PROCEEDINGS OF THE OPEN FORUM ON MANAGEMENT OF PETROLEUM REFINERY WASTEWATERS

PRESENTED BY

THE ENVIRONMENTAL PROTECTION AGENCY

THE AMERICAN PETROLEUM INSTITUTE

THE NATIONAL PETROLEUM REFINERS ASSOCIATION

THE UNIVERSITY OF TULSA



PROCEEDINGS

OF

OPEN FORUM

ON

MANAGEMENT OF PETROLEUM REFINERY WASTEWATERS

Presented by

The U. S. Environmental Protection Agency

The American Petroleum Institute

The National Petroleum Refiners Association

The University of Tulsa

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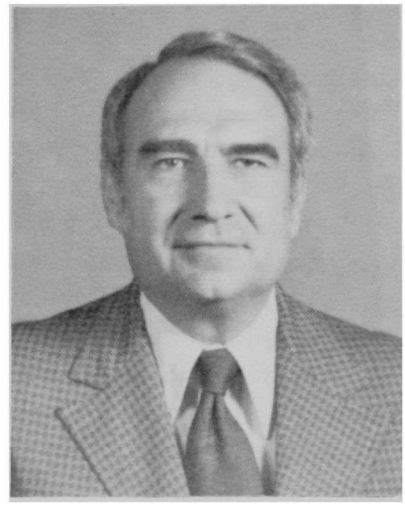
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Honored Guests, Ladies, and Gentlemen, It is a great pleasure to welcome you to the first 'Open Forum on Management of Petroleum Refinery Wastewaters." My hope is that this will be only the first of a continuing series of technical information exchanges between the industry, academia, governmental agencies at all levels, and the interested public. This conference, as you will note, is a series of sessions dealing with problems and solutions to protect the environment. In each session the program representatives have attempted to offer a balanced presentation of view points. The list of speakers is most impressive, and they are all quite knowledgeable in their fields.

Success or failure of any conference, however, can be linked to two action words -"participation" and "communication" by attendees. While not being an active part of any of the committees responsible for the symposium, I was close enough to experience the enthusiasm of your respresentatives from the American Petroleum Institute, the National Petroleum Refiners Association, the University of Tulsa, and the Environmental Protection Agency.

Last evening, upon entering the hotel, the undercurrent of expectation was very evident. Meeting old and new friends convinced me that you came to "participate" and "communicate". You have already, by your past and present actions, indicated the true welcome of this meeting; I have the priviledge of expressing that feeling. On behalf of the organization sponsoring this symposium, the working committees who planned it, the speakers for the various sessions, and our host, Tulsa University, I bid you welcome. May the next three days be as helpful to you as I expect them to be to me.

BIOGRAPHY



William C. Galegar holds a BS in Chemical Engineering from Oklahoma State University and an MS in Chemical Engineering from the University of Oklahoma. His career has included 11 years with Oklahoma Department of Health and 16 years with the Environmental Protection Agency and its predecessor agencies. Mr. Galegar is currently Director of the EPA's Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma.

KEYNOTE ADDRESS

"WASTEWATER CONTROL --- WHERE ARE WE, WHERE ARE WE GOING, AND WHY?

Milton R. Beychok
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I am sure that all of us must be impressed by the broad and diverse range of viewpoints represented by the speakers assembled for this conference. Very briefly, we have:

-- The EPA Divisional Directors for Effluent Guidelines and for Permits
-- The Chairman of the EPA's Effluent Standards and Water Quality Information Advisory Committee
-- The Program Director of the National Commission on Water Quality
-- A speaker from the Texas Water Quality Board
-- The EPA's Assistant Administrator for Research and Development
-- Speakers from a number of the major oil refining companies
-- Speakers from several well-known engineering and consulting firms
-- Eminent university professors
-- Key administrators from the EPA's Robert S. Kerr Research Laboratory

Aside from being impressive, these diverse viewpoints give us a unique opportunity to share perspectives and to explore important policy and technological questions related to industrial wastewater control. Toward that end, I would like to explore a few key issues in this 'keynote' address --- and one of those is the problem of the communication of viewpoints between industry and the federal EPA.

EFFECTIVE COMMUNICATION REQUIRES A TWO-WAY STREET

Effective communication works best on a two-way basis. That may be a cliche, but it is nevertheless true. Mr. Joe Moore of the NCWQ recently stated that (1), "We must not only listen, but we must also hear what is said." And I would add that we can accomplish much more by listening to each other than by shouting at each other.

In the three years since enactment of PL 92-500 (the Federal Water Pollution Control Act Amendments of 1972), at least 634 lawsuits have been instituted involving implementation of the Act (2). I submit that there would be far less court litigation between industry and the EPA if industry could effectively participate in developing effluent and emission control regulations --- and if industry viewpoints were truly given serious consideration. I fully realize that some industry viewpoints are non-productive and perhaps overly opposed to meaningful regulations. But the large majority of industry is willing to accept equitable regulations based upon realistic data and commercially-proven technology. The EPA should solicit industry viewpoints very early in their process of developing regulations, and provide industry a real opportunity to participate in their decision-making. It is not enough to merely invite formal written comments within a legalistic 30-60 days after publication of a criteria document or proposed promulgations --- especially not when those criteria or proposed promulgations represent months or years of work and many irreversible decision steps already taken by the EPA and their outside contractors. What industry wants is early involvement, face-to-face dialogues and a meaningful opportunity to help formulate proposed regulations through all the stages of decision-making. Formal comments made after the fact, or during public hearings conducted under

the rigid rules of law, are poor substitutes for a meeting of minds around a conference table. Formal comments and rigid public hearings simply invite adversary debate merely to establish a legal record --- what we need instead is the chance to voice, to hear and discuss valid viewpoints. I submit again that a working partnership between industry and the EPA would drastically reduce the court litigation involving PL 92-500. Obviously, the same participatory partnership between the EPA and the State regulatory agencies would be equally helpful.

It is probably too late to institute any working partnership of industry and the EPA involving the 1977 and 1983 effluent limitations mandated by PL 92-500. But it is not too late to learn some lessons from the past three years --- and apply them to the tasks and decisions that lie ahead of us. For example, what of PL 92-500's objective regarding the elimination of the discharge of pollutants (EOD) by 1985 --- the so-called 'zero discharge' goal? And what of the yet to be issued toxic pollutant standards called for in Section 307 of PL 92-500? And what of the recent decisions (3) by the Third and Seventh Circuit Courts of Appeal --- which made a clear-cut distinction between Section 301 effluent limitations as being 'minimum' levels of control and Section 304 guidelines as being 'factors or ranges' to be used by the permit issuers in deciding whether or by how much any individual permit is to be more stringent than the 'minimum' level Section 301 limitations? Do these Circuit Court decisions lend more validity to the matrix approach for Section 304 guidelines as advocated by the EPA's ES&WQIAC committee? Certainly, these are questions which must be of urgent concern to all of industry and there is still an opportunity to tackle these questions by a broad-based working partnership between industry, the EPA, and the State regulatory agencies.

WHERE ARE WE NOW?

I think most of us would agree that the tasks to be accomplished in order to achieve the mandated 1977 and 1983 goals of PL 92-500 are now defined in terms of the EPA's 1977 and 1983 Effluent Limitations and their New Source Performance Standards. Obviously, resolution of the recent Circuit Court decisions and of the pending backlog of litigation may very probably add new dimensions to the 1977 and 1983 regulations. But at least we have a framework upon which to assess where we are now, what we may accomplish by 1983, and what it may cost.

We are indeed fortunate at this conference that the National Commission on Water Quality has very recently released its Staff Draft Report. That Commission was created by Section 315 of PL 92-500 and charged with making a complete study of:

> "... all aspects of the total economic, social and environmental effects of achieving or not achieving the goals set forth for 1983."

The NCWQ staff draft summarizes PL 92-500 in terms of the Act's primary objective, two key goals and a number of specific policy statements. The primary objective of the Act is:

> "to restore and maintain the chemical, physical and biological integrity of the Nation's waters."

The two key goals of the Act are given by the NCWQ as: (4)

-- To reach, "wherever attainable," a water quality that "provides for the protection and propagation of fish, shellfish, and wildlife" and "for recreation in or on the water" by July 1983.

-- To eliminate the discharge of pollutants (EOD) into navigable waters by 1985.

Focusing on the 1983 goal, the NCWQ staff draft states that "much of the nation's waters are already of sufficient quality to meet the interim (1983) goal" as the result of pollution control efforts prior to PL 92-500 or as a natural condition (5). In order to be more definitive, the Commission selected certain minimum water quality criteria that would constitute meeting the 1983 goal --- one of which was a dissolved oxygen level of at least 4 ppm during 'worst case' conditions of seasonal low flow (5). Based on an assessment of 41 sites, the NCWQ developed the data in Table 1. These data indicate that 7-8% of the nation's waterways do not presently meet the 'worst case' dissolved oxygen criteria for satisfying the 1983 goal. Thus, in effect, we might define 'where we are now' by saying that 92-93% of our waters already satisfy a key criteria for meeting the 1983 goal of PL 92-500.

WHERE ARE WE GOING NEXT AND AT WHAT COST?

Clearly, where we are going next is to achieve the 1977 and 1983 goals. Table 1 tells us that achieving those goals will upgrade the 7-8% of our waters which do not presently meet those goals. But at what cost?

Table 2, developed from data in the NCWQ staff draft, sheds some light on the magnitude of the costs involved. The total capital expenditure required by industry and by municipally owned treatment systems will be about 233 billion dollars (1975 basis), and the annual operating costs will be about 16 billion dollars. I must stress that these figures do not include interest charges for borrowing the capital to finance this vast program, and that these costs will be spread over a period of at least 10 years. On the basis of about 65 million families in the nation, these costs amount to $3,600 of capital expenditure plus 245 $/year for each family --- or about 600 $/year per family for at least the next 10 years.

However, the costs will in fact be paid by each of us in the form of taxes and price increases for manufactured goods. Since tax burdens and buying power are graduated in terms of income level, Table 2 estimates that most of us in the middle and upper middle income brackets might expect to finance the 1983 goals by paying from 50-100 $/month for at least the next 10 years. But remember that these figures do not include interest charges of inflation. A simple 7% per annum interest charge for 10 years could easily increase that monthly payment range to 70-140 $/month per family.

The 1983 benefit will be an upgrading of 7-8% of our nation's waters. The cost might be 70-140 $/month per family for 10 years. Each of us will probably assess that balance from a different perspective in deciding whether it is an equitable balance.

WHY GO BEYOND 1983?

As mentioned earlier, the second goal of PL 92-500 is the elimination of the discharge of pollutants (EOD) by 1985. For simplicity, I will refer to that goal as EOD in my further remarks. What do we mean by EOD? The NCWQ staff draft uses the following definition:

> "The elimination of the discharge of pollutants shall apply to the removal of those constituents which are added during use of the water. The resultant discharge must be of equal or lower concentration than that of the original supply."

I cannot accept that as a satisfactory definition, since it does not define what constitutes a pollutant. Do pollutants include simple inorganic salts such as sodium and magnesium chlorides or calcium and magnesium carbonates and sulfates? If so, on what basis or criteria have these simple salts been defined as being 'pollutants'?

Nor can I accept the fact that the second part of the definition is not consistent with the first part. If we simply boil some water to produce steam, the resultant boiler blowdown will have a higher inorganic salt concentration than the original supply despite the fact that no salts were added during use of the water. Or if we simply evaporate some water in a closed loop cooling tower, the resultant cooling tower blowdown will have a higher salt content than the original supply again with no salts being added during use. Are these salts truly undesirable or toxic pollutants?

I am reminded of the following philosophical parable:

> First philosopher: "Why did the ancients consider the world to be flat rather than round?"
> Second philosopher: "I suppose simply because it looked flat."
> First philosopher: "Then how would it have looked to them if it had looked round?"

The point of my parable is that we had better take another look at this definition of EOD. Dissolved inorganic salts may look like pollutants to some people, but they don't look like pollutants to me. I would most certainly agree with defining pollutants to include phenols, cyanides, BOD, heavy metals and so forth --- but I cannot agree that simple inorganic salts are pollutants.

If we achieve the 1983 goal, presumably all of our nation's waters, "wherever attainable" will have a quality that "provides for the protection and propagation of fish, shellfish and wildlife ... and for recreation in or on the water." Then why go beyond that? What do we gain from EOD? Table 3 presents the answer to that question as given in the NCWQ report --- and the answer would appear to be that the benefits of EOD will be very minimal. The NCWQ report is very explicit on this point (7):

> "the predictable environmental effects (of EOD) would appear to be minimal, particularly in the absence of adequate control of nonpoint sources (urban and agricultural runoffs)."

On the question of costs for achieving EOD, the NCWQ report does not quantify total costs but only estimates unit costs in terms of $/1000 gallons for various innovative technologies that might possibly be used. However, the report does say that the costs would be (7):

> "prohibitively expensive, and the economic and social effect would be too severe to be absorbed within the foreseeable future."

The NCWQ report also points out that EOD technologies are considerably more energy intensive than those required to achieve the 1983 goals (8). Although energy requirements for the innovative EOD technologies are estimated in terms of KWH/1000 gallons, the report does not quantify the total energy requirements. However, I make my own estimate (in Tables 4, 5, and 6) based largely on the data within the NCWQ report. As shown on Table 4, I have estimated the total energy requirements to achieve EOD in terms of barrels per day of fuel oil --- and then expressed the fuel oil requirement as a percentage of our current oil imports of some 7 million barrels per day. If we assume a post-1983 industrial effluent flow of only 10% of the current nationwide industrial water intake, and if we assume we must produce at least a highly concentrated slurry for disposal by landfill or by land spreading, then the energy requirements to achieve EOD in the industrial sector will range from about 5-20% of our current oil imports.

Based on the NCWQ's projection of post-1983 municipal effluent flows, Table 5 presents an estimate of the EOD energy requirements for the municipal sector. Assuming that half of the municipal effluent can be disposed of as a 2 wt% brine (via ocean disposal, solar evaporation ponds, injection wells, etc.), and assuming that the other half must be concentrated to a slurry for land disposal, then the municipal sector energy requirements to achieve EOD will amount to about 10% of our current oil imports.

On Table 6, the total industrial and municipal energy requirements to achieve the 1977, 1983 and EOD goals are presented. The total will range from 1,430,000 to 2,660,000 barrels per day of oil, or about 20-38% of our current oil imports. The EOD requirements relative to the 1977 and 1983 requirements are very high. One must certainly agree with the NCWQ's statement that the EOD technologies are considerably more energy intensive than those required for the 1983 goals.

On the basis of costs versus benefits, the case against EOD appears overwhelming:

-- The environmental benefits would be very minimal.
-- The economic and social costs would be prohibitive and too severe to absorb in the foreseeable future.
-- The energy consumption would defeat any hopes we have of significantly reducing our dependence on imported oil.

Finally, in my opinion, the removal of simple water-soluble inorganic salts from our industrial and municipal effluents is a complete absurdity. As an intellectual engineering exercise, we very probably could remove those salts. But what a waste of the nation's wealth and genius! And after the salts are removed as a brine ... or a slurry ... or evaporated to dryness, how then do we dispose of them? In fact, how do we prevent their ultimate return to Mother Nature by dissolution in rainfall or by leaching into underground

aquifers? The NCWQ draft would seem to agree with me on this point:

> "The dominant consideration for achieving EOD relates to the removal of soluble salts. Removal of these salts creates large quantities of brine which must then be disposed of ... at very high costs."(8)

THE TOXIC POLLUTANT STANDARDS

"Toxic pollutant standards: paralysis or progress?" --- that was the title of a recent article in the Journal of the Water Pollution Control Federation (9). The purpose of the article was to analyze the delays in developing the toxic pollutant standards mandated by Section 307 of PL 92-500. Let us examine the chronological history of EPA's actions to date on these standards:

Published a list of 9 toxic pollutants	July 1973
Revised their criteria for selecting toxic pollutants, re-issued original list of 9 pollutants plus 25 other potential pollutants	Sept 1973
Proposed effluent standards for the 9 toxic pollutants	Dec 1973
Held public hearings on proposed standards	Apr-May 1974
Officially withdrew the proposed standards, and released a "Draft Advance Notice of Proposed Rule-making for Toxic Pollutant Standards" in which new proposed standards were presented on an informational basis	Nov 1974

In the 14 months since releasing that "Draft Advance Notice ...," no further official proposals have been issued. According to the schedule mandated in PL 92-500, the toxic pollutant list was to be published in Jan. 1973, the final standards were to be promulgated by Jan. 1974, and source compliance was to be achieved by Jan. 1975 --- some 12 months ago.

Much of the delay can be attributed to two factors: (9)

-- The lack of adequate scientific information on the effect of pollutants at extremely low concentrations in water.
-- The counterproductive provisions in PL 92-500 which required virtually impossible time schedules that were subsequently forced upon the EPA by court orders, and which required trial-type adjudicatory public hearings.

I can readily sympathize with the EPA on these points. But whatever the past reasons for delay, I would urge again that it is not too late to work with industry and with the State regulatory agencies in developing a practical set of toxic pollutant standards upon a firm base of scientific information.

EFFLUENT LIMITATIONS VS. EFFLUENT GUIDELINES

As I said earlier, recent court decisions (3) have made a clear-cut distinction between PL 92-500's Section 301 effluent limitations and Section 304 effluent guidelines. In the case of the American Iron and Steel Institute versus the EPA (10), the Third Circuit Court

of Appeals ruled:

> "Section 304 requires the EPA to develop effluent guidelines to assist permit issuers in setting individual point source discharge limits. Section 304 is not satisfied unless EPA specifies 'factors' and 'permissible ranges' of effluent limitations to be taken into account by the permit issuers in setting individual permit limits. These permissible ranges must be within the nationwide parameters established by Section 301 effluent limitations."

A few weeks after that ruling, the Seventh Circuit Court of Appeals in ruling upon a similar case issued a decision (10) which agreed with the Third Circuit's ruling on this point.

It would appear that these rulings (unless reversed by further appeal) mean that all of the EPA's effluent limitations promulgated to date are Section 301 nationwide parameter limitations --- and now the EPA must establish Section 304 effluent guideline 'ranges' and 'factors' within those nationwide limits. I hope that the Director of the EPA's Effluent Guidelines Division (who is our next speaker) will address this point --- because it should be of vital concern to industry.

It would also appear that these rulings should lead to a re-consideration by the EPA of the matrix approach for Section 304 guidelines which has long been advocated by the EPA's ES&WQIAC advisory committee. Mr. Leon Myers of the EPA's Robert S. Kerr Research Laboratory has been quoted as saying (11) that his group plans to study the application of the ES&WQIAC matrix approach to the petroleum refining industry. I hope that we may hear more about these plans from Mr. Myers when he speaks to us later in this conference.

Personally, I have very little knowledge of the ES&WQIAC matrix approach, and I have no opinions concerning the merits of that approach. But it was certainly disappointing that the work of the ES&WQIAC was not discussed or evaluated in depth anywhere within the 832 pages of the NCWQ staff draft report. That is an oversight which should be corrected in the NCWQ's final report.

THE PETROLEUM REFINING EFFLUENT LIMITATIONS

Leaving the area of broad issues, I would now like to focus upon a specific technical point which concerns the petroleum refining effluent limitations as applied to treatment plant design.

First, it would be useful to review how the refining limitations were developed. In 1972, the API and the EPA conducted an extensive wastewater survey of 167 refineries. 150 of those refineries submitted comprehensive data, and 136 were considered acceptable after screening. Upon eliminating those which used once-through cooling water for more than 3% of their process cooling, 94 were left in the final data base. That data base is probably the most realistic information ever collected for the wastewaters from the petroleum refining industry. However, the data were based on one-time samples and did not

represent attainable long-term performance. The EPA analyzed the data from the 94 refineries by statistical regression techniques to determine how refinery classification, size, and processing configuration affected the raw waste load. The regression analysis led to the five refinery subcategories, and the size and process factors, promulgated in the effluent limitations.

The next step by the EPA was to determine the attainable levels of long-term (annual) pollutant concentrations in the treated wastewater discharge from each of the five refinery subcategories, as well as the attainable long-term average wastewater flows. The data for these determinations were obtained by visiting refineries, reviewing monitoring records, and from various other sources.

Finally, data were gathered on the day-to-day and month-to-month variations in refinery wastewaters discharges. These data were analyzed by statistical techniques to arrive at variability factors which related long-term averages to short-term values. Thus, the attainable annual averages were multiplied by the applicable variability factors to arrive at the daily or 30-day averages in the final promulgated effluent limitations.

Unfortunately, the attainable long-term averages (flow and concentrations) and the variability factors are not included in the actual published EPA regulations (40 CFR 419). Due to the various amendments and revisions that have taken place, the unclear presentation in the original Development Document, and to the fact that the preambles to the various Federal Register promulgations are not included in the final Code of Federal Regulations --- it is virtually impossible at this point in time to determine the applicable long-term averages and variability factors with any degree of certainty. The waste treatment plant designer is left only with the amended short-term effluent limitations as published in the Code of Federal Regulations.

However, it is most important that the waste treatment plant be designed to achieve the more stringent long-term levels if the plant is not to exceed the allowable peak levels for daily and 30-day averages. For that reason, I have attempted to reconstruct (as best I could) the applicable variability factors and equivalent annual averages. Tables 7 and 8 present some of those reconstructions for:

1977 limitations for existing sources (30-day averages)
NSPS limitations (30-day averages)

These reconstructions reveal a number of anomalies. These anomalies may be due to my inability to correctly reconstruct the currently applicable information, or they may be due to inconsistencies which the EPA should correct. For example, in Table 7 for the 1977 existing source limitations:

--The annual average values were obtained from dividing the promulgated 30-day averages by the annual average wastewater flow and by the variability factor, and applying a conversion factor to arrive at ppm.
--We can see a number of trivial anomalies in values, most probably due to inconsistent round-off procedures.
--But in the COD values, the anomalies amount to as much as 20% between the extremes. I am fairly sure that the four COD values, shown enclosed in a box, were not meant to exhibit a 20% difference.

--Looking at the four NH_3-N values, shown enclosed in a box, I am at a loss as to why the more complex refinery subcategories (Lube Oil and Integrated) are expected to achieve 38% lower NH_3-N values than the less complex subcategories.

Table 8 illustrates the same anomalies for the New Source Performance Standards, and here the four NH_3-N values vary by a factor of 2-to-1.

Since the waste treatment plant design should be based on attaining the annual averages, I would strongly urge the EPA to:

--Publish a clear and explicit listing of the latest applicable values for long-term flows and concentrations in the format of Tables 7 and 8 -- for daily averages as well as 30-day averages, and for the 1983 limitations as well as 1977 and the NSPS.

--Publish a clear explanation of the COD and NH_3-N anomalies that appear to exist.

SUMMARY

In closing, I wish to express my deep appreciation for the opportunity to address this conference --- and for your patience with my lengthy address. I can only hope that it will stimulate some open discussion of the issues we face, and I look forward to listening to and hearing what the other speakers have to say.

REFERENCES

(1) Environmental Industry Conference, Council on Environmental Quality, Washington, D. C., December 10, 1975
(2) Staff Draft Report, National Commission on Water Quality, November 1975, page V-6
(3) American Iron and Steel Institute vs. EPA, Third Circuit Court of Appeals, November 1975
American Meat Institute vs. EPA, Seventh Circuit Court of Appeals, December 1975
(4) Staff Draft Report, National Commission on Water Quality, November 1975, pages I-1 and I-2
(5) Ibid, pages I-23 and I-24
(6) Ibid, page IV-10
(7) Ibid, page I-74
(8) Ibid, page 76
(9) "Toxic Pollutant Standards: Paralysis or Progress?", JWPCF, December 1975
(10) 8 ERC 1321, Environment Reporter, Decisions No. 10, November 28, 1975
8 ERC 1369, Environment Reporter, Decisions No. 11, December 12, 1975
(11) Environment Reporter, Current Developments, page 1252, November 14, 1975

DISCUSSION

Umesh Mathur: I found your comments extremely interesting. I work for the Indian Nations Council of Governments and we are a designated Section 208 planning agency. All of our guidelines (for Section 208 long-term regional planning) tell us to assume that industry will meet the EPA's effluent limitation standards. We can then evaluate the long-term effect of industrial discharges within our region on that basis.

However, if our evaluations on that basis indicate that long-term water quality goals will not be attained, what are we to do then? Can industrial NPDES permits call for more stringent limitations because Section 208 long-range planning indicates that more stringent controls may be needed?

Is there any real purpose in long-term planning based on receiving water quality when NPDES permits are issued on technology-based effluent standards?

Milton Beychok: I am not sure that I fully understand your questions. Each individual state already has the option of setting NPDES effluent limits which are more stringent than the established EPA guidelines. And the court decisions (which I discussed in regard to effluent limitations versus guidelines) seem to mandate a range of values to assist the permit issuers in deciding how stringent to make the individual permit. But I don't know how a Section 208 agency interfaces with the state NPDES permit issuers.

As for technology-based standards versus long-term receiving water quality, I guess that Congress crossed that bridge when they wrote PL 92-500 and decided upon technology-based standards.

Umesh Mathur: Perhaps we can have the EPA speakers address this point later on, because I think it is of great importance.

BIOGRAPHY

Milton R. Beychok is a consulting Chemical Engineer in the field of environmental technology. He has a B.S. degree in Chemical Engineering from Texas A & M University, and he is a registered professional engineer in California and Texas. He is a Diplomate of the American Academy of Environmental Engineers and is a member of the AIChE, Air Pollution Control Association and the Water Pollution Control Federation. He has served on the California Water Quality Control Board and consulted for the EPA, the National Science Foundation and the National Commission on Water Quality. Prior to entering private practice, he was with Fluor Engineers & Constructors for 20 years.

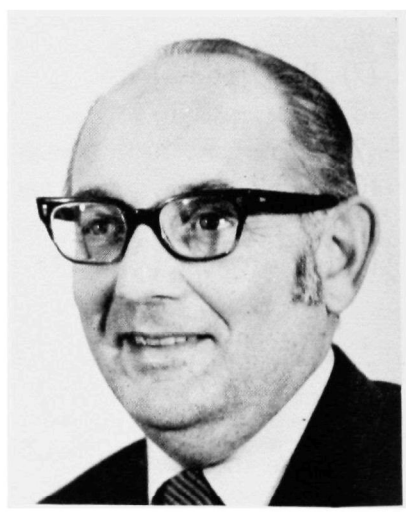
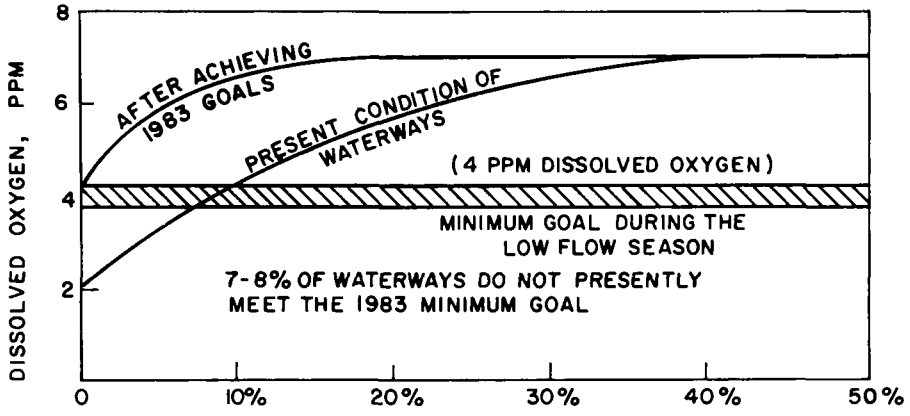


TABLE 1 "WHAT DO WE ACHIEVE BY 1983 GOALS?"



% OF WATERWAYS WITH DISSOLVED OXYGEN EQUAL TO OR LESS THAN LEVEL SHOWN
Reference: Page I-24, NCWQ Staff Draft Report, November 1975

*Involving 9,000 river and stream miles, 10,500 miles of coastline, 6,000 square miles of estuaries, and 6,000 square miles of lakes and reservoirs. The total surface of the watersheds where each of the sites is located encompasses 20% of the nation's land surface and a population of 80 million people (6).

TABLE 2 "WHAT WILL 1983 GOALS COST?"

	CAPITAL COST ($)	ANNUAL OPERATING COSTS ($)
ALL INDUSTRY (1)	75,000,000,000	13,900,000,000
MUNICIPAL SYSTEMS (2)	158,000,000,000	2,000,000,000
TOTAL	233,000,000,000	15,900,000,000

ESTIMATED MONTHLY COST PER FAMILY FOR NEXT 10 YEARS (3)
(IN TAXES AND PRICE INCREASES)

INCOME LEVEL:	MONTHLY COST
29,000 - 37,500 $/YEAR	$80 - 100/MONTH
20,700 - 29,000 $/YEAR	$50 - 65/MONTH
17,700 - 20,700 $/YEAR	$40 - 50/MONTH
13,100 - 17,700 $/YEAR	$25 - 30/MONTH

(INTEREST COSTS AND INFLATION ARE NOT INCLUDED)

(1) Page II - 81, NCWQ Staff Draft (2) Page II - 28, Ibid (3) Page III - 273, Ibid

TABLE 3 "BEYOND 1983 . . . WHAT DO WE GAIN FROM EOD?"

(By achieving EOD for point sources
after achieving 1977 and 1983 goals)

BOD REDUCTION - -	INSIGNIFICANT COMPARED TO UNCONTROLLED NON-POINT URBAN RUNOFF AND AGRICULTURAL RUNOFF
TOXIC SUBSTANCES REDUCTION - -	MINOR COMPARED TO UNCONTROLLED URGAN AND AGRICULTURAL RUNOFFS
EUTROPHICATION REDUCTION - - -	VERY LITTLE SINCE NON-POINT SOURCES CURRENTLY ACCOUNT FOR 80% OF TOTAL NITROGEN AND 50% OF TOTAL PHOSPHORUS ENTERING OUR WATERWAYS
SUSPENDED SOLIDS REDUCTION - - -	VERY LITTLE SINCE 90% OF THE LOAD ENTERING OUR WATERWAYS IS FROM NON-POINT SOURCES
OVERALL BIOLOGICAL IMPACT -	ONLY 6-10% OF WATERS PRESENTLY UNSUITABLE WILL BE UPGRADED. THUS, 5-10% of 7-8% OR PERHAPS ABOUT 0.4 - 0.8% OF NATION'S WATERWAYS WOULD BE UPGRADED.

Reference: NCWQ Staff Draft Report (Nov. 1975) Pages I-77 and I-78

TABLE 4 "HOW MUCH ENERGY TO ACHIEVE EOD FOR INDUSTRY?"

	GROSS USE	EVAPORATION, CONSUMPTION, LOSSES		
NET INTAKE (1)	ALL INDUSTRY	EFFLUENT	EVAPORATION TO A SLURRY	DISPOSAL OF SLURRY
15×10^9 gals/yr		ca. 10%/of INTAKE		

50-200 ------- KWH/1000 gals

EFFLUENT (AFTER 1983)		ENERGY CONSUMED TO ACHIEVE EOD			
% OF/INTAKE (1)	GALS/YR	KWH/1000 GALS (2)	KWH/YR	EQUIV./BPD OIL (3)	% OF CURRENT/IMPORTS (4)
10	1.5×10^9	200	3×10^{11}	1,371,000	19.6
10	1.5×10^9	50	0.75×10^{11}	342,750	4.9

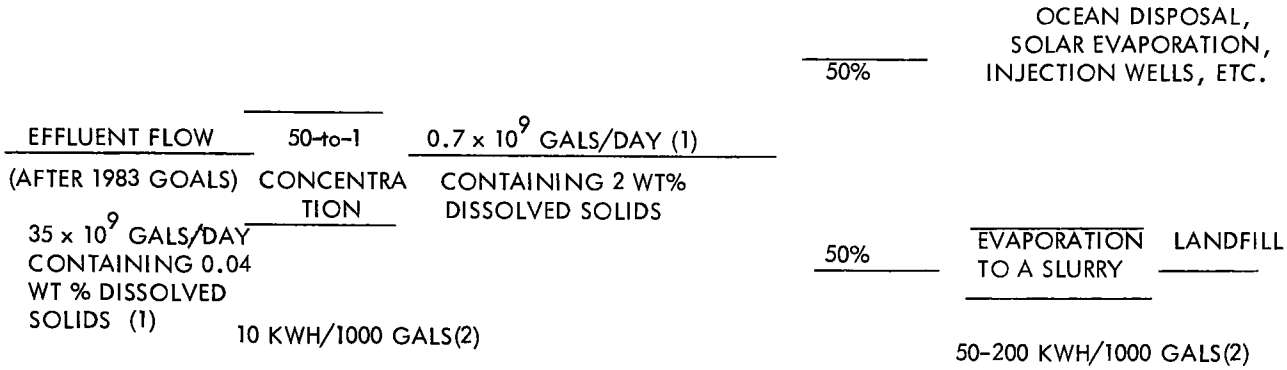
(1) CURRENT INDUSTRIAL WATER NET INTAKE = *ca.* 15×10^9 GALS/YR (p. II-53, NCWQ Staff Draft). EFFLUENT (AFTER 1983) ASSUMED TO BE 10% OF INTAKE.

(2) 50-200 KWH/1000 GALS (60-240 BTU/POUND) TO ACHIEVE A CONCENTRATED SLURRY (p. II-144, Ibid)

(3) EQUIVALENT BPD OF OIL = (KWH/YR) (10,000 BTU/KWH)/(365 DAYS/YR) (6×10^6 BTU/BBL OIL)
= (KWH/YR) (4.57×10^{-6})
BPD = BARRELS OF OIL PER DAY, WITH HEATING VALUE OF 6×10^6 BTU PER BARREL
10,000 BTU/KWH = FUEL CONSUMED IN GENERATING ELECTRIC POWER AT ca. 33% EFFICIENCY

(4) CURRENT OIL IMPORTS TAKEN TO BE ca. 7 MILLION BARRELS PER DAY

TABLE 5 "HOW MUCH ENERGY TO ACHIEVE EOD FOR MUNICIPAL EFFLUENTS?"



CONCENTRATION = $(35 \times 10^9$ GALS/DAY)(365 DAYS/YR)(10 KWH/1000 GALS)(4.57×10^{-6})
= 584,000 BPD OF OIL

EVAPORATION = $(0.35 \times 10^9$ GALS/DAY)(365 DAYS/YR)(50 to 200 KWH/1000 GALS)(4.57×10^{-6})
= 29,000 to 117,000 BPD OF OIL

TOTAL ENERGY REQUIRED = 613,000 to 700,000 BPD OF OIL
= 8.8 % to 10.0 % OF CURRENT IMPORTS

(1) Page II-155, NCWQ Staff Draft
(2) Page II-144, IBID

TABLE 6 "HOW MUCH ENERGY (NATIONWIDE) TO ACHIEVE 1977, 1983 AND EOD GOALS?"

	10^6 BPD OF OIL	% OF OUR CURRENT IMPORTS
Manufacturing Industry:		
1977 goal (1)	0.17	2.4
1983 goal (2)	0.20	2.9
Steam-Electric Industry:		
1983 thermal limitations (3)	0.02 - 0.13	0.3 - 1.9
Municipal Effluents:		
Treatment, collection, sewer control (4)	0.09	1.3
TOTAL TO ACHIEVE 1983 GOALS	0.48 - 0.59	6.9 - 8.5
EOD for industry (5)	0.34 - 1.37	4.9 - 19.6
EOD for municipal effluents (5)	0.61 0.70	8.8 - 10.0
TOTAL BEYOND 1983 (w/EOD)	1.43 - 2.66	20.6 - 38.1

(1) 376 trillion Btu/year (p. II-100, NCWQ Staff Draft)
(2) 446 trillion Btu/year (p. II-100, Ibid)
(3) 45 to 294 trillion Btu/year (p. II-106, Ibid)
(4) Page II-41, Ibid
(5) See Tables 4 and 5

TABLE 7 "1977 EFFLUENT GUIDELINES FOR PETROLEUM REFINING (1)"

EFFLUENT LIMITATIONS IN POUNDS/1000 BBLS OF CRUDE OIL (2,3)

SUBCATEGORY	BOD-5	TSS	COD	OIL	PHENOL	NH_3-N	SULFIDE	Cr	Cr^{6+}	
TOPPING	4.25	3.6	21.3	1.3	0.027	0.45	0.024	0.071	0.0044	
CRACKING	5.5	4.4	38.4	1.6	0.036	3.0	0.029	0.088	0.0056	
PETROCHEMICAL	6.5	5.25	38.4	2.1	0.0425	3.8	0.035	0.107	0.0072	
LUBE OIL	9.1	8.0	66	3.0	0.065	3.8	0.053	0.160	0.011	
INTEGRATED	10.2	8.4	70	3.2	0.068	3.8	0.056	0.17	0.011	
	EQUIVALENT ANNUAL AVERAGE p.p.m. CONCENTRATIONS (4)									(5)
TOPPING	15.0	10.2	79.9	4.9	0.10	1.8	0.10	0.25	0.02	20.0
CRACKING	15.5	10.1	115.2	4.8	0.10	9.6	0.10	0.25	0.02	25.0
PETROCHEMICAL	15.3	10.0	96.0	5.3	0.10	10.1	0.10	0.25	0.02	30.0
LUBE OIL	14.3	10.2	110.0	5.0	0.10	6.8	0.10	0.25	0.02	45.0
INTEGRATED	15.0	10.2	109.4	5.0	0.10	6.3	0.10	0.25	0.02	48.0
VF (4)	1.7	2.1	1.6	1.6	1.7	1.5	1.4	1.7	1.4	

TABLE 8 "NEW SOURCE PERFORMANCE STANDARDS FOR PETROLEUM REFINING (1)"

EFFLUENT LIMITATIONS IN POUNDS/1000 BBLS OF CRUDE OIL (2,3)

SUBCATEGORY	BOD-5	TSS	COD	OIL	PHENOL	NH_3-H	SULFIDE	Cr	Cr^{6+}	
TOPPING	2.2	1.9	11.2	0.70	0.016	0.45	0.012	0.037	0.0025	
CRACKING	3.1	2.5	21	0.93	0.020	3.0	0.017	0.049	0.0032	
PETROCHEMICAL	4.1	3.3	24	1.3	0.027	3.8	0.022	0.068	0.0044	
LUBE OIL	6.5	5.3	45	2.0	0.043	3.8	0.035	0.105	0.0072	
INTEGRATED	7.8	6.3	54	2.4	0.051	3.8	0.042	0.13	0.0084	
	EQUIVALENT ANNUAL AVERAGE p.p.m. CONCENTRATIONS (4)									(6)
TOPPING	14.8	10.3	80.0	5.0	0.11	3.4	0.10	0.25	0.02	10.5
CRACKING	15.6	10.2	112.5	5.0	0.10	17.1	0.10	0.25	0.02	14.0
PETROCHEMICAL	15.2	9.9	94.7	5.1	0.10	16.0	0.10	0.25	0.02	19.0
LUBE OIL	15.0	9.9	110.7	4.9	0.10	10.0	0.10	0.24	0.02	30.5
INTEGRATED	15.1	9.9	110.9	4.9	0.10	8.3	0.10	0.25	0.02	36.5
VF (4)	1.7	2.1	1.6	1.6	1.7	1.5	1.4	1.7	1.4	

NOTES FOR TABLES 7 & 8

(1) AS AMENDED ON MAY 20, 1975

(2) BEFORE APPLYING SIZE AND PROCESS FACTOR MULTIPLIERS. BASED ON 30-DAY AVERAGES.

(3) EXCLUDING ALLOCATIONS FOR RUNOFF AND BALLAST WATER

(4) EQUIVALENT ANNUAL AVERAGE p.p.m.

$$= \frac{\text{(30-DAY AVERAGE, LBS/1000 BBLS CRUDE) (120)}}{\text{(ANNUAL AVG. WASTEWTR. FLOW, GALS/BBL CRUDE) (VF)}}$$

VARIABILITY FACTOR (VF)

= RATIO OF 30-DAY AVERAGE TO ANNUAL (LONG-TERM) AVERAGE

(5) ANNUAL AVERAGE WASTEWATER FLOWS USED AS BASIS FOR 1977 GUIDELINES, PER EPA DEVELOPMENT DOCUMENT, EPA-440/1-74-014-a, APRIL 1974

(6) ANNUAL AVERAGE WASTEWATER FLOWS USED AS BASIS FOR NSPS GUIDELINES, PER EPA DEVELOPMENT DOCUMENT, EPA-440/1-74-014-a, APRIL 1974

SESSION I

"PETROLEUM REFINING GUIDELINES"

Chairman

William C. Galegar

Director, Robert S. Kerr Environmental Research Laboratory
U.S.EPA Ada, Oklahoma

Speakers

Allen Cywin

"Establishment of Petroleum Effluent Guidelines"

Martha Sager

"The Role of the Effluent Standards and Water Quality Information Advisory Committee (ES&WQIAC) in Furthering the Scientific and Technical Developments Towards Clean Water"

Joe G. Moore, Jr.

"The Role of the National Commission of Water Quality(NCWQ)

Robert T. Denbo

"Economic Impact of Wastewater Effluent Guidelines for Petroleum Refining"

"ESTABLISHMENT OF PETROLEUM REFINING EFFLUENT GUIDELINES"

Allen Cywin
Director, Effluent Guidelines Division
E.P.A., Washington, D.C.

Let me start by saying I am always pleased to be back in Oklahoma, having learned how to fly here in World War II at Norman; and I am always pleased to talk and participate in conferences with the petroleum industry. Mr. Brinegar, President of Union Oil was talking to me recently and said "You know you folks in the Environmental Protection Agency and the environmental movement ought to thank our industry as we got you started as a result of such incidences as the Tory Canyon and Santa Barbara oil spills." Well, of course, there are other industries and there are other reasons and we have had a whole series of laws in which this nation tried to tackle the problem of water pollution control.

Three years ago the Congress over Presidential veto enacted Public Law 92-500. Now why did they do so - why did the public demand cleaner water - why did the Congress intensely debate the issue for two years - why did they pass one of the most comprehensive pieces of legislation in order to establish new mechanisms and specific goals for water pollution control departing in significant ways from a whole series of laws passed just two, three, four, five years earlier? Now why does the law state in its very first sentences, in the very first page, that the objective of this Act is to restore and maintain the chemical, physical and biological integrity of the nation's waters? In order to achieve this objective it is hereby declared that consistent with the provisions of this Act, 1) it is the national goal that the discharge of pollutants into navigable waters be eliminated by 1985; now that is the goal. Is the national goal that wherever obtainable an interim goal of water quality which provides for the protection and propagation of fish, shell fish and wild life and provides for recreation in and on the water be achieved by July 1, 1983; now that's a goal also. It is a national policy that the discharge of toxic pollutants and toxic amounts be prohibited; now that's a policy. In order to accomplish these goals the Act created a new regulatory mechanism requiring uniform technology based effluent standards. As you know a level of standards for existing plants calling for Best Practical Control Technology is to be achieved by July 1, 1977 followed by a more stringent requirement to be achieved by July 1, 1983 which, and I am quoting from the Act, "shall require application of the Best Available Technology Economically Achievable for such category or class which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants." The Congress places faith in technology, practicable, available, and achievable by 1983. Why?

For one reason industrial wastes are the principal point source of controllable waterborne wastes. In terms of the generally quoted measurement of just BOD_5, the gross wastes of industries are about three times greater than that of the domestic sewered waste. Moreover the rate of U.S. industrial production is increasing at a rate of over four times of that of the population growth rate. But BOD_5 is just one consideration, industry also discharges the bulk of the metals, chemicals, toxicants, oils and greases to our waterways. Recent drinking water surveys illustrate the great amounts of noxious waste discharges that provide a threat to our drinking-water supplies. Therefore of paramount concern is that

public health now and in the future is at issue. Also at issue are other major beneficial uses of water - for agricultural purposes, for recreational purposes and indeed for use by industry itself. Industry which presently uses three times the volume of water required for domestic water supply is a major beneficiary of water pollution control.

Now let us look at the mechanisms for achieving industrial water pollution control in an equitable fashion on a national basis. As I have said industry has a stake in meeting the objectives of the Act since it not only is a water pollution control act but a water conservation act. The U.S. needs for industry, for agriculture and for domestic use, are increasing all the time, but as we all know, the volume of water available in the United States is finite. The 1972 amendments to the Federal Water Pollution Control Act, have as a goal the elimination or reduction of pollutant discharges through effluent limitations that encourage recycle and reuse and the law is to be implemented through a series of permits issued by the Federal Government and the States. At this date, we have more than half the states of the union implementing the program.

The industry effluent limitations are to be technology based; progress, not status quo, is to be emphasized. Two new terms are coined, best practical control technology available based on the average of the best practices within an industry or class or category of industries and best available technology economically achievable, which could be based on a single application within an industry. Technology transfer is permitted where there is little or no technology being practiced and, of course, we are interested in reducing the amount of pollution not just the measurement of pollution so mass units are used wherever possible for our limitations.

Now for industry, and by the way industry is required to do more than municipalities, best practical is to be achieved by July 1, 1977, best available by July 1, 1983 and also new source performance standards are to be established and the latter is to be based on best available demonstrated technology or technology transfer. Now these are for point sources that discharge directly to the waterways.

In addition to that, we are to establish pretreatment regulations and these could be and usually are somewhat different for existing plants that are tied into municipal systems and for new sources. By the way we have something like 40,000 industrial point source discharges and we have something like 300,000 commerical and industrial establishments on municipalities, but basically in going through the program we have had to establish some five different regulations, and there they are. Now the July 1, 1977 regulation, as I said before is to be based on the average of the best practices, and by the way these terms are not something we conceived at EPA. In establishing what a law requires one has to follow the history of the law and it does get complicated in our democracy because often times as the House works through its side it differs somewhat from the Senate; then there's a conference committee and a conference report and reports to the Senate and congressional record. These ideas and these thoughts on the effluent regulations are therefore based not only on public discussions of the issue, intense discussions and debate within EPA and within the federal establishment, but also on briefing the Congress on a very regular routine basis on these ideas and these thoughts throughout the development and history of this program. Everything that we have done from the very first definitions

has been supplied to the Congress. There are a number of factors that we have to take into account. By the way in establishing these kinds of regulations, no one had ever done this before and no one had taken into account many of these factors which became quite important as the country entered into inflation, recession and energy crises. But right from the beginning we did take into account as the law required the total cost versus the effluent reduction benefits, the age of the plants, where this was a factor, the reduction processes, where these were factors, process changes, engineering aspects, non-water quality environmental impacts, in other words what are the tradeoffs between transferring waste from one media to another, etc. There are only three places to put waste - air, land and water.

Now occasionally, as I said before, we do practice technology transfer. There are industries that are doing very little or nothing, yours is not one of these. The 1977 standard emphasizes end of process treatment but it does include in-process treatment where this is common practice and in very many industries there are very good housekeeping practices on-going and certainly should be used across the industry. The objective is to reduce the point source pollution discharge. Mr. Moore will be discussing the aspects of the Act which go to questioning whether or not this particular date or this particular goal should be achieved but the 1983 goal in the Act (the only way one could study this is to establish what the standards are) is quite a difficult one. It establishes that really you had better take the best available technology and apply this across the industry. The law which was passed on October 18, 1972 envisioned that there would be a ten year effort to reach that objective and in-process controls are suggested. Alternative water uses, water reuse conservation, by-product recovery, reuse of waste - water constituents, good housekeeping and quality control are all techniques in use in your industry and other industries and which can be utilized in many other applications. The objective in the Act, the ultimate objective is no pollutant discharge. Now in fact a few of our regulations do recognize that certain plants and certain industries are indeed achieving no pollutant discharge at the present time but in most cases the regulations do have limits and these limits are not zero. Now to go through the thought processes we take a major industry category, and some 28 were published as a minimum in the basic law, and within that industry we look at like families, or classes or categories (as the law states) of plants, by type, by size, or by age, or by climate, or by treatability or finished product and we call these sub-categories. We then establish what the raw waste loads are for these sub-categories, what the best or the average of the best in-plant controls are and the end of pipe treatment and come out with our standards. Once again there are five sets of standards. We look at the annual costs, both internal and external. This was a departure from previous rulemaking in most other agencies in that we actually took our costs and tried to establish what the economic consequences of these regulations were and these were considered and debated within and without the federal establishment before the regulations were promulgated. Now for publicly-owned treatment works, which are referred to in the law as POTWs, the law requires secondary treatment by July 1, 1977 and it can require industry pretreatment and it does say in the law that industrial waste which cannot be treated or will interfere with the operation of the municipal treatment plant or pass through untreated should be pretreated. The law established the technology based limitations as a minimum; it further stated that where water quality could not be achieved by applying the technology based limitations something more stringent may be

required. It also said that states may make their limitation more stringent than the Federal limits for whatever reasons occurred to the states. Now let me just explain some of the procedures we have gone through in order to come up with this. First of all the law itself expressed the view that for existing plants and at least for those 28 industries (and the petroleum refining was one), that we should publish proposed regulations twelve months after the law was passed from October 18, 1972 to October 18, 1973 and some four or five months thereafter the new source standards. We started the program building a little bit from the 1899 permit program. Recall that the Corp of Engineers suddenly discovered and we discovered about 1970 that the 1899 Rivers & Harbors Act called for a "permit" system for discharges to waters. For a variety of reasons no more than 20 permits were issued in that two year period and by that time Public Law 92-500 overtook the effort. Now if you recall the President vetoed the bill and the Congress overrode the veto on October 18, 1972. Because of that we were inhibited somewhat in building up the resources necessary to implement the bill as quickly as we would have liked to, but in any event starting with a secretary and myself about four years ago and still only with a real small handful of staff, we undertook to hire outside contractors to help us. We can start with the fact that good contractors were hard to come by in a hurry. With regard to previous comments by Mr. Beychok, I remember asking if Fluor wanted to participate and Mr. Beychok said "Oh no!", so we had to pick and choose the best we could. We also set up certain other review mechanisms. The law provides for us to consult with other federal agencies, states and other interested persons. Now of course the people affected by the regulations are the most interested persons, but you also have environmental groups and professional societies and others. Now EPA, in establishing what our program plan would be, where our deadlines would be, who our contractors and who our project officers would be, what our definitions would be, called in many groups, other federal agencies, states, industrial organizations, environmental professional groups and explained what we were going to do and solicited their cooperation. Now a lot of people didn't think the whole thing was for real although, of course, many did. Of course, the cooperation was spotty across industries and even between companies within industries. Within your industry, an environmental committee was established headed by Russ Mallett and we had a very good dialogue with that group throughout the rulemaking process. Now we also had to establish our effluent standards and water quality information advisory committee and get that set up and for a little while I was the executive/secretary/director of that committee and carrying water on both shoulders. We asked that committee to hold public hearings and Dr. Sager will go into that aspect of their operations. Faced with these deadlines, EPA set some very stringent timetables on the contractual efforts and we told our contractors that their very first draft report would be exposed to the public. Now this is highly unusual, I don't think anyone here would want to expose his first draft effort to the public, but we did. We did it for a purpose, part of the purpose went with a covering letter that went to the public. We said, that if you don't like what you see in this document, please let us know what you would like to see but give us your background, your data, your rationale -- for any changes, we just can't pluck things out of the air. In some cases this was successful, in other cases not so successful. In addition to that external review; within EPA, we tried to establish throughout the agency regional office and lab personnel who might be knowledgeable in a particular industry and we set up what we call working groups of these people for an internal review. These were technical task forces, and we ourselves -- (we just didn't wait for comments to come in) we ourselves went over these materials and in some cases wrote and rewrote these documents several times. We then

as an agency came out with a proposed regulation. This is the first time EPA's name appeared on it and a development document which was a manual which explained how we got from here to there. Everyone of the factors in the Act is a chapter, purposely written in that guise. We also took all of our background data, file cabinet loads, and made these available to the public in what we call a "freedom of information center," and once again we asked the public to tell us what it is they would like to see in there and give us their data, their background and their rationale, for any changes.

Now the timetable of 30 days or 60 days whatever they turn out to be were very short because during this period of time, not only were we faced with the congressional deadline which we didn't quite make (we made it for a number of regulations but not quite all) but the National Resource & Defense Council took us to court and the court set us on specific deadlines. Now what the court said is you will do competent professional work on this schedule and they told us what the schedule was. We have tried and so far we have stayed out of contempt, but in addition to that the court also added another 30 industrial categories, because the first 28 or 30 covered about only half the permit applications. Now in addition to all of that, of course, as I say there are some five regulations and we have established some well over 500 sub-categories so we have promulgated and proposed over 2500 regulations in less than four years. As a part of the regulation writing process in the United States in fact as a part of our very basic system of democracy we have three parts of government. We have the executive, the congressional and the judiciary and too many people lose sight of the fact that the rule-making procedures under the administrative procedures act and also under this Act, Public Law 92-500, call for public lawsuits if the public so desires. Now a number of our regulations were not sued, and a number of the lawsuits that were entered against us we have long since settled out of court, some for, to me, very trivial reasons. I will give you one. The textile industry sued us and before they did they came in and said we want to take on a research study to illustrate whether or not the projected numbers which we have reasonably agreed to for the 1983 standards could really be met through mixed media filtration. If we, the textile industry, do that would you look at the results and we said as public servants we are obligated to do that and the law tells us to look at this every few years. They said, well our lawyers tell us that we have to have this in writing for after all you might not be here by the time our results come in so they sued us and we and they developed a letter. We said if they come up with the results we will look at it and that was the way that suit was settled. Others were a little more complicated than that and others have gone right to the mat.

Now with respect to the two law suits previously mentioned by Mr. Beychok, I will give you my interpretation. Neither Milton Beychok nor I are lawyers, and perhaps this will all end up in the Supreme Court. The Seventh Circuit did not mention ranges and I think in my view I could not have written a better treatise for the position taken by EPA, than they did. The Third Circuit, although it did mention range, qualified that term by saying that we have to give very precise guidance to the permit writers as to how to apply anything over and above that minimum number. We will be wrestling with this issue in the months ahead. We have still to hear from several other Circuits. I think of great significance is the fact that we are all citizens and we have all expressed our views and indeed the House of Representatives had an oversight hearing on our program a year

and a half ago; something like the Church Committee on Intelligence. I would commend the report resulting from that hearing to your reading.

My summary of it is that the House said to itself; gentlemen this is a very complex law, people of goodwill are trying to work their way through it and let the process continue. With that I think I am on time to answer questions.

DISCUSSION

W. C. Galegar: We have talked primarily about history of the guidelines program, what do you think the future holds in this area?

Allen Cywin: Well immediately ahead if we did nothing else, we still have a number of industry categories to get out still in the court order deadlines, for example by January 30 (this Friday) we have to get out pulp and paper - phase II and we have a series of others to develop and these are all in process. Every time we promulgated a new source standard as law required we also promulgated a new source pretreatment standard. We have a very complex procedure in existence for pretreatment standards for existing sources and we have undertaken a program to try to clarify that somewhat better. So we still have a lot to do in the field of pretreatment. More than that last spring we proposed to the agency (I am just spinning this off and I know it is being taped so take this in the context of just discussion), a conception whereby 307a, would be used really as a last resort. For toxics in general, once they are established on a list, should be integrated into 301 and 306 as we go about reviewing and upgrading those regulations. Conceptually this seems to be taking hold in the agency and conceptually we are negotiating with NRDC and others on this issue. Here again we have been taken to court by the environmental organizations to get on with the job in both pretreatment and in toxics. So basically we still have a number of regulations to finish. The court suits themselves will give us a lot of work to do for example, the Eighth Circuit court remanded some of the standards in grain milling and just gave us an opportunity to go back and look at it again. As public servants, if our review had shown us to be wrong we would easily have admitted it, but in this case we felt we were correct and added 2500 more pages to the record to show that the standards were based on sound data. The lawyers again in responding to that for the other side said all you did was prove you were right in the first place and therefore you are arbitrary and capricious. So some call Public Law 92-500 the lawyers employment act and in some cases, the lawyers call it the engineers employment act. Perhaps it's both, but there is an awful lot of work to do to finish what we have started.

Frank Manning: Would you care to comment how you selected the parameters that were listed in your guidelines and promulgations, for example BOD, why did you choose that, instead of COD or TOC?

Allen Cywin: Basically, of course, it started with a look at the industry and the commonly regarded prinicpal pollutant parameters. Often times as we developed our regulations we dropped parameters because we thought it might cost too much to monitor and we knew that a certain amount of reduction would take place anyway if the technology was employed, so we tried to keep our parameters to a minimum. In the case of the petroleum refining

industry we had been discussing the parameters even before the law was passed with your technical advisory committee for a long period of time and we are in general agreement on the parameters that were selected.

Milton Beychok: Allen, I'm not sure whether you have had a chance yet to read the Commission's staff draft report but what is your personal opinion about the 1985 goals and the elimination of discharge as they relate to the removal of dissolved inorganic salts?

Allen Cywin: Well let me just say that the agency through testimony submitted by Mr. Ruckelshaus before the House in 1972, I guess even in 1971, gave its ideas about universal no-discharge. As I say some plants and some industries are achieving this now. Other places like storm sewers and for certain dissolved solids, I personally as an engineer, don't think we are going to achieve that for God knows when if ever in many industries. This does not mean that the goal is not a good goal you see. This does mean because of our population growth as the Commission reports and because of the industrial growth, we have got to get as close to that as is economically and technically feasibly possible. And for a lot of industries and a lot of plants this means from going from virtually unlimited discharge to something that is quite within the realm of possibility and is being practiced today. We have not suggested any technologies that those of us who have been working in this field for a long time have not worked with for a long time.

Morris Wiley: I believe Mr. Cywin that you stated that industry was discharging about three times as much waste as municipalities if I understood your statement. The National Commission on Water Quality indicated that the industrial water intake was a little more than half of the municipal waste discharges and the information that I would have would suggest that say in the oil and grease pollutant parameter that municipalities are larger sources than industry and probably true in BOD as well. What is the basis for saying that industry, apart from agriculture, discharges more pollutants and where can one find this information so that it can be examined by industry.

Allen Cywin: The basis of my information is the 1968 Department of Commerce report (and my three-times statement was in terms of BOD_5). If you will just think a large pulp and paper plant introduces in one plant as much BOD_5 as the population of a million people. A cow introduces ten times more BOD_5 than a person and so forth. I am including feed lots as they are very large industrial operations. The processing of animals (you can estimate in terms of petroleum refining) can get 100,000 chickens in one place you can get 10,000 cattle in one place and that's a large point source of discharge. I was looking at a film this morning just before I came down here on the Today Show for just a second and it was about California dairy operations. Everything was automated, cows came into a line, they got washed down, the machines were automatically applied, the machines were automatically taken off, they milk a cow in eight minutes - they just run them through this machine, there was an awful lot of cows in that place and a lot of residual material.

Anonymous: Where can you find population equivalents for livestock?

Allen Cywin: For that one number look at the 1958 census Department of Commerce. As far as the cattle and what not we have published some papers which give population equivalents and so has The Economic Commission for Europe of the U.N., but we are talking about concentrated animal feeding operations. The environmental protection agency was taken to court once again to include every cow and chicken not every farm, but we have established population equivalent limits based upon research, you know minimum limits, size limits and we have also established the fact that these have to be in concentrated areas.

J. Anthony Tallis: During your presentation you mentioned toxicity analysis is going to be factored into the guidelines in terms of cost. How is this a part of the policy of determination as to limitations? Maybe I can quote an example:-

> as to whether a dam should be built in a certain location is useful in comparison with alternative source of water supply, water supply being an absolute necessity for industry and municipalities.

In something like this, what is the break-off point?

Allen Cywin: Let me answer in two ways, first of all the term is cost versus benefits of effluent reduction. In other words, do you double the cost by taking out 2% more or 5% more of BOD, or of suspended solids, NUS was one of our contractors and they established a good series of graphs; for example, the iron and steel industry which showed what the levels of technology would be, what their costs were and how much tonnage on a model plant basis which would apply across the industry would delete from discharge to the water environment. As a part of this analysis, we had a separate series of contractors look at the economics of the industry as a whole. Now where are looking at the industry across the board with reference to what technology can achieve and in some parts of the industry you will find the smallest plants achieving let's say the best technology. Normally you will find in economics that the smallest plants are the most marginal and in many cases you will find in our regulations size cutoffs for example, where there is no or a lesser regulation because we don't feel that that segment of the industry should be regulated on a technology basis because the cost or the total economics across that spectrum of plants is prohibitive. Or you may find some differences by geography as for example in the Alaskan crab operations,we have a different limitation than the contiguous states. We have a number of variabilities throughout our regulations on this basis. I don't know the exact numbers for example and the history behind them but obviously that Mr. Beychok was showing and calling anomalies but I would guess that the average of the best practices in those sub-categories created those anomalies, since certain sub-categories especially more complex you perhaps have more sophisticated operations or designs and therefore are taking out more pollutants and you should because you have more in there than just BOD_5 and suspended solids. We have not identified the toxics at this stage but the more sophisticated chemical operations, petrochemical operations, are eventually going to have to address themselves to this point of toxics.

W. L. Ruggles: What is the future of toxicity in the guidelines?

Cywin: Amongst our own staff you will find different attitudes and different

statements. Toxics obviously are something that can get quite emotional. You see in Kepone for example, I think most of you have seen enough on TV recently of Kepone, and the emotions that this has generated. One of the reasons why EPA has not been able to come out under 307a with some real hard numbers as yet is because of the great divergence of opinion as to 1) what you can achieve and 2) the obvious economic costs that are involved. You run to two viewpoints, if it's my health that is in danger I don't care what the cost is, if it's your health I might not care either, but you most certainly would and I am sure that this kind of issue is going to be debated not only for water pollution but it is being debated for air pollution and OSHA and other regulations. It's a very hard thing to cope with because what is toxic to some people in toxic amounts or to the aquatic life isn't something we can prove quite easily across the board. There is a point of view that let's play it safe until we find out some more about it. Industry on the other hand obviously says well prove it and then we will do something about it. You get these two different points of view which EPA is trying to balance all the time. So let me say I think we will bring forth a balanced prospective when we finally get the thing out, I hope so.

BIOGRAPHY



Allen Cywin was appointed Science Advisor for the Environmental Protection Agency's Office of Water and Hazardous Materials in February 1976. Prior to this, Mr. Cywin organized and served as director of the Effluent Guidelines Division in the Office of Water and Hazardous Materials.

Mr. Cywin also served as Director, Division of Applied Science and Technology in the Water Pollution Control Research and Development Office, Assistant Commissioner for Operations and Engineering of the Community Facilities Administration, and Chief of the Saline Water Conversion Demonstration Plant Program of the Department of the Interior where he was responsible for directing the design, construction and operation of the Nation's first large saline water conversion plants.

Mr. Cywin has also worked for the Resarch Division of the Navt Facilities Engineering Command and is retired Seabee Reserve Officer.

"THE ROLE OF THE EFFLUENT STANDARDS AND WATER QUALITY INFORMATION ADVISORY COMMITTEE (ES&WQIAC) IN FURTHERING THE SCIENTIFIC AND TECHNICAL DEVELOPMENTS TOWARD CLEAN WATER"

Martha Sager
Chairman, ES&WQIAC EPA, Washington, D.C.

STATUTORY BASIS

The Effluent Standards and Water Quality Information Advisory Committee (ES&WQIAC) is a statutory Committee established under Section 515 of PL 92-500.

"Sec. 515 (a) (1) There is established on Effluent Standards and Water Quality Information Advisory Committee, which shall be composed of a Chairman and eight members who shall be appointed by the Administrator within sixty days after the date of enactment of this Act.	Establishment
"(2) All members of the Committee shall be selected from the scientific community, qualified by education, training, and experience to provide, assess, and evaluate scientific and technical information on effluent standards and limitations.	Membership
"(3) Members of the Committee shall serve for a term of four years.	Term

MEMBERS AND STAFF SUPPORT

PL 92-500, the "Federal Water Pollution Control Act Amendment", was enacted in October 1972. The ES&WQIAC members were appointed on February 3, 1973 for four year terms - which may be renewed. The committee is composed of a chairman and eight members. The staff consists of an Executive Director with administrative and secretarial support.

ACTIVITIES

The data bases and information relative to industrial point source effluent discharges are of such a particular technical nature that from its earliest meeting in March 1973, members of ES&WQIAC decided to work closely with the technical engineers and project officers in the Effluent Guidelines of the Office of Water Planning of EPA so that differing engineering viewpoints might be settled at an early stage in guidelines development to cut down the Administrators involvement in issues of such technical nature at the time of promulgation.

This relationship was developed in concert with the director of the Effluent Guidelines Division who arranged the first joint meeting with project officers of EPA early in April, 1973.

The Committee has carried out its statutory functions through public hearings; public

meetings; industrial workshops; critique and review of documents; special studies; and agency, industry, congressional; and public interest group liaison.

FIRST YEAR ACTIVITIES, MARCH 2, 1973 - MARCH 1, 1974

In its first year of effort the ES&WQIAC conducted 60 Industrial Workshops, 7 Public Hearings, and 15 Committee Meetings. It provided detailed comments on an extensive series of technical documents and proposed effluent limitations related to the initial 27 basic industries specified in PL 92-500, and proposed a new approach for developing effluent limitations for industrial point source discharges became later known as the Matrix Method.

MATRIX APPROACH
(BNA News Article 1973)

"This new matrix approach for establishing effluent limitations under the Federal Water Pollution Control was developed by ES&WQIAC and presented to EPA Administrator Russell E. Train September 26, 1973.

The new method entails a modification of the guidelines based on state-of-the-art waste water treatment technology. In addition to current subcategorization of industries, considerations which affect an individual industrial operation are included in mathematical models used to establish as best practicable technology. The current data base available from EPA and industry serves as a baseline for establishing raw waste load. The baseline is modified as additional data are generated and as predictive models of treatment technology are improved.

The subcategorization of industries considers four constraints on effluent standards of performance, these include treatment technology, operational characteristics, economic equity, and geographic and climatic considerations."

The matrix provides a quantitative, technically sound basis for subcategorization of industrial categories which is necessary to insure that effluent limitations are consistent with the requirements of the act and realistically achievable by classes and categories of point sources. This method for quantitatively determining effluent limitations could be interpreted as a National Guidelines.

Basic steps for development of an effluent standards model by the matrix method are outlined, as follows: (1) Develop statistical plots of raw waste load and flow for an industrial category. Determine if size, age, or type of process has a major effect and if so break the statistical plots accordingly. Eliminate plants which have extensive water reuse or product recovery not normally practiced in the industry. Base line flow/unit production is one standare deviation from the mean. (2) Determine from waste water treatment operating data on best practicable technology if the waste water characteristics have an effect on process performance under optional design operating conditions. If so, categories should be established with appropriate effluent qualities. (3) Define operation characteristics of the industry. Establish effluent qualities for each grouping. (4) Delineate geographical and climatic effects. Best practical technology in some cases can be defined by area if spray irrigation or evaporation ponds are applicable. However, in all cases an alternative for discharge

using waste water treatment should be considered because land availability or cost could mitigate against land disposal, waste water characteristics, particularly temperature, should be considered. (5) For each of the groupings defined in (1), the cost of compliance/unit production should be generated. Best practicable technology is defined and costs are computed by selecting the large plants with prevalent technology. Processes are selected and effluent quality defined for each grouping considering a reasonable cost equity. (6) As additional data is complied, it would be added to the data base for current best practicable technology. Treatment models would be updated as the state-of-the-art advances.

Industry support for this quantitative method was strong and was evidenced by several hundred letters and telegrams to the Administrator of EPA requesting its evaluation by the Agency.

In December, 1975, the matrix method was discussed by the EPA's R&D division at Ada, Oklahoma for review and revision, if necessary.

In addition the Committee developed data formats for information acquisition from industry and received and transmitted more than 320 communications to EPA regarding establishment of effluent limitations. Under its responsibilities for Section 307, i.e., on toxic substances the Committee: conducted special hearings; developed extensive lists of materials proposed for inclusion in the original toxic substances list by EPA; prepared a comprehensive bibliography of reference material on toxic substances and provided a position paper for EPA on toxic substances regulations. (Details are provided in the Committee's First Annual Report covering the period March 2, 1973 to March 1, 1974).

SECOND YEAR ACTIVITIES, MARCH 2, 1974 - MARCH 1, 1975

In the Committee's second year of operation a comprehensive Work Plan was developed covering 10 key areas of Committee interest in providing, assessing and evaluating scientific and technical information for the Administrator of EPA, according to its mandates. This FY'75 Work Program is shown in Table 1.

The Committee held 5 public meetings, and 40 industrial workshops to obtain technical information for assisting EPA in developing industrial effluent limitations. The Committee also provided comments and recommendations on 56 documents and rule-making packages developed by EPA for establishing industrial effluent limitations.

In April 1974, at the request of the House Committee on Public Works, the Committee provided comments on "Problems in Implementation of the Federal Water Pollution Control Act". The summary of this testimony follows:

The ES&WQIAC Members have been concerned with the following critical issues with regard to the effluent limitations for industrial point source discharges being developed by EPA under Sections 304 (b), 306, and 307 of PL 92-500; specifically:

(1) EPA's interpretations of definitive terminology and the effects of these interpre-

tations on the promulgated limitations, i. e., Exemplary Plants; National Standard; Guideline; Effluent Limitation; BPT; and, Zero Pollutant Discharge.

(2) The effectiveness of the methodology selected by the agency to develop industrial point source effluent limitations; i.e., selection of a descriptive and qualitative contractor's approach rather than a quantitative mathematical methodology.

(3) Specific items which resulted because of the definitions adopted by the agency amd the application of the methodology selected:

(a) % BOD reduction required of BPT by 1977;
(b) Factors excluded generally in establishing subscategories in many of the promulgated regulations;
(c) Economic equities largely imbalanced in favor of large "most exemplary plants";
(d) Lack of quantitative economic analysis of non-water impacts and energy requirements in the promulgated documents to date;
(e) Lack of economic and scientific substantiation with regard for Section 307 and toxic materials effluent discharges; and,
(f) Lack of cooperation by the Effluent Guidelines Division with the Committee efforts to provide, assess and evaluate scientific and technical information for the administrator of EPA according to the mandate for the ES&WQIAC in Section 515 of PL 92-500.

Special information gathering conferences were planned or conducted to facilitate exchange of technical information. In November 1974 the Committee sponsored a Federal Interagency Conference to determine the quantity and quality of technical information derived by EPA in establishing industrial effluent limitations. As a result of this conference, recommendations were made to the EPA Administrator for improvement in utilization of these government resources.

A special task force was constituted in December 1974 to review and provide recommendations to EPA on a newly proposed approach to developing Toxic Substance limitations. A report "ES&WQIAC Report on Review of Draft Advance Notice of Proposed Rule-Making on Toxic Substances" containing ES&WQIAC recommendations was subsequently transmitted to EPA.

THIRD YEAR ACTIVITIES, MARCH 2, 1975 - DECEMBER 31, 1975

During the Committee's third year of operation the Committee continued its activities of meetings, workshops, special task forces and reviews.

On March 6 a Hearing was conducted on "Privately Owned Sewage Treatment Works" including public interest groups, industry and Federal agency representatives.

A conference on radioactive wastes was conducted on April 3 with participation of all Federal Agencies with responsibilities in the area.

The Committee continued its detailed review and comments on all EPA documents

related to industrial effluent standards development and the associated rulemaking packages and evaluated 20 of these during this time period.

Public Meetings were conducted addressing industry problems of meeting Best Available Technology (BAT) specifications for 1983. The schedule for these meetings with milestones is shown in Table 2. The first meeting on BAT was held on April 24, followed by workshop/meetings in July, August, and September.

Four special studies were initiated by the Committee to provide additional information to EPA during this third year of operation: (1) Development of a Report on the Matrix Method for Establishing Industrial Effluent Limitations; (2) Development of an Approach for Establishing Best Available Technology (BAT) Under PL 92-500; (3) Analysis of Litigation on Implementation of PL 92-500; and (4) Analysis of Toxic Substances Legislation.

Five reports were prepared for publication in calendar year 1975:

(1) Second Annual Report - ES&WQIAC
(2) The Matrix Method - A Methodology to Assist in Establishing Industrial Effluent Limitations under Public Law 92-500
(3) Summary of Contentions of Industry in Litigation Pending Under Sections 304 (b) and 306 of Public Law 92-500
(4) An Analysis of Current and Proposed Federal Legislation Seeking to Control the Use of Toxic Materials
(5) An Approach for Establishing Best Available Technology (BAT) Under Public Law 92-500 - With Applications to the Organics, Synthetics and Plastics Industry

A new ES&WQIAC Toxic Substances Task Force was established in November 1975 to assist EPA in implementation of Section 307 of PL 92-500. A proposed rationale for implementation was developed. A workshop/meeting was also developed and scheduled for January 15 and 16, 1967 to review the EPA plans and ES&WQIAC proposal for implementation of toxic substances standards under PL 92-500.

CLOSURE

The ES&WQIAC is pleased with its output during its years of tenure since March 1973. We believe the evaluative techniques, methods of operation and range of inputs are uniquely different from the typical advisory committee pattern of operation and could possibly become a template for future operation of scientific and technical advisory committees in the Federal arena.

DISCUSSION

W. L. Ruggles: Will toxic-materials restrictions generally be even more severe than the present 1977/83 guidelines?

Martha Sager: The toxic limitations conceptually should be more stringent because of their direct relationship to the physiology of aquatic organisms and because of harmful effects in minute quantities.

Irvine W. Wei: Please describe the matrix approach.

Martha Sager: It is a little difficult to discuss the matrix method in a brief time. We are preparing a comphensive report on the "Matrix Method" which will be available shortly. Briefly the method utilizes a series of matrices in which the first matrix characterizes the individual inputs and leads to the definition of the standard raw waste load for each category or sub category. Then these results are input onto a second matrix which yields process designs for alternative choices as a function of the effluent quality. In turn these are then applied to the economic matrix which generates a series of costs versus effluent quality relationships for the alternatives from the second matrix. Through consideration of cost versus effluent quality policy decisions are next made in establishing the ultimate effluent standards for each sub category. This procedure is shown in Figure 1.

BIOGRAPHY

Dr. Sager is Chairman of the Effluent Standards and Water Quality Information Advisory Committee (ES&WQIAC), a statutory committee established under PL 92-500. She is also Professor and Director of the Environmental Systems Management Program within the Center for Technology and Administration, College of Public Affairs, at the American University, Washington, D.C.; Consultant in Environmental Management; Member, Air Quality Evaluation Panel; Technical Advisory Board, Department of Commerce; Panelist, Measures of Air Quality, National Bureau of Standards; and a Specialist in Environmental Engineering and Industrial Micobiology.

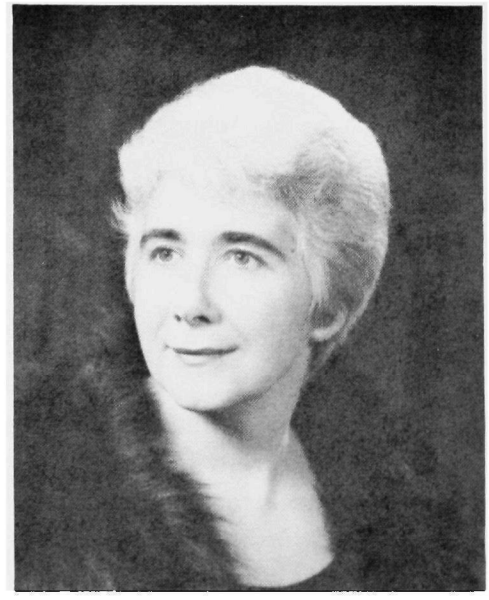


TABLE 1 "ES&WQIAC COMMITTEE WORK PLAN (FY75)"

It has been proposed that the following tasks and work plans be adopted for ES&WQIAC for the new fiscal year in order to accomplish the maximum production of end product in relation to providing, assessing and evaluating scientific and technical information for transmission to the Administrator of EPA.

I. Document Review

Overall engineering responsibilities for review of documents from Effluent Guidelines Division.

Don Bloodgood (coordinator)
Wes Eckenfelder
Ramon Guzman
Lloyd Smith

II. Early Inputs for Current Effluent Limitation Development

Early ES&WQIAC guidance on approach and document preparation for the development of effluent limitations. This will include workshops and special tasks for at least the following industries:

Miscellaneous Foods and Beverages
Machinery and Mechanical
Ore Mining and Dressing
Water Supply

(Others)

All Committee Members (Brossmar - Coordinate, development)

III. Anticipating Inputs for Future Effluent Limitation Development

Ongoing review for revision and updating of effluent limitations. Data input design and acquisition. Development of a broader base of data sources. Possible Matrix Workshops.

Glenn Paulson
Wes Eckenfelder
Blair Bower
Martha Sager
Martin Brossman (utilize additional technical staff support when available)

IV. Public Hearings for Public Interest Groups

Selected series of meetings involving public interest groups in relation to the possible economic implications and environmental impact on the public of PL 92-500. This task will have particular reference to ES&WQIAC responsibilities in order to advise the Administrator about public reception and response to the progress EPA is making on PL 92-500 in the area of industrial point source discharge.

Glenn Paulson
Bob McCall
Martin Brossman

V. Federal Liaison

Liaison with other federal agencies on positions and problems relating to PL 92-500 and preparation of reports for transmittal to the Administrator.

Martha Sager
Bob McCall
Martin Brossman

VI. Special Legal Tasks

Coverage and preparation of written reports to ES&WQIAC on hearings and legal actions related to designated industries and toxic materials. Maintenance of liaison with the General Counsel's Office in EPA and other federal agencies as required.

Blair Bower Rose Mattingley Bob Grieves

VII. Matrix Development

Coordination of development and implementation of matrix method by EPA.

Martha Sager Bob Grieves
Wes Eckenfelder Martin Brossman

VIII. Coordination with National Academy of Science

Coordination of National Academy of Science review of EPA in relation to impact on ES&WQIAC responsibilities (with special reference to the inclusion of the matrix in the EPA R&D Program).

Glenn Paulson Lloyd Smith
Martha Sager Martin Brossman

IX. Economic Analysis and Liaison with National Commission on Water Quality

Expansion of ES&WQIAC economic analysis inputs and coordination with NCWQ.

Blair Bower Martha Sager
Wes Eckenfelder Martin Brossman

X. Toxic Effluents

Review of effluent limitations, analysis of legal and technical aspects in liaison with other federal agencies on Section 307 of PL 92-500.

Lloyd Smith Martha Sager Glenn Paulson (participation dependent on current court actions)

TABLE 2 "BAT TASK FORCE SCHEDULE"
(Revised July 22, 1975)

(Organics, et al, and Paperboard)

ES&WQIAC MEETING DATE	LOCATION	MILESTONE	MEETING ACTION
July 18 & 19 (Fri./Sat.)	Univ. of Kentucky Lexington, KY	Completion of Data Collection	Review Data; Decide on Methods of Analysis
Aug. 18 & 19 (Mon./Tue.)	Vanderbilt Univ. Nashville, TN	Completion of Initial Analysis	Develop Report Outline
Sept. 25 & 26 (Thurs./Fri.)	ES&WQIAC Wash., D. C.	Completion of Draft Report	Review Draft Report, Revise, Produce Final Version
Oct. 30 (Thurs.)	ES&WQIAC Wash., D. C.	Final Action on Report	Agreement on Disposition of Final Report

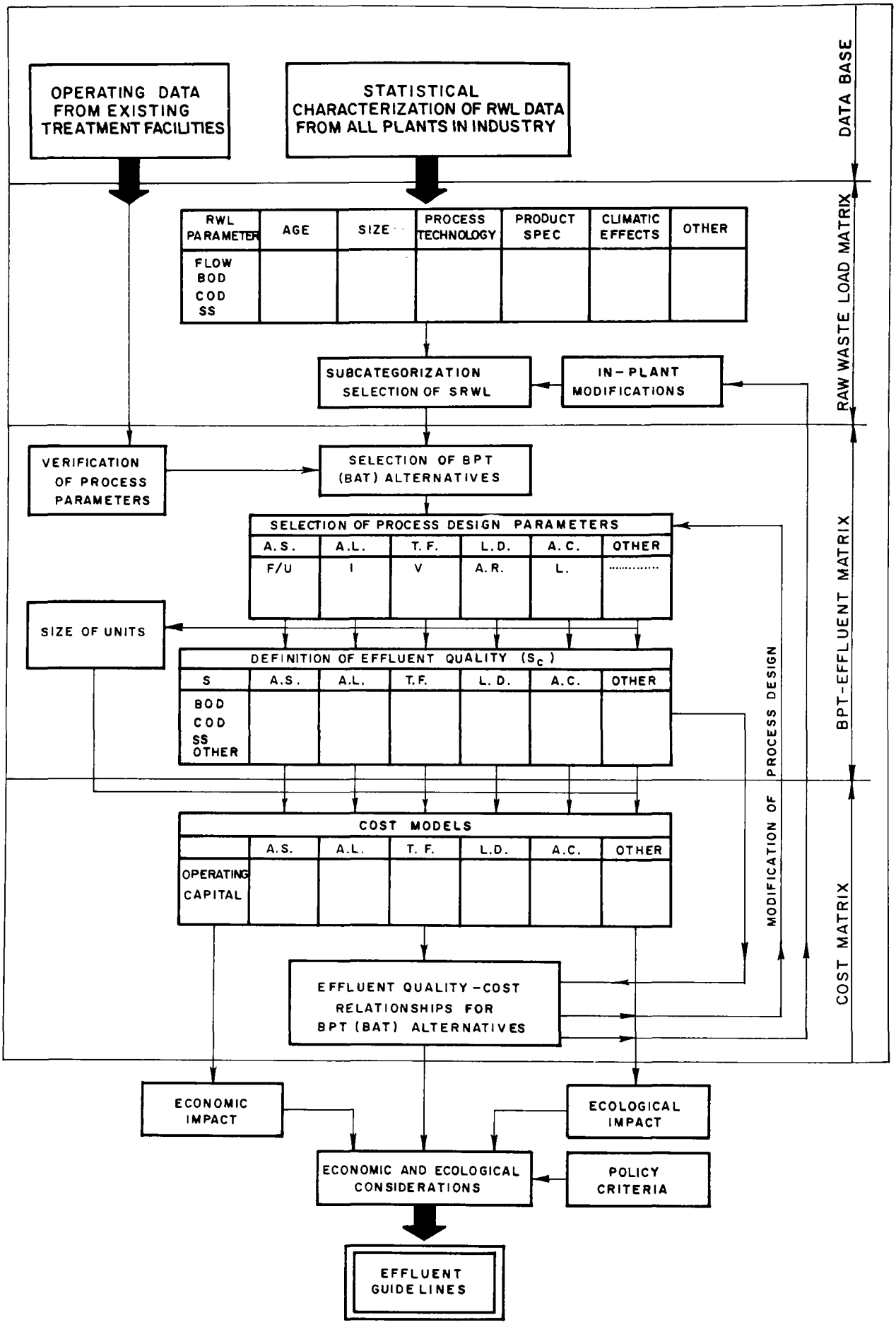


Figure 1. THE MATRIX METHOD

"THE ROLE OF THE NATIONAL COMMISSION ON WATER QUALITY (NCWQ)"

Joe G. Moore, Jr.
(formerly, Program Director, NCWQ, Washington, D.C.)
Head, Graduate Program in Environmental Science
The University of Texas at Dallas

Sometimes when I see what is going on today I wonder if the "good old days" were as good as we sometimes want to remember. My first experience with Bill Galegar had to do with the adoption of the Texas water quality standards. He had the proper federal view that nobody at the state level knew anything and I had the proper state view that we weren't going to have these "outlanders" telling us what we ought to do in our state. In one of the early conversations with him I said, "I want you to know that we don't like these foreigners coming down here telling us what to do." Bill sort of drew himself up and got a scowl on his face and said, "I want you to know that my forefathers welcomed your forefathers to this country when they came;" that did give me pause, I asked, "What do you mean by that?", and he said,"Well, you know I come from Oklahoma, you know Oklahoma was settled by the Indians. I happen to belong to a tribe of Indians who have not yet executed a treaty with the United States government."

How many of you know what the National Commission on Water Quality is? Well, may be I had better tell you something about this operation, with apologies to those of you who do know. The National Commission on Water Quality, created by Section 315 of Public Law 92-500 is made up of five members of the Senate, five members of the U.S. House of Representatives and five Presidential appointees. The Commission was created in the law with a statutory deadline to make a report to the Congress on or before October 18, 1975. As usual with government bureaucrats, we were two million dollars short and six months late, if the Commission manages to make its report in March of 1976. The Commission members -- and by the way, of the Congressional members you will recognize a large number of names involved in the development of Public Law 92-500 -- are as follows: the presidential appointees, Nelson A. Rockefeller, who was then governor of the State of New York and now Vice-President, has remained chairman throughout the life of the Commission; Dr. Edwin A. Gee, senior vice president of DuPont in the Wilmington, Delaware office; William R. Gianelli, a consulting engineer from Pebble Beach, California who is probably better known as the Director of the California Department of Water Resources, the agency responsible for developing the California water project; Mr. Raymond Kuduleis, the Director to the Department of Public Utilities for the City of Cleveland, Ohio and Mr. S. Ladd Davies, Director of the Arkansas Department of Pollution Control and Ecology; from the Senate, Muskie from Maine, Randolph from West Virginia, Bentson from Texas, Baker from Tennessee and Buckley from New York; and from the House of Representatives, Jones from Alabama, Jim Wright from Texas, Harold R. "Bizz" Johnson from California, Bill Harsha from Ohio, and James C. Cleveland from New Hampshire. There were three additional Commissioners, John A. Blatnik, a former Congressman from Minnesota, James R. Grover, a former Congressman from New York and Carl E. Wright the Chairman of the Arkansas Commission on Pollution Control and Ecology who died during the summer of 1973 and was replaced by the Director of that particular agency.

The Commission's charge in the statute is a very narrow one, "The Commission shall make a full and complete investigation and study of all of the technological aspects of achieving and all aspects of the total economic, social and environmental effects of achieving or not achieving the effluent limitations and goals set forth for 1983 in Section 301(b)(2) of this Act." That assignment was developed after some controversy in the conference committee on P.L. 92-500. By the time the Commission was actually operable, nearly a year after the passage of P.L. 92-500, attitudes even of the congressional members had changed, and the Commission early decided that in addition to taking a look at the narrow requirement for 1983, the Commission would also examine the progress being made under the 1977 requirement to the Act and examine as well the potential impact of the elimination of the discharge of pollutants -- the 1985 goal of the Act. After a great deal of discussion, the Commission, in February of 1974, published a study design stating what it intended to do in the time remaining to it.

The Commission appropriated or was authorized an appropriation of $15 million initially, has secured an additional $2 million authorization and a $2 million appropriation, so that by the time it concludes its work it will have spent at least $17 million. About $14 million of that total will have been spent on contract research projects defined by a professional staff to fulfill the stated study design and represented in some 90 contractor reports. I have one with me, or at least a part of the one with me on the petroleum refining industry. This is the contractor's report that went through two drafts and has now gone into the National Technical Information Service of the Department of Commerce. This does not include the Appendix which contains the data base; but if you can imagine, some of them run to four volumes this thick, so you can have some idea what sort of stack you'd get if you looked at all the reports. For any of you who may be interested in finding out about any report of the Commission, or getting a list of the reports, or getting a copy of the draft staff report or its summary, you should write to the National Commission on Water Quality, P.O. Box 19266, Washington, D.C. 20036, and we will be glad to send you a publication list. If we don't have a particular report, we can give you some idea about when it is likely to become available.

The contractor's report on the petroleum refining industry was done by Engineering Science of Texas, Inc. You have two staff people from that concern later on in your program talking about various waste treatment technologies, Davis Ford and Lial Tischler. Rather than take up my time trying to explain to you a technical subject from a person not versed in technical matters, I would suggest if you have questions you might catch them while they are here with regard to the actual technical aspects of the Commission's analysis of petroleum refining. Mr. Beychok, whom you have already heard, was a consultant to the Commission.

There were some 75 consultants used by the staff and an additional 30 or 40 specifically mentioned in the Commission's authorizing legislation.

The staff itself consisted -- the program staff -- consisted of some 30-35 professionals recruited by me and my deputy, Jim Smith, who came to the Commission from the Conservation Foundation. That professional staff oversaw the actual execution of contracts

for the various studies and then produced a report almost as lengthy as the one I have just shown you at some 900-1,000 pages; this report went through three publicly distributed versions, and probably three private versions that were prepared by the staff before any were released publicly. The staff draft report consists of several chapters; I am going to give you the general organization of the document. I have with me only the first chapter called Issues and Findings, this is the one that contains questions and answers conforming with the Commission study design. For those who wish merely a cursory examination of the Commission's work, this is some 82 pages long, and you can almost pick the subject in which you have an interest and take a look at it in that particular section. If you are more interested in the detailed subject matter areas I will give you the chapters so that you will know the contents of the full report. Chapter II is an analysis of the capabilities and cost of technology for achieving the effluent limitations required by 1977 and 1983 as well as what remains to be done after 1983, in a technological sense, toward achieving the 1985 goal of the elimination of discharge of pollutants. This is an assessment of the capabilities of the public and private sectors to apply the defined effluent limitations for 1977 and 1983 as well as those more stringent to protect water quality. Chapter III is an analysis of the economic effect of the cost of applying the necessary technologies on both a micro-economic and macro-economic scale as well as the social effect of these changes. Chapter IV is a description of present water quality and environmental water-based and related terrestrial conditions and projections of anticipated change which may result from implementation of the Act; this is where Mr. Beychok got some of the information he showed in the slides a moment ago. Chapter V is an identification of the effects of the Act in eleven selected regions in the nation. Chapter VI is an assessment of the public and private response as institutional segments finance, implement, manage and enforce the nation's water pollution control program. This Chapter concerns itself not only with the inter-governmental institutional relationships but also the response of the various regulated segments in terms of whether or not they can institutionally achieve the requirements of the Act.

In addition to the more traditional aspects of municipal and industrial technologies, economic effects and results, there is also discussion of the requirements related to agriculture, particularly with regard to feed lots, irrigation return flows and agricultural non-point sources.

Generally speaking, the Commission staff draft concludes that the cost of achieving the 1977 requirements and the 1983 requirements even in today's economic climate, are not insurmountable. However, the Commission staff draft inevitably has raised the question as to whether or not the incremental improvement to be realized from the achievement of the 1983 requirements, once the 1977 requirements have been met, is worth the probable cost. And so the question is, really, do the changes in water quality, as a result of the incremental requirements of 1983, justify the expenditure of the funds to achieve the 1983 requirements. Mr. Beychok did read for you the general conclusion of the staff with regard to the elimination of the discharge of pollutants.

Let me just give you some figures that relate to the petroleum refining industry in terms of the total. To reach the 1977 requirements for all refineries presently in place, the technology assessment staff concluded that the cost would be roughly a billion dollars. The economic impact analysis indicated that as a result of imposing these requirements there would be certain plants that would inevitably close or consolidations that would occur, and therefore the economic impact cost would be roughly $830 million as contrasted with a billion dollar cost. You must understand that the technology contractors were asked to price the various technologies for existing facilities. The economic impact analyses -- and by the way, they are contained in separate volumes, so this does not include the economic impact analysis -- the economic impact analysis would generally show lower figures because of in those industries that may be affected so as to cause plant closures, the economic impact figures are generally lower than the technology cost figures. To get that in perspective for the 1977 requirements, the total estimated economic cost is roughly $37 billion, so petroleum refining would account for roughly one billion of the $37 billion.

The operation and maintenance costs for those facilities once in place in petroleum refineries would be $142 million over and above whatever operation and maintenance cost there is in 1975 for waste water treatment facilities. The table you saw earlier assumed that the total of all these figures would represent the total O & M. There is a piece missing, simply because we were not always able to get the actual O & M figures for the base year. When you see O & M costs in Commission reports, these are incremental over the base line -- which is to say when we talk about 1977 O & M costs, we are talking about the requirements, the O & M costs attached to the billion dollars of expenditure that would be required to get to the 1977 requirements.

For 1983, the technology costs -- and unfortunately the economic analysis did not analyze in detail potential closures, primarily because most of them apparently occur in meeting the 1977 requirements -- the cost figures for both technology and economic impact are the same for the 1983 requirements. The total cost is roughly $1.2 billion for the refinery industry out of a total industrial cost of $23 billion for industry to achieve the 1983 requirements. In just comparing these two gross figures and assuming that the magnitude is reasonably valid, the cost to achieve the 1977 requirements is greater than the cost to achieve the 1983 requirements.

In addition to these two estimates, the Commission's staff, using a massive macro-economic model in which the staff does not have unlimited confidence, prepared a prediction as to the cost of new source performance standards for those plants that would be constructed between 1975 and 1983. For all new plants, the estimated cost is $20 billion, but the staff believes that that figure is much "softer" than the other two I have just given you. The O & M figures for the 1983 requirements would be $429 million over and above the incremental costs of 1977, and for new source performance standards, the estimate was $290 million for operation and maintenance.

I must emphasize that in any tabulation you see of costs produced either in the staff draft reports or analyses of the Commission's contractor reports or staff draft reports, it is inevitable that the cost figures are chosen or selected from a range. We did not attempt

to show all the ranges of costs that were selected or produced by the contractors; thus, you will occasionally see a variety of figures credited to the National Commission on Water Quality. What this means is that someone has chosen a series of figures from the ranges either in the contractors reports or supporting documentation and have put together a table of his own. For example, nowhere in the Commission staff draft work will you see complete tabulations of total costs to the nation including all three -- municipal, industrial and agricultural -- costs, simply because the number of variables or the range of figures is such that it is very difficult to do. For example, you saw the figure of $158 billion, for achieving the treatment requirements for publicly owned treatment works. The range from which that figure is chosen is somewhere between about $65 billion and $450 billion, so that the $158 billion is a figure that the staff chose as one that appeared to be reasonable in terms of the requirements of the Act. I must emphasize that for publicly owned treatment works there are six categories of eligible federal construction grant assistance. Depending upon which of those categories might be funded, one can account for a wide range of costs; for example, will municipalities be required to collect, contain and treat all urban storm water run-off. If they do, and they have to apply secondary treatment to that volume, you can regard that cost as one that contributed to that extreme figure of some $450 billion. I caution you that when using cost figures, it is difficult at best to get a series that may approach what you judge to be realistic, but you will see figures that vary considerably.

The important thing to remember is that the cost for achieving the publicly owned treatment works requirements of the Act are considerably higher if all categories are funded and are considerably higher than those for achieving the industrial requirements. At the same time it is obvious that industries have moved substantially farther towards achieving the 1977 requirements by the deadline in the statute than have municipalities, because the municipal program depends substantially upon the level of federal funding and whether or not Congress and the Administration are providing the intended level of federal participation.

Generally speaking, most industries believe that even the costs as I have given them to you are severely understated. There are those who believe, however, that the costs are overstated. As you might expect, Al Cywin and his group in EPA argue that we have substantially overstated the costs and therefore distorted the consideration of Public Law 92-500. There are those who believe, particularly in meeting the 1983 requirements, industries will strive for ways to minimize the costs through changes in production processes and that therefore the 1983 costs have been substantially overstated, which is to say that as the economics of waste water treatment approaches the point at which the costs become a significant factor in the original investment or changes in investment, then industries will find ways to adopt or adapt technologies that will be less expensive than those that have been analyzed by the Commission.

One of the issues that confronts anyone examining this subject is the question of the variability of the effluent limitations, and you have already heard some discussion of this topic this morning. The Commission generally concluded that in the petroleum refining industry EPA's effluent limitations, as presently stated, will preclude 100% compliance by all industries in which the technology specified may have been installed on a uniform

basis. This then raises the question, must the investment be doubled in order to ensure stand-by equipment for every piece of the wastewater treatment process? Of course, it is in examining these kinds of questions that disputes about cost arise.

Now without getting into the detail, let me just go to some general conclusions, then I am going to talk about what is likely to happen based upon Joe Moore's prognostication, since the Commission has not yet adopted any recommendations and now there may be serious questions as to whether the Commission itself will be able to agree on what should be recommended to the Congress. First of all I think it came as something of a surprise to those of us, at least in the Commission staff, that there is a greater cost for reaching the 1977 requirements and a greater water quality improvement from reaching the 1977 requirements than is estimated for the 1983 requirements and water quality changes. Recognizing that part of the difference may be accounted for in the methodology for making projections, I think it nevertheless came as a surprise to us that the greater step -- according to our analyses -- the greater step is to achieve 1977, and the smaller step is that to incrementally go to the 1983 requirements provided, of course, you ignore for the moment the new source performance standards which must be met over the entire period from 1975 until 1983.

You heard mention earlier of the four parts per million minimum dissolved oxygen level. Remember that that particular level is a minimum during sustained low flow conditions. Obviously, if that level of dissolved oxygen persisted in some places in the country for long periods of time, it is conceivable the biological integrity of that body of water could be substantially impaired. There has been some argument by environmentalists that we should not have chosen four parts per million but should have chosen six, which I presume would then suggest that we could compromise on five as a logical measure for dissolved oxygen. I mention that because there is in the basis for the Commission's analyses, grounds for differences of view, and so the Commission's results, I am sure, will undergo considerable discussion in the months ahead.

The Commission has just concluded five public hearings, the last one of which was held in Washington on last Monday and Tuesday. The general conclusion is that there was substantial support for the general thrust of the staff draft report with a great deal of quarrel about individual pieces. Each industry has generally argued that its costs have been understated and therefore the total should rise; environmentalists and public interest groups have argued that there should be no relaxation in the deadlines in the statute.

You heard some discussion this morning about the elimination of the discharge of pollutants; the staff early decided to us the "net" definition, that is, there should be no net increase in the constituents of the water from the intake to the discharge. You must also appreciate that the staff was only allowed to examine the elimination of discharge of pollutants after a great deal of Commission disagreement; finally there was a trade-off. Those who had objected to looking at anything but 1983 were concerned because of the delay in the publicly-owned treatment-works construction grant program and they agreed that the Commission could look at the elimination of the discharge of pollutants provided the Commission would also look at progress being made toward the 1977 requirement, particularly for publicly-owned treatment-works. While they did take a look at EOD (elimination of discharge), the Commission staff's effort was limited when compared with

the effort that went into looking at the 1983 requirements. Obviously, in the elimination of discharge of pollutants, one of the major concerns is what do you do with the municipal plants -- the publicly-owned treatment-works -- and obviously the question of dissolved inorganic salts becomes critical if EOD is to apply to municipal facilities. Strange as it may sound, most people who talk about elimination of discharge want to talk about it just in terms of industrial wastes and not necessarily in terms of the total waste stream from all point sources. Also, it is obvious from the Commission studies, that in some cases, not only will the point source controls be obscured by the contribution from non-point sources even with the 1983 controls in effect, but also if all dischargers also went to the elimination of discharge, the results from this step would in some cases be obscured by the contribution from non-point sources. The real question is one of balance between the 1977 requirement, the 1983 requirements, the elimination of discharge and what must be done for non-point sources where they now appear to be the major source of pollutants to the nation's waters.

Some discussion about the ESQUIAC Committees matrix approach might be appropriate. I must emphasize something about the way this Commission functioned. The question was presented early, should the Commission examine some other scheme for achieving national water quality objectives other than that contained in Public Law 92-500? As you should gather from the listing of the membership of the Commission itself, a majority was involved in the formulation and adoption of Public Law 92-500 and therefore they had already concluded that the structure of 92-500 was the preferable one for achieving water quality goals. For example, there was the question, should the Commission examine the prior program of water quality standards to achieve water quality objectives? Of course, the Congress believes it rejected that approach to the national water pollution control program in the 1972 Act and, furthermore, most of them that speak on the question will say that they became convinced that water quality standards were not achieving national water quality objectives. In other words, they tend to believe that water quality standards is an approach to a national pollution control program has been discredited. I say they believe that whether or not the arguments upon which they believe it are valid.

Thus in looking at the program, the staff was to some degree restricted in what it could examine.

Generally speaking, the technology contractors and the economic impact analysis contractors were asked to look at five levels of pollutant control; (1) BPT, "best practicable control technology currently available," generally as defined by the Environmental Protection Agency; (2) BAT, "best available technology economically achievable," generally as defined by EPA; and (3) the " elimination of the discharge of pollutants," as used in the definition I gave you earlier. There were two other levels for which we attempted to get technological costs, one somewhere between BPT and BAT or below BPT and one between BAT and EOD, so that, theoretically, there should be an analysis of at least five levels in every contractor's report. As a practical matter, the contractors achieved various degrees of success in their examinations. Fortunately, in petroleum refining, because there was a very good data base though, actually six levels were analyzed, primarily because of the question of the -- as I understand it -- of the use of activated carbon and the possible costs that might be imposed upon the industry for that requirement.

There was an attempt to look at various levels of treatment. However, the staff did generally not look at schemes for either achieving effluent limitations or for achieving national water quality objectives outside the general structure of Public Law 92-500. Thus we did analyze the ESQUIAC approach.

With that, let me go to the issues as I see them at the moment. First of all, will there be recommendations? Despite the fact that the majority of the Commission comes from those who sponsored the legislation and presumably therefore endorsed section 315, there is some indication that those who feel the general thrust of the staff draft report is inconsistent with their present or preconceptions about Public Law 92-500 believe that perhaps it would be advisable for the Commission to make no recommendations. Without recommendations they then do not have to contend with any suggestion other than what is presently contained in 92-500. There is a question even now as to whether or not there will be recommendations, and it takes interesting forms. We have a great deal of difficulty finding an agreeable time at which the Commission can meet, because if meetings can be postponed sufficiently long and the appropriation can be exhausted, then obviously the Commission cannot come to recommendations within the appropriated funds. The second question is, will there be recommendations that mean anything? Obviously if you can't stop the recommendations, then maybe the thing to do is to keep there from being any meaningful recommendations. The next question is, will there be any action in 1976? There are those who believe that 92-500 was a product of a political year and the worst thing that could be done would be to amend it in a political year. Those who may disagree with the general thrust of the staff draft can then argue in 1977 that the Commission staff's data base was in 1974, or 1973; that a great deal of time has elapsed and therefore the Commission's work is out of date -- another year has passed and so all those facts and figures don't really mean anything and what we should do is postpone any consideration of any changes until late in 1977. Think for a moment what that does with the deadline of July 1, 1977. The argument is being made, for example, that after all, 1983 is seven years away, and there is plent of time for Congress to act. My reaction is if they are as slow in considering changes to 92-500 as they were in adopting it in the first place, Congress should have started last September in order to consider amendments to 92-500 if they are going to get them out of the congressional process before the 1983 deadline.

The next series of statements are strictly mine and you cannot attribute them to the Commission. Without casting aspersions, I am going to use the phrase that we have come to use as a result of our association with the National Academy of Sciences and National Academy of Engineering Advisory Committee. I will credit the phrase to Dr. "Reds" Wolman, a professor at Johns Hopkins University. The phrase is, "If I were running the zoo," this is the way we could express our opinions and get them credited to us individually. And so, "If I were running the zoo," I would argue that there should be a delay in the requirement of "best available technology economically achievable" for industrial and agricultural point source discharges and a delay in "best practicable waste treatment technology over the life of the works" for publicly-owned treatment-works beyond the July 1, 1983 deadline, (1) provided that in the interim, every effort is made adequately to control toxics, either substances or pollutants -- recognizing that a large number of toxics are being controlled in permit conditions; (2) provided that there is an aggressive

program for the adoption, modification and enforcement of water quality standards wherever achievement of the 1977 requirements will not achieve adequate levels of water quality; (3) provided that there are stringent new source performance standards imposed upon all new plants constructed in the future; and (4) provided that there is an evaluation of the progress that will have been achieved by substantial compliance with the 1977 requirements before the course of the national water pollution control program is irrevocably committed to BAT.

I wish to make clear that that does not include an abandonment of the technology based effluent limitations in Public Law 92-500. In my view, the achievement of either a state or a national program requires the "marrying" or the joining of technology-based standards with individual discharger permits. I would like to mention that that has not always been the federal view. I was Chairman of the Texas Water Quality Board at the time we were negotiating with old Federal Water Pollution Control Administration for water quality standards and I was publicly chastised in a meeting in Houston, Texas in June of 1967 because of the Texas permit system for individual dischargers. That system was called by my predecessor, Mr. Jim Quigley, the process by which one grants "permits to pollute." I couldn't wait for an opportunity,and eventually caught Jim in an audience at a meeting with the pulp and paper industry in New York City, to remind him of what can transpire in eight short years in terms of national viewpoint and suggested that just as the nation had decided to go with Texas in that case, they might find other ways to go with Texas in terms of the national water pollution control program. I do think there must be a technology base and permits.

I do have some misgivings about permits administered from the Federal level, and I think the experience with 92-500 has demonstrated some of the problems. You see, as a practical matter, the flexibility that everybody argues for the effluent limitations for industrial categories very probably exists in the individual permit conditions. Those in EPA who develop the effluent limitations don't like to admit that their associates in the permitting process may not necessarily be following the effluent limitations in every detail. We have collected enough evidence to indicate that the permits do not always agree with the effluent limitations and may not be uniform across the country.

Now, "If I were running the zoo," there should be case by case exceptions to the 1977 deadlines, not only for publicly-owned treatment-works because of the delay of Federal construction grant funds, but also for industries as well, because our evidence indicates that industry will have to spend substantial sums of money or at least there will have to be substantial cash flow in the next two years if they achieve BPT; therefore there should be a delay for industry as well as municipalities conditioned upon good faith efforts to attempt to meet the 1977 requirements. Parenthetically, you should appreciate, from the discussion already of legal issues, that in some cases, the challenge either to the effluent limitations or of the permits themselves will not be concluded by July 1, 1977. In fact, there may be some that will then have judicially-applied schedules for achieving the BPT requirement which could extend as long as five years beyond the conclusion of the litigation -- which could very well run into the 1983 deadline -- just for achieving the BPT requirement.

All right, "If I were running the zoo," I think there should be priorities for the construction grant categories for publicly-owned treatment-works with a concentration of the funding where it should be. The nation is not likely to produce the kind of money that is contemplated in our estimates of the costs for publicly-owned treatment-works.

Generally, I believe there should be a retention of the elimination of the discharge of pollutants as a goal, simply because there are some cases in which this is a technological possibility. I should emphasize, in my view, that in most of those cases in which EPA has used elimination of discharge as a part of the effluent limitation, it more often than not is an elimination of the discharge of water as well as pollutants -- which is to say, closed cycle systems. I see no serious problem with retention of the elimination of discharge as a goal, retention of the 1983 interim goal -- the so called "fishable-swimmable" test, and even retention of the ultimate goal of "restoring the physical, chemical and biological integrity of the nation's waters." I do have a great deal of difficulty with the word "restore," and probably the goal would have more meaning in the administrative sense if it were changed to read "achieve and maintain" the physical, chemical and biological integrity of the nation's waters.

There should be flexibility in the regulations and some delegation of authority to state and local units of government, but that delegation should be conditioned upon an acceptance of the general philosophy of Public Law 92-500, adequate state and local resources to achieve those provisions of the statute and a post audit of performance by the Environmental Protection Agency. For agriculture, there should be some special way of controlling non-point sources; there must be some consideration of the effect these have upon the water quality of the nation.

I would like to close by suggesting that we not overlook that 92-500 has built into it a series of cycles. The effluent limitations are subject to review -- conscious review -- at intervals of five years. The permits are issued for maximum periods of five years except in the case of new source performance standards where the term is ten years; but there is a cycle in 92-500, and I think it might be well for EPA to recognize that cycle and make the necessary corrections or adjustments that should be made in effluent limitations and permits in the second round. I predict that if there are not relaxations in the deadlines and some adjustment in some of the rigid regulations issued by EPA, the entire statute faces the prospect either of becoming administratively impossible -- which is to say it would collapse by virtue of inability to administer it, or -- despite what some will say -- I think the Act will face serious challenges in the Congress -- if not in the next two years, certainly the next four. The very structure of the Act could be seriously weakened in any such challenge.

DISCUSSION

Umesh Mathur: In the business of pursuing permits, I think EPA policy has been traditionally to encourage the states to take over as much of this function as possible, and obviously this gives the state the responsibility of defining in some manner the existing water quality within the boundaries of the state. Now I know that the State of Oklahoma has declared that all the waters in the state are "water-quality limited" as

defined in the Act. The State of Kansas which is just upstream from us on the Arkansas has declared that every water body in their state is "effluent-quality limited" and I have not seen any determination as to whether or not either of these two designations are in fact valid. And to me what this means is that those of us who are in the planning business really have no ideas as to what EPA feels is the right attitude to take. Certainly if you are doing regional long-term planning for facilities as well as non-point sources in industries and storm water run-off, and you begin on the basis that the whole of the State of Oklahoma if really filthy and the State of Kansas is extremely pure, then I feel like you get into the contradictions and will have interstate battles eventually even if all the regulations came out in the right manner with all the right numbers. Because what one state adds on to the water leaving its state will be cumulative to what the next state adds on and so when you get to Louisiana you will never be able to do anything with water quality because of all the incremental additions that have been made along the way.

Joe Moore: You have hit upon what is in the statute, a difficult dichotomy. The construction grant program state allocations are based upon needs. You have states in the Southwest and generally the South that do not reflect substantial needs measured against a secondary treatment yardstick. The reason you have the declarations that waters are water-quality limited is to get the needs increased. The State of Texas, by the way, has done the same thing; most of its waters are classified as water-quality limited. The reason is that if it didn't do that and set higher requirements for publicly-owned treatment-works construction -- if you didn't get the needs increased -- it wouldn't get a very large share in the construction grant program. As you can gather from the list of names I read, with Bentson in the senate and Wright in the house, both on Public Works Committees from Texas, the decrease in Texas construction grant funds wasn't very well received when this first allocation was made under 92-500. The question of water quality limited waters, I think has largely been ignored by EPA; no judgment has really been made as to whether or not the designation is valid. That is the reason I used the words "an aggressive program of water quality standards with approval, actual approval by EPA." To show you what has happened, in the President's budget message that just came out this week -- if we properly understand the first language we saw, the construction grant program will hereafter -- if that recommendation is adopted -- will hereafter be limited to the achievement of secondary treatment only. There will be no advantage to a state declaring its waters "water-quality limited". You see, I think the "water-quality limited" designation is to get more construction grant funds, but affects every other activity in which you are engaged. Actually, "if I were running the zoo," I would recommend that the construction grant program be terminated on a date certain about ten or fifteen years from now, after which there would be zero federal funding in order to force, not only the Agency but also the Congress and the States to sort out their priorities for publicly-owned treatment-works. You asked an earlier question about section 208; you will find tremendous reliance among theoreticians on the whole planning structure of Public Law 92-500. Now I have been involved in government a long time, and planning is the ideal solution to budgeteers. If you are planning, you don't have to act and so you can plan for ever and you don't have to spend large sums of money. The problem with the planning provision of Public Law 92-500 is they will be worthless unless there is a linkage between the planner and the actor. The way the thing is structured at the moment, I don't think the linkage exists.

To show you how far-sighted the budgeteers can get, they have now decided that they will withdraw all federal funding for planning after another year. We will then have plans that will be out of date within two years, because plans in my view are worthless unless they are constantly updated. I hope I am proved wrong, but I am afraid that there is a tremendous amount of dust being stirred up under the guise of 208 that may settle on everybody and there will be no pollution control when it is over with.

Milton Beychok: You talked about the fact that the report, the staff draft, did not in any place put the total cost for municipal industry and I agree it didn't. You also talked or gave the caveats about the ranges, and I agree with that. I would point out that we have not only the Public Law 92-500 but the Clean Air Act, because essentially the American public believes in clean water and clean air as it believes in motherhood, and because it believes someone else will pay for it. Despite all of the caveats, all of the ranges you might have to attach to it, the greatest service your Committee could do to the American public in this election year, is to let them know that it might cost them $150 a month.

Joe Moore: I appreciate that comment. One of the statements that was made in the course of the Washington hearings was that for the first time, there was the cost of a program stated in terms that average citizens, ordinary folks, should be able to understand; for example, even in this section, (by the way this chapter is available like this bound in just an 82 page document and we distributed many more of these than we did the more detailed report), it actually says what the price rises are expected to be. You will always know if we have understated them, you can expect the price rise is going to be greater than that. There are some shortages that are mentioned. The industries and geographical areas of the country that are likely to be most severely impacted, insofar as we were able to analyze them, are stated; and just to show you the kinds of things you can get into, the analysis shows that generally industry will be most adversely affected in the northeastern and central part of the country and that there could very well be a shift of industry to the South and Southeastern part of the country. In these kinds of things, even with all the caveats, I agree that there is some value in being able to state things so that people understand them.

"ECONOMIC IMPACT OF WASTEWATER EFFLUENT GUIDELINES FOR PETROLEUM REFINING"

Robert T. Denbo
Coordinator of Environmental Control, Exxon Company, U.S.A.
Baton Rouge Refinery, Baton Rouge, Louisiana

This paper deals with the economic impact of the guideline requirements to the petroleum refining industry. The major points to be covered include:

- a summary study on costs of wastewater improvement for which a status report was presented to an API Division of Refining meeting in the spring of 1975.
- a case study of the experience of a major refinery in investment cost to achieve 1977 guideline requirements.
- insight into perspective of relative impact of discharges in terms of organic loading from the nation's petroleum refineries compared to discharges from other sources.
- suggestions for corrections to Public Law 92-500, the Federal Water Pollution Control Act amendments of 1972, will be presented.

The Environmental Protection Agency has issued the wastewater guidelines for Best Practicable Control Technology Currently Available (BPCTCA) to be achieved by U.S. petroleum refining by July 1, 1977. Based on a study sponsored by the American Petroleum Institute and completed in mid-1973, the petroleum refining industry will have invested approximately $1 billion to meet the requirements of BPCTCA. To arrive at this figure, the contractor made estimates on approximately 100 refineries and adjusted this investment to cover the entire 247 petroleum refineries in the country. Information available on the status of wastewater treatment trains as of 1972 was used and equipment was added to upgrade the treating sequences to include facilities estimated as being required to meet BPCTCA. The target treating sequence included facilities shown in Table 1. It is apparent that this treating sequence incorporates the latest in today's technology.

This paper will not discuss the merits and demerits of the most recent guidelines for petroleum refining. This is covered in detail in other places. Suffice it to say they are tough. Some refineries will have real difficulty in meeting the requirements, even with the target treating train, if they can meet them at all. Also, the daily variability requirements for some parameters are quite restrictive. The assumption of the cost study is only that the investment provides the industry with the BPCTCA treating sequence and not that guidelines are met.

By now many refineries are far enough along with their wastewater treatment programs to provide accurate investment information based on funds already expended or appropriated. It is of interest to consider the investment being made by the current largest U.S. refinery -- the Baton Rouge Refinery of Exxon, Company, U.S.A. -- to achieve BPCTCA. Total investment at this location since 1967, will amount to approximately $61,000,000. The breakdown of the investment is shown in Table 2. For this particular refinery the configuration of the sewer system made it less attractive to segregate clean, once-through cooling water than to eliminate it by conversion to a recirculating system employing cooling towers. This conversion cost $16,000,000.

In-plant source corrections to reduce wastewater flow and pollutant load cost $2,000,000.

Because of high annual rainfall, stormwater segregation and detention are quite expensive at this location. The cost of these facilities amounts to approximately $7,000,000.

The expansion of the sour water stripping facilities cost $1,500,000.

Site preparation was exceptionally costly, requiring expenditure of $7,000,000. Because of the shortage of adequate sites, it was necessary to reclaim 15 acres previously used for storing oily silt removed in past years from the separator system when silty river water was used for once-through cooling.

The $27,500,000 for the Wastewater Treatment Plant includes -- in addition to a two-train, activated sludge unit with aeration basins to provide 18-hour detention -- sewer segregation, a corrugated plate interceptor, equalization, dissolved air flotation, sludge dewatering and disposal and the associated utilities required.

The Baton Rouge Refinery came onstream some 66 years ago. These costs illustrate that solutions to retrofitting problems for an older refinery are expensive and are not of a nature that is readily anticipated in a generalized study approach such as the API study. The investment at the Baton Rouge Refinery to meet BPCTCA amounts to about $133,000 per 1,000 barrels of daily crude run, or almost twice the average for the entire petroleum industry in the API study. This comparison does not contradict the API study, but it does suggest that the API costs are not too high.

It has been established that the dollar costs for BPCTCA for petroleum refining are significant. Let's examine what we are getting for this money. This can be done in terms of investment per unit of cleanup. The $1 billion to go to BPCTCA reduces BOD_5 by some 357,000 pounds per day for the entire industry. This amounts to an investment of $2,800 per pound of BOD_5 removed each day.

At this point I would like to comment briefly on certain economic facts. When considering the costs of improvement of water quality, let's not forget who pays these costs. In the cases of municipal facilities, it is clear to us that we do -- as taxpayers. It is not so clear that we also pay the costs to industry since these costs are passed on as higher product prices to us as consumers. The essential difference is that it is usually easier to require industry to spend money than it is to increase taxes. Costs as higher prices don't have to be voted upon. The most important consideration in developing regulations should be whether the citizen is getting his money's worth.

It now appears that by the end of 1977, the largest portion of the U.S. petroleum refineries will have installed facilities to meet BPCTCA. If we decide to proceed with the 1983 requirements of Best Available Treatment (BAT) for petroleum refining, we will then be going after reducing BOD_5 at a cost per daily pound 3-5 times that of a daily pound of BOD_5 reduced by installing facilities to achieve BPT. And we will achieve a reduction of only about 126,000 pounds per day of BOD_5.

For perspective on the impact of petroleum refining, let's look at the total of all other sources - industrial and municipal. On this basis, the BOD_5 from total petroleum refining amounts to about 1% of the total. While it is true that BOD_5 may not be the best measure of pollutant load, it was the only parameter for which estimates of the other categories were available. One would anticipate that the relative amounts of total organic pollutants are roughly in the same proportion as BOD_5.

Some of my numbers are rough and can be verified when final data become available from studies by EPA. The figures are probably good enough to provide perspective. If all of the petroleum refiners in the U.S. would suddenly disappear and we could get the required energy from sunlight, the overall impact on the nation's waterways would be almost indiscernible.

One other comment on the relative impact of petroleum refining. None of the comparisons have included the impacts of pollutants in runoff from feed lots, agricultural runoffs or from land disposal operations. It becomes more obvious what constitutes the greatest potential for cleanup.

SUGGESTIONS FOR MID-COURSE CORRECTIONS TO PUBLIC LAW 92-500

Now for some suggestions for mid-course corrections to Public Law 92-500.

It is generally believed that all responsible citizens agree with the objective of environmental legislation if it is to protect human health and well-being. It appears that there is much that is right with Public Law 92-500 in working toward this end. However, it is not clear that technology-based guidelines uniformly applied are the right answer for correcting the pollution problems of the nation's waterways. Suggestions are in Table 3.

The assessment of pollutants in drinking water known to affect human health should be completed, and then high priority should be set for removing the known problem pollutants.

In order to avoid wasting of our technical expertise, natural resources and money, what is done after this first step should be reevaluated. For each contemplated regulation questions like the following should be answered:

- For example, does the impact of a water regulation on land destroy the net benefit anticipated by the author?
- Does the regulation require consumption of excessive energy?
- Does the manufacture of equipment necessary to implement the regulation cause excessive pollution somewhere else?
- Do the effects of inflation, balance of payments and possible infringements on other social goals destroy the desired impact?
- Are we taking control steps in priority order? We should insist on this since we are paying the bill.

These questions should be adequately answered before proceeding in our control program. This is a business-like approach. We have the time, the expertise and the

commitment to do this and do it correctly. Improvements from BPCTCA will have bought the time for us. We can't afford to take the chance of wasting the very natural resources we are trying to conserve.

DISCUSSION

Shariff Khan: As you know, the refinery industry has generally installed electrostatic collectors to control the FCC effluents whereas Exxon is the only company which has installed a wet-gas scrubber. Would you be able to outline the economic and the technological benefits plus any comment on the legal aspects?

R. T. Denbo: Yes. We are discussing control of FCC particulate emissions to the atmosphere. Since it is wet-gas scrubbing, then I guess it would qualify as a water topic. On that basis, I will consider this a just question and we will go ahead with it. Let me mention the reason for the development in the first place. An engineer who had been an expert in the catalytic cracking area for some time was not satisfied with the previous experience with electrostatic precipitators. He felt there must be a better way to achieve the Clean Air Act requirements that were implemented by the States. Further, some States such as New Jersey required the removal of so-called condensible particulates in early regulations for cat cracking emissions. Steel and some other industries had employed wet gas scrubbing successfully for years and the application was considered for cat cracking. The Baytown and Baton Rouge refineries of Exxon Company, U.S.A. participated in pilot plant work that indicated that wet-gas scrubbing had several advantages over electrostatic precipitators since you could remove SO_2 and condensibles in this system. So, consequently an economic comparison was made that indicated that investment and an operating cost were about breakeven with electrostatic precipitators. Consequently, the major refineries in Exxon have decided to install these facilities.

BIOGRAPHY

Robert T. (Bob) Denbo is the coordinator of environmental control at Exxon Company, U.S.A. Baton Rouge Refinery. In this capacity, he is responsible for development of long-range goals for air and water conservation and solid waste disposal problems. Mr. Denbo received a B.S. degree in chemistry from Louisiana State University in 1948, finishing the work for his degree after spending four years in military service during World War II. Mr. Denbo has been with Exxon in Baton Rouge since 1948. He is currently chairman of an Exxon committee concerned with environmental control for all Exxon refineries. He is vice-chairman of the API Committee on Refinery Environmental Control, a member of the Subcommittee of the API Division of Environmental Affairs Water Quality Committee and other industry committees.

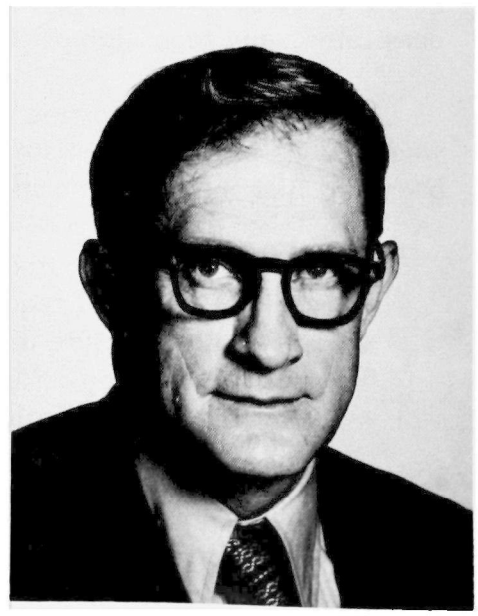


TABLE 1

- efficient in-plant water use practices
- segregated storm runoff and detention
- sour water stripping
- gravity separation
- equalization
- added removal of suspended oil and solids by either dissolved air flotation, filtration or coagulation
- activated sludge biological treatment
- postfiltration
- facilities for dewatering oily and biological sludges and sludge disposal

TABLE 2 "INVESTMENT REQUIRED TO ACHIEVE BPCTCA AT THE EXXON COMPANY, U.S.A., BATON ROUGE REFINERY"

Project	Purpose	Investment $
River Water Replacement Project	Eliminate the use of once-through cooling water to reduce effluent rate by about 90%	16,000,000
In-Plant Waste Load Reduction	To further reduce flow and abate pollution at the source	2,000,000
Storm Water Handling	Segregate, detain and treat storm water	7,000,000
Sour Water Stripper	Remove ammonia and H_2S from effluent	1,500,000
Reclamation of Old Oily Silt Storage Pond by Sand-Lime Stabilization	Develop site for Wastewater Treatment Plant	7,000,000
Wastewater Treatment Plant (Activated Sludge)	Provide treatment to achieve BPCTCA	27,500,000
	Total	61,000,000

TABLE 3 "SUGGESTED MID-COURSE CORRECTIONS TO PUBLIC LAW 92-500"

(Steps assume BPCTCA is implemented as currently scheduled in mid-1977.)

Complete the assessment of pollutants known to affect human health.

- Determine sources and abate.

At that point provide an adequate period for reassessment of any additional steps.

- For each new, contemplated regulation evaluate:

    the impacts of that regulation on other areas of the environment -- air; water; land

    energy consumption

    use of natural resources to install the control facility

    impacts in other segments of the economy

Impose only those regulations that are determined to provide net benefits that justify the net costs to society, with special consideration for the specified uses and the assimilative capacity of each waterway.

SESSION II

"PERMITS FOR THE POINT-SOURCE CATEGORY"

Chairman

Jerry T. Thornhill

Regional Representative
Office of Program Integration
U. S. EPA, Region VI, Dallas, Texas

Speakers

Carl J. Schafer

"The Environmental Protection Agency's Permit System

Robert F. Silvus

"Current Approach to Refinery Permits"

William K. Lorenz

"Petroleum Industry Experience With The NPDES Permit System"

Harless R. Benthul

"The Enforcement of Permits"

F. T. Weiss

"Measuring the Parameters Specified in Permits"

BIOGRAPHY Jerry T. Thornhill

Jerry T. Thornhill holds a B.S. in Geology from the University of Texas at Austin. Mr. Thornhill has been with the EPA in Dallas, Texas since 1969. During this time he has served as: - Contingency Plan Officer; Chief, Federal Activities Branch; Chief, Oil & Hazardous Substances Branch; and Deputy and Acting Director, Hazardous Materials Control Division - before assuming his present position of Regional Representative, Office of Program Integration in 1974. Mr. Thornhill has also served with the Texas Water Development Board as Water Quality Specialist and as Assistant Director, Ground Water Division; the Texas Water Commission; and the Texas Board of Water Engineers.

THE ENVIRONMENTAL PROTECTION AGENCY'S PERMIT SYSTEM

Carl J. Schafer, Acting Director
Permits Division
Office of Water Enforcement
U. S. Environmental Protection Agency
Washington, D. C.

Created by the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500), the National Pollutant Discharge Elimination System (NPDES) replaces and improves upon the old permit system under the 1899 Refuse Act. It is part of the comprehensive effort set in motion by the 1972 law to prevent, reduce, and eliminate water pollution.

After listening to all the excellent speakers this morning, I have to tell you they make up a hard act to follow. I thought, too, of all sorts of clever opening remarks as I sat in the audience but as I stand here, they've either vanished or have been used by somebody else. I would just like to say that it is a pleasure to be here, and it is a special pleasure to renew acquaintances with many of you with whom I have worked in years past in setting up some of the initial considerations for permit limitations before there were guidelines. The Permit Program is established under Section 402 of the Federal Water Pollution Control Act as amended in 1972 and constitutes one cornerstone of a comprehensive program to insure that the intent of the Act is complied with by all point source dischargers to the waters of the United States. Under the Act, National Pollutant Discharge Elimination System (NPDES) permits specify effluent limitations and schedules of achievement which involved both compliance monitoring requirements on the part of the discharger and compliance monitoring on the part of the regulatory agency, be it State or Federal. Obviously, the purpose of all NPDES compliance monitoring is to assess whether or not the limitations are being met and, if not, whether enforcement actions are necessary.

The Program is designed for ultimate delegation to each State, and State participation with and without delegation has been most gratifying. While the States retain primary responsibility to combat water pollution, they do so within the framework of the Federal law. Wherever States encounter difficulties in administrating the NPDES, the Environmental Protection Agency may intervene to assist in resolving the problems, be they legal, technical, or administrative. Currently, a total of 27 States manage their own NPDES programs, all of which are monitored constantly by Federal EPA Water Enforcement personnel. The Environmental Protection Agency is a highly decentralized effort in itself as it delegates authority to its ten regional offices, each of which exercise a high degree of autonomy.

I'd like to address today the actual substance and content of NPDES permits. By and large, you can break an NPDES permit down into four general components: (1) the limitations; (2) the compliance schedule; (3) the self-monitoring and reporting requirements; and (4) the boiler plate. Limitations, of course, are based upon effluent guidelines, or

water quality standards in their absence, under Section 402 (a) (1) of the Act. The individual determination by EPA for a particular plant regarding what constitutes Best Practicable Treatment (BPT) is generally written in pounds, depending upon production levels at the time the limitations are determined. Concentration limits are also specified depending upon various other requirements. Compliance schedules cite specific steps to achieve compliance with the Act by July 1, 1977, as well as reports of progress on the achievement of each step and, in particular, reports of failure to make progress.

Each of the requirements in an NPDES permit, whether it be interim or final, is legally enforceable. Each permit is for a fixed period of time not to exceed five years and application for renewal must be made 180 days prior to the expiration date. Most of the major permits were issued by December 31, 1974, and we therefore expect the next round of permit issuances to take place during 1979 and 1980.

I would like to give you a little bit of insight into where we stand right now, what the status of the program is, and what is going on. There has been a great deal of interest expressed regarding the Seventh Circuit Court decision by Judge Flannery on feedlots and I don't think we know yet exactly how many new point source discharges this is going to add to the list, but for the time being at least - - that not withstanding- -we have a total of 59,048 identified dischargers requiring permits. Permits have been issued for 43,420 of that number, which is a 74% issuance rate. The breakdown on those figures indicates that 16,000 municipal permits have been issued out of 19,000 dischargers identified and in the non-municipal field, which includes industrial, agricultural and Federal facilities, we have issued just under 26,000 permits out of the approximately 40,000 dischargers that have been identified.

Out of the 59,000 permits to be issued, of which EPA has issued 43,000, you might be interested in what our adjudicatory hearing experience has been. To date there have been 1,863 adjudicatory hearings requested. In other words, only 3 percent of all the permits issued have been contested. Of those adjudicatory hearings requested, 1,105 are still pending. A look at those pending requests reveals that it is not necessarily the major discharges that give us the most grief, because by and large we will have devoted more time and energy and thought to the limitations going into those permits. The minor dischargers, on the other hand, pose some very difficult problems in peripheral areas which must be resolved before a reasonable permit can be issued. Such is the case for petroleum bulk terminals, two or three other sub-categories, some water treatment plants and other classes of permits which make up a good portion of the 1,105 adjudicatory hearing requests yet to be resolved. It is also interesting to note that only ten of the 750 adjudicatory hearings that have been resolved required the use of all the formal adjudicatory proceedings available under the law. By far, the majority of all adjudicatory hearings requested are settled prior to trial.

Insofar as the petroleum refining industry is concerned, most - - if not all - - of the approximately 250 petroleum refineries in the nation have now been issued NPDES permits. Of those, only about 20 are currently pending under the adjudicatory hearing request review process, having been contested on some requirement or condition of the permit. Typical issues in the adjudication of petroleum refining permits include deep well injection

controls, storm water runoff treatment, supply-water silt disposal and other miscellaneous items.

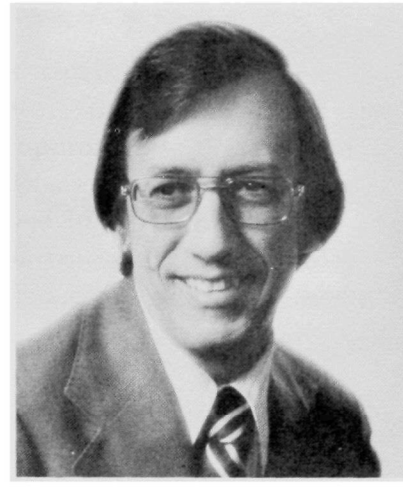
Overall, the NPDES program has proven quite workable in the petroleum refining industry. The basic requirements for Best Practicable Treatment of process water do not seem to have constituted a major source of disagreement between the industry and EPA. Earlier statements provided at this Forum give further proof that the industry as a whole is well on its way to achieving the installation of the equipment necessary to meet Best Practicable Treatment.

To sum up, NPDES requirements were designed to make sure that discharges of pollutants into the nation's waters are subject to uniform minimum controls and that the restrictions, terms, and conditions of a permit are substantially the same whether issued by EPA or a State. In brief, water pollution is a national problem, and the permit system is part of a national program to combat that problem.

I will be happy to take any questions at this time.

BIOGRAPHY

Mr. Schafer received his degree in Chemical Engineeeing from Georgia Institute of Technology, and has extensive experience in industrial production and development with Shell Chemical Company (Petrochemicals, Houston, Texas) and Celanese Figers Company (cellulose fibers, Cumberland, Maryland). He joined EPA in January 1972, and is currently Chief of the Permits Assistance Branch, Office of Water Enforcement, in Washington, D. C. As such, he is responsible for quality control,technical assistance and policy coordination and policy coordination for EPA regions and states writing National Pollutant Discharge Elimination System permits for industrial point source discharges.



"CURRENT APPROACH TO REFINERY PERMITS"

Robert F. Silvus
Texas Water Quality Board, Austin, Texas

HISTORY

Much of Texas is water short, and water is a valuable resource which has always needed protection. The first official recognition in Texas came in 1860, when a law was passed to make water pollution illegal. But, it wasn't until the 1930's that the degree of allowable pollution was quantified by a State Health Department requirement of secondary treatment of sewage effluent from cities. From that time until 1967, the State Health Department was responsible for water pollution control in Texas. The Texas Water Pollution Control Board functioned (as a part of the Health Department) from 1961 to 1967 and initiated a permit system for both municipalities and industries. The Texas Water Quality Board was established by the legislature as an independent agency in 1967. It presently performs the administration of the Texas Water Quality Act and the Solid Waste Act and has responsibilities under the Subsurface Disposal Act. The Board is composed of three public members and representatives from four other State agencies with interest in water.

Most State permits were written 10-15 years ago and revised since then as water quality problems were recognized, plant expansions occurred, etc. The initial efforts were more of a cataloging operation to denote the location and approximate quality and quantity of discharges. State law requires control of effluent volume as well as average and instantaneous quality. A self-reporting system was established in 1970, and computerized data for each outfall of each discharger is available for review. Traditionally, the State has relied on treatability studies to set limitations for industrial permits with the overall goal of "good secondary treatment".

SINCE EPA

There has been quite an impact on the State permit system since the implementation of the NPDES permit program beginning in 1972. The nationwide guidelines adopted by EPA provide another and important means to check industrial permits for reasonableness of effluent requirements and equity among permit holders. The State permit format has been revised to resemble the NPDES format, and a working agreement established with the EPA whereby we write most NPDES permits for the EPA for Texas dischargers. Currently, we consider (1) waste load evaluations and allocations for the various stream segments, (2) stream standards, (3) treatability studies, (4) self-report data, (5) the existing State permit and (6) guidelines in considering a permit revision. It should be emphasized that before the guidelines were issued most refiners in Texas had either already built or contracted for wastewater treatment plants which can now meet or exceed guidelines. In fact, six of the twelve exemplary refineries used to develop the guidelines are located in Texas. These are Coastal States and Champlin at Corpus Christi, Union Oil at Beaumont, Marathon at Texas City, Shell at Deer Park (near Houston) and Phillips at Sweeney. Most treatment systems include oil-water separators, dissolved air flotation units, equalization basins, biological treatment units, clarifiers, and a sludge handling system.

Having taken care of the major treatment problems during the late 1960's and early 1970's, most Texas refiners can concentrate their efforts on the remaining problems of storm water handling and hazardous metals control and should be able to meet guidelines in 1977 without additional major expenditures. However, a few old refineries do not yet have adequate treatment facilities and will have difficulty meeting even the 1977 guidelines. It is almost impossible to carry out a large wastewater handling and treatment program over a period of years without the continuous commitment of corporate management to the program. The State strongly advocates a management policy which encourages timely investments in concrete and steel rather than in a good staff of attorneys.

PERMIT PREPARATION

Now that you know how we arrived at our current 1976 state of affairs, you would probably like to know what is involved in the preparation of a waste discharge permit. The Texas Water Quality Board has divided the various water bodies in the State into segments and each segment is regularly monitored. A set of stream standards was adopted in 1967 and subsequently revised several times. Those stream segments which have problems are designated "Water Quality Segments", and some special limitations designed to correct the problem are placed on all dischargers to the segment. In the case of the Houston Ship Channel, a computer model was developed, and a waste load allocation expressed in pounds of BOD_5 and ammonia-nitrogen was established by the State for each discharger (including municipalities). The EPA reviewed and concurred with these limitations. In addition, the State has issued several special statewide orders which affect many dischargers. Chief among these is the Board Order governing the discharge of hazardous metals. The latest revision of this order is stringent and may require special treatment to remove or replace catalysts or cooling water additives which were previously discharged. When an engineer first begins to draft a permit, he looks at the stream standards, waste load allocations and special orders to determine their applicability.

A second question for existing dischargers concerns their current performance. The Texas Water Quality Board has 12 district offices around the State staffed by about 100 employees. By reading their inspection reports and reviewing the self-reporting data from the permittee, the engineer can answer questions about current performance. What he does not know is whether refinery operations were normal and whether the refinery was operating near its capacity. This information along with unit capacities, etc. is usually obtained by direct contact with the company.

There is an existing State permit for each refinery. Most State permits were written to include concentration limitations and dry weather flow. The engineer will calculate the limitations (in pounds) which are established in the existing State permit for later comparison with guideline calculations. The guideline numbers will be used in the new permit unless the existing State permit requires something more restrictive.

From the NPDES or Corps of Engineers application, we would attempt to determine the unit capacities so that size factors and process configuration factors can be calculated. Frequently, additional information from the company is required. A storm water

management plan is normally a very important ingredient in every permit, and a ballast water treatment system is important in many cases. Storm water runoff can be estimated from a plot plan of the refinery and historical rainfall data. A better source of data is historical in-plant concentration and volume measurements on storm sewers. Historical ballast water receipts can be used to estimate the ballast water contribution to the permit. Ballast water is being treated successfully in combination with other refinery wastewaters.

Normally, storm water data is the most difficult item to quantify in a permit. Since storm water runoff is a problem common to all refiners, some further elaboration of the type of recommendations which we make is in order. First, we recommend that process and storm water sewers be separate. Second, we recommend that all storage tanks be diked and that tanks not be drained into the diked area; draining water from tanks into the firewall area has been common practice at some locations. Third, we recommend that all process areas be curbed and provided with drains so that contaminated storm water will not be discharged without treatment. It has been the practice in many plants for operators to rinse sample bottles and pour the contents down the drains or on the slab and to drain equipment which is opened for maintenance on the slab. If it rains before this material is flushed to a treatment unit, the storm water will be contaminated. Our fourth recommendation is that all contaminated storm water be captured for eventual treatment and that clean storm water be discharged directly. The permit usually defines clean storm water in terms of (1) pH, (2) TOC and (3) Oil and Grease content, and this storm water can be released without treatment. As mentioned earlier, historical volume and quality measurements provide the best data on the magnitude of the storm water treatment problem. Impoundment of the contaminated runoff is the most common approach. This allows the collected water to be treated over a period of time; this reduces the hydraulic loading of the treatment plant which, in turn, reduces the investment.

Impoundment is not always practical because of the geography of the plant or availability of land. In such cases, exceptionally good housekeeping practices are necessary, and the additional investment for an oversized treatment plant may also be necessary. A final recommendation is that runoff from non-point sources including those areas held for future development be diverted away from potentially contaminated areas through an adequate system of dikes and ditches. In many cases, efforts expended in preventing the contamination of rainfall runoff can greatly reduce the magnitude of the problem.

Another common problem involves the compliance with chromium limitations. Limitations are usually based on the volume of chromium-treated cooling water discharged and not on the total plant effluent. Since not every refiner has had success in substituting other water treatment chemicals for chromium, some plan to continue to use chromium but to treat the cooling water blowdown prior to discharge. There are three processes under evaluation to achieve removal. These are (1) chemical precipitation and clarification, (2) ion exchange, and (3) electrolysis. Chemical precipitation with clarification is the most proven process but each has its advantages. Each of the processes will be installed at some manufacturing plant in Texas before July 1, 1977, so we will soon learn how well they perform in routine service. It is very difficult for a company to meet the required chromium levels if the discharges are not confined to a few large volume streams. For this reason, the engineer who prepares the permit will consider each plant situation individually.

Having reviewed the stream standards, waste load allocation, Board orders, operating history, NPDES applications and other company input, and the existing State permit, the engineer will simply compare the calculated limitations using the existing State permit or allocation with calculations using the guidelines and pick the more stringent limitations for the July 1, 1977 requirements. Limitations are normally placed on BOD_5, TSS, COD, oil and grease, phenol, ammonia-nitrogen, sulfides, chromium and pH. Volume limitations and requirements on other hazardous metals, temperatures, and occasionally on chlorides and sulfates are added. Interim limitations (until July 1, 1977) are usually based on self-report data, field reports, current State permit limitations and federal applications. Limitations for each time period on individual samples and on volume are also placed in the State permit. At this point, it is normal to discuss the proposed permit with the company to determine the accuracy of assumptions, applicability of particular guidelines to the refinery, currentness of the data, time required for compliance, and approved expansions or other major changes to take place during the five year period covered by the permit. Once all points have been explored, the State permit is set for public hearing and a similar NPDES permit is sent to the EPA for review. The two permits then proceed through the various public notice and hearing procedures where they may be modified as a result of new evidence introduced by the public or other governmental agency. Finally the permits are adopted by the Texas Water Quality Board and the EPA. With good communication between EPA and the State during the public hearing procedures, the permits will contain the same limitations and the same sampling and reporting requirements.

These procedures have been completed for most refineries in Texas, and 1977 objectives are set. There remain questions concerning 1983 limitations. It is assumed that final filtration will be a standard treatment step if the 1983 guidelines remain unchanged. Additional biological treatment or physical-chemical treatment or some combination will also be required. The technology is available, and considering the excellent progress which most refiners have made in the last decade and the knowledge accumulated during this period, I feel that the major problems in meeting the 1983 guidelines will be financial and not technical.

ENFORCEMENT

State enforcement action is initiated primarily by the district offices around the State. In addition to regular inspections, all dates in permit compliance schedules are entered into a computerized data system which is regularly checked. It is an understatement to say that it is more difficult to achieve a continuous quality level with biological treatment units than with other refinery unit operations. Recognizing this fact, the State has not normally pursued enforcement actions for isolated violations of permits caused by weather changes, etc. However, where repeated violations occur, enforcement action will be taken. This frequently involves an enforcement hearing and subsequent recommendations to the Texas Water Quality Board for remedial action. Flagrant violations are normally referred to the Attorney General for prosecution either directly or following an enforcement hearing. It remains the intent of the State to enforce State permit requirements.

SUMMARY

A partial picture of the background and current procedures for the development of permits for petroleum refineries has been presented. Most State permits were originally issued 10-15 years ago and revised as necessary. Traditionally, the State of Texas has relied on treatability studies to set limitations with the overall goal of "good secondary treatment". Following the establishment of EPA, a working agreement was reached whereby the State drafts most NpDES permits for Texas dischargers along with a parallel State permit. Current permits are derived by combining information from waste load evaluations, self-report data, existing State permits, NPDES applications and guidelines and company input. Most refiners already have secondary treatment systems which will meet or exceed 1977 NPDES requirements. In general, storm water handling and chromium and zinc removal constitute the problems to be solved by 1977.

BIOGRAPHY



Robert F. Silvus is Branch Chief of the Industrial Permits Branch, Central Operations Division, Texas Water Quality Board. He received a B. S. degree in Chemical Engineering and an MBA degree from the University of Texas at Austin. He is a professional engineer registered in the State of Texas. He had 15 years of industrial experience in Research and Development with Ehtyl Corporation and Jefferson Chemical Co., Inc. before joining the Texas Water Quality Board.

PETROLEUM INDUSTRY EXPERIENCE WITH THE NPDES PERMIT SYSTEM

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ABSTRACT

Sun Oil reviews its experiences with refinery NPDES permits. This discussion emphasizes the special problems encountered with water quality limited streams, effluent sampling, laboratory analysis, and self-reporting requirements. Recommendations are made that may simplify negotiation and compliance with future NPDES permits.

INTRODUCTION

Most of the 250 U.S. petroleum refineries have now been issued final National Pollutant Discharge Elimination System (NPDES) permits. Compliance and enforcement are now actively underway. Over the last three years, the refining industry has had many problems with the NPDES permit system and has hopefully learned many important lessons.

We are speaking with you this afternoon primarily on the basis of Sun Oil Company's experience at our six domestic refineries. Sun has accepted final NPDES permits at all six refineries. Our permits are based almost entirely on the EPA petroleum refining effluent guidelines with certain more stringent conditions based on water quality-related effluent standards.

We are planning to achieve our 1977 permit limitations through the use of conventional treatment technology including sand filtration. At this time, we are not certain that this technology can achieve the daily 24-hour maximum effluent limitations for all parameters. Sun's largest refinery at Marcus Hook, Pennsylvania will join a regional treatment plant in early 1977. We believe this experience is typical of the problems encountered by most U.S. refiners. Many of these experiences are also relevant to the marketing and production phases of the oil industry. The purpose of this paper is to discuss our most significant NPDES problems and to make some recommendations that may simplify negotiation and compliance with future NPDES permits.

Several of the more vexing NPDES problems occur throughout all the stages of the refinery NPDES permit process. For clarity, we will discuss these issues on a functional basis, rather than chronologically. Table 1 lists the three subject headings we feel are worthy of special discussion at this conference. We have excluded reference to the EPA petroleum refining effluent guidelines, and will limit our discussion to the basic NPDES problems which are somewhat independent of any specific set of effluent regulations. Further, we assume our audience has some experience with the NPDES permit system so

that we will not dwell on the procedural and legal aspects of negotiating and appealing NPDES permits.

1. Water Quality Limited Streams

According to the Engineering-Science Report for the National Commission on Water Quality, 68 refineries, having a cumulative crude capacity of 6,800,000 bbl/day, now discharge to water quality-limited streams (Table 2). Thus, over one-third of U.S. refining capacity is partially, if not totally, controlled by water quality standards, rather than the EPA technology-based effluent standards.

The impact of the water quality-related effluent limitations can range anywhere from Best Practicable Control Technology Currently Available (BPCTCA) limitations to zero discharge. Individual states are responsible for classifying specific river segments as effluent quality-limited or water quality-limited on the basis of EPA-approved state water quality standards.

For a refinery discharging into a water quality-limited segment, permit negotiations can be a complex and frustrating experience (Table 3).

First, it is necessary to establish the water quality standards upon which the effluent limits are based. We have found that these standards are not always available in specific form in the legally-promulgated state regulations. In some states, the regulations are narrative with the specification of numerical water quality standards up to the state agency. In the latter case, it is very important to determine if the internal state agency decisions have been open to public comment according to the relevant Administrative Procedures Act.

The states have employed a variety of methods for calculating the total allowable effluent load that will achieve water quality standards on a particular stream. These techniques range from sophisticated computer models to mere educated guesses. No individual method is satisfactory for all circumstances. A major stumbling block appears to be the unavailability of historical data. The important fact is that the individual company must analyze the state methods in sufficient detail to determine if there is an adequate basis for establishing its effluent standards.

The next step is to allocate to all individual dischargers on the stream segment a portion of the total allowable segment load determined by the mathematical model or educated guesswork. This process opens up a complex set of economic equity problems. Mathematical models are available to set load allocations in a variety of ways. As you all know, it is very difficult to quantify the relative environmental impacts of a variety of different effluents to an individual stream segment; thus, it is almost impossible to objectively determine individual abatement schedules. Nevertheless, these decisions are being made every day and all dischargers, municipal and industrial, should play an active role in setting load allocations.

Water quality-limited river segments will also be classified for the 1983 water quality standards. We can expect that our next round of NPDES permits will also include a significant number of refineries discharging to these river segments.

2. Effluent Sampling and Laboratory Analysis

One of the most significant changes brought by the NPDES system is the imposition of uniform requirements for measuring wastewater flows and the obtaining and analyzing of representative effluent samples (Table 4). Prior to PL 92-500, all Sun refineries had evolved their own monitoring programs based on local and state regulations. However, some waste streams like tank farm storm runoff were never measured or sampled before the 1972 Federal Water Act.

As you know, in most cases the interim and final refinery effluent limitations are based on mass-weight (lb/day) discharge rates. This requires that the flow measurements, sampling techniques and analytical methods be of comparable precision and accuracy. It makes no sense, whatsoever, to monitor a multi-million dollar treatment facility with trained chemists using sophisticated analytical instruments if the flow measurements are only within $\pm$ 20% of the real flow rate.

Inadequate historical flow data is one of the main reasons that our refineries have had some non-compliance incidences with interim permit conditions. Such problems stem from both the lack of the quality and quantity of historical flow data. Hopefully, these problems will not reoccur since we are now establishing flow measurement systems that should provide an adequate amount of accurate and precise flow data. For example, our Marcus Hook, Pennsylvania refinery will join a large municipal-industrial regional treatment system that requires us to install a flow meter accurate to within $\pm$ 1%.

Prior to PL92-500, our refinery practices were about evenly split between grab and composite samples. We are now running more composite samples as required by NPDES permits. However, we expect to continue taking grab samples on segregated storm runoff. In developing our specifications on sampling methods and sample preservation, we have relied on the guidance of the EPA technology transfer handbook entitled, "Monitoring Industrial Wastewater." This reference is quite complete and is an excellent source of information on sampling equipment and flow measuring devices.

Laboratory testing is rapidly becoming the most critical part of the NPDES compliance monitoring system.

As an example, we are all spending a lot of money to build sophisticated treatment systems. We measure our performance by laboratory results. But what does it all mean if another laboratory analyzes an identical sample and obtains results five or ten times higher than our own? This is a very significant problem

if the second laboratory happens to be an EPA laboratory and the samples are being analyzed as part of an EPA annual site inspection.

We have only begun to look into the areas of analytical precision, analytical accuracy, and interlaboratory variability. Our fundamental interest is in producing reliable information that is legally defensible in administrative and judicial proceedings. If we really do have a non-compliance situation, we need accurate data to identify and solve the problem. On the other hand, if we are in compliance with the effluent limitation, we must have accurate data for use in any governmental enforcement action. In the long run, we need accurate and precise effluent data so that the 1983 Best Available Technology Economically Achievable (BATEA) effluent standards better reflect reality.

By way of example, the State of Texas is now implementing an analytical quality control program for use in NPDES compliance monitoring. Once this program is operational, the State will back up its effluent sampling results with information on the precision and accuracy of the test method. If an industrial discharger wishes to challenge the State analytical results, he will be at a distinct disadvantage without comparable precision and accuracy data on his own laboratory. These quality control programs are expensive and time-consuming to operate, but they may be necessary in order to maintain a balance in the enforcement of NPDES permits.

3. Enforcement of Self-Reporting Requirements

As we all know, the bases for the enforcement of NPDES permits are the many self-reporting requirements that the permittee must satisfy. Table 5 shows the major headings of a typical NPDES permit issued in EPA Region VI. The format may vary throughout the country, but the main subjects are included in all NPDES permits.

Part 1, Section A details the specific effluent limitations and monitoring requirements, but does not stipulate the form or frequency of any self-monitoring reports.

Part 1, Section B sets forth the specific timetables for implementing the limitations in Part 1, Section A. These timetables require progress reports from design of facilities through the attainment of operational levels. We have been successful in negotiating reasonable compliance schedules, but still recognize that the interim dates are only educated guesses based on very little prior experience in designing and building refinery wastewater treatment facilities. As long as the final deadline is satisfied, we believe that the interim dates should have some flexibility. The EPA or the states cannot now agree to interim date modifications without formally modifying the permit including proper public notice. We suggest that some red tape could be cut by a revision in EPA's regulations to allow them some internal flexibility in modifying interim compliance dates as long as final deadlines can be achieved.

Part 1, Section C covers the details of analytical test procedures, reporting of results and retention of records. Under this section, the report of all analytical results is prepared for EPA or the states every three months. The regulatory agencies can seek enforcement actions against the permittee on the basis of the quarterly report.

The procedures and reports of this section do not reflect the accuracy and precision of the compliance monitoring process nor the problem of interlaboratory variability. We know that the EPA effluent guidelines attempt to reflect the variability of wastewater effluents. However, we are not satisfied with the EPA methodology. The total variability of a wastewater effluent must be broken down into its component parts. Basically, we need to differentiate between the controllable vs. uncontrollable sources of variability. Then, a compliance monitoring system could be developed that 1) does not try to limit the uncontrollable variability and 2) does attempt to limit the controllable variability sources in a probabilistic manner. We are still learning about the variability issue and have no specific systems to offer at this time. But, we are convinced that the existing data base is not adequate.

Part II, Section A includes a subheading on non-compliance notification. Within five days that a permittee becomes aware of exceeding any daily maximum effluent limitation, the permittee must notify the agency. This notification must describe the problem and specify what, if any, remedial actions are being taken. We consider this requirement to be an example of unnecessary red tape. Further, we have had some difficulties in implementing the five-day requirement, especially when commercial laboratories are performing the analyses. After all, it is our legal responsibility to achieve both the daily maximum and monthly average effluent limitations. Why should we have to take special steps on the daily maximum limitations and not on the monthly average limitations? Each daily non-compliance is a separate violation subject to considerable fines and adverse publicity. We believe that we can manage our wastewaters without the added burden of this daily maximum non-compliance notification. Our recommendation is to delete this provision from NPDES permits.

The remaining sections of the NPDES permits do not include any specific self-reporting requirements that are worthy of specific mention in this paper.

CONCLUSIONS

This concludes our prepared remarks on experiences with petroleum refinery NPDES permits. To sum up:

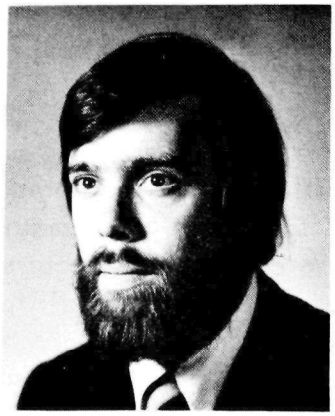
1. Over one-third of all U.S. refining capacity discharges to water quality-limited streams. Special considerations must be taken in order to negotiate an optimum set of permit conditions. Water quality-limited discharges will also be an important factor in the 1983 permit negotiations.

2. Effluent sampling and laboratory analytical procedures are now becoming more standardized and more sophisticated. All phases of the compliance monitoring system must be of comparable precision and accuracy. Analytical quality control programs and round-robin testing may become a necessary part of the NPDES permit process.

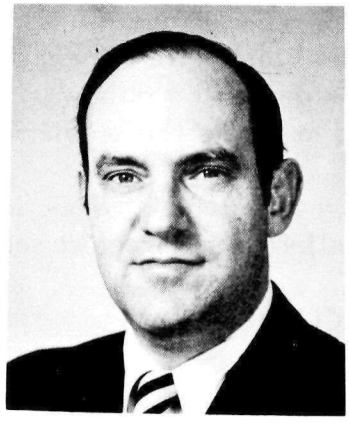
3. Self-reporting is the primary basis for enforcing NPDES permits. Most of the existing requirements are necessary, but some improvements can be made to cut red tape and improve the identification of an actual non-compliance incident.

We believe that our experiences are typical of other refiners and also relate to problems that will be encountered by the marketing and production activities of the oil industry. We have purposely not dwelled on the EPA effluent guideline regulations believing that these criticisms are being handled in a separate forum.

BIOGRAPHIES



William K. Lorenz is Senior Environmental Engineer in the Environmental Affairs Department of Sun Oil Company. Bill holds the following degrees: Bachelor of Chemical Engineering from Villanova University, Master of Science in Environmental Engineering from Drexel University, and expects to receive a Masters in Business Administration from Drexel University in 1977.



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Mr. Elkin has served on the Pennsylvania Air Pollution Commission, advisory panels to EPA, and numerous industry environmental committees.

TABLE 1 SELECTED PROBLEM AREAS IN NPDES PERMITS

I - Water Quality Limited Segments
II - Sampling and Laboratory Analysis
III - Enforcement of Self-Reporting Requirements

TABLE 2 DISCHARGE LOCATION OF REFINERIES IN THE U.S.

Type of Effluent Limitation	Number of Refineries	Crude Throughput 1,000 bbls/Stream Day
Effluent Quality Limited	106	5,729
Water Quality Limited	68	6,954
Municipal System	34	1,720
Zero Discharge	38	615
TOTALS	246	14,918

Source: Engineering Science, "Petroleum Refining Industry Technology and Costs of Wastewater Control" Table II -- 6, page II-25

TABLE 3 WATER QUALITY BASED EFFLUENT LIMITATIONS

- o Applicable State Water Quality Standards
- o "Modeling" Techniques
  - Computerized River Model Studies
  - Manuel Computation River Model Studies
  - Educated Estimates
- o Individual Load Allocations

TABLE 4 EFFLUENT SAMPLING AND ANALYSIS

- o Lack of Historical Data
- o Flow Measurements
- o Analytical Quality Control
- o Interlaboratory Variability
- o Legally Defensible Monitoring Programs

TABLE 5 OUTLINE OF NPDES PERMITS

EXAMPLE: EPA REGION VI

PART I
- A - Effluent Limitations and Monitoring Requirements
- B - Schedule of Compliance
- C - Monitoring and Reporting

PART II
- A - Management Requirements
- B - Responsibilities

PART III - OTHER REQUIREMENTS

"THE ENFORCEMENT OF PERMITS"

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Before I get into the substance of my discussion I would like to extend personal thanks to Bob Silvus. He did something in his talk that I have been waiting for for some time, and that is Bob acknowledged that two people, non-lawyers presumably, can look at the same piece of information or the same data and reach different conclusions. I had heard since I got a law license that it was unique to attorneys that we could look at the same piece of English language and forever argue two different conclusions, but I am grateful to Bob that he has made progress for us, who knows tomorrow we may be considered people as well. I am going to talk a little bit about enforcement of federally issued NPDES permits. Federally issued because in the Region where I work, Texas and the four bordering states, we don't yet have a state which has been formally delegated NPDES permit authority, although we do work with those states on various cooperative bases. Nevertheless my discussion will be on enforcement of federally issued permits.

We are now just over three years from the enactment of public law 92-500. Many of the deadlines of the Act have come and gone. Others are yet before us - you as the operators of regulated facilities, we as EPA the regulatory agency. Two deadlines are of specific interest today. They are first, the December 31, 1974 moratorium expiration date which became the target by which all major permits (and some others) were to have been issued and second the July 1, 1977 requirement for attainment of best practicable control technology currently available (BPT).

The December 31, 1974 date saw the issuance of virtually all permits for major dischargers in Region VI and EPA nationally. What is a major industrial discharger is a matter of evolution. It has included generally large production facilities such as refineries, chemical plants, certain power plants, metal processors and others, not based solely on size or diversity of waste, but on the strength or toxicity of waste or effect on the receiving stream. Those to be added to the major permit list in the future will probably be based on considerations such as potential harm to the receiving stream, significance of pollution abatement facilities, extent of hazardous material handled and the like. Finally, it should be remembered that designation of major permits is in large part a label for purposes of allocation of our resources.

The number of such industrial permits in Region VI, is now about 340. It should be noted that the claim of having issued those permits rests in part on the procedural system which allows uncontested portions of permits to become effective notwithstanding the fact that an adjudicatory hearing is pending on other portions of the permit. Depending upon the day of the count, the number of such pending adjudicatory hearings is around 100 in Region VI and about 1100 nationally.

Parts of almost all of those 100 contested permits, all the other 200 plus majors, as well as many minor industrial and some municipal permits are effective. They have been

effective for a year or more in many cases. As you are aware all of these industrial permits require the discharger to attain effluent limits equal to BPT by the statutory date of July 1, 1977 or other more stringent limitations established pursuant to Section 301(b)(1)C based on water quality standards or other federal or state law. BPT may be defined by effluent guidelines promulgated pursuant to Section 304 or in the absence of guidelines on a case by case basis by application of professional engineering judgment.

As is well known to this particular group, many effluent guidelines remain in litigation. Yet if one can detach himself from this hopefully temporary delay in our joint implementation of the Act, it is clear that if the July 1, 1977 mandate is to be realized, one thing that must be done is to uphold the credibility of the issued permits.

Parenthetically, I would point out that EPA administrator Russel Train recently in a case involving Bethlehem Steel, concluded that the July 1, 1977 date is a mandatory date and permits must require permitees to meet it. This position upheld a previous decision of the general counsel. That was No. 26 if you want to look at it or have your attorneys look into it. Enforcement of these permits is an element of maintaining that credibility and enforcement is well under way.

The principal legal basis for enforcement of NPDES permits is generally Section 309 of the Act. I am not going to bore you by reading that whole page, I will read a section of it of particular importance. Potentially available also for direct enforcement of permits is Section 504. Also available for collateral support of a municipal permit is Section 402(h) by which injunctive relief is available to prohibit additional pollutant load being introduced where there is an existing violation of that municipal permit.

However for most violations of NPDES permits, Section 309 will be the primary enforcement tool. Since we are here concerned with federally issued permits the parts of Section 309 of most immediate interest are Sections 309(a)3, 309(a)4 and 309(b),(c) and (d). This results from the fact that Sections 309(a)1 and (2) are concerned with state-issued permits and 309(e) deals with municipal permits. I will not in this discussion deal with enforcement of true municipal permits where there are violations caused by industrial or other non-domestic waste contributors. There are other classes of permit holders which claim some attributes of municipalities as defined in the Act, but treat almost exclusively industrial waste. These applicants have been in our Region and will continue to be dealt with on the basis that each industrial contributor is a party to the permit and responsible directly to EPA along with the applicant for performance of the permit. These permits are not generally addressed here either. Thus we will be dealing with enforcement of single-party, federally-issued permits for industrial facilities.

Section 309(a)3 reads as follows,

> "Whenever on the basis of any information available to him, the administrator finds that any person is in violation of Section 301, 302, 306, 307 or 308 of this Act, or is in violation of any permit condition or limitation implementing any of such sections in a permit issued under Section 402 of this Act by him or by state, he shall issue an order requiring such person to comply with such

section or requirement, or he shall bring a civil action in accordance with subsection (b) of the Act."

A few remarks are in order about word usage in this section. First, the word "any" appears twice in the first two lines preceding both information and person. This would appear to be all inclusive and cover self-reported, agency-discovered and citizen-reported information (information relating to violations). Then note that the language encompasses both violations of certain enumerated sections of the Act and violations of permits which implement those sections. Then follows the directive to the administrator. He shall issue an order requiring compliance or he shall commence a civil action in accordance with Section 309(b) (emphasis added). I will touch later on this directive language. The authority to so act has been delegated to regional administrators. Section 309(a)4 provides for sending a copy of these administrative orders to states; it provides that service of orders shall be by personal service, that they shall state with reasonable specificity, the nature of the violation and it also puts an outside limit of 30 days on the time for compliance. This section also creates a right on the part of the recipient of the order, to a conference as a condition to effectiveness of the order relating to a violation of Section 308. Section 308 deals with monitoring, reporting, sampling, inspection and the like. Parenthetically I would say that in orders we have issued dealing with monitoring requirements of the permit or violation of monitoring requirements we have been very careful, we think, to be sure to post date the effectiveness of those orders and to explicitly advise people that they had a right to a conference before the order became effective.

Section 309(b) authorizes civil actions for what is called "appropriate relief", including (but not limited presumably to) injunctive relief for any violation for which an order could have been issued under Section 309(a)3 (that is the section I read just a minute ago). Section 309(b) also establishes venue, that is where the suit is to be filed for such proceedings and requires immediate notification of the appropriate state.

Section 309(c)1 contains the criminal sanction for violation of enumerated substantive provisions of the Act or a permit implementing them. The criteria for Section 309(c)1 criminal conduct is "wilful or negligent". Liabilities of $2500 to $25,000 or up to one year in prison or conceivably both, per day of violation are imposed and the limits are double for a second offense.

Section 309(c)2 makes criminal a knowing false statement, representation or certification of certain documents filed or required to be maintained under the Act. Tampering with monitoring equipment is a criminal offense. Penalties range up to $10,000 or six months imprisonment or both.

Section 309(c)3 adds for the purpose of 309(c), any responsible corporate officer to the general definition of the term 'person' as contained in Section 502(5). 502(5) defines person generally for purposes of the Act. 309(c)3 adds to that definition for the purposes of 309(c), the term "responsible corporate officer".

Finally, Section 309(d) creates a civil penalty of up to $10,000 per day of violation

of the same sections listed in 309(a)3 or a permit condition implementing them. On its face this liability, the civil penalty liability, is strict. That is, it applies without the necessity of proof of fault on the part of the violator. The question of how many penalties are assessable for multiple violations in one day has been addressed so far by only one court that I am aware of. That was the Detrex case which indicates a $10,000 penalty per day only may be assessed. That is, not several $10,000 penalties in the same day for multiple violations and that is based on a comparison of language in Section 309 and Section 311 which is the oil-and-hazardous-material section. One case addressed the point and that was the result. In my opinion there will be more heard on that point as to whether more than one $10,000 penalty could be assessed for more than one violation - for instance, for violation of two different effluent parameters.

Let me talk now about the mandatory aspects of Section 309(a)3 which was again the language that I read for you out of the statute a few minutes ago. I have referred previously to Section 309(a)3 as directive in nature. This is because it says that the Administrator shall, and I emphasize shall, issue an order or commence a civil action upon the finding that any person is in violation of a permit as well as in violation of the enumerated sections of the Act. Literally read, there is no discretion except as to which remedy to exercise - issue an order or commence a civil action.

To date we have had to exercise some discretion because there have been more violations (of various levels of seriousness I should add) than we have had resources with which to develop orders or prepare referrals or court actions. Consequently we have tried to issue orders and commence civil actions in cases where we felt it most important to do so. We have noticed others by warning letter. Notwithstanding resource limits on the part of EPA and the States for that matter, the language of Section 309(a)3 remains what it is.

This language using the term "shall" is pretty clearly mandatory upon the Administrator once there is a finding of a violation. The requirement of 309(a)3 is qualified elsewhere in Section 309 only if a state agency has been delegated NPDES authority by the provisions of Section 309(a)1. Now if you refer to Section 309(a)1, it suggests the argument that the only circumstances where the Administrator has an alternative, and I will come back to that in a minute, to issuing an order or bringing a civil action under 309(a)3, is where a state has been delegated NPDES authority. However the EPA may be free to seek civil or criminal penalties in addition to the order or civil action contemplated by 309(a)3. In any event if we are operating under 309(c)1, where a state has authority to issue permits under this law, even then the alternative to issue an order or commence a civil action appears to me to be limited to a 30 day waiting period after giving notice to a state of a violation to see if the state does or does not commence appropriate action. This option is not available where, as here, we are dealing with federally issued permits. Now the word alternative that I used, was used advisedly because of language in another section of the Act, 505(a) of the Water Pollution Control Act, which authorizes citizens suits to compel the administrator to perform any act or duty which is not discretionary, and I will risk boring you by reading part of section 505. It reads - "except as provided in sub-section (b) of this section, any citizen may commence a civil action on his own behalf against any person including the United

States and any other governmental instrumentality or agency, to the extent permitted by the eleventh amendment to the constitution, who is alleged to be in violation of a) an effluent standard or limitation under this Act or b) an order issued by the Administrator or state with respect to such standard or limitation, or against the Administrator where there is alleged a failure of the Administrator to perform any act or duty under this Act which is not discretionary with the Administrator". Then it goes not to say that federal district courts will have jurisdiction without regard to the amount in controversy or citizenship of the parties to enforce such an effluent standard limitation or such an order or to order the administrator to perform such act or duty as the case may be herein to apply any appropriate civil penalties under Section 309(d). Well, so what does all that legalese get for us? Referring back to 309(a)3, which is the part you will recall that said that on the finding of a violation by any person the administrator shall issue an order or commence a civil action, a compelling argument can be made that once a finding of a violation has been made on the basis of any information available by the Administrator in a pre-NPDES delegation situation, he has no discretion but to issue an order or commence a civil action per 309(a)3 and that such duty is enforceable by a citizen through Section 505(a).

This argument is very similar to the result of a case that was decided under the Clean Air Act called Wisconsin Environmental Decade versus Wisconsin Power and Light et al; one of the et als being the administrator of the EPA. This was in the U.S. District Court for the western district of Wisconsin and decided in 1975. You will pass it on to your attorneys that case is printed in volume 7, Environmental Reporter Cases, page 2022. Here the court construed part of Section 113(a) of the Clean Air Act an conferring a non-discretionary duty on the Administrator to issue a notice of ciolation, which duty is enforceable under citizen suit provisions of the Clean Air Act. Now I am going to bore you again with some reading, which I think you will find interesting. This is Section 113(a)1 of the Clean Air Act.

> "Whenever on the basis of any information available to him, the administrator finds that any person is in violation of any requirement of an applicable implementation plan, the administrator shall notify the person in violation of the plan and the state in which the plan applies of such finding. If such violation extends beyond the 30th day after the date of the administrator's notification, the administrator may (emphasis added) issue an order requiring such person to comply with the requirements of the plan or bring a civil action in accordance with sub-section (b)."

The "may" that I read refers to what can be done after the 30 days expires. "Shall" was back up earlier - whenever on the basis of any information the administrator finds that any persons in violation he shall notify the person in violation. It reads very much in words like 309(a)3 in the water act which we have been reading. The citizen suit provisions of the Clean Air Act are very very similar to Section 505(a) of the Water Act which I read to you. The court in the Wisconsin case also indicates that the act of the Administrator 30 days after the notification is discretionary and that the initial finding which generates the notice of violation must be a good faith effort based on investigation of any evidence available. By analogy, and I emphasize by analogy, similar criteria

could apply to a founding of a violation in connection with Section 309(a)3 orders or civil actions. The case is also interesting in the fact that the violation was on alleged violation of a state implementation plan as compared with an NPDES permit. The court holds that the EPA may, in determining whether a violation has occurred which requires that a notice of violation be issued, defer to the state's interpretation of its plan as long as the state's interpretation is reasonable and consistent with the Act.

Thus there appears to be a compelling conclusion, if not inescapable, on the basis of this analysis and that case that I have cited, that the 309(a)3 requirement to issue an order or commence a civil action is non-discretionary once a violation is found to exist and that that duty is enforceable by citizen suit through Section 505. In checking this last week, I discovered the existence of one unreported case in a Federal Court in the northern district of Alabama which reached a contrary result on whether this is a discretionary or non-discretionary duty. I would caution that the result was reached on a preliminary motion and that the case is on appeal. It has not turned up in the reporters yet to my knowledge.

Now this is not to suggest that issuing an order or commencing a civil action such as an injunction under 309(a)3 is an exclusive remedy. We believe, and we have operated on the premise that the civil penalty and criminal sanctions of 309(c) and (d) compliment, in appropriate cases, Section 309(a)3. There has been one case that held that the 309(a)3 remedies are not exclusive. That is a case which was decided, I believe, in the District Court for the district of Arizona where it was claimed that EPA had issued an administrative order and therefore was not entitled to collect penalties for violations that were covered by the administrative order. The judge said that's not right, the two go together.

Finally, it should be noted in the face of all this grimness that there may in fact be, and may in law be, a place in the execution of Section 309 for what has traditionally been called prosecutorial discretion. However, the extent to which this may be engrafted onto the Act when Congress used the language it did presumably being aware of the concept of prosecutorial discretion remains to be seen. And also if there is discretion it may lie in the area of the finding of a violation. I think this is sort of hinted at in the rational behind the Wisconsin case that I mentioned. Time and experience will tell. This doesn't mean that we, EPA, are going to issue administrative orders on trivial violations and it doesn't mean we are going to refer bad cases to the U.S. attorneys, but that we see our enforcement responsibilities as rather explicit and rather demanding. I would like to conclude by making a few observations on some of our experience to date in enforcement of permits. We have been attempting to enforce these permits in Region VI, and I think nationally, as long as we have had them issued. During fiscal year 1975, approximately 65 administrative orders were issued to a variety of dischargers for various violations. Beginning in fiscal year 1976 or July 1975, a greater emphasis on enforcement of permits has taken place. During the first six months of fiscal year 1976, that is July to December 1975 inclusive, we have issued 48 administrative orders involving 38 violations of effluent limits, 13 violations of reporting requirements and 6 violations of schedule of compliance. During the same period there were a total of 4 referrals to U.S. attorneys for prosecution. The prosecutions have all been for civil penalty

collections and one case for injunctive relief involving a manicipality. The referrals involve for the most part, violations of effluent limitations or serious bypassing, that is running waste around the treatment plant, and we have recommended collection of civil penalties for each day in violation.

It is worthy of observation that a problem keeps recurring which we are trying to discourage by making referrals as it comes up in appropriate cases. The pattern is that a difficulty of some nature will arise within a production facility or perhaps independent of production, but in any event the facility operator is faced with a choice of whether to discharge untreated or partially treated waste in violation of his permit or curtail production. In the instances we have had occasion to carefully examine so far, we have concluded that a referral was in order. I should say in some of the cases, not all of the cases. The point we are trying to make is that if there is a choice of violating a permit and keeping production going, then that choice is in all likelihood going to have a price attached to it, and that concludes my prepared remarks. I will attempt to answer questions if anyone has any.

DISCUSSION

Milton Beychok: I have a question and I am not sure whether it should be addressed to you or one or more of the previous speakers. We have heard a great deal this afternoon about compliance schedules for industry, violations by industry and enforcement of sanctions against industry, be they discretionary or non discretionary. I would like to put the shoe on the other foot. There is one part of PL 92-500 that places what is in my opinion the mandatory responsibility upon the EPA and it says that before granting a new source permit the EPA must develop an environmental impact statement. So I have two questions, how many new source permits has the EPA granted, and how many environmental impact statements have they written?

Harless Benthul: In Region VI, we have granted, I want to say a handful of new source permits and by that I think and I really honestly don't know, I think the number is on the order of maybe 10 or perhaps less or perhaps a few more. How many impact statements have we prepared? I don't believe we have published any impact statements Mr. Beychok. We have asked for and have received environmental assessments in at least some of those. In one or two cases that come to mind, we have received an impact statement for review which has been prepared before the facility owners got to us because they had to get a federal license or permit earlier in the game. Now if I may, let me add one other point. The requirement is as I recall not that self executing that automatically-if it's a new source, there must be an impact statement. As I recall 511(c), it says that only two things are "major federal actions" under this law, one of which is issuance of new source permits. Well given that it is a major federal action because it is a new source permit then there may or may not be a requirement for an impact statement depending on the various criteria that are contained in NEPA and in the cases that have developed under NEPA. Does that answer your question?

Milton Beychok: Well I understand that you could have a negative declaration and get around the EIS and that is what you are really saying that all it required was that NEPA

apply. Are you saying then that out of the ten new source permits, if there were no impact statements written, that in each case a negative declaration was filed. And simply telling me that you asked for one doesn't answer the question because it is EPA who must prepare that statement.

Harless Benthul: Your latter statement is correct. We do have responsibility for preparing the impact statement. We have asked for and received the assessments in those cases. What I was trying to say to you was in at least some of those, and don't hold me to the ten, that is a matter of memory and I honestly don't know if there were ten or less or more, but in some of those, by the time the people got to us, there had already been an impact statement prepared as a result of their dealing with some other agency, before they got to us, and some other agency had to do something like granting a license of one kind or another which they felt like required an impact statement.

Milton Beychok: Just one further question, does PL 92-500 spell out any sanctions against the EPA, should they not follow Section 511 properly?

Harless Benthul: Well we are back to 505; if need be. The sanctions I think are there in abundance under NEPA, if we take a major federal action significantly affecting the human environment and don't prepare the 102(2)C statement its "back to go" for us. Whether 505(a) of the Water Pollution Control Act applies I honestly don't know. I would have to give some consideration to whether or to what extent preparing an impact statement is discretionary and again, horseback, off the top of my head, I would say there is a good likelihood it is not discretionary, that if a court found that we issued a new source permit to a facility which was a major federal action significantly affecting the human environment and we hadn't prepared an impact statement, I would say the judge would say go back and prepare it.

Frank Manning: You have mentioned many times in your talks when a violation occurs. Is this always cut and dried, doesn't a violation occurring depend upon a measurement and analysis? Don't you find cases where one analyst might say yes it's over a guideline, another might say it's under, in sort of a case like this. One, do these kind of cases occur and if they do occur, what do you do then?

Harless Benthul: The answer is that yes both on the self-reporting data and as a result of our own inspections we turn up apparent violations which are to use an electronics term "in the noise level", either because it's such a small percentage over the limit or because it's within the accuracy of the analytical technique or in another area if a schedule of compliance date is missed by a week or two weeks or a month, technically that is a violation. As a practical matter, going back to what I said earlier, we try not to issue administrative orders on relatively trivial violations and we hopefully are not going to send any bad cases to the U.S. attorney. So again as a practical matter there is some discretion exercised. Does that answer your question?

Umesh Mathur: I noticed in your presentation that you stayed away from the whole area of pretreatment, particularly for toxic materials. Obviously the NPDES permit system applies only to a direct discharger to the navigatable waters. And so if somebody

was to say, Well if I am going to have to discharge to the river then obviously I am going to have to get a permit from EPA, so why don't I just discharge into the sanitary sewer system because there is no regulation that covers that, except EPA's 40CFR128 which is really saying nothing, because 40CFR128 does not specify concentration levels or any of the mass loadings permissible per unit of production, and so this area has been very grey and so what I would like to point out here is that the construction grants program under Title 2 has been running around all over the country requiring municipalities that are going to get federal funds for building facilities to pass ordinances that will supposedly control these pollutants. Now the problem of that is that there is no uniformity in these various and sundry ordinances that have emerged and as a result of that nobody in industry that is using sanitary sewers for discharging what are called incompatible or toxic pollutants depending upon what you choose, has any idea as to what those numbers are going to say eventually when and if EPA comes around to defining pretreatment standards for these materials. Now the difficulty that I am trying to point out here is very real because once an industry was given an ordinance which stayed in effect for two years, if EPA took two years to determine what pretreatment they should require, and this industry went in and built pollution control facilities to meet both standards that have been established on a completely arbitrary manner in the face of any definitive guidance from EPA, then for the municipality to go back to the industry and say look now that EPA has come out with a new set of numbers you are going to have to shoot for this new set of numbers; I feel is going to cause a management problem for the municipalities involved. I was wondering why the construction grant problem cannot be restrained and told not to require facilities that are going to require federal funds to necessarily have the industrial waste pretreatment ordinance in the face of the fact that EPA itself is under suit to produce those pretreatment guidelines and they have failed to do so for I think they are already two years too late, and they have still not produced and so what is the point of forcing municipalities to do it.

Harless Benthul: Well thank you for raising a very pertinent point in this whole discussion. I can't very reliably answer your question as it relates directly to the construction grant program. Hopefully, I can give you some reassurance with respect to the rest of it. The pretreatment regulations generally required that as of the end of the three year period which I think about upon us in the order of a year or so, contributors of incompatible waste or waste which would pass through or interfere with the operation of the treatment works, have some pretreatment satisfactory to prevent that happening implemented. Now you are quite correct that that is not implemented is a general rule or any specific basis, that is in terms of limitations in either concentrations or flow or pounds per day from the industrial contributor to the municipal treatment facility. Nevertheless the regulation is there, it has been on the books for a period long enough that we feel like it is about ready to be implementing. Coincidentally, we had a crew investigating a municipality in an industrial facility last week which fits this circumstance, and there very well may be some enforcement activity resulting from that. It doesn't by the way concern anybody in this room. It is not a petroleum or refinery operation. The rest of the reassurance is, I hope, that is something I mentioned earlier in my talk, and that is that category of industry permit applicants which has some attributes of a municipality under the Act, that is they are a creature of statute under state law, they have bond-issuing powers and the like, but treat totally if not largely, industrial waste. We are

permitting those applicants on the basis that the contributors of that waste is a party to that permit and is therefore directly responsible to us for a violation of that permit. My answer to you is not specific as it relates to the grant program. What it is, is that we think we have some enforcement power on pretreatment by virtue of the regulation which you mentioned and by virtue of the reference in Section 309(a)3 to violations of that portion of the statute that requires pretreatment. So I would have to agree that pretreatment has probably not been implemented on a specific uniform basis to the degree that you would like or that EPA would like, but we do recognize that there is a problem and we try to deal with it to some degree at least.

Pete Hoffman: The question I have deals with those permits which have not been given by the EPA, on applications that were filed say back in the original Corps of Engineers which I think was July 1971. If during the period of time in which this permit is pending conditions change significantly, on that discharge, what is the burden upon the operator to file a revised permit or revised application on changing conditions on a permit that has never been issued in the first place and secondly, is it not true what you were saying that if a citizen wants to they could file suit and force the EPA to fine that company for not having a permit?

Harless Benthul: I will answer your last question first. Yes it is possible. Again the citizen has to prove that or has to show, make a prima facie showing that the duty involved is not discretionary and that we haven't performed it. You are describing a facility for which there was an application filed under the Refuse Act Permit Program and which has never been permitted?

Pete Hoffman: Yes

Harless Benthul: I didn't think there were any of those left around Mr. Hoffman. Alright, you filed the application timely, I assume, and you say there have been some changed conditions. Have you notified us of those changed conditions? Therefore, if we were to proceed to issue a permit tomorrow, we would be issuing a permit based on facts which are not current. Would that be a fair assumption?

Pete Hoffman: Yes, Sir

Harless Benthul: Mr. Hoffman, I would have sworn that we have issued permits to all your facilities, but obviously we haven't. I would say that, and had very good experience with you in doing it I would add, if there have been changed circumstances I think I would make a record of it if nothing else by letter to the Regional Office and at least by doing so you have put us on notice that the facts are different than we apparently think they are. Someone else was going to help me and far be it from me to turn down any help. Whoever was going to Mr. Hoffman I would like a little expansion on that last thinking.

Bob Funk: We have a similar situation to Mr. Hoffman. Being specific we have a number of offshore production facilities which have permits filed which have never received a permit from Region VI and these kind of facilities are subject to change as

time goes on due to the nature of the discharge. You mentioned a letter to inform EPA of what the change is, what level of change would trigger a letter, this is our real problem.

Harless Benthul: While I doubt you are ready for this, what I am referring to is a major change, significant change and those are only words, I realize. You are talking about offshore facilities, you are absolutely right you haven't got any permits for those and Mr. Hoffman are you talking about minor industrial facilities, not what we would probably call a major permit? You are right there is a bunch of applications lying around for minor, what we have in the past called minor discharges, and they have not been issued. Several have, on the order of 1500-2000 in Region VI total. We will get to you sooner or later and again, if there has been a change in circumstances, again for the like of a better phrase, major, significant and I know that is not much help, but those you should notify us.

I am delighted to hear it and thank you.

Bob Funk: During your discussion you cited a court case limiting penalties for violations to $10,000 per day regardless of the number of violations and you mentioned that you felt like there would be further challenges to this interpretation. Can I draw the conclusion that Region VI would contemplate requesting penalties above $10,000 a day for multiple violations?

Harless Benthul: Yes, you can draw from that we think we will encounter some cases where it is appropriate to ask for a penalty, conceivably $10,000 per day for more than one violation which results in conceivably $20-$30-$40,000 per day violation. I don't believe we have done that yet. I don't think we have asked for more than $10,000 per day, but it has been because we haven't run across a case where we think it fits. I do believe though that there will be cases where it is appropriate even within the language of the judge in that Detrex case to ask for penalties, multiple penalties, for multiple violations on the same day.

Morris Wiley: I have a question I think that concerns many of the audience here about the pretreatment requirement. EPA in publishing the guidelines for municipal secondary treatment has included fewer parameters than they have in some of the other industrial guidelines. For example, COD is not included in municipal secondary treatment but it is included in the refinery guidelines. Now if the refinery or other industrial plant discharged a pollutant to a municipal treatment plant which is required by its guidelines to treat for implementation of the 77 standards, but is not included in the municipal monitoring program, what would be the view of the pretreatment requirements which might be required of that discharger?

Harless Benthul: Sounds like it might be a case where it would be in order to put a COD limit on the municipal permit.

Morris Wiley: Is that being done at all?

Harless Benthul: It is being done in those, that class of cases I mentioned earlier which are sort of quasi municipal type permits. I don't know that it is being done in ordinary municipal permits. We have a case pending in one of the states in this Region, where that is precisely the issue. We have a court decree from a couple of years back that imposed a requirement on a municipality and us as parties to the settlement, that there will be certain pretreatments of metals and influence limits on metals coming into the treatment plant and it also is a requirement that there be effluent limits on those same metals which, of course, would be significantly above what you normally see in a municipal permit as you are aware. And that one is still up in the air, I don't know where it is going to wind up.

Morris Wiley: Metals would be a good case in point because the refinery effluent guidelines do place a limitation on chromium and it is well known that this is removed by either a municipal or industrial primary and secondary treatment and yet I don't think there is any basis for evaluating what chromium limit municipalities should discharge in a permit.

Harless Benthul: Well I wouldn't place the greatest emphasis on the fact that one set of guidelines requires controls of COD and chrome and lead and another one might not. Those as you undoubtedly know, vary from sub-category to sub-category. For instance, one of the organic chemicals or may be all of them for instance, don't have a BPT limitation for COD, it doesn't come up until 1983. Well I personally don't know about that, but nevertheless that is what the regulation says.

Morris Wiley: If the COD limitation were placed on a municipal discharge and they received discharges from both the refinery and the organic chemicals plant then how would that be resolved to determine who was responsible for what pretreatment?

Harless Benthul: The total COD load coming from the municipal treatment plant couldn't be any more than what would be BPT for those two industrial facilities. So how you translate that back up through the municipal treatment plant, back to the effluent from the two industrial facilities, I am to many years away from engineering to know if I ever did and I probably didn't. Sorry.

Bob Wortman: Isn't the intent of the law where you have an industry discharging into a municipal system the actual intent I would think is that any discharge in the system should not cause any harm to the sewer or harm to any of the biological treatment processes. And yet the effluent from the sewage treatment plants should meet stream quality standards and I would think if you meet the intent of the law this would be the essential thing to do regardless of all of the other parameters.

Harless Benthul: Well I go along with you up to the point where you said it would be sufficient if you met the stream standards, remember we have technology standards which would apply to the municipality for starters. If you start backing away from placing requirements on however many industrial dischargers there are to the municipal facility, if you'd start backing away much from the technological standard that they would otherwise be required to meet, then you are placing them at a competitive advantage with

the people who are discharging and treating their own waste and just that advantage might or might not be offset by the cost recovery ordinance under the construction grant, assuming there is one.

Bob Wortman: But I thought that was one of the concerns to encourage more centralization of treatment processes and to me there should be some built in advantage to an industry going to the city, otherwise he is not going to go and you are going to have more permits, more administrative expenses and everything. In other words there are a lot of things to consider here.

Harless Benthul: You are right there are and one of them is not placing people at relative advantages or disadvantages when they should otherwise be similarly situated.

BIOGRAPHY

Harless Benthul holds a B.A. from Texas A&M University and a Bachelor of Law degree from S.M.U. in 1964. He has vast experience in the engineering field, seven years total and has been in the private law practice four years and three years in the practice of corporate law. His present title is Chief of the Enforcement Legal Branch in Environmental Protection Agency Region VI in Dallas.

"MEASURING THE PARAMETERS SPECIFIED IN PERMITS"

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ABSTRACT

Much effort has been expended in recent years to develop and evaluate methods for the determination of wastewater parameters. It is important to review the validity of the analytical methods and to determine that they relate to the ecology of the receiving waters. The detailed procedures of the methods must be carefully standardized and cooperatively tested on samples representing actual effluents.

INTRODUCTION

In order to establish and enforce environmental regulations it is necessary that there be a reliable, accurate and meaningful measuring system. The measuring system is composed of a complex interrelation of several factors. First, of course, are the test methods themselves. These should be chosed to determine those components and properties of the effluents for which there is a need for measurement. The methods must be carefully examined to determine the significance of procedural operations and standardized by interlaboratory comparisons. Precision of the methods should be determined from interlaboratory testing and accuracy determined, if possible, from analysis of Standard Reference Materials. Well established procedures must be set up and followed to provide for proper sampling and to ensure stability of the samples prior to actual analysis. Analytical chemists should always be a part of the overall planning process.

A essential consideration in establishing a meaningful measuring system is to make certain that the analytical data obtained on the effluents relate to the ecology of the receiving waters. Factors that should be considered in assessing the health of the receiving waters include processes acting upon the components of the effluent, as it passes into the receiving water, as evaporation, dilution, chemical reactions, and biological degradation.

ORIGIN OF THE METHODS

The methods specified in the permits represent various stages in the history of analytical technology, some quite current while others derive from an earlier period of water analysis methodology. Among the more current techniques are atomic absorption for determination of metals and specific ion electrodes for determination of individual ionic species. These powerful new techniques now permit the determination of specific components with a higher degree of accuracy. Examples of test methods which derive from an earlier period of technology in water analysis include the determination of oil and grease and of biochemical oxygen demand. It is interesting to review the history of these older

methods in regard to the significance of their present applications.

The present methods for determination of oil and grease in water stem from a committee review held in Los Angeles by the City Bureau of Engineering some years ago. The paper covering their work (1) was published in 1941 and used the now familiar extraction methods for determination of grease in sewage sludges and industrial wastes. The procedure described initial acidification of the sample, extraction of the grease with a solvent, evaporation of the solvent, and weighing the residue. The extraction procedure itself, however, was taken from yet an earlier method published in 1933 by the American Petroleum Institute (2) for the analysis of oil-field wastewaters.

The history of the test for biochemical oxygen demand (BOD) in water analysis goes back many more years. The test was recommended in 1912 by the British Royal Commission on Sewage Disposal (3). Almost fifty years ago, in 1928, it was possible to present a review paper entitled "Technic and Significance of the Biochemical Oxygen Demand Determination" (4) and, even then, make the statement that the BOD determination had been in use for many years. The dilution method, taken from the 1917 issue of "Standard Methods" (5), is essentially the BOD method in current use. The data reported (4) were taken from analysis of sewage effluents, the drainage canal of the Chicago Sanitary District, and of an effluent from a corn products manufacturing plant.

A characteristic of these older methods, and that also of certain others being used as test procedures, is that the results are empirical. The data obtained are dependent upon the test variables themselves and do not provide compositional data. In certain of these methods, the parameter being measured is defined by the methodology itself.

STANDARDIZATION GROUPS

The long history of the analysis of water led inevitable to a confusion of methods and interpretation of results. To overcome these problems, standardization groups were organized many years ago. A committee of the American Association for the Advancement of Science reviewed methods for the analysis of water and published a report (6) in 1889 which covered methods for determination of "free" and "albuminoid" ammonia, nitrites, nitrates, and oxygen-consuming capacity. Further developments led the American Public Health Association to appoint a committee who produced in 1905 the first edition of the now familiar "Standard Methods". Revised and enlarged editions of "Standard Methods" have been produced over the years under the combined sponsorship of the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation (7).

The American Society for Testing and Materials (ASTM) made a review in 1925 and established that there was a need for cooperative testing in the sampling and analysis of industrial waters (8). As a result, ASTM Committee D-19, on water analysis, was established in 1933 with eleven members and has grown in scope and membership, particularly in the past ten years. Membership now is over 500 and the number of methods currently printed are 135 (9). Active groups meet twice yearly to review and introduce methods covering such topics as biological monitoring, sampling techniques, radiochemical

analysis, determination of inorganic and organic components, analysis of brackish water, and the identification of waterborne oils. An essential part of the ASTM process is inter-laboratory comparison of results on practical samples in round-robin fashion to determine precision and reliability of the methods. Such testing goes on during the course of the year and results are reviewed at the semi-annual meetings.

The U. S. Environmental Protection Agency (EPA) has developed a valuable Manual covering "Methods for Chemical Analysis of Water and Wastes" (10) now in its second edition. This set of methods was collected, reviewed and published by the Method Development and Quality Assurance Research Laboratory at the National Environmental Research Center at Cincinnati, Ohio. Assistance was provided by other governmental laboratories, both state and federel. The Manual is a basic reference for monitoring water and wastes in compliance with the Federal Water Pollution Control Act. Although other test procedures may be used, it is stated in the Manual that the methods therein described will be used by the EPA in determining compliance with applicable water and effluent standards.

European standardization groups are also active in promulgating methods for the analysis of wastewaters, but their publications do not directly impinge upon the practice in the United States on measuring wastewater parameters. Exceptions, of course, will be with the development of new analytical technology or in topics which have a large geographical impact. For instance, the characterization of waterborne oils has been the subject of activity not only by the ASTM and others in the United States, but also by the Institute of Petroleum in England (11).

FEDERAL GUIDELINES FOR ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

The specific approved test procedures to be used for measuring the parameters specified in permits derive from Part 136, Title 40, Code of Federal Regulations. Section 136.3 identifies the test procedures which must be used in any permit application pursuant to sections of the Federal Water Pollution Control Act. Updated lists of approved methods in the Code of Federal Regulations are published from time to time in the Federal Register. The most recent proposed amendments to the test procedures for aqueous samples were published in the Federal Register issue of June 9, 1975 (12).

These proposed amendments covered a great deal of ground since they include not only correction of minor errors but also allowed new techniques and added a considerable number of additional parameters for possible measurement. The corresponding proposed table of approved test procedures from the Federal Register of October 16, 1973 (pages 28759 and 28760) lists 71 parameters for measurement. The 1975 table lists 115 parameters. Although the text briefly reviews the fact that additional parameters have been added, the magnitude of the additions is obscured by the way in which the 1975 table was constructed. In the effort to keep the parameter listings of the 1973 table unchanged, the 44 new parameters have been introduced as subheadings. For instance, the new listing of Rhodium is introduced as 35 (b) under Potassium (35) and Potassium - dissolved (35a). Ruthenium is then introduced as 35 (c).

The recent issue of the Federal Register is an example of a way in which test

procedures have been introduced without undergoing a thorough standardization process and interlaboratory review. For example, a number of the new test procedures which have been introduced are directed to the determination of the dissolved portion of metal components, generally using atomic absorption for final measurement. The procedures differentiate between the portion of the metallic constituents which will pass through a 0.45 micron filter and those which will be retained. In nearly all cases the reference is to a single page of the EPA Methods Manual (10). This Manual does not provide sufficient procedural details for method standardization. In fact, a note is included in the EPA Methods Manual in the general method detailing techniques for atomic absorption which suggests the need for (unspecified) special precautions for stabilization of certain types of metal containing samples. Large differences can be expected in behavior between metal components of such diverse properties as sodium, for example, and titanium. Because of these factors new sets of proceudres should always be subjected to careful and detailed review and proper standardization and validation before being applied to the permit process. This should include crosstesting of samples amongst a group of laboratories for intercomposition and development of data on the reliability of the procedures.

Although the current Federal Register lists 115 parameters, in actual practice considerably fewer are used for control of petroleum refinery wastewaters. Table I lists twelve parameters which are most commonly required with a brief statement of the method recommended.

REQUIREMENTS FOR SATISFACTORY TRACE ANALYSIS

Measurement of certain components specified in the permits is a practical example of trace analysis which is generally considered to be the determination of a component or components in a sample vastly diluted by other materials. Many methods have been used for trace analysis. (13), (14) During 1972 an intercompany project was initiated to develop techniques for measuring trace concentrations of metals in oil (14). Although their analytical medium was different from water, their detailed studies of the principles of trace analysis apply to the determination of trace components in water.

Sampling. It is well acknowledged that analytical results can be no better than the sampling and preservation techniques employed. It cannot be overstressed that samples must accurately represent the conditions existing at the point of sampling and that samples must be properly preserved in that condition until the analysis is made. Although each of the reference compilations provides guidelines on sampling, in actual practice good sampling techniques are not always employed. For accurate results in trace analysis, clean sampling containers of the proper material, caps, thorough sampling procedures, and proper preservation techniques must be carefully established and rigorously follwed in actual use. If these points are not properly observed, the results obtained can be meaningless. It must be emphasized that anything which contacts the sample, whether apparatus, storage, or shipping containers and closures, the reagents or the atmosphere can serve as a potential source of elemental contamination or provide a sink for loss of some components, such as by adsorption.

Storage and Stability. The instability of dilute aqueous solutions has been widely observed. (10, 14) The best rule is to analyze samples as soon as possible after they have

been taken. Changes that take place in a sample can be due to chemical or biological reactions. Metal cations may precipitate, form complexes or adsorb onto surfaces. Organics, including hydrocarbons,may undergo biochemical oxidation. A general rule to increase the stability of aqueous samples is to acidfy approximately to a pH of 2. $HgCl_2$ can be added for bacterial inhibition. Refrigeration at temperatures near freezing or below can be helpful in preserving a sample which cannot be analyzed immediately.

Standards. The best means to evaluate laboratory performance is the analysis of a standard sample in which the composition of the determined component is known exactly. A series of quality control samples is available on request from the Environmental Protection Agency (15) for the determination of many components including certain trace metals, ammonia, nitrate, phosphate, pH, and so on. These have been widely used to provide checks on reagents and laboratory procedures. More exact primary standards are the Standard Reference Materials being prepared by the U. S. National Bureau of Standards for trace metals in water. The composition of NBS Standard Reference have been certified by at least two independent analyses. Suitable Standard Reference Materials are the best means of evaluating the entire proceudre and to establish its accuracy. In the absence of a standard sample, "spiked" samples prepared by adding known amounts of a constituent to an effluent can be used.

SIGNIFICANCE OF THE DATA

It is important to divide the test results into those which provide compositional data and those which are empirical. In the first category, compositional, are included those methods for determination of ionic constituents such as dissolved metals, nitrogen compounds such as ammonia, nitrite or nitrate, and sulfide ion. Since these are all defined components and determinable by at least two independent analytical methods, their concentrations can be determined with some degree of accuracy and the effect of interferences investigated on the precision and accuracy of the results. Interlaboratory comparisons of methods and data, preferably, by several techniques can establish the validity, accuracy, and precision of the data.

On the other hand, those methods which provide empirical results, including the determinations for oil and grease and biochemical oxygen demand, defy a definition of accuracy. For the empirical methods the best that can be done is to standardize the procedural descriptions and then determine precision by interlaboratory round-robin testing under exactly defined conditions. It is not possible to run any of the empirical tests by two sets of procedures to determine accuracy since the results are defined by the procedures themselves.

Relationship to Ecology of Receiving Waters. The prime consideration in establishing effluent standards should be to relate the analytical data of the effluent wastewaters to the ecology of the receiving waters. The factors which should be considered in the receiving water are toxicity (both acute and long-term) to the flora and fauna, depletion of oxygen, odor, and detrimental changes in the esthetics of the receiving waters and the adjacent land areas. Factors that should be considered in assessing the effects of effluent composition on the receiving waters include such processes as evaporation, dilution, air-water interchange, chemical and photochemical reactions, and biological degradation.(16)

The relationship between laboratory bioassays and actual results in the field are not necessarily straightforward. For example, the chemical form in which a trace metal is released or the form it adopts after release is highly significant in its biological impact (17). There is an increasing body of evidence indicating that there are natural processes operating to reduce both the concentration and toxicity of trace metals dissolved in water. In order for a heavy metal to be toxic it must be in the ionic state. (18,19,20) In most natural waters much of the free metal ions would probably be rapidly bound to organic substances, naturally present in the water, decreasing the relative percentage of the ionic species There is indirect evidence that organically chelated heavy metals in aqueous solutions do not have as great an effect upon organisms as do solutions of the metal salts. (20) This could be due either to the fact that the organo-metallic complex is too bulky to enter a biological system or it could be due to the lack of availability of the metal for reaction with enzymes within the cells.

Precision of Data. From the standpoint of quality control and agreement with regulatory standards it is important to have an understanding of the significance of precision of the results obtained by the various methods. Both ASTM Committee D-19 (21) and the Methods Development and Quality Assurace Research Laboratory of the Environmental Protection Agency (22,23,24,25) have practices for evaluating analytical methods for water. After a method has been sufficiently investigated to determine the significant variables and establish their control, it is possible to organize an interlaboratory, round-robin testing program. A written copy of the method being investigated plus the necessary samples for each test are supplied to each laboratory. From the interlaboratory tests, it is possible to derive terms for method precision, which is usually done by calculating standard deviations. Standard deviation is the measure of the dispersion of the data around their average, expressed as the square root of the quantity obtained by summing the squares of the deviations from the average of the results and dividing by the number of observations minus one. The standard deviation is generally given as a measure of the precision of methods which have been subjected to comparative evaluation. The next factor to consider is the confidence level of the data obtained at two different laboratories. As Youden (26) points out, it is well known that a reasonable number of measurements must be made to give confidence in the results. A number of factors enter into establishing confidence limits on data sets. At a 95 percent confidence level an approximate rule (26) is that, for sets of 4 or 5 determinations, average results between two laboratories should not differ by more than approximately 3 times the standard deviation. When analytical methods are used at or near their lower level of sensitivity, there is a greater tendency to error and loss of reproducibility.

PROCESS-TYPE INSTRUMENTATION

The use of continuous monitors to determine effluent parameters on flowing systems is particularly valuable, if it can be made effectively. Such continuous measurements provide for the fully automatic regulation and control of certain parameters and avoid the delay and error in sample taking and handling. It is always necessary to carefully review the operation of a continuous monitor under field conditions for a sufficient period of time to make certain its behavior is satisfactory and that its response is to the parameter to be measured and not to an artifact in the system.

Continuous instruments are available and have been commonly used for many years for measurement of pH by use of the glass electrode (ASTM D 1293). Commercial process-type water quality analyzers are currently becoming available for a number of other components. These include the use of specific ion electrodes for ammonia and sulfide, and ultraviolet spectroscopic instruments for phenols. An excellent detailed coverage of such instruments was recently published by the Lawrence Laboratory of the University of California (27).

EXAMPLES OF CRITICAL ANALYSES

Oil and Grease Determination. A considerable number of methods have been applied over many years for determination of "oil and grease" or extractable materials in aqueous samples. Table II provides a summary of the principal features of some twenty such methods. For each of these, more detail is given in a recent report (28) prepared for the American Petroleum Institute. The kind of results that may be obtained from use of this large array of empirical procedures may be quite different. For instance, Methods 4 and 10 both involve initial extraction with Freon 113. Method 4 utilizes a gravimetric determination following solvent evaporation, which causes also some evaporation of light hydrocarbons. Method 10 utilizes an intrared spectrophotometric measurement and does not involve evaporation. Consequently, it can be anticipated that comparative measurements, where light hydrocarbon components are present in the sample, can be higher with Method 10. It is interesting that the Federal Register of June 9, 1975 (12) lists both the gravimetric and infrared methods as alternative procedures without commenting on differences that could be anticipated in results.

Another area of concern is the relative solvent power of common solvents for petroleum constituents. The components of wastewater are a complex mixture of compounds of different nature and are not all equally dissolved by different solvents. For instance, Freon appears to extract less material of an asphaltic nature and a "rag" or undissolved oily film has sometimes been noticed.

Another significant difference in results can be obtained when an absorbent is used to separate polar from nonpolar materials. Methods of this type can provide for the determination of hydrocarbons in effluent waters. A review of Table II shows that there are several available methods utilizing adsorbents to separate polar materials from hydrocarbons to allow the more specific determination of the latter. These involve different applications of adsorbents such as the use of alumina (Method 5), Florisil (Methods 11 and 17) or silica gel (Method 13). An extensive round-robin test was recently managed by the Robert S. Kerr Laboratory of the Environmental Protection Agency, Ada, Oklahoma to ascertain the validity and reproducibility of Method 13. It is generally the experience that the efficiency of separation of polar organics from aromatic hydrocarbons may depend to a considerable extent on the polarity of the solvent, the activity of the adsorbent and the adsorbent/sample ratio. A study of this type has been recently published (29) and indicates that the variables should be carefully established with such methods for accurage and meaningful results.

Continuous monitors have been considered for determination of small quantities of oil in effluent waters. The principles and experience with several of these techniques are indicated under Method No. 21. Most of those methods involve interaction of the components of the sample with light of several wavelengths. It is important that the spectral

region (that is, ultraviolet, visible, or infrared) relate properly to the components of the samples. Although these techniques do show promise, several have shown limitations in field use in that they may be somewhat fragile and some tend to undergo fogging in the optical path. It is necessary that the optical instruments properly discriminate between oil and interferences such as suspended solids.

ASTM Committee D-19 is currently conducting interlaboratory comparisons with many participants of several of the methods of oil and grease analysis. Samples being circulated are practical effluents and contain both petroleum and non-petroleum constituents.

Chemical Oxygen Demand. The dichromate oxidation method for chemical oxygen demand is another empirical test with a history of use of some years (30. As is pointed out in "Standard Methods" (7) it is important to follow a standardized technique since only a part of the organic matter is oxidized. This is particularly important with nitrogen compounds since the extent of their reaction can be variable, depending upon structure, as can be seen from Table III. The data in Table III are taken from references being reviewed for consideration in the ASTM D-19 Committee studies on the method for Chemical Oxygen Demand. Because of the way the test is performed, volatile, nonpolar components, such as benzene and toluene can be partially lost. The limited reaction of many nitrogen compounds depend upon the structure of the compound. For instance, pyridine with one heterocyclic ring is essentially nonreactive while quinoline undergoes extensive reaction, no doubt due to initial attack on the homocyclic ring.

Biochemical Oxygen Demand (BOD). As pointed out earlier, this empirical method has a long history of use in the analysis of wastewaters. The test has significance as an index to the susceptibility of the components of wastewater to biodegradation. The test involves measurement of the amount of oxygen consumed in a 5 day period after the sample has been inoculated with sewage bacteria. Despite its long history of utility, the BOD method has been recognized to have many limitations (31). The limitations include such factors as the differential rates of biochemical oxidation of various compounds, including the effects of nitrifying bacteria which convert nitrogen compounds to higher forms. The rates of reaction may vary markedly with different sources of inocula. "Standard Methods" (7) points out that the BOD test is of limited value in measuring the actual oxygen demand of surface waters. The extrapolation of test results to actual stream oxygen demand is highly questionable since the laboratory environment does not reproduce actual field conditions, particularly as related to temperature, sunlight, biological population, water movements, and oxygen concentrations.

ASTM Committee D-19 came out with a similar assessment of the BOD method. The action of the ASTM was to discontinue without replacement, ASTM D 2329, "Test for Biochemical Exygen Demand of Industrial Water and Wastewaters". (9) The ASTM group concluded that the BOD concept is important in determining water quality but that the laboratory bottle incubation procedure typified by the usual BOD test is ill defined, producing data which are limited. The ASTM recommends several alternate tests which have been better standardized to assess pollution potential. These tests include those for Total Organic Carbon (ASTM D 2579) (9) and Total Oxygen Demand (ASTM D 3250) (9). The subject is still under close review by this ASTM group.

Cyanide Determinations. The issue which has become of concern in the determination of cyanide in effluents is the differentiation between simple cyanide and complexed cyanides. In common practice simple or "free" cyanide is defined as the CN^- ion or the HCN molecule. Complex cyanide is taken to mean any molecular composition in which the CN group is bound to a metal through coordinate bonds. Examples of complex cyanides are those of iron: $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$. The practical distinction between simple and complex cyanides depends upon the production of HCN under relatively mild conditions. For example, the procedure of Roberts and Jackson (32) provides for distillation of hydrogen cyanide, in the presence of zinc acetate, under reduced pressure. Under the conditions of the test the decomposition of ferrocyanide is completely prevented. The cyanide in the distillate is determined by colorimetric pyridine-pyrasolone procedure.

There is currently an extensive effort in ASTM Committee D-19 involving interlaboratory round-robin tests with many participants examining several of the methods which have been recommended for cyanide determination. The aim of this testing program is to establish the validity and precision of the cyanide methods and to establish the significance of interferences.

CONCLUSIONS

1. The large scope of the procedures for measuring the parameters of aqueous effluents has given rise to methods whose variables have not all been completely understood or standardized. Results from some of these methods are dependent upon the procedural steps employed.

2. It is important to review and decide on what components in effluent waters should be measured. The purposes and definitions of the measurements must be tied to real needs relating to the ecology of the receiving waters.

All methods must be thoroughly examined to determine the significance of the procedural operations. The final methods must be carefully standardized and cooperative testing on samples representing actual effluents.

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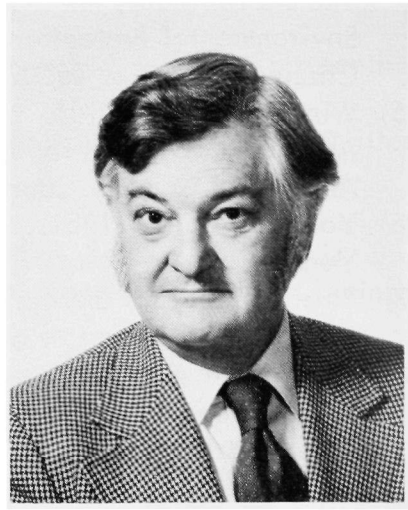
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DISCUSSION

Larry Echelberger: I am wondering what Shell does to ensure the accuracry of its numbers. What do you do at the individual refineries? Do you spike samples or periodically on a routine basis, for example, send them to independent laboratories? What do you do or what do most of your refineries do to ensure accuracy of your results?

Fred Weiss: In the Company for certain types of analyses we have for some years run our own type round-robining for some product materials. For effluents, which I take your question to be, because the transport of effluent samples is very difficult, we do run cross comparisons with commercial laboratories in each of our areas. The data I have seen from a number of the cross comparisons is generally fairly good. Another thing that we have done, although I don't know how widely it is done throughout the refinery laboratories, is to get those samples from the EPA that are essentially standard materials. There are a whole series which have been made available and we have run those.

BIOGRAPHY



Fred Weiss is Senior Staff Research Chemist, Analytical Department, Shell Development Company, Houston, Texas. He holds degrees in Chemistry from the University of California at Los Angeles (B.S., 1938) and from Harvard University (M.A., 1939 and Ph.D., 1941). He has been involved in research with the Shell Companies since 1941. His special interests have been in the detailed analysis of organic compounds and the application of methods to trace analysis. In recent years much of his work has been devoted to environmental measurements.

TABLE 1 PARAMETERS COMMONLY REQUIRED FOR PETROLEUM REFINERY PERMITS

Parameters	Method
Biochemical Oxygen Demand 5 day (BOD_5)	Modified Winkler or probe
Chemical Oxygen Demand (COD)	Dichromate reflux
Oil and Grease	Extraction
Total suspended solids	Glass fiber filtration
Total Organic Carbon (TOC)	Combustion-infrared
Chromium, Total	Atomic absorption or colorimetric
Chromium (VI)	Extraction and atomic absorption, colorimetric
Cyanide	Distillation and colorimetric
Phenols	Colorimetric
Ammonia	Several techniques
Sulfide	Titrimetric or methylene blue
pH	Electrometric

TABLE II

SUMMARY OF ANALYTICAL METHODS FOR DETERMINATION OF OIL & GREASE [a]

TYPE	NO.	METHOD DESIGNATION	REFERENCE	STATUS	CONDITIONS OF EXTRACTION	EXTRACTANT	ADSORBENT	COSTS
GRAVIMETRIC METHODS	1	Chloroform Extractable Matter	ASTM D-1178	Discontinued	pH 3-4	Chloroform	None	Moderate
	2	Solvent Extraction	ASTM-2778	Limited Use	pH Variable	Any Solvent	None	Moderate
	3	Soxhlet Extraction	EPA Manual 00550	Wide Use	pH - 2 Soxhlet	Hexane or Freon-113	None	Moderate
	4	APHA Oil & Grease	APHA - 137	Wide Use	Acidic	Freon or Pet. Ether	None	Moderate
	5	Hydrocarbon and Fatty Matter	Std. Methods P. 413	Limited Use	Follow Method 4	Freon-Hexane	Alumina	Moderate
	6	Reflux Distillation Method	ASTM D-1340 [a]	Discontinued	Acidic	Benzene, Others	None	Moderate
	7	Petroleum Ether Extraction		Limited Use	No pH Adj.	Petroleum Ether	None	Expensive
	8	Hexane Extractable Material	ASTM D-1891	Discontinued	pH-4	Hexane	None	Moderate
VOLUMETRIC METHODS	9	Flocculation - Extraction Method	API 732-53	Limited Use	pH-4	Ether	$Fe(OH)_3$Floc	Inexpensive
INSTRUMENTAL METHODS	10	Oil and Grease - Freon Extractables	EPA - 00560	General Use	pH-2	Freon 113-IR	None	Expensive
	11	Hydrocarbons in Water or Soil	Concawe I/72	Limited Use	Acidic	CCL_4 (IR)	Florisil	Expensive
	12	Combined Methods	API O & G Comm	Proposed	pH $< 7 \geq 7$	CCL_4 (IR)	None	Expensive
	13	Petroleum Hydrocarbons	1975 EPA Study	Proposed	Acidic	CCL_4 (IR)	Silica Gel	Expensive
	14	Volatile and Non-Volatile Oily Material	API-733-58 & Lit.	Limited Use	Acidic	CCL_4 (IR)	None	Expensive
	15	Ultraviolet Fluorescence		Limited Use	None	CCL_4-Hexane (UV)	None	Expensive
	16	Ultraviolet Absorption		Limited Use	Acidic	Hexane (UV)	None	Expensive
	17	Gas Chromatography	Concawe III-72	European Use	Acidic	CCL_4 or Pentane (GC)	Florisil	Expensive
	18	Visible Color Method	Hach Handbook-1973	General Use	None	3-4 Solvents	None	Inexpensive
	19	Color Comparator	Champion Chem. Co.	Very Limited	None	Special Chemical	None	Inexpensive
SAMPLING	20		EPA, ASTM, APHA	Wide Use	pH Control, Refrigeration, Time-Dependent, Glass Bottles			
CONTINUOUS MONITORS	21	Ultraviolet		Specific Applications	None	As Received	None	Moderate
		Visible						Inexpensive
		Infrared						Expensive
		Fluorescence						Expensive
		Light Scattering						Moderate

[a] For more information, see Reference 28.

TABLE 3 BEHAVIOR OF VARIOUS TYPES OF ORGANIC MATERIAL IN ASTM METHOD D-1252 FOR CHEMICAL OXYGEN DEMAND

Component	Reactivity, Percent of Theoretical			
References (a)	(1)	(2)	(3)	(4)
Aliphatic Compounds				
Acetone	98	96	94	-
Acetic Acid	-	98	-	-
Dextrose	95	-	-	-
Diethylene Glycol	-	-	70	-
Ethyl Acetate	-	-	85	-
Methyl Ethyl Ketone	-	-	90	-
Aromatic Compounds				
Acetophenone	89	-	-	-
Benzeldehyde	-	-	80	-
Benzene	60	41	-	-
Benzoic Acid	98	-	100	100
Dioctyl Phthalate	83	-	-	-
Ortho Cresol	95	-	95	-
Toluene	-	-	45	-
Nitrogen Compounds				
Acrylonitrile	48	-	44	-
Adenine	-	-	-	59
Aniline	80	-	74	-
Butyl Amine	57	-	-	-
Pyridine	0	1	-	2
Quinoline	-	-	-	87
Trimethylamine	1	-	-	-
Tryptophane	-	-	-	87
Uric Acid	-	-	-	64

(a) References:

(1) Unpublished data.
(2) Dobbs, R. A., Williams, R. T., Anal. Chem. 35, 1064 (1963)
(3) Buzzell, J. C., Young, R. H. F., Ryckman, D. W., "Behavior of Organic Chemicals in the Aquatic Environment: Part II, Dilute Systems," Manufacturing Chemists Association, April 1968, page 34.
(4) Chudoba, J. and Dalesicky, J., Water Research, V. 7, No. 5, 663, (1973).

BANQUET

Master of Ceremony -- Dr. J. Paschal Twyman
President
The University of Tulsa, Tulsa, Oklahoma

Paschal Twyman: "I am Paschal Twyman, and, as President of the University of Tulsa it is my privilege to welcome all of you to this Open Forum Banquet. As you are well aware this highly successful symposium on "Management of Petroleum Refinery Wastewaters" is co-sponsored by the EPA, the API, the NPRA, and T.U. Just before this banquet I was told that T.U. were the only initials which should be spelled out as Tulsa University; because the others - E.P.A., A.P.I., and N.P.R.A. - are so well known to all of us.

"As your M.C. for this banquet it is my pleasure to introduce to you the people at the head table. Starting at my left, that is your right, they are:"--

Fred Pfeffer, of the R. S. Kerr Environmental Research Laboratory, Ada, Oklahoma. Fred is the Project Officer for the EPA Grant sponsoring this Open Forum.

Milton Beychok, Consulting Engineer, Irvine, California. Our distinguished keynote speaker.

Herb Bruck, Technical Director, N.P.R.A. Herb is representing the NPRA, who are, of course, one of the sponsors of this symposium.

Nick Gammelgard, Senior Vice President, Environmental Affairs, A.P.I. Nick is our banquet speaker and is also representing the A.P.I., the other industrial sponsor of this symposium."

"Now on the other side starting at my right hand is:"--

Bill Galegar, Director, R. S. Kerr Environmental Research Laboratory, Ada, Oklahoma. Bill, as you remember, welcomed us this morning.

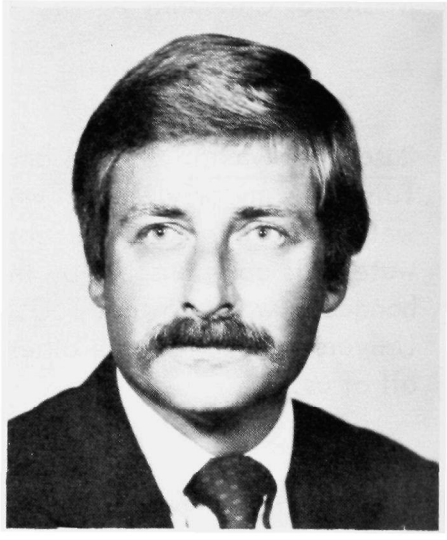
Nancy Manning, Research biochemist at St. Francis Hospital in Tulsa. Dr. Nancy Manning is also Mrs. Frank Manning.

Frank Manning, Professor of Chemical Engineering at Tulsa University. Frank is Project Director for the EPA Grant financing this Open Forum."

"Frank Manning will now introduce the banquet speaker."

Frank Manning then introduced Mr. Gammelgard. Mr. Gammelgard's address and biography follow on page 107.

BIOGRAPHY J. Paschal Twyman



Dr. Twyman holds the following degrees from The University of Missouri at Kansas City: B.A. in Sociology; M.A. in Educational Administration; and a Ph.D. in Education. Dr. Twyman served as a Professor of Education and Associate Director of the Research Foundation at Oklahoma State University and as Director of Research, Assistant to the Chancellor and Professor of Education at University of Missouri at St. Louis, before joining Tulsa University in 1967, as Vice President for Research and Development. Dr. Twyman became President of Tulsa University in 1968.

Dr. Twyman has extensive research experience and has published extensively on higher education. Dr. Twyman is also most active in numerous educational, charitable and community-service organizations.

BANQUET ADDRESS

"LET'S CHANGE COURSE AND SPEED"

P. N. Gammelgard, Vice President
American Petroleum Institute, Washington, D. C.

I am very glad to have been invited to participate in your Forum here in Tulsa. The wastewater management subjects that you will be discussing in your sessions this week are matters of great concern to refiners in this country --and, I have found, in other countries as well. On a recent trip to the USSR, for example, I found Russian refiners talking about some of the same things that you are talking about here.

A good many of the wastewater management problems that refiners face in this country can be traced to the Federal Water Pollution Control Act. That is hardly news. At the time of the passage of the 1972 Act, Congress was frustrated by the lack of progress that had been made under earlier versions of the Act. It determined that major legislation, with teeth in it, was necessary. But it also knew perils and pitfalls would be involved, as is the case with all legislation of such broad sweep and bite.

In this case, for example, many important water pollution control problems had not yet even been clearly defined. And certainly, to meet the ambitious goals of the Act, it would be necessary to develop new control technology, always a tricky business. Back in 1972, therefore, Congress wisely built into the Act some mechanisms that would facilitate making any necessary changes that might be indicated in the future.

Among other things, Congress established the National Commission on Water Quality. As you know, the Commission has just completed hearings on the staff draft of its report to Congress, which is due in March. As a result, some of the tools needed for making the kinds of changes envisaged by Congress are now at hand. I am referring to the really impressive amount of data in the draft report itself and the public hearing record.

This evening, I would like to offer for your consideration a general proposition which I believe would be helpful to bear in mind as we go about making such changes. Briefly, it is that our country is best served by the kind of environmental legislation that responds to clear environmental needs, has been carefully weighed against other pressing national needs, and promises to yield benefits commensurate with the costs involved.

In light of this proposition, I would like to talk with you, first, about the impact of the Federal Water Pollution Control Act on the petroleum industry -- and on the economy as a whole, for problems like the ones you are discussing here have reprecussions far beyond the refinery gate. Second, I would like to make some suggestions for amending the Act in ways that will enable this country to move ahead toward reasonable water quality goals, efficiently and effectively.

First, regarding impact, as this audience is well aware, life under the Act is very difficult for the regulated industries now and, unless some sound changes are made, will

be a great deal more difficult in the future. As things presently stand, the EPA Administrator must require what is, in his judgment, the best practicable control technology currently available to be installed by 1977 and the best available technology economically achievable by 1983. Beyond that date, the Act sets a national goal of elimination of discharge of pollutants, or EDOP, for 1985. Implicit in these three dates and in the increasingly stringent requirements for each date is a rapidly rising cost forecast that is of great concern to the petroleum industry and, indeed, to all affected industries.

That concern is justified. Many of you are familiar with the cost findings of API's 1973 Brown and Root study of the economics of refinery wastewater treatment. The study concluded that the cumulative capital investment in refineries alone to achieve the three levels of wastewater treatment required by the Act, adjusted to 1974 dollars, would reach $2.5 billion in 1977, $4.7 billion in 1983, and $6.7 billion in 1985.

Of even greater concern to us in the petroleum industry is the fact that much more attention needs to be given to the cost-benefit ratio associated with water pollution control requirements. The Brown and Root study plotted capital costs against water pollution reduction - - measured in terms of the three increasingly stringent levels of treatment technology and Biochemical Oxygen Demand, or BOD, discharges. The cost per annual pound of BOD removed from refinery effluent streams by the first level of control is estimated, again in 1974 dollars, to be about $10. The cost of application of the second level of technology for 1983, although it would bring only a small reduction in discharges, would just about double to some $20 per annual pound. And the cost of elimination of discharge of pollutants by 1985 would soar to more than $80 per annual pound - - about eight times the cost of the first level of control. That, in our judgment, is completely unreasonable.

The industry expenditures on water quality have already been substantial - - some $2.8 billion between the years 1966 and 1974. The very serious question now arising is whether, after already making notable progress, the petroleum industry should be required to continue to commit ever larger amounts of money to achieve even smaller reductions in water pollution. The anticipated reductions are so small, in fact, that in many, if not most cases, they could not even be accurately measured in the receiving waters.

In other words, whatever degree of success the petroleum industry and other industries should attain, at whatever cost, the quality of the receiving waters - - the name of the game, after all - - would remain about the same.

That bleak outlook is not the petroleum industry's alone. A few months ago, the Environmental Reporter carried a story on several of the regional assessment studies sponsored by the National Commission on Water Quality. These studies confirm the dismal cost-benefit picture. With regard to the Commission's study of the densely populated and industrialized Houston Ship Channel-Galveston Bay area, for example, the Reporter had this to say:

> The study concludes that the costs of meeting 1983 and 1985 scenarios would be disproportionate to the benefits of achieving the goals of the Act. Changes in water quality and hence recreational opportunities, number of aquatic and terrestrial biota, and aesthetics would be minimal . . .

Yellowstone country, on the other hand, is far from being densely populated and industrialized. Yet here, too, the Commission's investigators reached the same conclusion. Again according to the Environment Reporter:

> The report for the Yellowstone River Basin . . says the high concentration of nutrients in the river basin appears to be of natural origin. The river's tributaries contain high concentrations of sediments and total dissolved solids, mostly from natural and diffuse nonpoint sources . . . and they would not be significantly affected by implementation of the Act.

With so little to be gained in the way of improving actual water quality, even after heavy expenditures, it would seem wise -- indeed mandatory -- to assess our position in light of genuine environmental needs, other national needs, and, especially, costs and expected benefits.

Everyone I know in the petroleum industry is acutely aware of the need for such assessment. The primary mission of the industry, of course, is to help supply this country's energy needs. That is our reason for being. And we know that environmental expenditures on the order of magnitude required by the Act are bound to have an adverse effect on the industry's ability to generate the capital necessary to maintain a satisfactory growth pattern and meet future energy needs.

Capital formation is one of the most important problems -- possibly -- facing the petroleum industry. In the years ahead, if the nation is to achieve reasonable energy self-sufficiency, the industry's capital needs are going to be staggering. It is therefore essential that legislators and government environmental planners -- at some point along the ling, and the sooner the better -- consider all of the industry's environmental expenditures together and then relate them to the industry's expected capital requirements for all purposes.

The plain fact is that the amount of capital available to the industry in a given year is limited. The capital used to meet environmental requirements simply is not available to meet other pressing requirements, including, particularly, exploration and production -- the bedrock upon which a major part of the nation's energy supply structure is built.

What these environmental costs are likely to mean is becoming clearer and more urgent by the day. In the same year that the Brown and Root refinery study was completed, API did what it has long been recommending that legislators and government environmental planners do. It embarked upon a much broader study covering all environmental costs to all segments of the industry. Phase I of that study, a literature survey, was published in 1974. Phase II, forecasting environmental costs to the industry for present and future environmental regulations, is now being finalized.

According to the preliminary findings of Phase II of the study, the cost of meeting anticipated federal, state, and local environmental regulations between 1975 and 1985 to the petroleum industry -- expressed in 1974 dollars -- will be $20.1 billion. This figure, incidentally, does not include the cost of the 1985 goal of EDOP, which, again, we

believe to be unreasonable and most probably unattainable. Excluding EDOP, the cost of meeting water quality regulations is estimated to be about $8 billion, or some 40 percent of total environmental expenditures.

The magnitude of the additional $20.1 billion environmental investment for the 1975-1985 period can be put in perspective by comparing it with recent and projected levels of total capital spending by the petroleum industry. That $20.1 billion, for example, is almost as much as the $21.3 billion that the U.S. petroleum industry laid out in total capital and exploratory expenditures during the two-year period 1972-1973. In the next decade, however, and for as far ahead as we can see, the industry's total capital requirements -- in current dollars, with a five per cent inflation factor -- are expected to be on the order of $40 billion a year. The question is: Where is all of that capital going to come from?

The coming capital bind is there for all to see. The pool of funds available to the nation for pollution control is limited -- including, certainly, funds for water pollution control. We simply do not have the wherewithal to accomplish all that has been promised by the Federal Water Pollution Control Act within the time frame specified.

I would like to turn now to some suggested amendments to the Act. Like everyone else who must deal with the provisions of the Act, we in the petroleum industry have compiled a long list of such suggestions. This evening, however, I want to mention just three of the most important ones, designed to provide some of the things now sorely lacking -- namely, achievable deadlines, realistic water quality goals, and ensuing environmental benefits commensurate with the costs to society:

1. Extension of the 1977 Deadline. EPA has already concluded that because of lack of funds, 50 per cent -- some 9000 -- of the municipalities that will be serving 60 per cent of the 1977 population will not be able to comply with the 1977 sewage treatment requirements of the Act. The Agency therefore recommends that the 1977 deadline be extended to about 1983 -- for municipalities. That may or may not be the optimal date, but we in the petroleum industry agree that an extension certainly is indicated. We also feel, however -- and very strongly -- that the deadline should be extended for industry, too, especially since such extension would not prevent EPA or the states from requiring earlier compliance where possible through the individual permit program.

As you know, a part of the problem is that some refineries and smaller facilities like terminals and service stations discharge to municipal sewers. Such facilities must rely on municipal treatment plants for removal of compatible pollutants in order to comply with 1977 requirements. It is worth adding that industry must bear 100 percent of the costs, while municipalities need bear only 25 per cent of the capiral costs for federally approved projects. Clearly, to extend the deadline for municipalities and not for industry would be inequitable in the extreme.

2. Modification of the Requirement for Best Available Technology Economically Achievable for 1983. Once both municipalities and industry are in compliance with the first treatment level requirements -- at whatever date compliance is achieved -- it would be unwise to continue to require application of tremendously expensive second level technology everywhere, indiscriminately. The National Commission on Water Quality's studies

show that water quality is improving faster than expected and that implementing the 1977 requirements of the Act will produce better water quality than was anticipated at the time of enactment. The Commission's studies also show, as I mentioned earlier, that the benefits of implementing the second level of technology would not in general be commensurate with the costs. The limitations and other controls imposed by the Act for second level technology, therefore, should be applied only in those cases where they are necessary to achieve receiving water quality and then only when the environmental benefits exceed the costs to society.

3. Redefinition of the Term "Pollutant." In general, the Act fails to distinguish between natural and man-made pollutants. The Act also fails to recognize that substances now termed pollutants are not in all cases harmful Salt and suspended solids, for example -- whether natural or resulting from man's activities -- often occur without harm to waters or to the biota in them. What is needed is a definition of "pollutant" which excludes substances which are discharged in quantities too small to cause damage. It would then be possible to establish -- not the Act's present national goal of elimination of discharge of pollutants, which just is not going to happen -- but a national goal of elimination of discharge of harmful quantities of pollutants, which well could happen.

These amendments, if enacted, would not solve all of the nation's water quality problems. They would clarify some of the nation's water quality goals and set reasonable deadlines and procedures for attaining them. And from clear goals and reasonable deadlines come the capacity of regulatory agencies to regulate wisely and the capacity of industry and municipalities to comply at acceptable cost.

This position was championed last week by Bill Ruckelshaus, "Congress has an almost neurotic fixation for setting deadlines on environmental matters that are unachievable. Then by promising something we cannot achieve we become incapable of measuring progress. A delay of one year in meeting the standard that denied reality to begin with makes it look as if EPA is copping out and all the progress that has been made is ignored. Adjustments to some of the schedules are necessary for a sane and a reasoned approach to such a vital national goal. The question should not be whether an environmental law is tougher but whether it is wise and in the best interests of the whole country."

John Quarles, last December, also espoused these views in a letter to me, "On the side of disappointment, we are all now wiser but sadder as to the ability and solve national pollution problems quickly. It is now evident that the work of cleaning up pollution will require intensive efforts throughout the next ten or fifteen years and that many important environmental goals will not be reached any sooner than that. Passing a law does not by itself solve a problem. Manpower, money and in some cases technica, advances must also be provided and experience leads me to conclude that in a national program tackling complex problems the achievement of results takes patience as well as persistence. The risk this creates is that if the intensity of effort weakens along the way some of the goals may never be achieved."

The national badly needs to move ahead toward its water quality goals at a more considered pace, allowing ample time to take into account all of its peoples' needs and

how best and most economically to meet them. To answer to that need, let's change course and speed.

BIOGRAPHY



Peter N. Gammelgard is the Vice President of the American Petroleum Institute responsible for Industry Affairs. He holds a B.S. degree in Engineering from Northwestern University. He served as a Commander in the U.S. Navy during World War II. He has been a Vice President of the Air Pollution Control Association and past President of the National Petroleum Refiners Association. He has participated in environmental conferences around the world and has been active in the affairs of the World Energy Conference.

SESSION III

"BIOLOGICAL TREATMENT"

Chairman

George W. Reid
Regents Professor of Civil Engineering
University of Oklahoma, Norman, Oklahoma

Speakers

W. Wesley Eckenfelder

"Activated Sludge Treatment of Petroleum Refinery Wastewaters an Overview"

James F. Grutsch

"A New Perspective On The Role Of The Activated Sludge Process and Ancillary Facilities"

Charles E. Ganze

"Case History On Biological Treatment Of A Petroleum Refinery Wastewater"

Mohammed A. Zeitoun

"Optimization Of The Activated Sludge Process Through Automation"

Fred M. Pfeffer

"The National Petroleum Refinery Wastewater Characterization Study"

BIOGRAPHY

George W. Reid, born 1917, Indianapolis, Indiana, attended Shortridge High School, Purdue, Harvard and Johns Hopkins Universities, studying Civil and Sanitary Engineering. Employed by the Indiana State Health Department, a sanitary engineer with USPHS, MCWA and CDC. Has taught at Purdue, Johns Hopkins, Florida and George Tech. Currently teaching at the University of Oklahoma as Regents Professor of Civil Engineering and Environmental Sciences and is the Director of the Bureau of Water and Environmental Resources Research. Holds degrees from Purdue and Harvard Universities.

Has published numerous articles, etc., in the field (170); is and has been consultant to the USPHS, EPA, Interior, USAF, WHO (PAHO), AID and others in water and public resources systems. Recently involved in extensive research on modeling of natural and man-made public systems. Lectures at r recent Urban Water Systems Conferences and seminars in Colorado, New Mexico, Bogota, Lima, Europe, etc.

ACTIVATED SLUDGE TREATMENT OF PETROLEUM REFINERY WASTEWATERS AN OVERVIEW

W. Wesley Eckenfelder, Jr.
Distinguished Professor of Environmental and Water Resources Engineering
Vanderbilt University, Nashville, Tennessee

This discussion will consider aerobic biological treatment in the activated sludge process. The two basic equations which describe the aerobic biological mechanism are:

$$\underset{(s)}{\text{Organics}} + \overset{(a')}{O_2} + N + P \xrightarrow[(k)]{\text{cells}} \text{new cells} + \overset{(a)}{CO_2} + H_2O + \text{nondegradable soluble residue} \quad (1)$$

(BOD, COD, TOC)

$$\underset{(X_v)}{\text{Cells}} + \overset{(b')}{O_2} \xrightarrow{(b)} CO_2 + H_2O + N + P + \text{nondegradable cellular residue} \quad (2)$$

Equation (1) is the synthesis equation and occurs in the presence of degradable organics and biological cells with oxygen, nitrogen, and phosphorus present. Equation (2) is the endogenous breakdown of the biological cells, and occurs continuously in an aerobic environment.

In order to design an aerobic biological process it is necessary to balance equations (1) and (2). Since petroleum refinery wastewaters contain an unknown mixture of organics, it is necessary to operate a laboratory or pilot plant program to define the coefficients to balance these equations. In some cases experience elsewhere may be employed. The pertinent parameters for design purposes in equation (1) are the coefficient a' which is the fraction of organic matter removed in terms of BOD, COD or TOC oxidized for energy; the coefficient a which is the fraction of organic matter removed converted to new cells expressed as volatile suspended solids; the rate coefficient k is a measure of the rate of oxidation of the organics present in the wastewater. The coefficient b in equation (2) is the fraction per day of the biodegradable volatile suspended solids oxidized. Since it requires approximately 1.4 pounds of oxygen to oxidize one pound of biological cells as volatile suspended solids, the coefficient b' is generally approximately 1.4b. For all practical purposes organic matter removed in the process is either oxidized for energy or converted to biological cells (except for the small fraction of organics which result in nondegradable by-products as shown in equation (1)). Therefore, on a COD or ultimate BOD basis, the coefficients $a + a' = 1$. As shown in equations (1) and (2), the biomass as volatile suspended solids is denoted by the symbol X_v and the organics expressed as BOD, COD or TOC by the symbol s. It should be noted that the nondegradable soluble residue indicated in equation (1) results from the accumulation of nondegradable organic by-products from the biological oxidation process. It has been found that the magnitude of this value usually falls between 1 and 5 percent of the influent COD. The nondegradable cellular residue as shown in equation (2) will amount to approximately 23 percent by weight of the volatile

suspended solids generated in equation (2). It can therefore be concluded that the pertinent parameters required for bio-oxidation design are those indicated in equations (1) and (2), namely a', a, k, b and b'. Typical values found for petroleum refinery wastewaters are summarized in Table 1. These reactions as they would occur in a batch oxidation system are shown in Figure 1.

Figure 2 illustrates the breakdown of 1 pound of degradable COD in accordance with equations (1) and (2). Analysis of the wastewater in Figure 2 indicates that the COD/BOD_5 ratio is 1:0.75; a' and a are 0.5 on a COD basis. It is assumed that 1.4 lbs O_2 will oxidize 1 lb cell mass as VSS.

DESIGN RELATIONSHIPS

As can be deduced from equations (1) and (2) nondegradable volatile suspended solids will accumulate in the process as auto-oxidation of the cellular mass proceeds.

In order to develop process design relationships it is therefore first necessary to define the degradable fraction, x, of the volatile suspended solids (biomass) in the aeration process. The degradable fraction is a function of the sludge age or the length of time the volatile suspended solids are in the process as shown in Figure 3. Sludge age in the activated sludge process can be defined by the relationship:

$$\text{Sludge Age} = \frac{X_v \ \text{(lbs)}}{\Delta X_v \ \text{(lbs/day)}} \tag{3}$$

in which ΔX_v is the volatile suspended solids wasted per day from the process. As the sludge age is increased the nondegradable materials accumulate and the degradable fraction decreases as one would expect. The relationship shown in Figure 3 represents average conditions for a petroleum refinery wastewater.

The kinetic relationship employed for the design of a completely mixed activated sludge process is based upon the removal of most soluble simple organic compounds as a zero order reaction. In a multi-component wastewater a number of zero order reactions occur concurrently. The summation of these zero order reactions can be expressed in an exponential form for a batch reaction or employing equation (4) for a completely mixed continuous flow reactor.

$$\frac{S_o - S_e}{X_v t} = k S_e \tag{4}$$

In cases where the influent concentration of the wastewater varies markedly, equation (4) may be modified to equation (5) which considers variable influent wastewater strength.

$$\frac{S_o - S_e}{X_v t} + k S_e/S_o \tag{5}$$

When COD or TOC are employed as a parameter of organic strength, the nondegradable portion of the TOC or COD must be substracted from the total as shown in Figure 4. It

should be noted that the reaction coefficient $\underline{k}$ in equations (4) and (5) relates to a specific wastewater composition. If the wastewater composition varies the reaction rate coefficient $\underline{k}$ may also be expected to vary.

It should be noted that the effluent concentration defined by equations (4) and (5) are soluble concentrations. In order to determine the total BOD in the effluent it is necessary to add that contributed by the effluent suspended solids. While the BOD contributed by the effluent suspended solids will be a function of sludge age (increasing sludge age decreases the degradable fraction) for most activated sludge processes in the petroleum refining industry, a value of approximately 0.3 mg BOD/mg SS may be used.

The total oxygen requirements in the biological process are related to the oxygen consumed to supply energy for synthesis (equation 1) and the oxygen consumed for endogenous respiration of the biological cells (equation 2). Total oxygen requirements can therefore be defined by equation (6) and shown in Figure 5.

$$O_2/\text{day} = \underline{a}' (S_o - S_e) + \underline{b}' x(X_v) \tag{6}$$

If nitrification is occurring in the process this oxygen will also be included in equation (6) and considered in the coefficient $\underline{a}'$.

Sludge accumulation from the biological treatment of petroleum refinery wastewaters can be similarly calculated. Volatile suspended solids accumulation, ΔX_v, is equal to that resulting from synthesis (equation 1) plus the influent volatile suspended solids not degraded in the process, minus the volatile suspended solids oxidized by endogenous metabolism (equation 2). This relationship is shown in equation (7) and Figure 6.

$$\Delta X_v = \underline{a} (S_o - S_e) + S_i - bx(X_v) \tag{7}$$

One further consideration in the activated sludge process is that the biological sludge generated in the process flocculates, settles and compacts in the final clarifier. In most cases the sludge settling characteristics have been found to relate to the organic loading to the process (F/M) expressed as pounds of BOD applied per pound of MLVSS.

$$F/M = \frac{S_o}{X_v t} \tag{8}$$

In order to insure good settling properties, the F/M should be maintained within an acceptable range as shown in Figure 7. If the F/M becomes too high, frequently non-settling filamentous growths will result creating sludge bulking. If the F/M remains too low, autooxidation of the biological floc and resulting floc dispersion causes an increase in effluent suspended solids and a bulking condition.

The final clarifier is an important consideration in the process design of the activated sludge process. The solids flux to the clarifier and hence the underflow solids concentrations attainable are related to the zone settling velocity of the biological sludge mixture. These relationships are shown in Figure 8.

ATTAINABLE EFFLUENT QUALITY

Considering the performance of biological treatment plants the primary factors which will affect effluent quality are aeration basins, temperature, changes in organic loading (as reflected in the F/M) and changes in product mix (as reflected in the $\bar{k}$ value). Where temperature is critical for effluent quality during winter operation the aeration system should be selected to minimize heat loss, usually a submerged aeration system. By contrast, high temperatures during summer operation can be minimized by the use of surface aerators which maximize heat loss from the aeration basin. Covered basins as employed in the high purity oxygen process will maintain high temperatures during cold weather operation.

Changes in organic loading can best be dampened by equalization. Since, all other things being equal, the effluent BOD will be directly proportional to the influent, the equalization basin can be designed for whatever maximum effluent levels are permissible. Variations in organic loading can also be compensated by increasing the sludge recycle, thereby maintaining the F/M constant. The most difficult effect to assess is changes in the reaction rate $\bar{k}$ due to changes in wastewater composition. In some cases the plant operating conditions can be modified for a change in plant production schedule. Equalization will also help to dampen this variability. While the effects of temperature and organic loading variation can be calculated from the design relationships, it is not possible in most cases to calculate the effect of product mix. In this case a statistical approach using operating data is necessary.

Long-term case histories of a number of activated sludge plants in the petroleum refining industry have been reported in a study for the National Commission on Water Quality (2) and are summarized in Table 2. The variability in effluent quality which might be expected for these parameters are shown in Table 3.

It may be expected, therefore, that as a refinery becomes more complex there will be a greater variation in wastewater composition and hence a greater variation in $\bar{k}$. The net effect of this considering equations (4) and (5) is to increase the variability in effluent concentration, S_e, on a daily basis. Refineries in the northern part of the United States would be expected to have a greater monthly variability due to seasonal temperature effects than those in the south.

LIST OF SYMBOLS

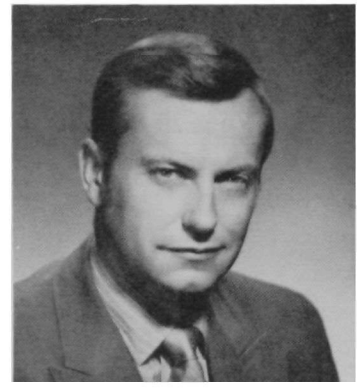
$\bar{a}$ lbs VSS produced per lb BOD, COD or TOC removed
$\bar{a}'$ lbs oxygen required to oxidize one lb of BOD, COD or TOC
$\bar{A}$ Area
b lbs VSS destroyed per day per lb oxidizable MLVSS
$\bar{b}'$ lbs oxygen per day per lb oxidizable MLVSS
$\bar{C}_L$ Oxygen concentration in the basin
F/M Food-to-Microorganism Ratio
hr Hour
k Organic removal rate coefficient, $days^{-1}$
MLVSS mixed liquor volatile suspended solids

N oxygen transfer coefficient, corrected for field conditions
N_o Oxygen transfer coefficient under standard conditions
OR Clarifier overflow rate (gpd/sq ft)
Q Flow rate
R Recycle flow
S_e effluent organic concentration
S_o Influent organic concentration
t Time
T Temperature
T_w Basin temperature
S_i Average influent suspended solids
X_v Volatile suspended solids
α Ratio of oxygen transfer rate of waste to water

REFERENCES

(1) Eckenfelder, W. W., "Principles of Biological Treatment," Vanderbilt University, Nashville, Tennessee, 1975.
(2) Engineering Science, Inc., "Petroleum Refining Industry Technology Costs of Wastewater Control," Report to the National Commission on Water Quality, June, 1975.
(3) Engineering Science, Inc., "Activated Sludge Treatability of Petroleum Refinery Wastewaters," 1975.

BIOGRAPHY



W. Wesley Eckenfelder holds a B.E. from Manhattan College; a M.S. from Pennsylvania State University; and a M.E. from New York University. Professor Eckenfelder has served on the faculty of Manhattan College, the University of Texas at Austin, the University of Delft in Holland, and is now a Distinguished Professor of Environmental and Water Resources Engineering at Vanderbilt University. Wes is also Board Chairman of AWARE, Inc. and has written over 200 publications and 11 books on water quality management. Professor Eckenfelder has received many awards.

DISCUSSION

Bob Worton: Would you care to comment on the effect of polyelectrolytes on keeping suspended solids down in the final effluent when operating with a high degree of nitrification.

Wes Eckenfelder: The polyelectrolytes probably would not help much, since denitrification occurring in the final clarifier would lead to floating sludge due to the nitrogen gas bubbles released during the process of denitrification.

Bob Worton: Do you know any research in this area?

Wes Eckenfelder: Specifically on nitrification, no. I think the answer to this problem, however, is to remove the sludge from the final clarifier before active denitrification sets in.

Juanito Chavez: My first question is also on the polyelectrolyte injection. In commercial application is there any specific point where you would inject the polyelectrolyte in such a way that you effect good distribution and at the same time not destroy the biological floc.

Wes Eckenfelder: To my knowledge, I know of no full-scale plant that has been using polyelectrolytes for effluent suspended solids control for long periods. All of the experimental studies that I have been associated with have injected the polymer prior to going into the final settling tank. In view of the fact that most of these have not been pre-engineered to optimize the process, much of the data is erratic.

Bill Oberman : Would you care to comment on the use of dissolved air flotation instead of secondary clarification, where poor settling sludges are involved?

Wes Eckenfelder: Some years ago I was involved in engineering an activated sludge system employing BAF in lieu of secondary clarification. While a reasonably concentrated sludge was obtained for re-cycle, the effluent suspended solids from the flotation unit were highly variable. It is possible that advances in flotation practice may overcome this problem to date.

Larry Eckelberger: What type of variability factors can be achieved in your opinion?

Wes Eckenfelder: I quote here data that generates out of the Petroleum Industry report to the National Commission on Water Quality. Monthly variability in BOD is 2.7 times the average with daily variability in BOD being 5.4 times the average. For effluent suspended solids, monthly variability is 2.5 and daily variability 3.8. I consider these realistic limits.

John Garner: This question may be a little premature and may be that it will be answered later, but I have found in raw waste BOD that I require 20 to 25 aeration horsepower and in practical application I find I need 50-55 horsepower.

Wes Eckenfelder: I have no figures specifically for the petroleum refining industry, but in the pulp and paper industry, we generally estimate 45 pounds of BOD removed per day per horsepower as a rule-of-thumb. I see no reason why this would be markedly different in petroleum.

TABLE 1 "BIOLOGICAL TREATMENT COEFFICIENTS FOR PETROLEUM WASTES (3)"

Refinery Category (EPA)	Size (MBPD)	k* 1/days BOD	k* 1/days COD	Sludge Growth Coefficients BOD Basis a	Sludge Growth Coefficients BOD Basis b'	Sludge Growth Coefficients COD Basis a	Sludge Growth Coefficients COD Basis b'	Oxygen Requirements Coefficients BOD Basis a'	Oxygen Requirements Coefficients BOD Basis b'	Oxygen Requirements Coefficients COD Basis a'	Oxygen Requirements Coefficients COD Basis b'	Influent mg/l BOD	Influent mg/l COD
E	406	4.15	2.74	-	-	-	-	-	-	0.57	0.1	244	509
C	60	--	7.97	-	-	0.5	0.06	-	-	0.06	0.11	575	980
D	90	--	5.86	-	-	0.5	0.06	-	-	0.34	0.06	396	782
C	63	--	2.92	0.5	0.08	0.44	0.1	-	-	0.35	0.08	153	428
E	427	0.595	5.0	0.5	0.05	0.26	0.03	0.47	0.28	0.46	0.05	600	170
B	205	--	7.79	-	-	0.2	0.08	-	-	0.40	0.01	--	563
C	88.4	--	7.24	-	-	0.43	0.10	-	-	0.52	0.14	345	806
-	--	3.84	--	0.6	0.05	-	-	0.88	0.10	-	-	160	--

* at 24°C k = organic removal rate at 24°C
' based on total VSS

TABLE 2 "LONG TERM EFFLUENT CONCENTRATIONS FROM THE ACTIVATED SLUDGE PROCESS (2)"

Sub-category	Capacity (1000b/S_d)	mg/l BOD	COD	TSS	Oil	Phenol	NH_3-N	$S^=$
C	60	13	174	78	9.4	.053	1.1	0.27
C	63	16	130	30	9.0	.15	6.7	--
B	135	18	132	23	--	--	--	--
B	63	28	183	41	--	--	--	--
B	205	12	112	15	9.9	.04	8.2	--

TABLE 3 "VARIABILITY OF EFFLUENT LEVEL IN ACTIVATED SLUDGE TREATMENT (2)"

		BOD	COD	TOC	TSS	Oil	Phenols	NH_3-N
Daily	Min	3.8	1.9	--	2.4	3.9	4.5	9.5
	Max	7.6	5.0	--	5.2	5.2	5.2	10.9
	Ave	5.4	3.6	3.5	3.8	4.7	4.9	10.2
Monthly	Min	2.2	1.5	--	1.5	1.8	1.4	2.1
	Max	4.6	1.9	--	3.3	2.9	3.4	4.1
	Ave	2.7	1.8	2.9	2.5	2.2	2.5	3.4

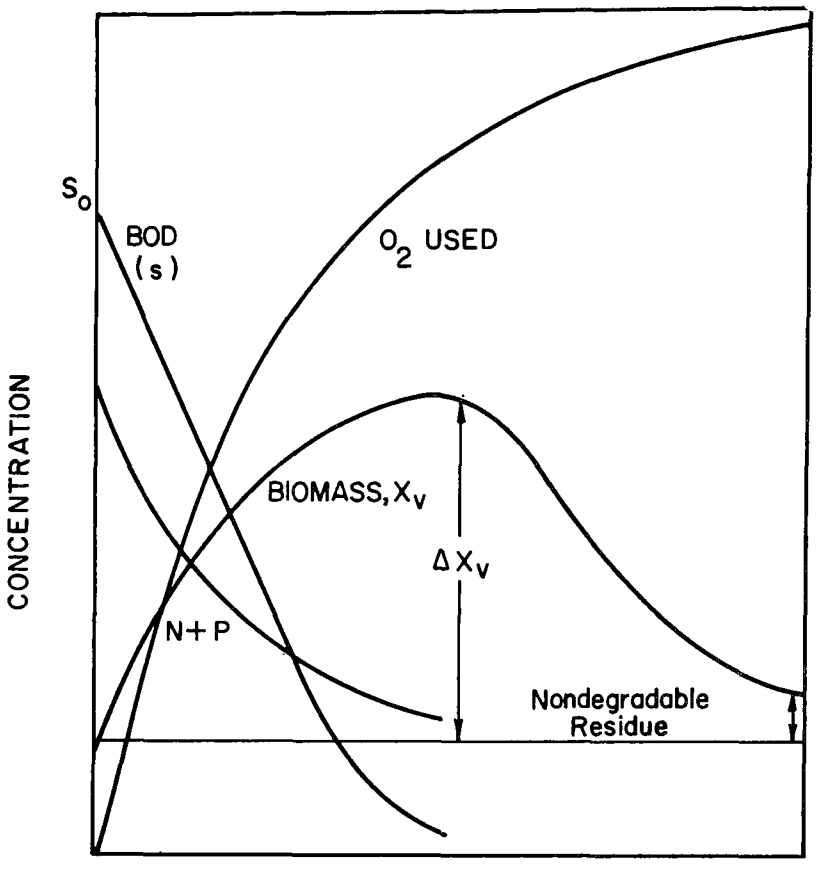


Figure 1. SCHEMATIC OF AEROBIC BIOOXIDATION PROCESS

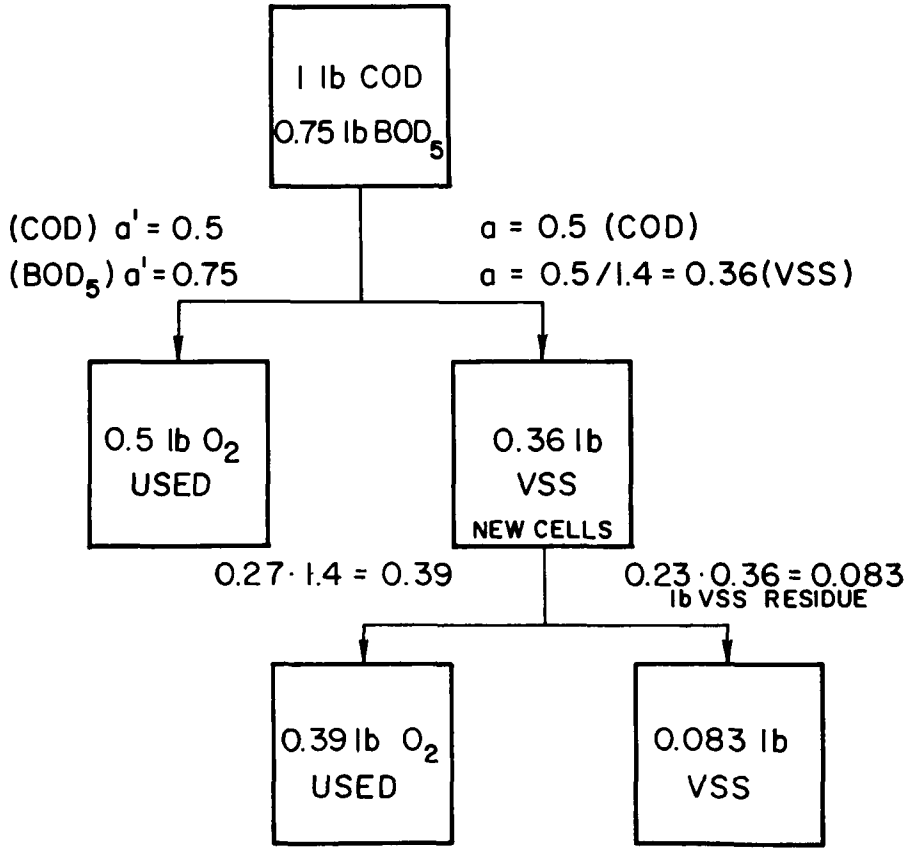


Figure 2 .

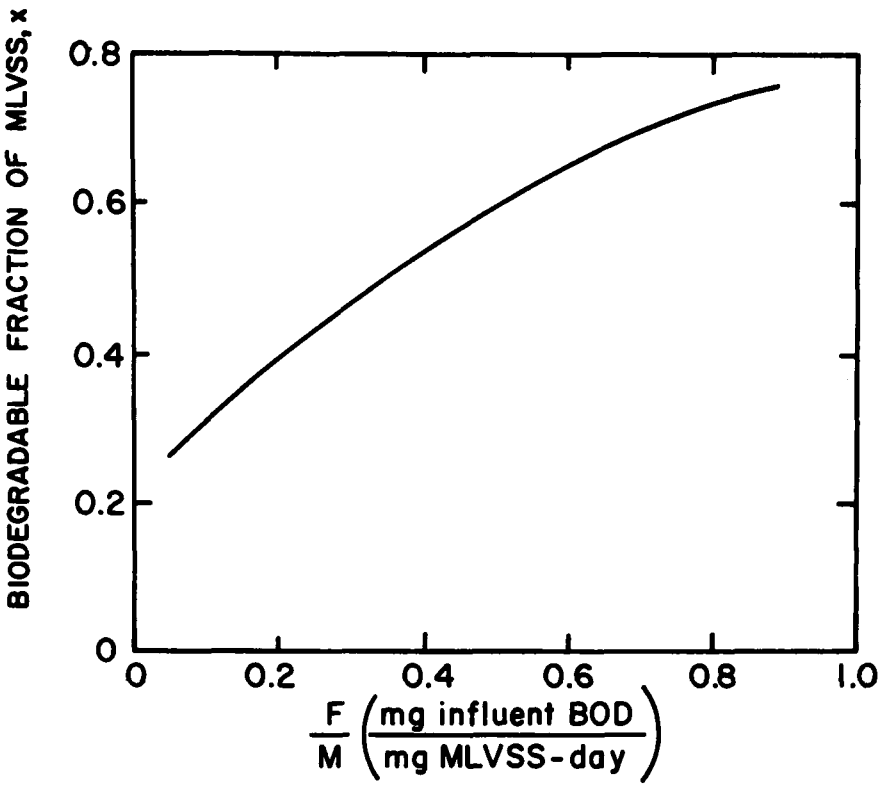


Figure 3. CORRELATION OF BIODEGRADABLE FRACTION OF MLVSS, x, WITH ORGANIC LOADING, F/M.

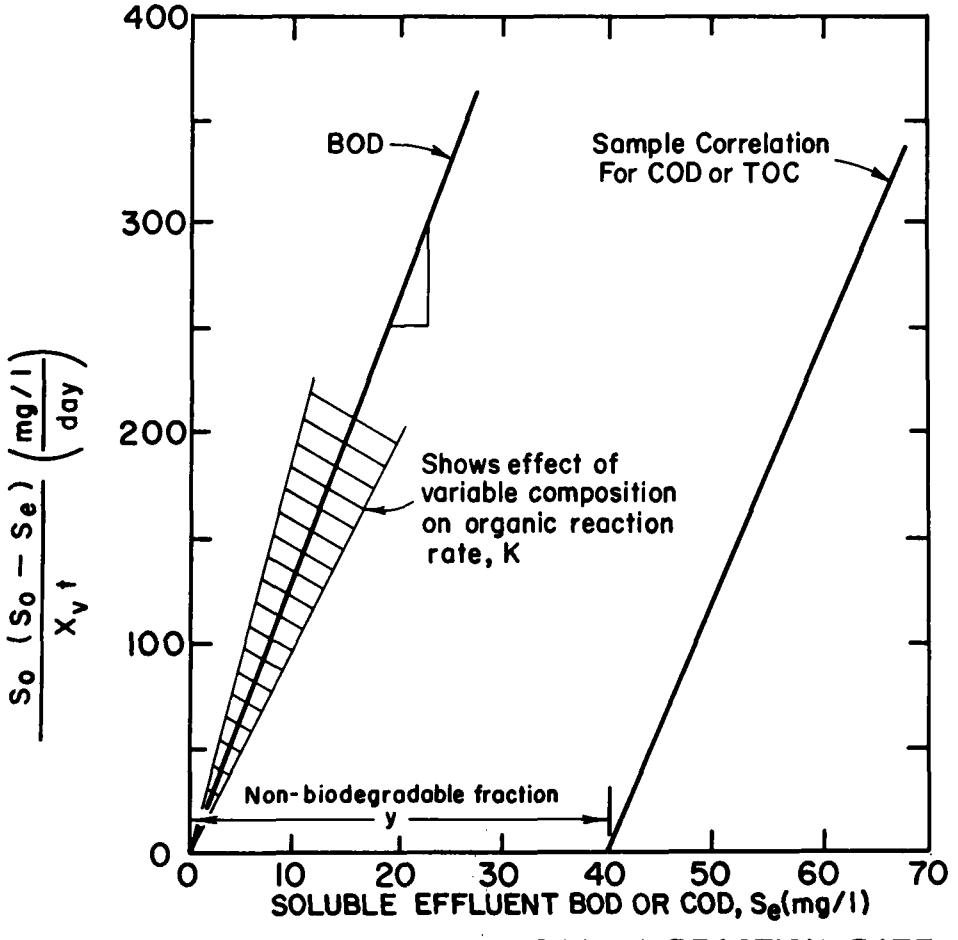


Figure 4. DETERMINATION OF ORGANIC REACTION RATE COEFFICIENT (EQUATION 5)

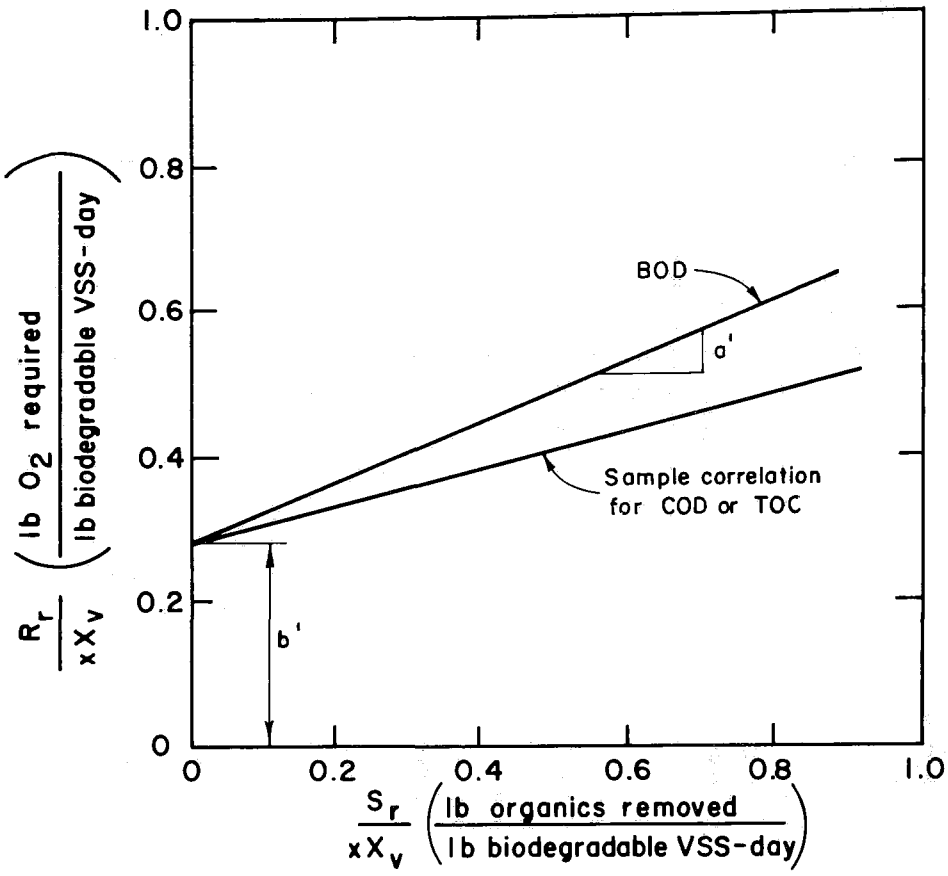


Figure 5. DETERMINATION OF OXYGEN UTILIZATION COEFFICIENTS (EQUATION 6)

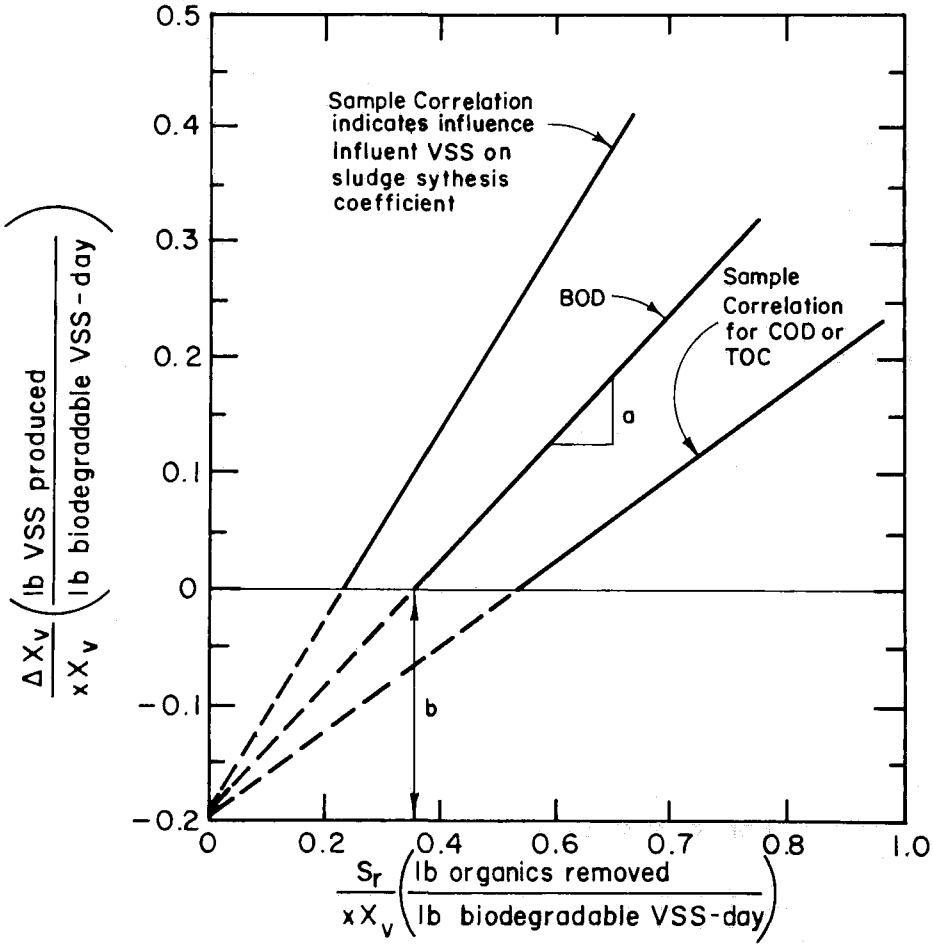


Figure 6. DETERMINATION OF SLUDGE PRODUCTION COEFFICIENTS (EQUATION 7)

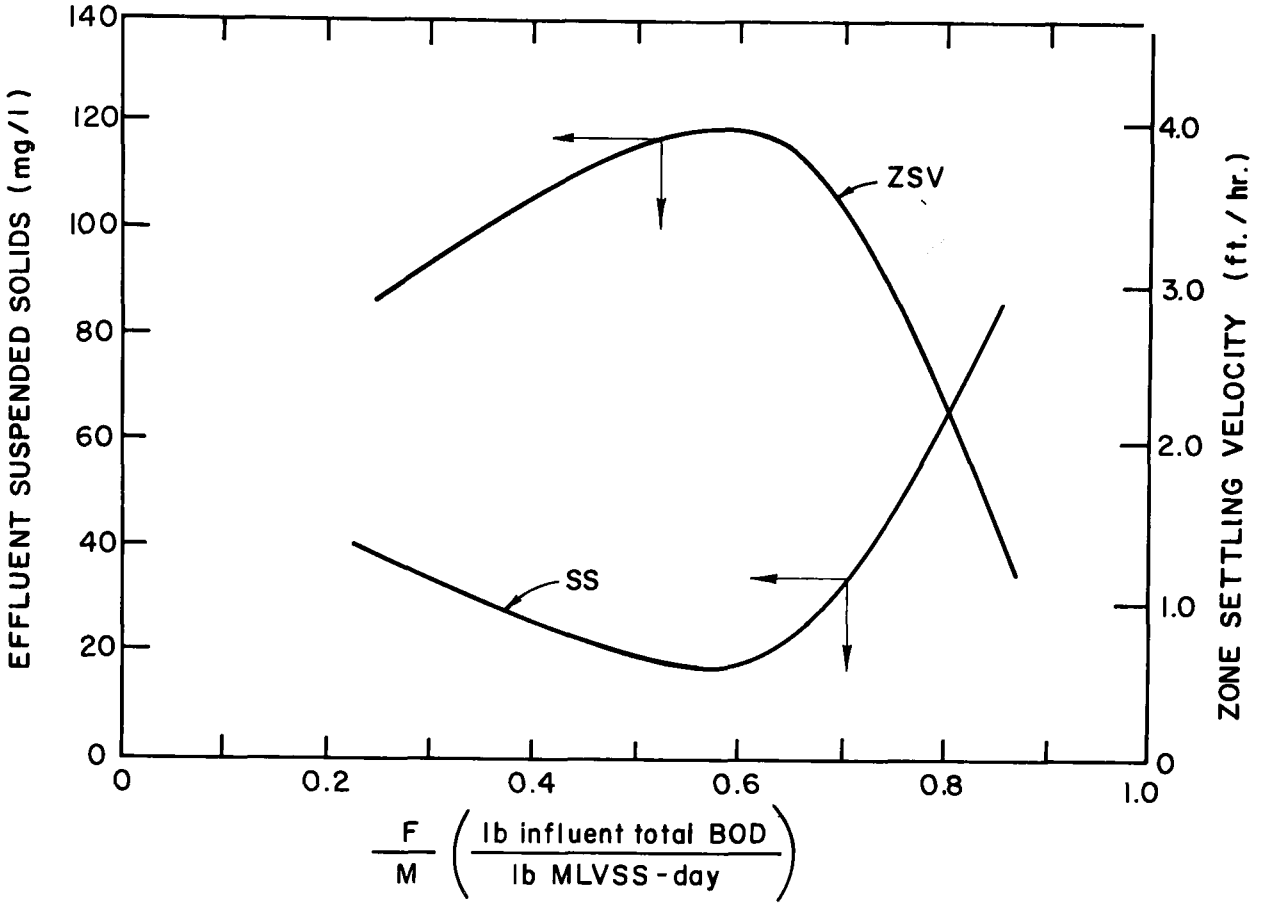


Figure 7. CORRELATION OF EFFLUENT SUSPENDED SOLIDS AND ZONE SETTLING VELOCITY WITH F/M.

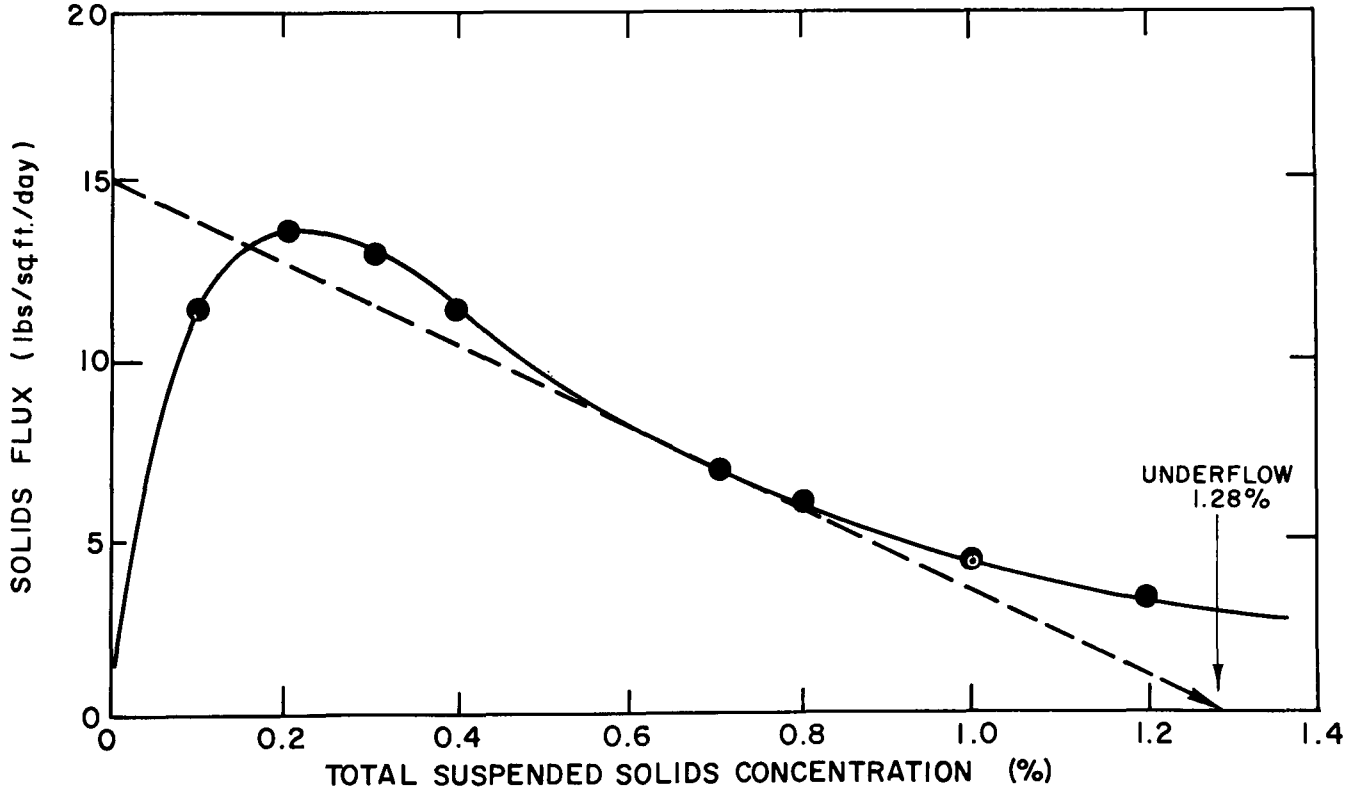


Figure 8. BATCH SOLIDS FLUX CURVE FOR CLARIFIER DESIGN

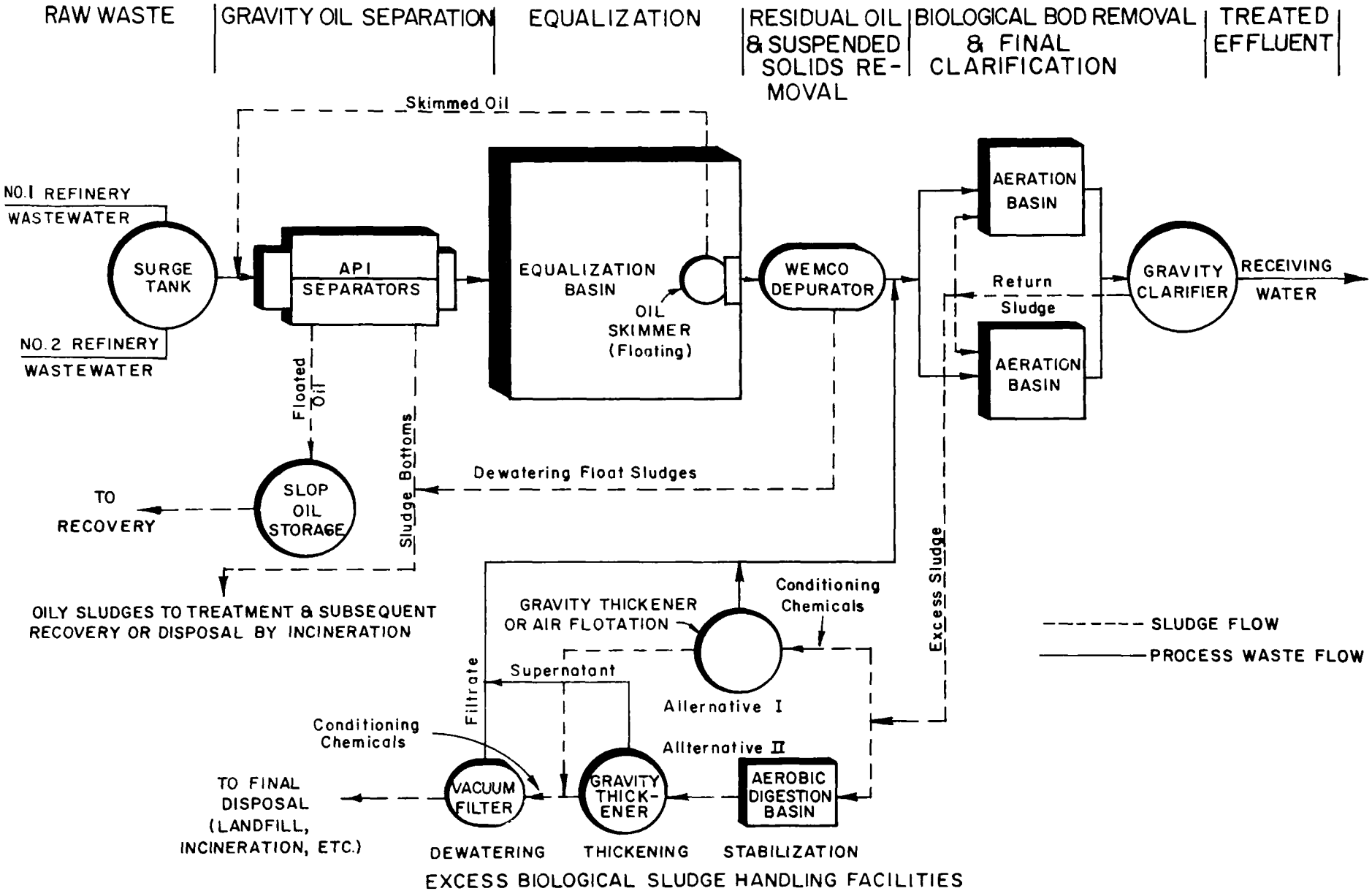


FIGURE 9: SCHEMATIC PROCESS DESIGN FLOWSHEET FOR ACTIVATED SLUDGE SYSTEM

"A NEW PERSPECTIVE ON THE ROLE OF THE ACTIVATED SLUDGE PROCESS AND ANCILLARY FACILITIES"

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Refiners have found the activated sludge process (ASP) to be a very effective and broadly applicable process. The versatility of the ASP has impressed many users and emphasis has been placed on this aspect of the process. However, design and operation of the ASP have not proceeded in a direction that is optimum for meeting future effluent quality goals. The ASP is generally used to achieve major reductions in suspended and colloidal material, as well as dissolved substances. When the refiner is almost wholly dependent on ASP to achieve end-of-pipe treatment objectives, this operating mode may achieve the best overall reduction in contaminants. In the future, however, the refiner will be confronted with very restrictive effluent limits on suspended solids, BOD, COD, ammonia, and some bioresistant materials, as well as variability limits for each parameter as conditions for obtaining an NPDES permit. Under these conditions, the ASP becomes only one of a series of process steps required to meet the objectives. When viewed in this context, the ASP can be optimized to achieve further control of process variability and increased removal of soluble contaminants to concentration levels below that achievable by activated carbon. The key to optimizing the ASP in this new mode is to design and operate the preceding end-of-pipe process facilities for maximum removal of interfering colloidal and suspended contaminants.

APPLICABLE REFINERY TREATMENT TECHNOLOGY

Best practicable control technology currently available (BPCTCA), as defined by the federal Environmental Protection Agency (EPA) for petroleum refineries, is based on both in-plant and end-of-pipe control technology. Suggested in-plant controls include:

1. Installation of sour water strippers to reduce the sulfide and ammonia concentrations entering the treatment plant.

2. Elimination of once-through barometric condenser water by using surface condensers or recycle systems with oily water cooling towers.

3. Segregation of sewers, so that uncontaminated storm runoff and once-through cooling waters are not treated normally with the process and other contaminated waters.

4. Elimination of polluted once-through cooling water by monitoring and repair of surface condensers, or by use of wet and dry recycle systems.

EPA recognizes also that good housekeeping practices and precautionary measures

taken during the turnaround of operating units are important considerations that can have a substantial impact on waste loads discharged to end-of-pipe water treatment facilities.

BPCTA end-of-pipe treatment technology is based upon the existing waste water treatment processes currently used in the industry. Although various options are possible, as shown in Figure 1, the most sophisticated and complete end-of-pipe treatment sequences usually make provision for equalization and storm water diversion; initial oil and solids removal in API or parallel plate separators; further oil and solids removal in filters, clarifiers, or dissolved air flotation units; carbonaceous wastes removal by any of several biological oxidation processes or combinations thereof; and a final clarification or polishing step, consisting of chemical coagulation or destabilization and either dissolved air flotation or granular media filters for phase separation. For BATEA, in 1983, the contaminant concentrations achievable by an additional activated carbon process element is an indicated objective.

More specifically, the principal objectives of the end-of-pipe treatment sequence for process design considerations are as follows:

1. Maximize removal of soluble contaminants contributing to biochemical oxygen demand (BOD).

2. Maximize ammonia removal.

3. Maximize removal of contaminants contributing to chemical oxygen demand (COD).

4. Maximize final effluent clarity.

Achieving these primary objectives gives rise to some secondary design objectives:

5. Effect the efficient removal of gross quantities of solids and oil.

6. Provide for hydraulic and chemical equalization of refinery wastes.

7. Minimize the generation of excess biological sludges.

8. Minimize any odor and bulking problems from biological sludges.

9. Minimize IOD (Immediate Oxygen Demand) of water entering secondary treatment.

10. Minimize sulfides in the effluent.

11. Discharge an effluent containing dissolved oxygen and a good threshold odor number.

SECONDARY TREATMENT IS THE KEY TO OPTIMIZING THE END-OF-PIPE TREATMENT SEQUENCE

If the overall treatment sequence is to be optimized, the principal objectives listed above point to secondary treatment as the key end-of-pipe treatment element. Various other process steps are designed to enhance its performance. Further, in contrast to prevailing practice, secondary treatment must focus on removal of only soluble contaminants. This limited objective for secondary treatment requires the objectives of the remaining elements in the treatment sequence to be defined, establishes a basis for operating conditions that maximizes the performance of each treatment element, thereby optimizing the effectiveness of the overall treatment sequence. Adherence to this design philosophy can yield an effluent quality superior to that achievable with an add-on activated carbon treatment element.

OPTIMIZING PRETREATMENT PAYS OFF

Optimizing pretreatment not only permits the ASP to be designed and operated in an especially attractive mode of exceptionally high sludge age as will be described later, but major savings in energy costs and capital costs can be made. Consider, for example, the indicated raw waste load in Figures 2-4 to be average data. These quantities are highly variable in a refinery and may be increased five to ten fold by many situations including, for example, (1) an occasion of high pH or excessive sulfides which contributes to increased colloidal matter with high zeta potentials, (2) sulfonate waste from an alkylation unit, which peptizes and disperses contaminants, (3) loss of catalyst fines that remain dispersed in water, (4) loss of residual oils, coke fines, wax, clay, or lube stocks and additives, which emulsify oil and solids and tend to escape the API separator, (5) loss of efficiency in the API separator by hydraulic overload, etc. Excessively high raw waste loads from the API separator are characterized by the fact that they consist primarily of discontinuous phase materials. Adequately providing for chemical and physical equalization in the intermediate treatment section will provide a more consistently uniform quality effluent over a very wide range of raw waste loads.

Maintenance of high sludge age in the ASP requires that the feed be free from oily inerts that accumulate in the activated sludge mass and impart undesirable properties to it that preclude operation in the high sludge age mode. In large and complex refineries the oil and grease in the raw waste load can vary over a year's time as shown in Figure 2. Whereas the 50% probability (median) is only 70 mg/l oil, about 5% of the data may be in the 600+mg/l range due to causes previously outlined. Optimized ASP operation at very high sludge ages has been achieved with excellent sludge properties when all discontinuous phase oil and solids are removed. Pretreatment can achieve these oil levels indicated in Figure 2 when treatment consists of chemical destabilization and filtration.

Removing oil from the process water effluent prior to biological treatment recovers the oil in a sludge much easier and less costly to handle than if the oil is commingled in a waste activated sludge. Waste activated sludge is costly enough to dewater but when commingled with oil, the oil blinds precoat filters, increases significantly the volume of waste sludge to be dewatered, and makes the final disposition of dewatered oily sludge more troublesome.

Equalizing feed quality in terms of organic loading can also be achieved by the same pretreatment as shown for BOD/COD data in Figures 3 and 4. Colloidal and suspended matter contributes significantly to the total BOD/COD;and periods of storm flow which flushes sludge and silt from sewers, high pH, loss of emulsifiers, coke fines, clay fines, etc., typically give a highly variable raw waste load which is frequently underestimated because of sampling and testing difficulties. Removal of the discontinuous phase contaminants can have a large impact on reducing the total organic load and the variability in quality of water entering secondary treatment.

Equalizing the organic loading results in substantial savings in capital and operating costs, simpler operations, and better effluent quality with less variability in quality of water leaving the secondary treatment facilities. For example, data from Figures 2, 3, and 4 are as follows:

Contaminant	Treatment After	% Probability Less Than Indicated Value		
		50	95	98
Oil and Grease, mg/l	Primary	70	600	800
	Intermediate	4	10	12
BOD, mg/l	Primary	185	380	400
	Intermediate	80	96	105
COD, mg/l	Primary	400	980	1,400
	Intermediate	220	310	350

An engineer faced with design of an ASP to operate in the nitrification mode at 2 mg DO/l with uniform effluent quality faces an almost insurmountable challenge, both economically and performance-wise, if he has to deal with the variability of the raw waste load. Considering that data in the preceding table represent a year of operations, they also reflect (1) seasonal, (2) weekly, (3) daily, and (4) hourly cycles. The final design of an ASP based on primary effluent would be such a compromise that year-round operation would be unsatisfactory, yet the unit would be expensively over-designed. If, for example, a guideline of 1 lb. O_2/lb. COD is used and the 98% probability COD value is selected as a design basis, the raw waste would require four times the aeration horsepower the intermediate treated waste does. Actually, it would require substantially more, because the alpha (oxygen transfer) characteristics of raw waste are not as good as the intermediate treated waste.

Another example of the impact of the representative data on the ASP is recognition that, for the same sludge age, the equilibrium solids level in the ASP relates directly to organic loading. One critical aspect of clarifier design is the solids flux rate. The increased solids circulating at the higher organic loading can increase substantially the clarification capacity required. Thus, once the engineering and operating details of an ASP unit are addressed, the designer soon recognizes that proper design of the intermediate treatment section will contribute to lower costs, improved and simpler operation of the secondary treatment facilities.

PROCESS CONTROL OF THE ACTIVATED SLUDGE PROCESS

A key to designing and optimizing the operation of an ASP unit as an integral part of an end-of-pipe treatment sequence is first, to recognize that it is only a part of the treatment sequence, and operation of each part should be optimized in light of what it can do best, or is required to do by another part to perform optimally; and second, to provide for use a method of process control that optimizes performance.

Performance of the ASP in terms of BOD/COD removal relates to organic loading; i.e., the food-to-mocroorganism (F/M) ratio. Eckenfelder (1) has summarized concisely the effect of organic loadings on ASP performance when treating domestic wastes in the manner shown in Figure 2. These data and the work of others (2,3) show that better BOD removals, total oxidation, nitrification, and less excess sludge are achieved with lower F/M ratios. The consideration which most often limits the ability to produce a high quality effluent is development of an activated sludge mass with poor settling characteristics at organic loadings under .2 F/M, where increasing values of SVI are observed. Sludge volume index (SVI) is a measure of the sludge settling characteristics and is the volume occupied by 1 gm of sludge after the aerated liquor settles for 30 minutes. While the SVI test has shortcomings beyond the scope of this discussion, it can be a useful process indicator. On the basis of these data, optimal ASP operating conditions are usually cited as F/M loadings in the range of 0.2 to 0.5.

Our ASP development work has shown that optimum ASP operating conditions are achieved by removing essentially all the dispersed colloidal contaminants by chemical destabilization and filtration prior to ASP treatment. With removal of colloidal matter in the feed, the SVI of the activated sludge did not increase at sludge ages well in excess of 35 days, but consistently measured 70-80 with excellent flocculating and settling properties.

Thus, contrary to comments in the literature that operation at high sludge age (F/M $<$ .2) results in unsatisfactorily poor sludge properties related to development of "dispersed biological growths", we find that the sludge properties do not deteriorate. Additionally, the biological population dynamics improve substantially.

Our experience indicates the chief reason for the deterioration at high sludge ages observed in the literature relates to the accumulation of excessive amounts of negatively charged colloids in the sludge mass; negatively charged colloids, of course, typifies the suspended matter in the effluent from primary treatment. Forster (4) has related the sensitivity of the activated sludge mass to accumulation of negative colloids by relating the zeta potential (ZP) of particles in the activated sludge mass directly to SVI as shown in Figure 6.

Biological processes such as activated sludge are cited as examples of agglomeration of dispersed colloids induced by slight, though definite, reduction of the negative ZP.

Thus, it is hypothesized that the deterioration of the SVI of activated sludge with decreasing F/M (higher SA), as summarized by Eckenfelder, is chiefly due to the accumulation in the sludge mass of sufficient negatively charged, non-biodegradable colloidal

material that intensifies the zeta potential and enhances the dispersion of the biomass. Forster's ZP-SVI relationship in Figure 6 shows SVI to be remarkably sensitive to ZP and it is easily perceived how the highly negative charged particles in refinery primary effluents cause the SVI to deteriorate.

For refinery effluent waters, the impact of accumulating colloidal solids in the activated sludge mass must not only be addressed, but dispersed phase oil and oily solids also must be considered. Oily materials contribute to electrokinetic effects and destabilization of the oily colloidal system allows the agglomeration and coalescing of the oily matter into the activated sludge mass; this, in turn, leads to other deleterious effects. For example, the coalesced oil matter associating with suspended solids can cause so little gravity differential with water that the associated materials pass through the clarifier to the effluent. The coalescing of the oily materials also encourages the formation of a stable, voluminous emulsion mass consisting of oil, water, solids and air. Typically this mass floats on the surface of the aeration tank and the discontinuous emulsion phase builds rapidly because its surface properties encourages agglomeration of like materials. The emulsified mass does not biodegrade significantly. Dispersion, or redispersion, of emulsified material in the aeration tank typically causes the material to enter the clarifier where it collects on the surface. If the clarifier is not designed to trap floating material, the material escapes in the effluent causing a significant degradation in effluent quality.

Well-settling activated sludges have been observed to have a density of about 1.016. When associated with oily matter, it is misleading to simply calculate the final sludge density from composition and component density data, because the oily, emulsified mass is much more buoyant than calculated, due to entrapped air.

ASP PROCESS CONTROL DYNAMICS

The amount of colloidally dispersed inert solids and oil entering the aeration tank affects the degree of process control available to the operator. Colloidal and suspended matter in the influent to the ASP at quite low concentration levels can make the process non-operable at the optimum conditions.

The ASP process control is via the food-to-microorganism (F/M) ratio, or perhaps more practically the sludge age (SA). The sludge age and F/M ratio are related as follows:

$$\frac{1}{SA} = \frac{a(\Delta F/\Delta T)}{M} - b \qquad \text{(Equa. 1)}$$

where, a = the sludge yield coefficient,
b = the endogenous rate coefficient,
M = the mass (lbs) of microorganisms in the system,
SA = the sludge age (days), and
$\Delta F / \Delta T$ = the mass (lbs) of food (BOD or COD) supplied per day.

The F/M process control involves measurement of the BOD or COD load ($\Delta F/\Delta T$) per day and adjustment of the sludge inventory (M) to maintain a desired ratio. The sludge age method of process control can provide a simple hydraulic means to achieve the same end

by sludge wastage. The sludge wastage rate to maintain an indicated sludge age is calculated from the equation:

$$\text{Wastage (MGD)} = \frac{1}{\left(\frac{X_r - X_e}{X}\right)} \left\{ \frac{(V_A + V_c)\, X_A}{SA} - QX_e \right\} \qquad \text{(Equa. 2)}$$

where, X_r = sludge concentration in recycle

X_e = sludge concentration in effluent

X_A = MLSS

V_A = volume of aeration tank, MMGD

V_c = volume of clarifier, MMG

Q = feed volume, MMGD

The sludge age method of process control has many advantages which are discussed in detail by Walker (5).

The accumulation of negatively charged colloids, inerts and oil in the activated sludge mass is hypothesized to be a principal cause of poor sludge settling properties (SVI) and dispersed solids, thereby limiting the effective SA or F/M operating range. The sensitivity of the ASP to influent inert solids can be readily demonstrated. For example, if undesirable materials such as heavy oils, catalyst fines, clay, coke fines, metallic sulfides, etc., escape preceding treatment at the rate of 30 mg/l, become flocculated by activated sludge and accumulate, their effect can be predicted. Assuming for simplicity of calculation that the inerts can escape only via sludge wastage and not via the clarifier overflow, the equilibrium concentration levels in the waste and recycle streams and aeration tank can be estimated using equations (1) and (2).

The quantity of inert suspended materials flocculated by the activated sludge mass at equilibrium is shown in Table 1 for two cases; one in which the cell yield is 0.4 lbs/lb COD removed and the second in which the yield is 0.6. For each case, equilibrium conditions are calculated for sludge ages from 5 to 45 days. In columns C through J equilibrium data are shown for only soluble substrate (COD), and in columns K through S the impact of the inert suspended matter accumulating in the system for a rate equivalent to 30 mg/l in the feed.

Not expressly illustrated by the data in Table 1 is the desirable change in biological population dynamics when operating at the higher SA. At low SA, bacteria predominate in the activated sludge mass. As SA increases, organisms which are comparatively slow reproducers accumulate to a greater extent. One effect of operation at high SA is to allow accumulation in the activated sludge mass of nitrifying and other organisms to degrade the more "bio-resistant" contaminants present. A second effect is the accumulation of protozoa in the activated sludge mass. In an ASP operating at high SA, the role of protozoa is chiefly effluent clarification achieved by predation on the dispersed bacteria; i. e., those tending to carry out in, and thereby contaminate, the clarifier effluent (6). Bacteria within the floc are relatively immune to predation.

The soluble BOD/COD/TOC remaining in the effluent from an ASP relates importantly to the SA in the treatment of refinery effluents. As described earlier, the COD/BOD ratio for refinery effluents may be quite high. As shown in Figure 7, the BOD is usually removed quite readily by the ASP with little attention to process details. However, operating at comparatively low SA's usually results in an effluent containing substantial remaining contamination measured as COD. Operating the ASP at increasingly higher SA results in increasing COD reductions, as shown quantitatively in Figure 7. The TOC removal curve is similar to the COD curve. Dickenson and Giboney (7) in a study of refinery effluent treatment observed that, with sufficiently long periods of acclimation, the organisms in an ASP can acquire the capacity to metabolize components normally biorefractory. A specific example of such a material was found to be tertiary butyl alcohol, which took a 5-month acclimation period before degradation was obtained. Many other such observations are reported in the literature and have been experienced by the authors. Thus, operating at high SA will continue to reduce significantly the COD, whereas the observed effect on the BOD may be slight. Additionally, we have achieved total organic carbon (TOC) levels below 10 mg/1, superior to that achievable with activated carbon.

BIOLOGICAL REASONS FOR LIMITING THE OBJECTIVE OF BIOLOGICAL TREATMENT TO REMOVAL OF SOLUBLE CONTAMINANTS

Only soluble organics can be absorbed through the cell membrane of the microorganism. Above certain minimum "saturation"concentrations (typically perhaps 5-10 mg/1) of degradable organics, the rate of removal is independent of degradable organics concentration, but directly proportional to the amount of microorganisms present. Thus, the rate of biodegradable organics removal is determined by the rate of metabolism of the microorganisms down to certain minimum concentrations. Below these minimum "saturation" concentrations, the rate of biodegradable organics removal is determined by their rate of passage through the cell membrane. As the concentration gradient across the cell membrane decreases, the rate of mass transfer decreases, and further biodegradable organics removal under these conditions involves increasing the reaction time.

Large particles of biodegradable organics are removed by two possible mechanisms: (1) the microorganisms can evolve a mechanism for engulfing or directly passing large molecules into cells where confined enzymes initiate oxidative biochemical reactions, or (2) they excrete the necessary enzymes causing the reaction sequence to be initiated outside the cell membrane. These exoenzymes are produced and controlled by mechanisms not understood, and in the activated sludge process it is not possible to predict the influence of process variables on the kinetics of colloid and large particle biodegradation. This latter mechanism involves bacteria, and is believed to be the principle mechanism operative in the activated sludge process.

STRUCTURE OF THE BACTERIAL CELL

Figures 8 and 9 are schematics of a bacterial cell and bacteria cell walls and membrane which are useful in picturing the extreme complexity of biological oxidation. The food material must pass through the cell wall and the cell membrane. The outermost surface of most bacteria is a slimy capsule varying in thickness up to 100,000+ A°. The composition of capsules varies with species and may consist of polymers of glucose or other sugars, amino

acids and sugars, or polypeptides. Capsules generally consist of about 98% water, and the capsular layer probably serves the microorganism as an osmotic barrier; i.e., a mechanism for guarding against too rapid an influx or efflux of water (8).

The soft outer layer of the cell wall is 100-150 A° thick and consists of an outer layer of proteins and polysaccharides and inner layers of lipids and possible lipopolysaccharides and proteins. The acidic polysaccharides are partially responsible for the negative electric charge on the bacteria surface.

The rigid layer is about 50 A° thick and is comprised mainly of heteropolymers of peptidoglycans arranged in a coarse three-dimensional foraminous mesh which provides rigidity and strength to the cell wall.

These outer layers offer no obstacle to inward passage of molecular oxygen, minerals, amino acids, glucose, and large organic molecules. Cell wastes can pass outward unobstructed (9).

The periplasmic space is about 100 A° thick and, in some bacteria, contains degradative enzymes which break down the larger molecules passing through the cell wall into simple sugars, amino acids and other low molecular weight fragments. These lower molecular weight fragments are transportable across the cell membrane by transport systems.

Membranes consist almost entirely of proteins and lipids (14). The proteins serve as enzymes and provide the distinctive functional properties. The lipids provide the gross structural properties and are a permeability barrier.

FUNCTIONS OF THE CELL MEMBRANE

The cell membrane is about 100 A° thick and serves three key functions: It acts as an osmotic barrier and is impermeable to ionized substances and nonionized substances with molecules larger than glycerol; it provides a housing for active transport systems, and provides a site for key enzymic reactions involved in energy metabolism. Cell membranes, therefore, are highly selective in regard to the substances that may pass through them, inward or outward (10).

Substrates may be transported through cell membranes counter to concentration gradients. This process is called active transport because it requires added energy. Active transport is accomplished by enzyme transport systems sometimes called permeases. These systems are so efficient for concentrating metabolites that the osmotic pressure in the cell can reach 300 psi (14). Like other enzymes, permeases are specific for the substrate involved and are inducible.

REACTIONS WITHIN THE CELL

With reference to Figure 8, transport of the substrate through the cell wall and membrane is only a small part of the over-all biological system. Once inside the cell, the substrates are acted upon by systems of enzymes called endoenzymes. There are several thousand different enzymes within the cell of a single bacterium (15). Endo-

enzymes undertake two general types of processes inside the cell; synthesis of cell components in food reserves, and the release of energy from food stuffs. The energy is either stored in special molecules like adenosine triphosphate (ATP) inside the cell or is immediately used for any of the active processes of the cell. Recently it has been discovered that bacteria can energize the active transport of many substances by the oxidation of various chemical substances without the transfer of phosphate groups (17).

Endoenzymes do not act individually but as parts of coordinated and sequentially operating systems. Whatever effects one portion of the intracellular enzyme system has some effect on all parts. The activity of an enzyme is inhibited by accumulation of the end-products of the enzyme catalyzed reaction. In a sequentially operating enzyme system excessive accumulation of a reaction product may inhibit the reaction not only of the enzyme manufacturing the reaction product, but all prior enzymes in that sequence. This is an important form of automatic control called feedback inhibition. In the presence of excessive amounts of end-products, not only is enzyme activity inhibited but the actual synthesis of the enzymes themselves may be repressed. If a cell normally synthesizing a certain substance is artifically supplied with that substance from an extraneous source, not only is activity of the enzyme inhibited, but synthesis of some or all of the enzymes in the production sequence for that substance is repressed until the enzymes are needed again. This is called feedback repression. Differentiation is made between inhibition of the action of the enzymes by their end-products (feedback inhibition) and repression of the synthesis of the enzymes themselves by the accumulation of end-products (feedback repression) in the enzyme sequence (Figure 10). In a sequentially operating system the end-product of each enzyme can be the inducer of the next enzyme in the series and the inhibitor or repressor of the preceding enzyme, thus carrying forward the work of the enzyme factory (18).

In the cell, energy is derived from the enzymic bio-oxidation of foods, and the energy liberated is transmitted by high energy compounds, notably certain organic phosphates; or directly as recently discovered. The exact manner in which energy is transferred from low energy level oxidized foods into high energy foods is not yet fully understood, but it has been suggested that the participating enzymes are perhaps hundreds in number and must have a specific orientation to each other in the cell (18).

REACTIONS EXTERNAL TO THE CELL

Suspended and colloidal matter require solubilization by exoenzymes preparatory to transport into the cell. Many enzymes probably exist free in colloidal suspension in the fluid matrix of the cell. Some of these are secreted to the exterior of a cell. They are called exoenzymes. Exoenzymes are mainly digestive in function. By hydrolysis they decompose complex organic matter, such as proteins, cellulose, and fats, to simple soluble molecules of amino acids, glucose, glycerol and fatty acids. These relatively small molecules can be transported through the cell membranes of many microorganisms, there to be utilized as food. Among the lower fungi, algae, and bacteria, digestive enzymes are to a large extent excreted aimlessly into the surrounding fluid where they may or may not come into contact with food. They may be wholly dissipated by dilution, convection currents, or other factors (12).

STRUCTURE OF ENZYMES

Enzymes are large complex molecules with molecular weights ranging from about 10,000 to more than 1,000,000 and consisting of two components; a colloidal protein part called apoenzyme, and a non-protein, noncolloidal, low molecular weight, thermostable part called coenzyme (organic) or cofactor (inorganic). The two components constitute the complete active enzyme called holenzyme but commonly referred to by the term enzyme. Coenzyme molecules generally carry the distinctive reactive portion of an enzyme. Acting with the apoenzyme, the coenzyme brings about the specific substrate reaction that is characteristic of that particular enzyme. In many coenzymes the distinctive reactive portion is a familar vitamin; nicotinic acid or its popular derivative niacin; others are vitamins of the B complex such as thiamine which is vitamin B_1 or riboflavin vitamin B_2. In fact, all vitamins that function physiologically have been found to act as a reactive group of one or another coenzyme (13, 19).

ENZYME MECHANISMS

In most enzyme reactions, the specific apoenzyme involved appears first to attach to the substrate at certain specific sites involving only 10-20 amino acid residues confined to an area of surfaces perhaps 15-20 A° in diameter (19). These sites represent reciprocally corresponding physical structure and anionic and cationic groups in the molecule of the substrate. This preliminary combination appears to place certain bonds in the substrate under stress. The coenzyme, because of its appropriate molecular structure, then combines with a part of the substrate. For example, a halogen ion or amino group, etc. This ion or group is then either passed by the coenzyme to another coenzyme or to a different substrate molecule, or may be liberated as waste into the surrounding fluid. The final result depends on the nature of the reaction being catalyzed. The enzyme, freed of the altered substrate residue, is then ready to combine with another substrate molecule and repeat the process. If any energy is released by the reaction, it is partly lost as heat and in part taken up into the cell substance by the formation of energy-rich compounds that contain certain types of bonds as organic phosphate bonds, thioester bonds, and some others in certain coenzymes. The energy stored in such energy-rich compounds is later used by the cell in motility and cell synthesis.

ENZYME STEREOCHEMISTRY

All known enzymes are globular proteins whose active site is either a crevice, shallow depression or a pit and, stereochemically, conform to the principle of the "hydrophobic in, hydrophilic out" protein model. All charged, and most uncharged, polar groups are on the surface and the great majority of the nonpolar hydrophobic groups are buried in the interior. This has a profound chemical purpose in that the reactant molecules can be taken out of the water where water molecules keep charged molecules apart, and into the enzyme which is made up of hydrocarbons with a low dielectric constant. In the organic solvent of the enzyme, strong electrical forces can be brought to bear on the reactant causing them to react rapidly (15).

Being colloidal proteins, enzymes are macromolecules that may consist of hundreds of the 22-24 amino acid residues linearly linked in different arrangements. Trypsin,

chymotrypsin and carboxypeptidases, for example, contain 200-300 amino acid residues per molecule, or between 3,000 and 5,000 atoms. The active site involves perhaps less than 20 of the acid residues and the three dimensional structure of the entire molecule is necessary for maintaining the stereochemical structure of the active site. Changes in the three dimensional structure of the protein are typically accompanied by a loss of enzymic activity. Since each enzyme is different from all others with respect to molecular configuration, each is unique or specific. Each enzyme can react only with certain particular substrates that have a corresponding stereochemical structure. Specificity of enzymes varies greatly in degree (19).

Lysozyme, the first enzyme to have its detailed molecular structure worked out, ribonuclease, and carboxypeptidase A are examples of "small enzymes" of molecular weights -- 14,600, 13,700, and 34,600 respectively. These enzymes are ovid shaped and carboxypeptidase A has dimensions of about 40 X 44 X 52 Angstroms. Most enzymes are far larger than these (16).

GENETIC INFLUENCE ON ENZYME PRODUCTION

Each species of living cells has a genetically determined natural endowment of certain functioning enzymes. These are characteristic of and constantly present in all of the cells in that species of cell. Such inherited enzymes, part of the normal constitution of the cell, are called constitutive enzymes. In addition, many cells possess genetic determinants or genes for the synthesis of such enzymes which are genetically repressed. These genetically repressed enzymes are manufactured only when an inducing substrate or related substance enters the cell. In the presence of the inducer the repressor of the appropriate synthesizing mechanism is removed and the enzyme specific for the inducer substrate is synthesized. Such enzymes are said to be inducible. Therefore, although genes determine the full enzymic potentialities of a cell, environmental factors in the form of inducers, determine just which of the latent enzymic potentialities of a cell shall appear under any given circumstances. The cell is evidently not under the necessity of synthesizing all its potential enzymes but only those needed (11).

ENZYME MEDIATED REACTION EQUILIBRIA

Enzymic reactions are reversible. The accumulation of products affects the action of any enzyme in either direction, as would be expected in chemical equilibria. Under any set of constant conditions, the equilibrium point for an enzyme catalyzed reaction is constant. There is a constant relationship between concentration of enzyme and concentration of substrate. Up to the point of "saturation", the rate of reaction increases with increase of ratio of one component to the other. With a constant amount of enzyme, increase of substrate increases rate of reaction until every molecule of enzyme is fully saturated with substrate. Further additions of substrate cannot increase the rate of reaction. Conversely with a fixed amount of substrate, rate of reaction increases with the additions of enzyme until all molecules of substrate are in contact with enzyme. Further additions of enzyme do not effect the rate of reaction. In many instances enzyme catalyzed reactions appear to proceed in only one direction because the equilibrium is never reached. Under normal conditions in the living cell, enzyme reactions are constantly pushed in this manner toward the one or the other side of the reactions. Theoretically reversible reactions cannot

actually reverse when large differences in energy levels are involved, since resynthesis cannot be brought about by the same enzymes because they cannot restore the lost energy. To reverse the reaction requires that work be done by other systems of enzymes that capture new energy from other sources (11, 20).

ENZYMES SENSITIVITIES AND INHIBITIONS

Enzymes are sensitive to all of the various precipitating and coagulating factors that effect proteins in general: temperatures above 80°C, excessive concentrations of heavy metals or of hydrogen or hydroxyl ions, active chemicals like chlorine, and strong alkalis quickly destroy all types of proteins. In addition to being sensitive to deviations in temperature, enzymes are very sensitive to variations in pH, osmotic pressures (salinity), and UV and other radiations. Whatever affects enzymes, of course, affects microorganisms.

The functioning of some enzymes may be inhibited by certain non-metabolizable substances whose molecular structure is analogous to that of a true, metabolizable substrate. Such metabolites like inhibitory agents are called metabolite antagonists and because of their molecular structure, can pre-empt the specific combining site on a particular enzyme protein to the exclusion of the true metabolite. The enzyme or coenzyme is not necessarily destroyed but it can no longer function.

ENZYME CHEMISTRY

A key to recognizing the important process design responses which must be made in an integrated end-of-pipe treatment sequence in which the activated sludge process is an element, is recognition of the complex enzyme systems operative and their requirements. Exoenzymes excreted aimlessly into the surrounding water by bacteria for hydrolysis of colloidal and suspended solids into smaller soluble molecules so they can pass through the cell membranes to be utilized as food, not only may be dispersed and lost in the effluent, but are exposed to and unprotected from environmental changes in pH, salinity, and other conditions impacting on the stereochemical conformation or properties of proteins, causing deterioration in their functioning. Endoenzymes on the other hand, are at least partially protected from these environmental changes by the bacterial cell wall and membrane. Thus, using the biological process for removal of only soluble contaminants, as we recommend, is consistent with obtaining a stable system less influenced by transient changes in environmental conditions. An additional important consideration contributing to capacity and process stability is that activated sludge units utilizing only soluble contaminants can be operated at very high sludge ages. This permits much higher biological cell inventories, which in turn increases stability, capacity, and purification while minimizing generation of excess biological cells.

SUMMARY

1. A systems optimization of a refinery end-of-pipe treatment sequence points to the activated sludge process (ASP) as the key element.

2. To achieve maximum water quality, system optimization points to reversing the historic work horse role of the ASP; i. e., it should be used only for

the removal of essentially soluble contaminants.

3. Reversing the role of the ASP yields a dramatic series of beneficial effects:

   a. The SVI characteristics of the activated sludge mass are excellent at very high sludge ages; i. e., over 40 days.
   b. Process control is greatly simplified by operating at a very high sludge age; i. e., greater than 40 days.
   c. Using very high sludge age for process controls eliminates the need for many process control tests.
   d. Operating at very high sludge age produces an exemplary effluent very low in TOC and other contaminants.
   e. The cell yield coefficient is remarkably low at very high sludge age.
   f. At very high sludge age the population dynamics of the sludge mass improve.
   g. Maximum ASP capacity for purification is achieved by operating at high sludge ages.

4. Systems optimization wherein the key element is using the ASP for removal of only soluble contaminants permits clear definition of the roles the other elements play; i.e., colloidal and suspended matter must be essentially all removed in pretreatment sections.

5. The technology is available to handle the new requirements made by the process operations in their changed roles.

6. Current research developments on cell membranes and enzyme systems support strongly this new role for the ASP.

7. Cell genetics, wherein inducible enzymes or mutant species are required, support operating the ASP at very high sludge age for maximum purification capacity.

8. Bacteria are essentially enzyme factories. Enzymes are sensitive to temperature, pH, excessive concentrations of heavy metals, oxidizing agents, salinity, UV, and other radiations. Using the ASP for removal of only soluble contaminants is consistent with obtaining a stable system less influenced by transient changes in environmental conditions since the endoenzyme systems are at least partially protected from these environmental changes by the bacterial cell wall and membrane.

9. This recommended systems optimization saves significant energy and other operating and capital costs of the end-of-pipe sequence.

10. This recommended systems optimization minimizes the generation of solid wastes, and the solid wastes generated are amenable to disposition.

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DISCUSSION

Milton Beychok: Jim, what you have really said is that if you filter well ahead of the activated sludge unit, you can cycle up in sludge age and the process behaves much better in terms of capacity, effluent quality, and operating simplicity because it's only working on soluble BOD.

Jim Grutsch: Yes.

Milton Beychok: What do you do in your DAF (dissolved air flotation) or filter unit that is different than other people so you can achieve this?

Jim Grutsch: We address the water chemistry. Essentially everything in nature has a negative electrical charge on the surface. Colloidal particles exist because they are repelling each other and resist agglomeration which would facilitate phase separation. In a filter, for example, the surface of a granular media filter is also negatively charged. If we just attempt to filter out negatively charged solids with a granular media filter, a large fraction of the negatively charged colloids will be repelled by the media and rapidly break through to the effluent. Similarly with a DAF unit, the flotation air has a negative electrical charge. This is the most important reason why Wes Eckenfelder's DAF unit wouldn't do a very good job clarifying activated sludge from mixed liquor; the negatively charged fine particles in activated sludge repel the negatively charged flotation bubble resulting in poor phase separation efficiency.

The key to making DAF units or filters work effectively, therefore, is to reduce the electrical charge on the colloidal particles so that they can agglomerate and be trapped in granular filter media, or separated by attached air bubbles. There are some excellent chemicals available for this purpose at reasonable cost. Determination of the most cost-effective chemical treatment is easily done by comparing zeta potential titration curves. The use of zeta potential titration curves is, unfortunately, in its infancy but this tool will see greatly increased use in the coming years.

Anonymous: Do you encounter any problems from oil and grease?

Jim Grutsch: The electrical charge on oil particles is also negative and the previous discussion on colloids also applies to oil and grease particles. Granular media filters should be protected from gross slugs of oil, and the equalization basin does this. The higher the ratio of inert solids-to-oil in the feed to the DAF of filter unit, the lower the oil in the effluent.

Robert L. Wortman: Would you care to comment on the effect of polyelectrolytes on keeping suspended solids down in the final effluent when operating with a very high degree of nitrification?

Jim Grutsch: This question is central to the main thrust of our paper and I would like to develop the response in some detail so that the importance of optimizing the end-of-pipe sequence as described is not overlooked.

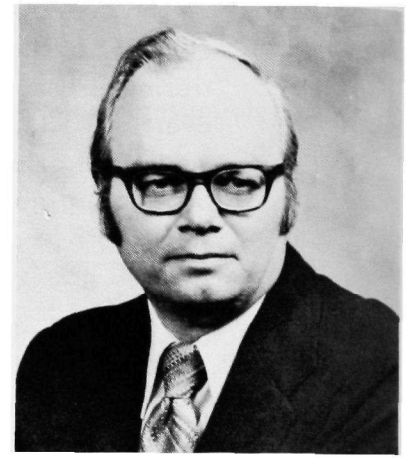
1. We have no experience using polyelectrolytes in the activated sludge unit clarifier at high sludge ages because the need doesn't exist when proper prefiltration is used. The average amount of total suspended solids in the clarifier overflow is less than 10 mg/l , and less than 5 mg/l from a final stage of granular media filtration (also not using chemicals). This is due principally to the excellent SVI maintained of about 80, with no "arms and legs" in the supernatent. A wide-well clarifier is used, but it is typically fully loaded; i.e., overflow rates greater than 70 gpd/s.f. and solids flux rates greater than 25 lbs/D/s.f. Actually, the design capacity of the clarifier in this service has not been determined.

2. "A very high degree of nitrification" specified in Mr. Wortman's question equates to operation at a high sludge age (or low F/M). With reference to Figure 5 and Wes Eckenfelder's data, under these operating conditions the SVI of the sludge increases which presumably gave rise to the question. A reason for the deterioration of the SVI is shown in Figure 6; i.e., the electrical properties of the sludge are deteriorating.

   Electrical properties (ZP) of the sludge deteriorate because of increasing accumulation of electrically charged inerts in the activated sludge mass at increasing sludge age. This can be visualized better by plotting some of the data in Table 1 as I have done in Figures 11 and 12. Data from Part A of Table 1 is plotted in Figure 11. The curve for inert solids shows the effect of capturing only 30 mg/l by the sludge mass. Thus, for this comparatively weak waste, by comparing the ratio of inert solids to biological solids it is observed that at 20 days sludge age half the sludge is inerts,and at sludge ages greater than the biological fraction. This inert fraction has a negative zeta potential, and at some ratio of inerts to biological solids the capacity of the biopolymers to destabilize the solids (i.e., keep the zeta potential of the sludge mass low enough so that fine particles are not repelled and thereby dispersed) is surpassed and the SVI deteriorates (Figure 6) and "arms and legs" appear in the supernatent. Without the inerts in the activated sludge mass, excellent SVI's are achieved at very high sludge ages. Our objective, therefore, is to remove completely suspended matter in the influent to the activated sludge unit.

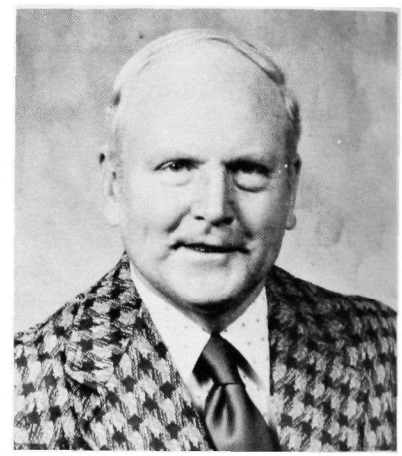
   Figure 12 shows the mixed liquor solids characteristics for the conditions of Part B, Table 1.

BIOGRAPHY



James F. Grutsch is Coordinator-Environmental Projects, Standard Oil Company (Indiana). He holds undergraduate and graduate degrees in chemistry from Indiana University. Prior to his present assignment with Standard, Jim served successively as Group Leader for finishing, blending and reclamation at the Amoco Oil Whiting refinery, and Coordinator of Waste Disposal for Amoco. Jim taught undergraduate chemistry for six years at Indiana.

BIOGRAPHY



Russell C. Mallatt is Manager-Environmental and Energy Conservation, Standard Oil Company (Indiana). He holds degrees in chemistry from the University of Illinois and the University of Rochester. Prior to his present assignment with Standard, Russ served successively as Chief Chemist, Chief Process Engineering and Technical Services Superintendent of the Amoco Oil refinery at Whiting, Indiana.

TABLE 1 "MATERIAL BALANCES AROUND ACTIVATED SLUDGE PLANT FOR VARIOUS OPERATING MODES"

Basis: Flow = 20 MM GPD; Total Aeration and Clarifier Tank Volumes = 10 MMG; Thickened Sludge From Clarifier = 8000 mg/l; No Solids Loss in Clarifier Overflow; COD = 150 mg/l

A. Basis: a = .4; b = .05; COD Removal = 25000 lbs/D (150 mg/l)

Case	Sludge Age (days)	Equilibrium MLVSS mg/l	Equilibrium MLVSS Total lbs	F/M	Wastage Rates lbs/D	Wastage Rates gpd @ .8% Solids	Sludge Yield lbs/lb COD	MGD Clarifier Draw @ .8% Solids	Clarifier Flux, lbs. Solids/Day
1	5	480	40,032	.625	8006	120,000	.32	1.2	84,868
2	10	800	66,720	.375	6672	100,000	.267	2	146,784
3	15	1029	85,783	.292	5719	85,716	.229	2.57	193,693
4	25	1333	111,200	.225	4448	66,666	.178	3.33	259,365
5	35	1527	127,375	.196	3639	54,541	.145	3.82	303,352
6	45	1662	138,572	.181	3079	46,148	.123	4.16	334,884

30 mg/l Inert Suspended Matter in the Incoming Water Have the Following Effects

Inerts in Wastage, mg/l	mg/l MLSS Inerts	mg/l MLSS Total	Inerts/MLVSS ratio	MGD Clarifier Draw @ .8% Solids	Equilibrium MLSS, lbs.	Clarifier Flux. lbs Solids/Day	Wastage Rates lbs/D	Wastage Rates gpd @ .8% Solids
5000	300	780	.625	1.95	65,052	142,789	13,010	195,000
6000	600	1400	.750	3.5	116,760	274,386	11,676	175,000
7000	900	1929	.875	4.82	160,879	399,300	10,725	160,750
9000	1500	2833	1.125	7.08	236,272	639,825	9,451	141,650
11000	2100	3627	1.375	9.07	302,492	879,344	8,643	129,541
13000	2700	4239	1.625	10.6	353,533	1,081,810	7,856	117,750

B. Basis: a = .6; rest as above in A

Case	Sludge Age (days)	Equilibrium MLVSS mg/l	Equilibrium MLVSS Total lbs	F/M	Wastage Rates lbs/D	Wastage Rates gpd @ .8% Solids	Sludge Yield lbs/lb COD	MGD Clarifier Draw @ .8% Solids	Clarifier Flux, lbs. Solids/Day
7	5	720	60,048	.417	12010	180,000	.48	1.8	130,905
8	10	1200	100,080	.25	10008	150,000	.4	3	230,184
9	15	1543	128,674	.195	8578	128,567	.34	3.86	307,045
10	25	2000	166,800	.15	6672	100,000	.267	5	417,000
11	35	2291	191,062	.131	5459	81,820	.218	5.73	491,622
12	45	2492	207,859	.12	4619	69,230	.185	6.23	545,145

30 mg/l Inert Suspended Matter in the Incoming Water Have the Following Effects

Inerts in Wastage, mg/l	mg/l MLSS Inerts	mg/l MLSS Total	Inerts/MLVSS ratio	MGD Clarifier Draw @ .8% Solids	Equilibrium MLSS, lbs.	Clarifier Flux. lbs Solids/Day	Wastage Rates lbs/D	Wastage Rates gpd @ .8% Solids
3333	300	1020	.417	2.55	85,068	191,828	17,014	255,000
4000	600	1800	.5	4.5	150,120	367,794	15,012	225,000
4667	900	2443	.583	6.11	203,746	531,981	13,583	203,583
6000	1500	3500	.750	8.75	291,900	839,213	11,676	175,000
7333	2100	4391	.9167	11	366,209	1,135,249	10,463	156,821
8667	2700	5192	1.083	13	433,013	1,428,942	9,623	144,222

FIGURE 1

Optional Refinery Treatment Sequence

Treatment Objectives	Pre-or Inplant Treatment: Phenolics, $S^{=}$, NH_3, RSH, F^{-}, Acid Sludge, Oil Etc., Removal & Water Reuse or Waste Equalization	Primary Treatment: Free Oil and Suspended Solids Removal	Intermediate Treatment: Emulsified Oil, Suspended and Colloidal Solids Removal	Secondary Treatment: Dissolved Organics Removal	Tertiary Treatment: Variable Objectives
Processes	Unit Separators	API Separators	Chem. Coagulation & Air Flotation	Trickling Filter	Chem. Coagulation & Air Flotation
	Steam Stripping	CPI, PPI Separators	Chem. Coagulation & Filtration	Activated Sludge	Chem. Coagulation & Filtration
	Fuel Gas Stripping		pH Control	Oxidation Pond	Activated Carbon
	Air Oxidation		Immediate Oxygen Demand Reduction	Aerated Lagoon	
	Neutralization		Equalization of Wastes		
	Surge Ponds	Sludges	Sludges	Sludges	Sludges

FIGURE 2. Probability Plots of Oil & Grease Data Before and After Intermediate Treatment

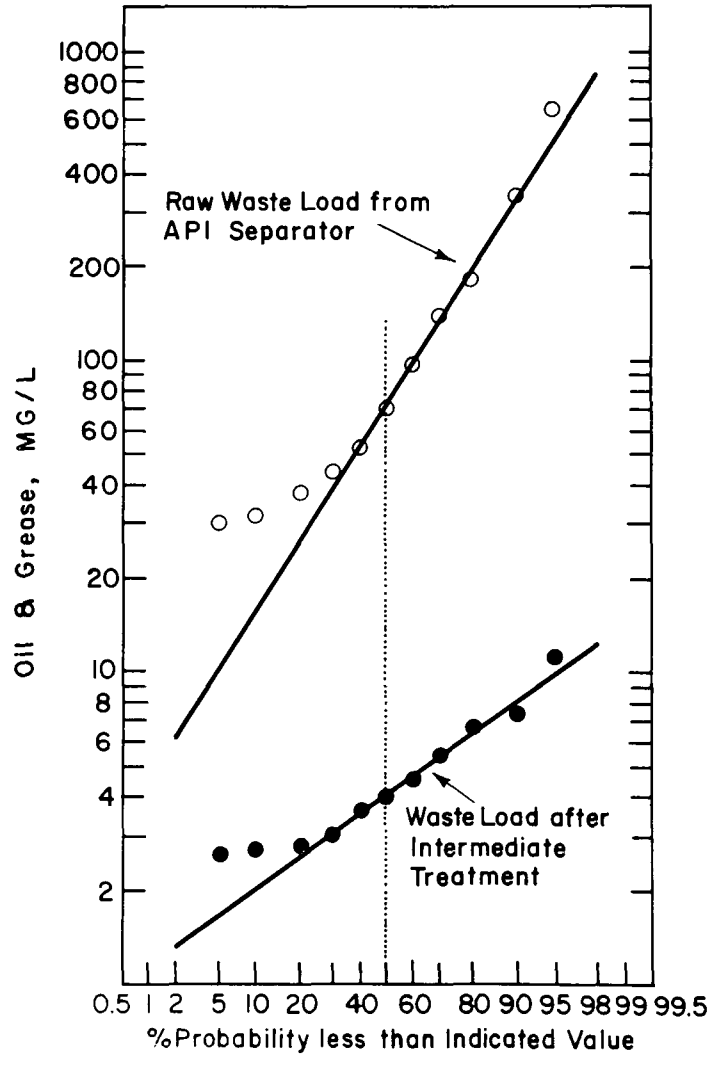


FIGURE 3

Probability Plots of BOD Data Before and After Intermediate Treatment

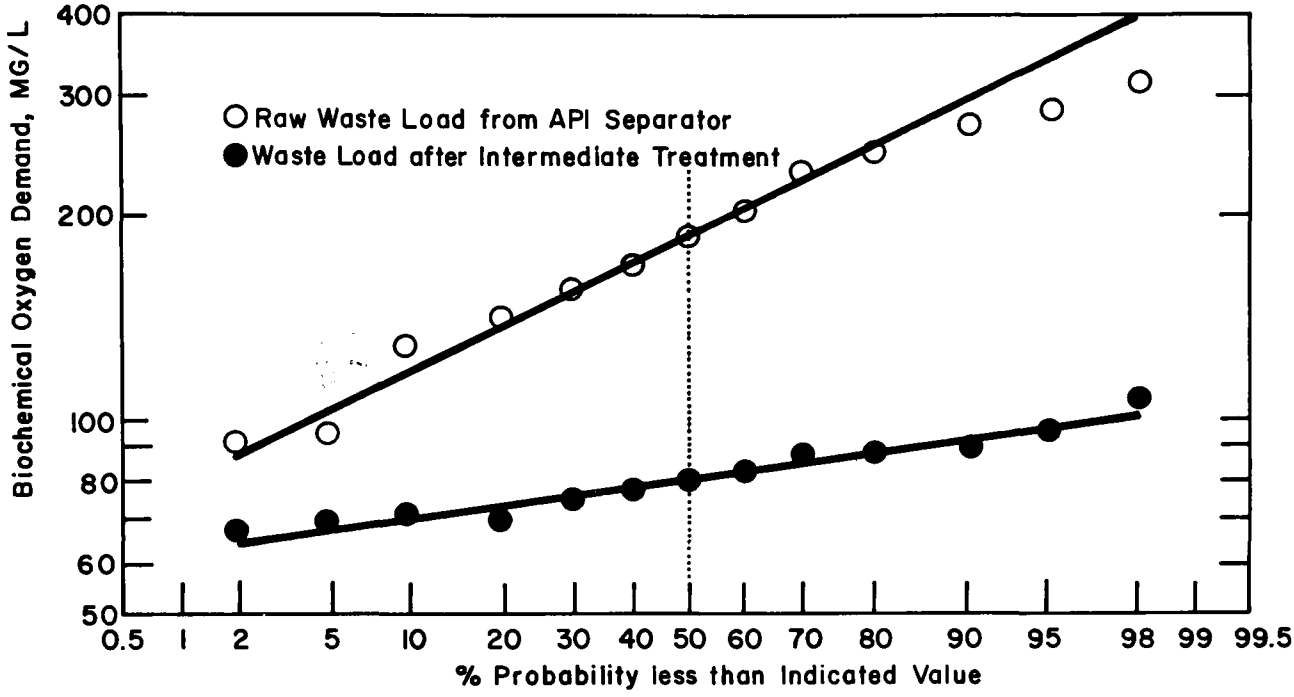


FIGURE 4

Probability Plots of COD Data Before and After Intermediate Treatment

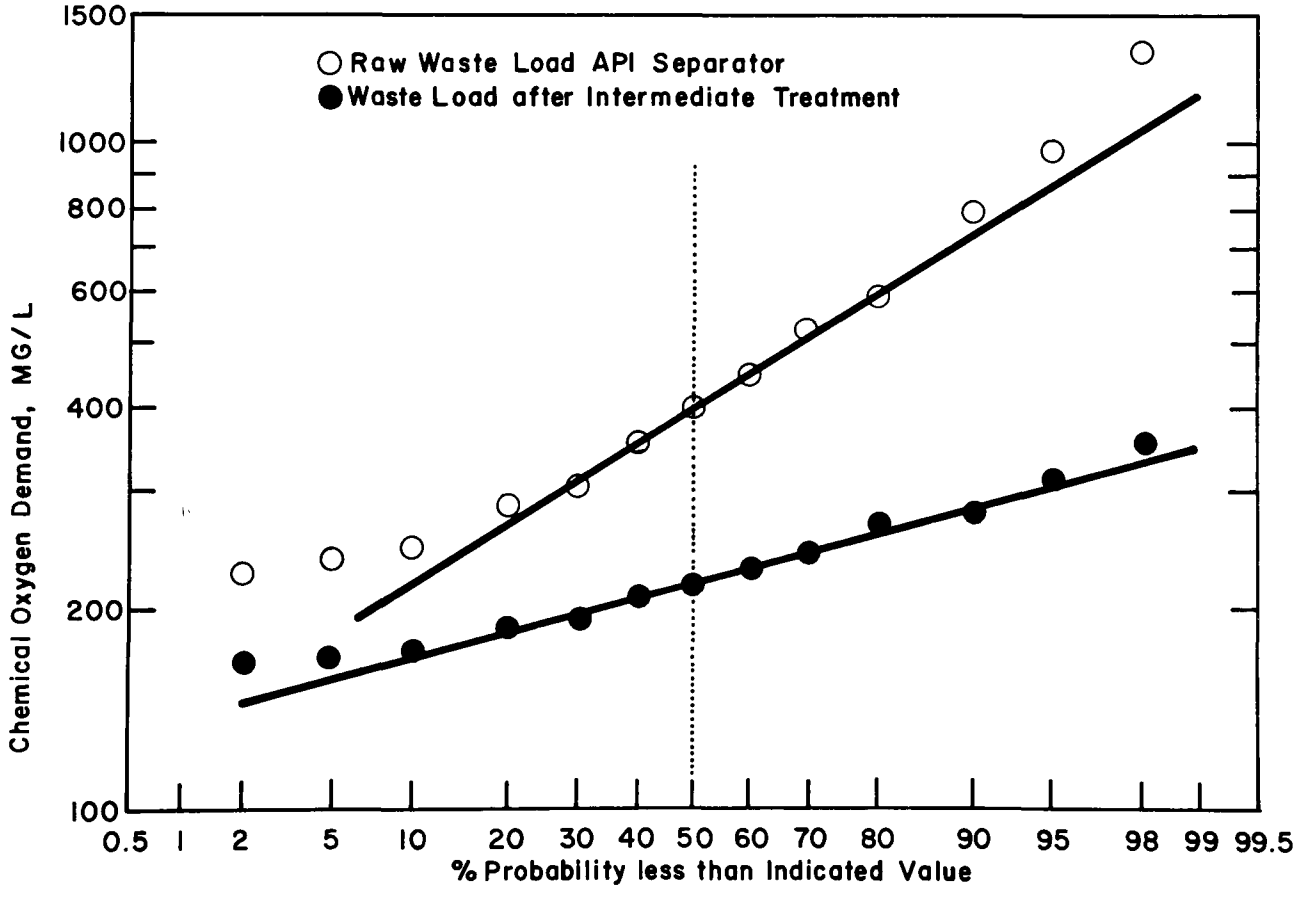


FIGURE 5

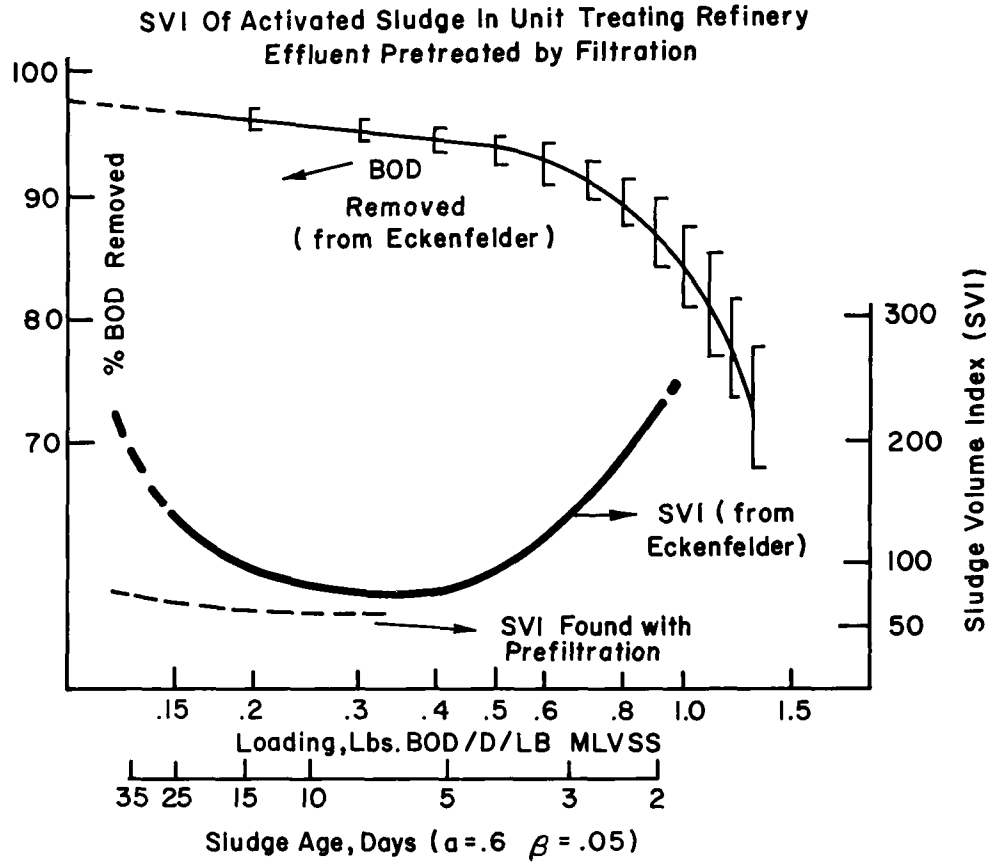


FIGURE 6

Relationship of Activated Sludge
SVI with Zeta Potential In-Situ(Forster)

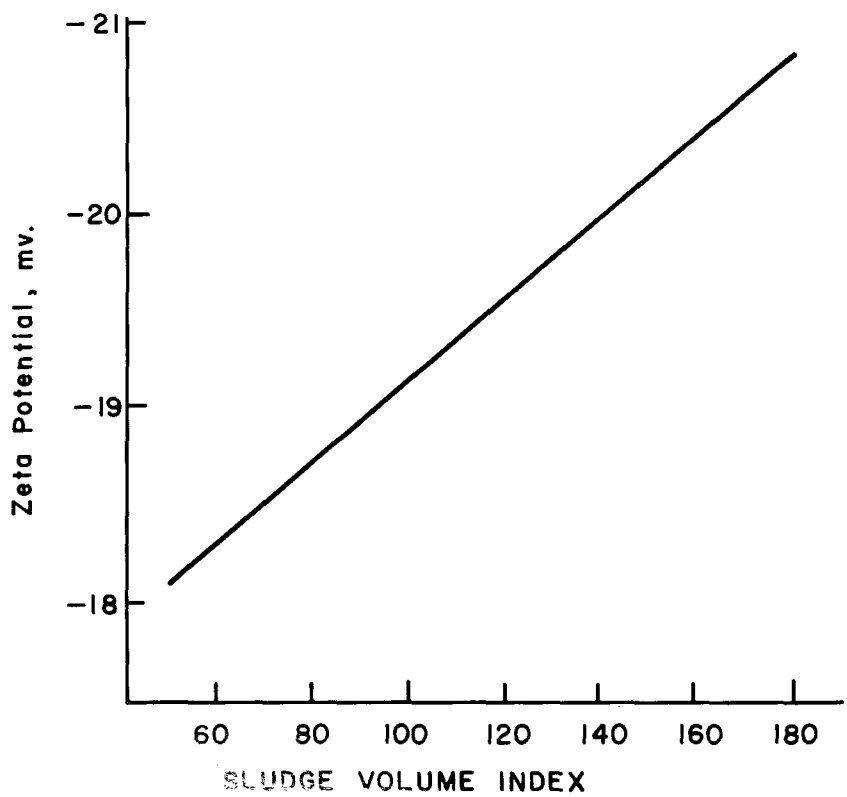


FIGURE 7

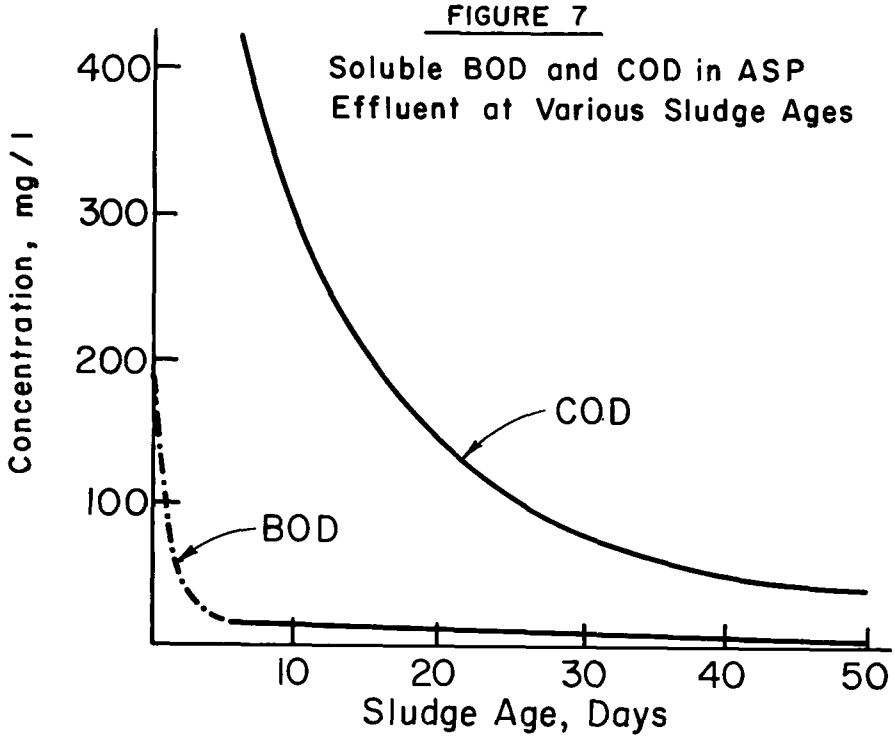


FIGURE 8

Schematic of a Bacterial Cell, Its Biochemical Activities, and Exoenzyme Solubilization of Insoluble Substrates

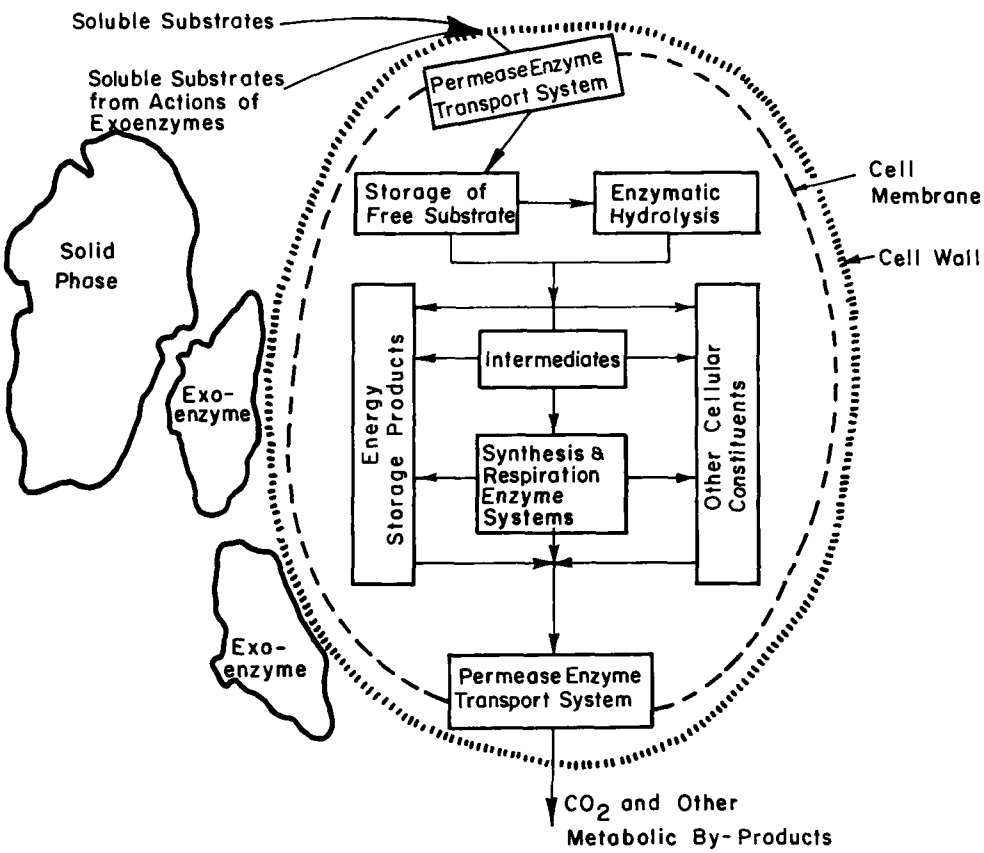
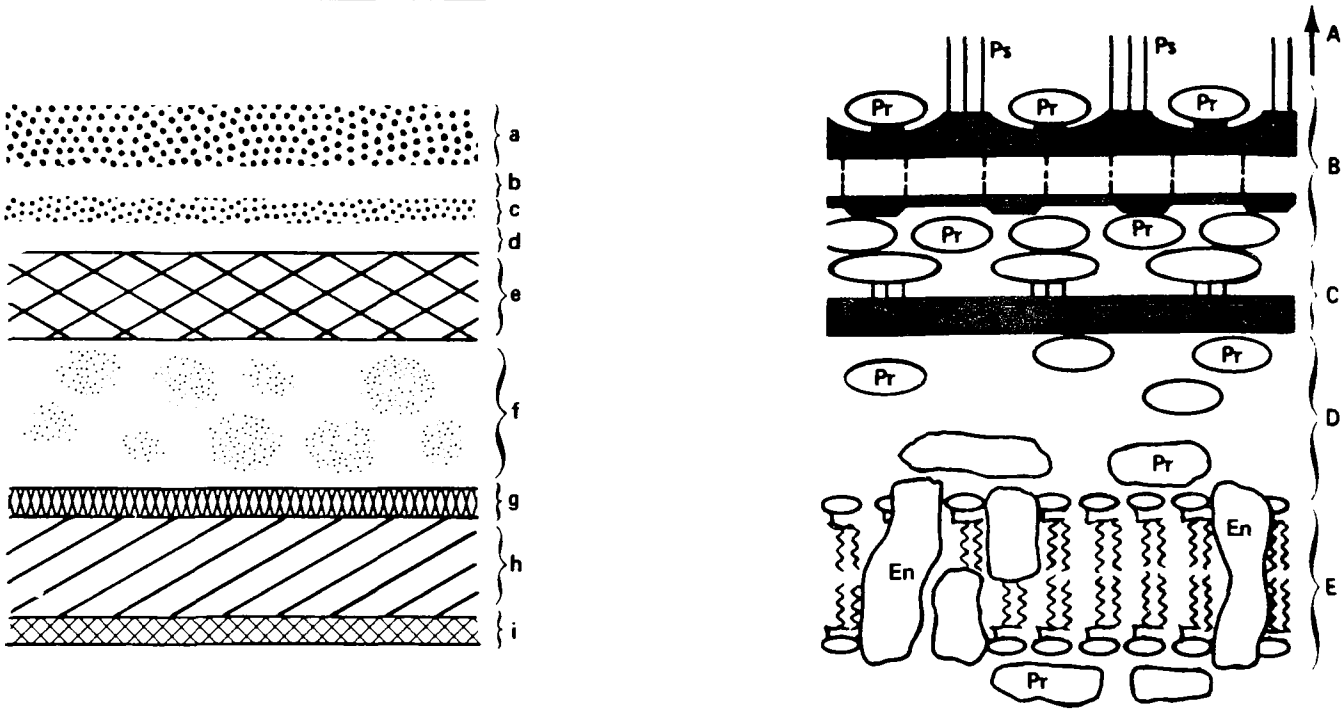


FIGURE 9

Schematic of Layers Observed in Bacteria Cell Walls and Cytoplasmic Membrane (Approximately to Scale)



a Outermost Layer, Proteins and Polysaccharides
b Lipids
c Possibly Lipopolysaccharides
d Possibly Proteins
e Fibrous Heteropolymers of Peptidoglycans
f Periplasmic Space Containing Degradation Enzymes
g Outer Layer of Cell Membrane
h Middle Membrane Layer, Bimolecular Phospholipid Layer
i Inner Layer of Cell Membrane (~25 A°)

A Capsule Material; 200-100,000+ A°
B Soft Layer; 100-150 A°
C Rigid Layer; ~50 A°
D Periplasmic Space; ~100 A°
E Cytoplasmic Membrane; ~100 A°
P_r Proteins
P_s Polysaccharides
E_n Enzyme Transport Systems (Permeases)

FIGURE 10

Enzymes Work in Sequentially Cooperating Systems

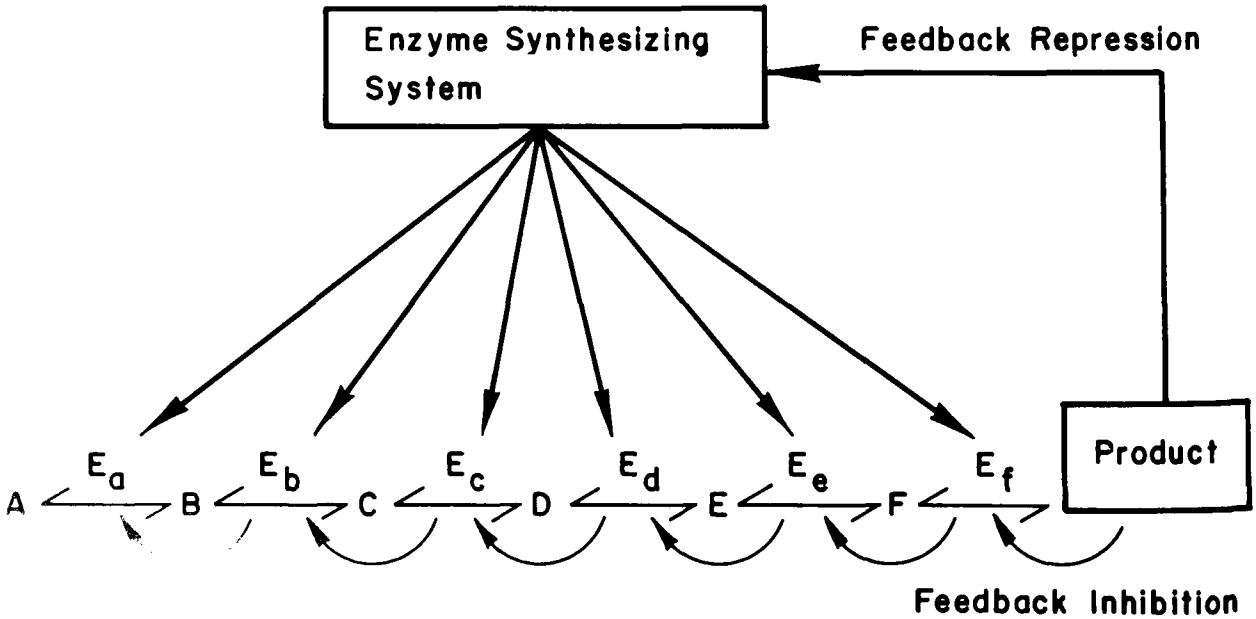


Figure 11

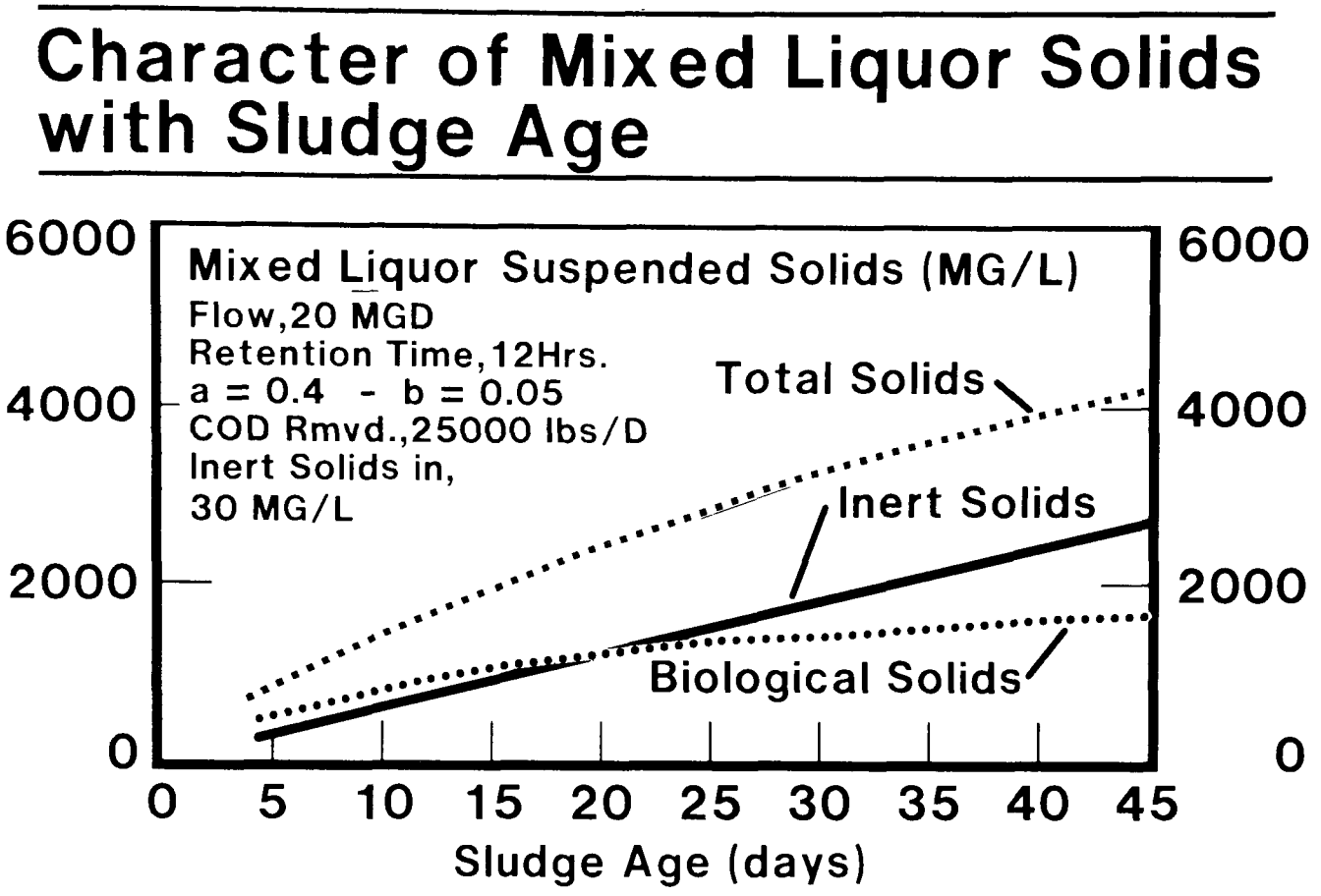
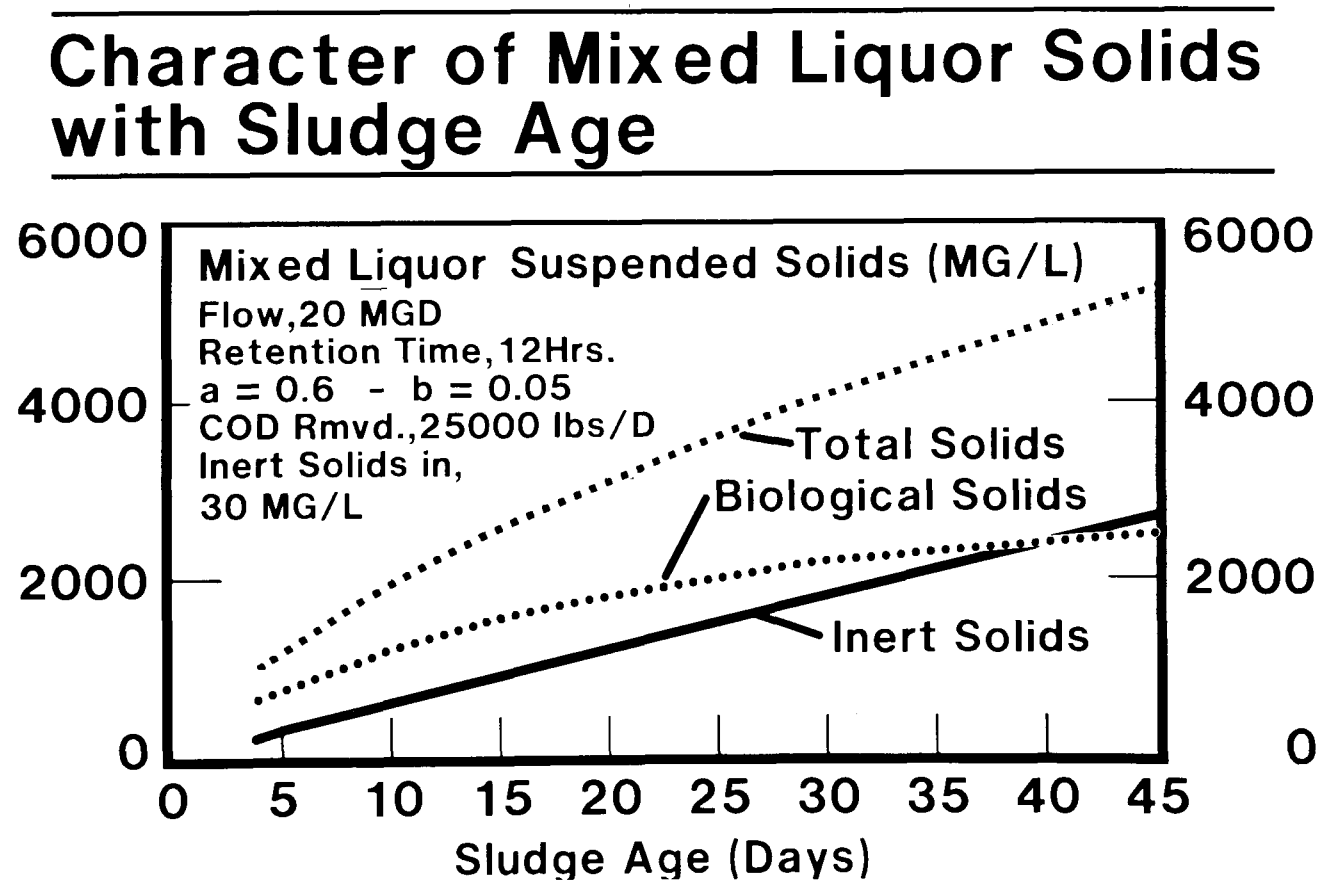


Figure 12.



CASE HISTORY ON BIOLOGICAL TREATMENT OF A PETROLEUM REFINERY WASTEWATER

Charles E. Ganze, Facilities Supervisor
and
Joe P. Teller, Deputy General Manager
Gulf Coast Waste Disposal Authority
Houston, Texas

Gulf Coast Waste Disposal Authority's American Facility located in Texas City, Texas, provides intermediate, secondary and tertiary treatment for a 23 million gallon per day waste stream.

The Research and Development and Process Design work was done by Amoco Oil and its Parent Corporation, Standard Oil of Indiana. A number of process patents have been applied for, with several granted and others pending. Williams Brothers Construction has been licensed to construct similar facilities incorporating the patented processes.

The wastewater treated at the American Facility is generated primarily by Amoco Oil Company's Texas City Refinery which currently processes approximately 350,000 barrels of sweet crude per day. In addition to the wastewater generated in the crude refining processes, sulfuric acid concentrating unit, cokers, and other refinery related process, this treatment facility treats wastewater generated by Amoco Chemical Company's Texas City Plant "B", other Amoco Chemical Company processing units located at the Refinery and all storm water collected in the 500 plus acres inside the battery limits of both Amoco Oil and Amoco Chemical Company's Plant "B".

To characterize the influent wastewater, parameters listed in the wastewater discharge permits are used. The data presented represent the values actually observed over 7 months operation.

Influent Characteristics

	Average	Maximum	Minimum
BOD, mg/l	183	1,110	36
TOC, mg/l	118	620	30
TSS, mg/l	234	1,908	32
O & G, mg/l	11	110	1
NH_3-N, mg/l	39.4	100	9
Phenols, mg/l	6.7	85	1.2
Sulfides, mg/l	0.4	4.0	0.07
pH		11	2

The various waste streams have received primary treatment prior to reaching the Gulf Coast Facility. In many cases, streams have passed through unit oil separators for the removal of gross quantities of oil before being discharged to the refinery's collection system, and then at the end of the collection system, all wastewater is processed through

API Separators for removing the remaining oils and the bulk of the suspended solids. As is generally the case with refinery effluents, the waste treatment system receives a waste stream that varies greatly in both quantity and quality. The process design was based on a knowledge that the treatment system would experience a highly variable waste load and that more stringent effluent requirements could be expected in the future.

To describe the waste treatment system, it is broken into three steps: Intermediate, Secondary, and Tertiary. The intermediate step incorporates the use of physical and chemical processes which are designed to protect the secondary or biological step. It consists of equalization with pH adjustment and prefiltration. As in many waste treatment facilities treating industrial wastes, equalization is considered a necessity. It serves several functions: first, it helps smooth out some of the variations in types of wastes and waste strength; second, it helps protect the secondary facilities from sudden surges in flow; and third, it helps reduce the overall treatment chemical costs by allowing the various wastestreams to mix, and, in many cases, neutralize each other, especially in the case of pH. The 4-hour equalization time provided is considered minimal for adequate protection to the biological system.

Prefiltration in this system is performed by pressure-type multimedia filters. The design hydraulic loading to the prefilter system is 5 GPM per square foot. Using only organic polyelectrolytes as filter aids, the prefilters are designed to remove the suspended solids and oils that remain after primary treatment and removal of much of the colloidal materials. The logic in keeping an extremely high quality water as a feed to the biological step is: first, to reduce the organic loading by removing the suspended solids, colloidal materials and oils; and second, to reduce the amount of inorganic solids that are put into the system. When the inorganic solids and oils are kept out of the biological system, the settling characteristics of the biological sludge is improved; with a better settling sludge, a higher sludge age can be attained; thus we then start attacking the more difficult to treat organic compounds and ultimately obtain biological nitrification.

The backwash from the prefilters is clarified with the overflow recycled to the equalization basin and the underflow (sludge) mixed with digested waste-activated sludge and pumped to a land farm for disposal.

The product water from the prefilters passes into the second step of our treatment system, the biological system. At this point, two aeration tanks, which operate in parallel, provide 12 hours retention time at design hydraulic loading. This reasonably long retention time improves the treatment capabilities for handling shock loads. Aeration is provided by ten 150-horsepower, floating, low-speed surface aerators. From the aeration tanks, the mixed liquor passes into the secondary clarifiers. The two 140-foot diameter, 18-foot side-water-depth-wide feed well clarifiers operate in parallel. The hydraulic loading on the secondary clarifiers is 600 gallons per square foot per day, which is generally considered adequate. The sludge removal mechanism is the multiple pick-up, sludge sucker type. The return sludge is pumped by centrifugal, recessed-impeller type pumps. Waste sludge is pumped to a gravity thickener where the underflow passes into an aerobic digester, and the thickener overflow is recycled to the equalization basin.

The overflow from the secondary clarifiers then flows to the third step of our treatment

system, the tertiary. The tertiary step consists of polishing filters. These final or post filters are designed simply to remove the biological solids that escape the secondary clarifiers. These gravity type, dual media filters operate at a design hydraulic loading of 4 GPM per square foot with the backwash pumped back to the aeration tanks as the solids are of biological origin.

Operations began before all construction activities were complete; we have experienced and are continuing to experience, the usual start-up mechanical and design problems. Among the significant mechanical problems are electrical switch gear malfunctions, an aerator gear box, backwash sump pumps, a clarifier scum pump motor, and the underdrain nozzles on the final filters. Design problems that we have noted to date include: no special provision for operating in sub-freezing weather (freezing sample lines, service water lines, caustic lines, and wet-leads to instrument-primary devices); and a widely fluctuating float in the Parshall Flume which is caused by excessive turbulence as a result of too short an approach to the throat. Even without all equipment and facilities fully operable, a number of interesting observations have been made. Over a three month period, when mechanical problems were at a minimum, we observed what we consider phenomenal reductions for a secondary waste treatment facility.

BOD	92%
TOC	85%
Ammonia-N	88%

These removals were experienced while maintaining the following conditions:

MLSS	3400 mg/1
Sludge Age	Approximately 50 days
F/M	0.07 pounds BOD/pound MLSS

with no apparent deterioration in sludge settleability (Average SVI -85).

The average performance for the first seven months of operation was as follows:

REMOVALS	
BOD Reduction	88%
TOC Reduction	77%
TSS Reduction	94%
Oil & Grease Reduction	91%
Ammonia-N Reduction	51%
Phenols Reduction	96%
Sulfides Reduction	72%

It should be emphasized that much of the data collected for these calculations do not reflect a stable operation.

We feel that by completing the remainder of the construction, clearing up all the initial mechanical problems generally associated with start-up, and by continuing to improve on our own operational procedures, we can meet the conditions set forth in the existing permits which extend through June 30, 1979. Beyond this, we foresee even more

stringent requirements for BOD, TOC, and Ammonia-Nitrogen. Provided our treatment capabilities improve as expected, this facility will produce an effluent that will comply with anticipated future requirements.

DISCUSSION

J. J. Chavez: How much ammonia do you have in your raw influent and in the final effluent stream and where do you think you get the bulk of ammonia removal in your system?

Charles Ganze: The ammonia is removed, biologically, in the aeration tanks. The average influent concentration (feed to the aeration system) was about 40 ppm with a maximum of about 100 ppm or so.

J. J. Chavez: How about the final effluent?

Charles Ganze: The final effluent - it would go into the .05 ppm range, very difficult to analyze.

Anonymous: Please discuss your choice of filters.

Charles Ganze: Economics is one thing. The pressure type filters are a little more expensive. You can give them a little bit higher loading. The multimedia does give us some advantages on handling the colloidal materials and the suspended solids. Now the gravity-type filter again is used on the effluent, again the only thing that we anticipated getting from that were biological solids.

G. T. Minnick: How do you dispose of your aerobically-digested sludge?

Charles Ganze: The sludge that we actually waste is a very minimal amount. As Jim indicated we observe very low sludge yield, we are operating again at 50-day sludge age at an elevated temperature and we have a low sludge yield. The aerobically digested sludge is mixed again with this back wash from the prefilters and it is pumped to a land farm area. Now we call this a land farm and not a land fill. It is actually tilled into the soil. At this facility we have some 150 acres dedicated to this activity. We just take a tractor with a disk out there and till it into the soil.

R. A. Farnham: What are the calculated variability factors associated with your process?

Charles Ganze: We don't think we have enough data to try to put together any thing like that, I only showed you some maximums and minimums that we have observed over this relatively short period of time, which is seven months, and we haven't tried to put together any probability type numbers.

Anonymous: What is the loading on your secondary clarifier?

Charles Ganze: 600 gallons per day per square foot, surface loading.

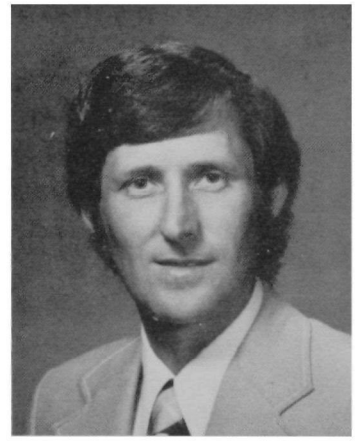
Leonard Orwin: At the beginning of your talk you mentioned that there were several features of this plant for which you had applied for patents, I wonder if you are able to point out any of those?

Charles Ganze: Standard Oil, since they did the R & D and design work, has applied for the patents. I'll ask Jim Grutsch if he will come back up here and speak on that for just a moment.

Jim Grutsch: More than 20 claims are allowed in the patent covering areas of (1) pretreatment, (2) the activated sludge process, and (3) the integrated end-of-pipe treatment sequence. Some of the specifics are as follows: Pretreatment (1) The use of a portion of the pretreatment basin for reduction of immediate oxygen demand (IOD). (2) The use of certain catalysts for IOD removal. (3) The addition of colloid destabilizing chemicals followed by filtration of suspended solids and oil and grease to levels of 10 mg/l and less. Activated Sludge Process (1) Two stages of sludge treatment in facilities for one unit; i.e., recycle of part of the clarifier return sludge to: (a) the aeration tank rundown line, and/or (b) a thickener thence to the aeration tank rundown line, and/or (c) a thickener, aerobic digester, thence to the aeration tank rundown line. (2) Operating at a sludge age greater than 10 days. (3) Pretreating the activated sludge unit influent to 10 mg/l or less suspended solids and oil and grease. (4)Using air or oxygen between stages of the activated sludge unit. For example, turbulence in the wide well region of the clarifier was visible in the slide. This turbulence is intentional. Air is educted into the buried rundown line so that the air/water mixture is under a hydrostatic head to improve oxygen transfer. When the air is released in the wide well clarifier, it provides flocculating energy. Process. A process consisting of an equalization section incorporating hydraulic equalization, pH control, pre-aeration, colloid destabilization, and filtration to 10 mg/l or less of suspended solids and oil and grease, followed by an activated unit incorporating two stages of sludge recycle and interstage aeration, in which the average sludge age is greater than 10 days.

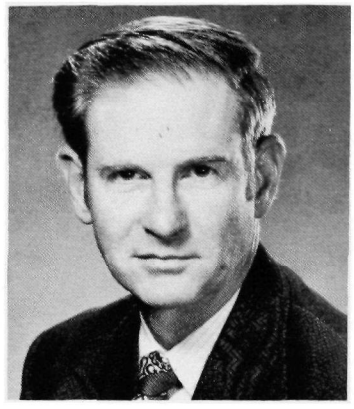
A Tulsa based firm, William Brothers Waste Control, is authorized to use these features.

BIOGRAPHY



Charles W. Ganze is Facilities Supervisor at the Gulf Coast Waste Disposal Authority's 40-Acre and American Facilities in Texas City, Texas. He has acquired two degrees from East Texas State College. He holds a B.S. in General Science/Biology and a M.S. in Earth Science with a minor in Biology. Charles taught science in the LaMarque Independent School District (1967-1968) and the Andrews Independent School District (1966-1967) and was employed by Union Carbide Corporation as a Secondary Waste Treatment Research Worker prior to his employment with the Gulf Coast Waste Disposal Authority in 1973.

BIOGRAPHY



Joe P. Teller is Deputy General Manager in charge of Operations at the Gulf Coast Waste Disposal Authority in Houston, Texas. He holds a B.S. Degree in Civil Engineering from Texas Technological College and a M.S. Degree in Sanitary Engineering from the Georgia Institute of Technology. Mr. Teller was employed as Deputy Director of the Texas Water Quality Board in Austin before joining the staff of the Gulf Coast Waste Disposal Authority in 1972.

OPTIMIZATION OF THE ACTIVATED SLUDGE PROCESS THROUGH AUTOMATION

Mohamed A. Zeitoun
The Dow Chemical Company, Texas Division, Freeport, Texas

As an introduction, I would like to go over our accomplishments in extending the application of the activated sludge process for the treatment of brine wastewaters.

ACTIVATED SLUDGE TREATMENT OF WASTEWATERS OF HIGH SALT CONTENT

Many petrochemical processes produce organically contaminated wastes of up to 12% NaCl. Glycols and glycerine made by the chlorohydrin process result in a brine waste of 6-10% NaCl and constitute the major organic waste load at the Texas Division of The Dow Chemical Company.

Up to 1969, operation of the activated sludge process was believed to be possible at salinities less than 2% NaCl. Although numerous bacterial species living in very high salt concentrations were known, utilization of halophilic bacteria in a biological oxidation process was lacking.

Under an EPA grant (1969-1971) we started with a fill and draw procedure to find the minimum dilution required. We started with sewage sludge and slimes from ditches and holding ponds exposed to the wastewater from the glycol production facilities, and at 2% NaCl concentration. Then we raised the NaCl concentration gradually, over a period of 6 weeks, to 10% salt. To our surprise, no dilution was required. Then we operated laboratory continuous units, obtaining 80-88% TOD removal at a residence time of 12 hours, a good settling sludge, but a turbid effluent. A chemical flocculation step was required to clarify the effluent and maintain low suspended solids.

We then built a mini-plant on a skid for a flow rate of 0.5 to 1.0 gpm and fed it continuously from the production facilities. We then learned the necessity of good equalization. The mini-plant (Figure 1) is essentially equalization-aeration-bio-settling-flocculation and a final settler.

At that point in time we believed that activated sludge can be extended to the treatment of brines up to 12% salt content. The operation was checked in a pilot plant (150 gpm) using commercial size equipment. Its operation continued for over two years where several sludge handling methods were tested and it served as a technology center for the design of several treatment facilities around the world. We spent about $1 million on this testing facility.

In the Texas Division at Freeport, Texas, we utilized existing holding ponds and built a mammoth aerated lagoon system using submerged Kenix mixers. It is treating 20,000 gpm in 45 acres of aerated basin at a capital cost of about $5.5 million. Now we are adding air flotation, settling tanks and pressure filters to remove the suspended solids from the aerated lagoon effluent at a capital cost of $7 million.

At Stade near Hamburg, Germany, we built an activated sludge plant to treat a mixed effluent of glycol, glycerine, and other minor streams, which were tested in mini-plant operation. This plant has been in operation for about 2 years. It is designed for 9,500 gpm at a cost of $7 million. Another plant built at Sarnia, Canada, has been in operation for about 4 months, and is treating 3,000 gpm at a capital cost of $4.5 million.

The Louisiana Division at Plaquamine is building a Unox activated sludge plant at a cost of $8.5 million for treating 8,500 gpm and is scheduled to start early 1977. A total of $33 million has been invested in plants treating 60 million gallons per day, (Table I), of brine wastes all over the world. All this resulted from an initial study sponsored by an EPA grant costing the taxpayer $150,000. This is the story of the best spent $150,000 by EPA.

AUTOMATION OF THE ACTIVATED SLUDGE PROCESS

The problems of automated control of activated sludge plants lie in selecting parameters for control and developing sensors for these parameters. The common practice of monitoring plant operations with random daily or weekly analysis is inaccurate and clearly inappropriate for control and optimization. Parameters to control the process must be measured on a continuous basis or must be obtained rapidly enough on a repetitive basis so that updated data are available for use within the time constraints of the process.

The objectives of the reported study were to develop on-line control systems that will (a) add nutrients (N &P) in proportion to the total carbon in the feed, (b) control the sludge recycle rate by an F/M signal that is measured as the ratio of the total carbon in the feed to that in the mixed liquor, (c) control the chemical flocculant addition at the end of the process in proportion to the turbidity of the bio-settler overflow, (d) divert the feed to a holding pond if a toxicant is detected in the feed by an instrument "Biological Inhibitor Detector", that measures the oxygen uptake of the biota on repetitive basis.

The existing, skid-mounted mini-plant was renovated and new electrical circuits for the instrumentation were added. The control panel (Figure 2) included three 2-pen recorders. The influent flow, set manually at the board, and the pH of the influent were both recorded. The sludge recycle was manually controlled and recorded. The alum flow rate and the turbidity of the final effluent were both recorded and controlled at the board. The pH of the final effluent was both recorded and indicated on the board.

Influent pH Control

The influent pH control system (Figure 3) was designed for fast response in a well mixed system. By coupling the pH feedback loop around the recycle feed pump, the loop capacity, mixing time and measurement lags were kept to a minimum. The pump also served as the feed pump to the aeration basin and provided the feed at the proper pH independent of the volume and pH of the influent in the equalization tank. The pH control system had a high and low limit switch that closed the feed valve if the pH got out of control and automatically opened the valve as the control range was regained.

Food to Microorganisms (F/M) and Nutrients Addition Controls

The F/M control system is shown schematically in Figure 4, together with the nutrients addition control system. An Ionics Model 1212 Total Carbon Analyzer was used to measure the total carbon in the feed and that of a homogenized and diluted mixed liquor sample from the aeration basin. To achieve this, the sample handling system of the carbon analyzer was modified to accommodate two sample streams, one a continuous flow and the other a batch sample. A schematic of the sample handling system is shown in Figure 5. A continuous sample of the feed passes through a 3 micron Cuno(R) filter, through a valved rotameter and through a two-way solenoid valve (A). It then passes through the Analyzer sample injection slide valve to a 3-way solenoid valve (B) and on to drain. A 1:1 dilution of the mixed liquor sample aids in the homogenization step required to obtain a representative sample. Two timers operate sequentially to first operate pumps to provide the aliquot and next operate the Virtis(R) 45 homogenizer. Upon completion of the homogenization time, another sample pump empties the homogenizer contents into the stand-pipe above solenoid (B), which allows deaeration of the sample before analysis. All three solenoid valves are energized at this moment; two-way solenoid (A) is closed and the drain connections of valves (B) and (C) are closed. The homogenized sample passing through the stand-pipe above valve (B) flows by gravity through the sample injection valve and into the stand-pipe above solenoid valve (C) until the stand-pipe levels approach equilibrium. Flow in this direction flushes the prior feed sample from the injection valve. Upon injection of the homogenized sample, all of the solenoid valves are de-energized, restoring the flow of the continuous feed sample stream through the system. Meanwhile, the batch sample in both stand-pipes is drained.

The output from the Total Carbon Analyzer is converted to a pneumatic F/M signal with a 0 to 1 range. The signal is fed to a recorder-controller which adjusts an output pneumatic signal proportional to the offset between the desired and actual F/M valve. The output signal controls the percent energized time of a 60-second cycle timer, that operates a normally closed solenoid valve allowing the flow of the recycled sludge to waste. The system also includes a high signal selector and regulator that is set to designate a maximum waste flow rate independent of the F/M controller. This safety device prevents bacteria washout in case of control system failure

Nutrients Addition Control: Constant nutrients addition, based on flow rate, will occasionally result in excess or insufficient nutrients addition. Insufficient addition decreases bacterial viability and decreases the organic carbon removal efficiency. Excess nutrients addition, besides being economically unsound, can cause downstream algae blooms and subsequent pollution problems. High nutrients residual may also prevent the recycle of industrial treated effluents.

The activated sludge mini-plant was operated with varying flow of nutrients to the aeration basin based upon the measurement of the total carbon in the feed. Ammonia and phosphorus concentrations, in the biosettler overflow, were analyzed routinely to determine the optimum C:N:P ratio, for the waste water being treated. Figure 6 shows the relationship between ammonia consumption and microbial growth. Although the

experimental data reflects the ammonia consumption for cellular growth plus the ammonia absorbed onto the bio-floc, the experimental value of 0.133 compares closely with the theoretical value of 0.15 according to cell formula $C_5H_7O_2N_1$.

In order to determine the minimum nutrients requirement, the ratio of nutrients addition to feed total carbon concentration was progressively lowered until analysis of the bio-settler overflow showed a very low concentration of N and P. The results shown in Figure 7 indicate a large adsorptive capacity of the mixed liquor bio-floc for values of N :C greater than 0.2. The C:N:P ratio of 100:9:0.54 was found to be optimum for the 8% salt containing wastewater. Using this proportionally the nutrients control system assured microbial viability and the effluent concentration was maintained below 5 ppm ammonia and 1 ppm phosphorus.

F/M Control System: A transient or unsteady state model of the completely mixed activated sludge process is developed to simulate the dynamics of the F/M control system. The Monod kinetic equations are incorporated into the substrate and microorganisms material balance equations around the aeration basin. The substrate degradation is assumed to occur only in the aeration basin.

The scheme of F/M proportional control is inserted into the model as a function of the wasted sludge flow rate.

$$W = A\ (F/M) + B,\quad 0 \leq W \leq W_{max.}$$

where W = wasted sludge flow rate
A and B are constants related to a specified gain.

A maximum waste flow rate, $W_{max.}$ is imposed to prevent complete cell washout in case the control system should fail. The control is related to the recycle flow by:

$$T = R + W$$
$$R = T - [A\ (F/M) + B]$$

where T = total biosettler underflow rate
R = recycle flow rate

The dynamics of the unsteady state bio-settler operation are computed in terms of a constant compaction ratio, X_r/X. There are obvious limitations in using a constant ratio to describe the unsteady state performance of a biological settler, however it was adequate for the predictionof the bacteria concentration in the aeration basin. Figure 8 shows that the sludge compaction ratio remained relatively constant during a 50% increase and decrease in feed concentration.

The Monod type kinetic equations were found adequate in simulating the dynamics of the activated sludge treatment of propylene glycol waste water because of four basic reasons:

1. The Monod model was developed to describe the behavior of pure cultures. In the fresh water glycol system, 80% of the microorganisms present were of one species, Pseudomonas. In the brine (6-8% NaCl) glycol system 90% of the culture was identified as one halophilic bacterium.

2. The propylene glycol represented the only soluble carbon source in the feed.

3. The carbon energy source was rate limiting. Deficient nutrients (N&P) were added by the nutrients control system.

4. The pH and temperature were regulated for the optimum rate of biological growth.

Sludge growth coefficients and substrate removal kinetic constraints were determined for freshwater glycol feed and saltwater glycol feed. For the freshwater biota, the yield coefficient $Y = 0.21$ gm VSS/gm TOD removed, and the decay coefficient $k_d = 0.06$ day^{-1}, while for the saltwater bacteria, these values were 0.133 and 0.02 respectively. The substrate utilization rate for the freshwater system is best described by:

$$\frac{dF}{dt} = \frac{k \times S_1}{K_s + S_1}$$

where $k = 5.0\ day^{-1}$

and $K_s = 117$ mg/l as TOD

For the saltwater bacteria, K_s is very large compared to S_1 (substrate concentration in the aeration basin), and the rate equation reduces to:

$$\frac{dF}{dt} = k \times S_1$$

where $k = 0.0132\ (mg/l\ TOD)^{-1}\ day^{-1}$

Testing of the F/M Control System: The mini-plant test runs were started with the F/M controller on manual, i.e., constant recycle and sludge waste flow rates were set. The system was allowed to approach a steady-state condition, in terms of reactor microorganism concentration, substrate removal efficiency, and bio-settler characteristics such as sludge concentration and sludge blanket height. The system was then put on automatic control and a step increase in the concentration of the feed was made by adding an aliquot of industrial grade propylene glycol to the equalization tank.

An automatic Total Carbon analysis was made every six minutes during these runs, with alternate analysis of feed sample and homogenized mixed liquor sample. To reduce the volume of data, each F and M concentration plotted in this section is represented as the average of five total carbon analyses. Waste, recycle and F/M data are also hourly averaged values.

A blank F/M test in which no control is affected shows the dynamics of cell growth under continuous flow conditions and is used for comparison for F/M control test system

response. Figure 9 shows the mixed liquor total carbon and F/M response to a 47% increase in loading. The solid lines are the predicted responses using the transient state computer model. A very good fit is obtained for the increase in mixed liquor total carbon. Because of a non-linear calibration of the total carbon instrument above 50% of scale, data for F/M signal lie below the computer prediction of F/M, till the mixed liquor total carbon values reach the same non-linear range as the feed values, then the predicted curve agrees with the experimental data.

The results of one of the control tests made with freshwater glycol feed are presented in Figures 10 and 11. The initial conditions of this test run compare closely with those used in the blank test (Figure 9). The model prediction of the increase in mixed liquor total carbon ($t = 0$ to $t = 27.5$ hours) fits the data well. The F/M signal data lie above the predicted F/M curve for the first several hours following the step increase and below the predicted curve following the step decrease, because an average value of feed concentration is used in the simulation, rather than individual data points. A good representation of recycle and wastage response is obtained with a fast F/M response (Figure 11). The prediction of the transient biological state after the step decrease in feed concentration ($t = 27.5$ hours) is not accurate because of an inadequate representation of the bio-settler dynamics. However, the final steady state computer prediction ($t = 50$ hours) fits the data well.

In order to have a meaningful basis of comparison for the F/M control tests, it is necessary to have a blank run with identical initial conditions. The initial steady state must be the same in terms of feed, recycle and waste flow rates, substrate concentration, reactor and bio-settler underflow microorganisms concentrations, temperature, and physiological conditions of the biota. While this is difficult to achieve experimentally, a valid comparison can be made by using the mathematical modeling which predicts the transient accumulation of microorganisms.

The computer simulated curves in Figures 12 and 13 show the differences in response characteristics for the freshwater propylene glycol system with F/M control versus the system with no control. For the case of an 8.5-hour hydraulic residence time with an initial recycle ratio of 0.55 it takes 17 hours for the controlled system F/M to return to within 20% of the set point after the step increase in loading (Figure 12). This represents a 63% reduction in response time. Figure 13 represents the system having a 6.95-hour hydraulic residence time and an initial recycle ratio of 0.3. The F/M ratio returned to within 20% of the set point in 10 hours, less than a third of the time required for the system without control. The larger mass of waste sludge available for recycle allowed a 69% reduction in response time.

One of the most important achievements of this control system is maintaining the effluent quality. Figure 14 shows the relationship between substrate concentration in the aeration basin for the blank and the F/M control simulation of Figure 13. The control enables a fast return to the desired effluent quality.

Figure 15 shows the simulation of an F/M blank test and an F/M control test for the brine propylene glycol waste water system. Low volume of waste sludge is available for

additional recycle, due to the lower yielding halophilic bacteria, which results in the rather long response time of 33 hours with F/M control. Manual adjustment of the recycle and waste flows would be adequate for loading control because of the long response times involved. On-line F/M control for high salt systems does not seem justifiable unless an aerated sludge storage or stabilization tank is available to supply additional recycle in periods of high loading.

Chemical Flocculation Control System

The overflow of the bio-settler is too turbid, especially in case of saline wastewaters, and needs additional clarification. A chemical flocculation control system was used to remove the suspended and colloidal matter from both the fresh water and the highly saline biologically treated effluents.

The schematic in Figure 16 illustrates the flocculation controls and process flows. The proportional control was based on a turbidity measurement. Aluminum sulfate was used as the flocculant, and the pH was controlled (proportional-integral) at the level corresponding to the optimum for alum flocculation. Both feed forward and feed back modes of control were tested. A Hach Surface Scatter Turbidimeter, No. 2426, operated better than other types tried because it has no contact between the sample and the optical surface.

The optimum pH for alum flocculation was determined by a series of jar tests at various pH values, on samples having the same initial turbidity. The optimum alum dosage was found to increase above pH 6 and below pH 5. At a pH above 7.0, the settled floc was more fluffy and had a higher subsidence line.

A stoichiometric relationship was found between the bio-settler overflow turbidity and the optimum alum dosage, at constant pH (Figure 17). Comparing point 5 with point 6 in this graph illustrates the effect that the physiological condition of the bacteria has on the alum requirement for optimum flocculation. Data point 5 represents a series of jar tests on a sample of bio-settler overflow whose initial turbidity was increased from 25 JCU to 44JCU by adding aeration basin mixed liquor. Thus the sample contained larger bio-colloids of older microorganisms. On the other hand, data point 6, where the higher optimum alum dosage was required, represents a case of finely dispersed microorganisms, as the sample was collected during a period of very high growth rate of microorganisms in the aeration basin.

Because of the lag time of several hours associated with the flocculator and final settler, control stability was a major problem in feed back control. The feed forward mode of proportional control resulted in a high quality effluent and stability was not a problem.

The feed forward control was tested on both the propylene glycol fresh water system and the glycol-salt waste water. Typical performance is given in Tables 2 and 3 respectively. An average of 98% of the suspended solids were removed by the floc-

culation step in the fresh water system and 85% were removed in the salt system. The chemical flocculation step increases process efficiency in terms of TOD removal. For the fresh water system the overall process efficiency increases from 90.9% TOD removal to 93.4%. The turbidity of the final fresh water effluent was reduced to 2 to 3 JCU whereas the bio-settler overflow turbidity was typically 15 to 25 JCU. The bio-settler overflow turbidity for the saline waste water system was reduced by 85%, from 35 to 80 JCU to 5 to 10 JCU.

Biological Inhibitor Detector

The objective was to develop an upstream sensing device for toxic loads or spills to an activated sludge process. If the presence of a toxin in the feed to the plant can be detected rapidly enough on a repetitive basis, the feed could be diverted to a holding pond until the toxin is identified and eliminated, or bled at a low rate to the treatment plant.

Oxygen uptake rates, both Warburg and oxygen electrodes, have been used to measure the effect of toxins and inhibitors on activated sludge. Tests were conducted to determine an oxygen uptake measurement cycle that would be sensitive to the presence of a toxic substance in the feed to an activated sludge plant and that could be automated to rapidly detect the toxic effect on a repetitive basis.

The oxygen uptake rate and the total oxygen consumed by propylene glycol standard solutions containing various concentrations of toxic substances were measured as 10 ml of the sample was introduced in 500 ml of activated sludge under controlled conditions of mixing, aeration, and temperature.

The sensitivity and reproducibility of the total oxygen consumed, as determed from the area under the oxygen uptake curve, was found superior to that of the oxygen uptake rate, as determined from the initial slope of the oxygen concentration curve when the aeration was cut off. The rate of oxygen uptake was more dependent on the concentration of the viable biomass than the total oxygen consumed. The automation of a measurement cycle utilizing the area under an oxygen uptake curve was simpler since it did not require cutting off the air every time a test sample was added.

In order to utilize the area under the oxygen uptake curve to monitor the toxic effects of a feed to an activated sludge plant, it is necessary to distinguish between the changes due to the varying concentrations of the substrate in the feed and the presence of toxic substances. A comparison of the oxygen uptakes of two standard propylene glycol samples before and after the exposure of the bacteria to a feed sample was the measurement cycle adopted to measure the toxic effects of the feed. The oxygen uptake of the first standard established a reference activity of the bacteria sample, which was then exposed to the feed to the process for long enough time to degrade the substrate in the feed. Then the same bacteria sample received an equal volume of the standard and its oxygen uptake, compared to that of the first standard, was expressed as an activity ratio in response to the feed sample.

Figure 18 is a schematic illustration of the measurement cycle (60 minutes), when the feed contained no toxic substance. The activity ratio would be approximately equal to 1.0. Figure 19 shows a measurement cycle when the feed contained a toxic substance resulting in an activity ratio much less than 1.0.

Several models of an instrument based on the automated measurement cycle of three oxygen uptake curves were built in-house and used extensively in screening the biodegradability and toxicity of industrial waste waters, organic and inorganic substances. The instrument can be regarded as a differential respirometer, and has the added feature of measuring a BOD value of the feed in less than one hour. The feed BOD value, calculated from the ratio of the feed oxygen uptake to that of the first standard multiplied by the BOD of the standard, compares very well with BOD_5 for values of 100 to 800 mg/l (Table 4).

PROCESS DESIGN CONSIDERATIONS - CONTROLLED ACTIVATED SLUDGE

The development of on-line control systems for the activated sludge treatment process opens up many possibilities for flexible and innovative process design.

Figure 20 illustrates a conceptual design of an activated sludge treatment system including the F/M control system and the biological inhibition detection (BID) system.

Equalization dampens fluctuations in the organic content, in flow, in pH, and in other physical-chemical characteristics of the feed, thus it is part of the F/M control system. The equalization tank is also part of the feed forward inhibition detection control system. It provides a time delay, together with dilution of a possibly toxic feed during the biological activity analysis period. A toxic feed would be diverted to a holding basin by the BID control system. After determination of the chemical nature of the toxin, it could either be bled back into the system or treated by other means. Pre-treatment could include chelation of toxic metals and sorption of toxic organics.

The F/M control system, based on flow measurement and organics concentration, includes an aerated waste stabilization tank which supplies additional microorganisms for recycle in periods of high loading. The stabilization tank may be located in the sludge waste line as shown in Figure 20, or it could be located in the sludge recycle line; depending on which site is more adequate in terms of microorganisms viability and effects on bio-flocculation.

If the feed sample for F/M control is taken before the equalization tank, F/M control will be more anticipatory in nature with very short response time. The control system could then include a mini-computer which would be programmed to calculate the hydraulic effect that the equalization will have on the feed flow and composition and would affect F/M control on this anticipatory basis. Hence, extra sludge recycle could begin before the higher loadings affect the aerated biomass.

Another available control system that needs to be incorporated into the plant design is an aeration basin oxygenation system that optimizes oxygen allocations and controls the oxygen supply to the stabilization tank.

Nutrients and pH control would be provided when required. Turbidity control would be provided for designs that employ flocculation as the tertiary treatment for colloidal and suspended solids removal.

In conclusion, future plant designs have to incorporate both control systems and predictive models in order to optimize the operation of the activated sludge process to be able to meet the more closely regulated effluent limitations. Both design and operation of sophisticated plants depend upon the availability of reliable sensors and the instrumentation necessary to control the processes.

REFERENCES

Details of the research reported in this paper are given in two reports published by U.S. Environmental Protection Agency and are for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

(1) "Treatment of Wastewater from the Production of Polyhydric Organics," 12020 EEQ 10/71 Water Pollution Control Research Series (1971), includes 18 references.

(2) "Optimizing a Petrochemical Waste Bio-Oxidation System through Automation," EPA-66-/2-75-021 Environmental Protection Technology Series (June 1975), includes 61 references.

ACKNOWLEDGEMENTS

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These projects were partially supported by a grant from the Water Quality Office of the Environmental Protection Agency. Appreciation is expressed to the personnel of Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, for their cooperation and assistance.

DISCUSSION

Morris Wiley: Was this a calcium or a sodium brine?

Mohamed Zeitoun: Mainly sodium chloride.

Morris Wiley: Have you tried treating this in combination with other organic waste?

Mohamed Zeitoun: Yes.

Morris Wiley: Is that desirable or undesirable?

Mohamed Zeitoun: That depends on the same factors governing the possible combination of fresh wastewaters. Our aerated lagoon treats a mixture of organic waste that were tested in the laboratory and determined to be compatible and treatable. Some organic wastes were found to be non-toxic to the system, but don't degrade in the presence of the main substrate which is glycol and glycerine.

Morris Wiley: Do you notice either positive or negative synergism between the wastewaters, by that I mean you get enhanced activity or decreased activity by mixing the brine waste and other types of waste?

Mohamed Zeitoun: Do you mean by other type of waste, that which is less saline?

Morris Wiley: Yes.

Mohamed Zeitoun: Micro-biological tests showed that the optimum salinity of this halophitic bacteria is 6-7% NaCl.

Morris Wiley: Do you have problems with salinity swings causing osmotic pressure difficulties on the organisms?

Mohamed Zeitoun: Gradual changes of salinities up to 10% and down to 4% have very slight change of activity. Practically, this is not a problem.

BIOGRAPHY



Mohamed A. Zeitoun is a senior research specialist with the Dow Chemical Company, Texas Division, Freeport, Texas. He holds the following degrees in Chemical Engineering: B.Sc. Cairo University, Cairo, Egypt (1950), M.S. and Ph.D. (1958) Texas A&M University. He taught at Cairo University and Texas A&M. Mohamed has been conducting research work in desalination and industrial waste water treatment since 1962 and has been with Dow since 1966.

TABLE 1 BIOLOGICAL OXIDATION PLANTS TREATING BRINE WASTES IN THE DOW CHEMICAL COMPANY

Process	Location	Design Flow Rate, gpm	Capital Cost Million $	Remarks
Activated Sludge Pilot Plant	Freeport, Texas	150	1.0	Incl. 2 years operation
Aerated Lagoon	Freeport, Texas	20,000		
Aeration			5.5	
Sludge Handling			7.0	Start-up late 1976
Activated Sludge	Stade, Germany	9,500	7.0	
Activated Sludge	Sarnia, Canada	3,000	4.5	
Unox Activated Sludge	Plaquamine, LA	8,500	8.5	Start-up early 1977
TOTAL		60 MGD	$33.5 million	

TABLE 2 ALUM FLOCCULATION SYSTEM PERFORMANCE*
GLYCOL-FRESH WATER SYSTEM

Day of Operation	Effluent Before Chemical Flocculation MLSS mg/l	TOD Removal %	Effluent After Chemical Flocculation MLSS mg/l	TOD Removal %
1	45	88.8	4	89.7
2	22	95.5	0	96.0
3	20	93.5	0	95.8
4	20	89.3	0	93.0
5	11	92.0	0	93.9
6	36	95.2	1	95.4
7	52	84.1	0	87.7
8	86	90.7	0	94.9
9	34	88.3	0	94.0
10	55	91.7	0	93.9

* proportional control with optimum alum dosage according to Figure 17.

effluent turbidity maintained at 2 to 3 JCU

TABLE 3 ALUM FLOCCULATION SYSTEM PERFORMANCE*
GLYCOL-SALT WASTE WATER SYSTEM

Day of Operation	Effluent Before Chemical Flocculation MLSS mg/l	TOD Removal %	Effluent After Chemical Flocculation MLSS mg/l	TOD Removal %
1	91	76.2	24	91.9
2	164	78.9	17	91.9
3	52	63.2	0	65.9
4	43	66.6	3	-
5	23	90.3	0	90.8
6	214	75.8	18	96.3
7	66	71.5	0	-
8	43	69.0	19	-
9	52	75.4	21	80.3
10	40	78.4	18	81.0

* alum dosage at optimum (10% greater than doses in Figure 17)

TABLE 4 COMPARISON OF INSTRUMENTAL BOD AND BOD_5

BOD_5 mg/l	Instrumental BOD* mg/l
190	197
536	482
588	565
815	839

* Standard propylene glycol of 400 mg/l BOD_5 used for the instrument calibration.

Figure 1

ACTIVATED SLUDGE MINI PLANT

Flow Diagram

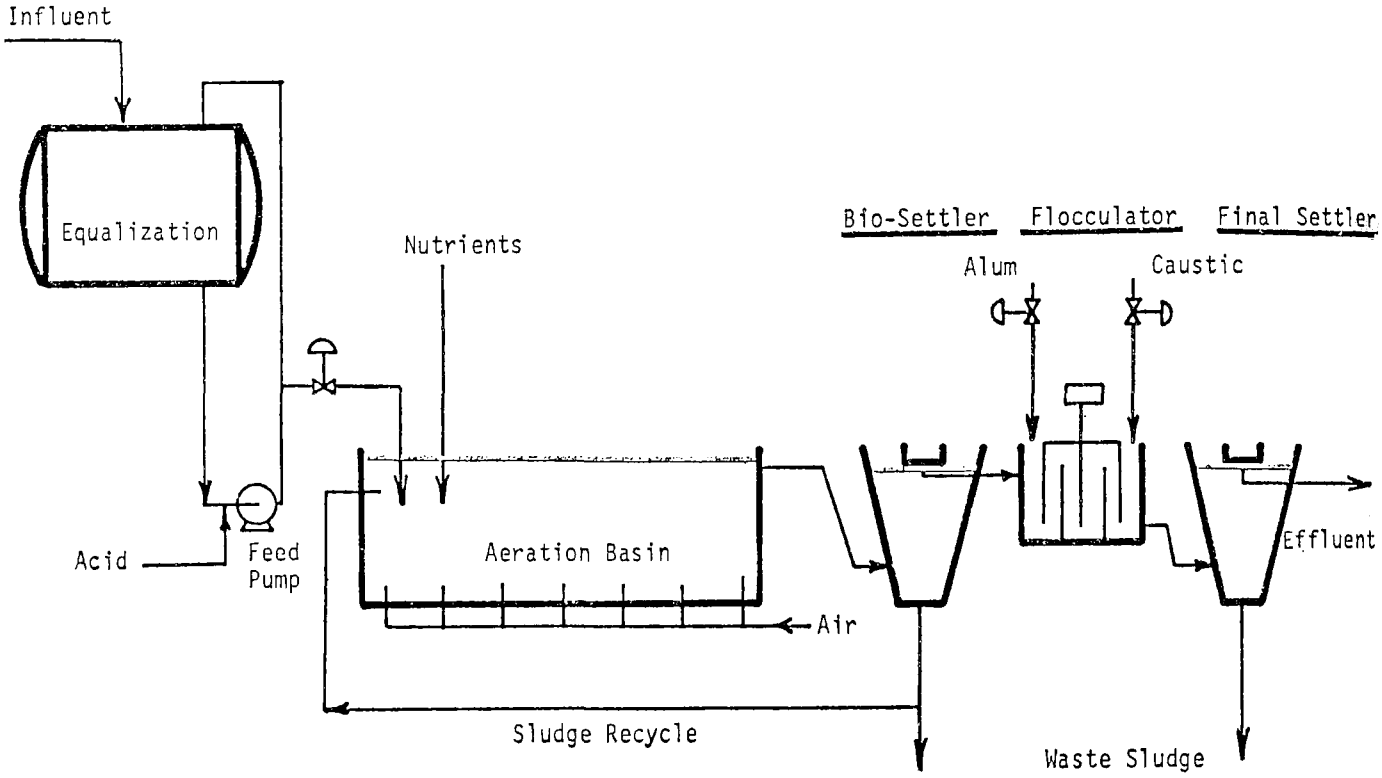


Figure 2.

ACTIVATED SLUDGE PILOT PLANT

Side View

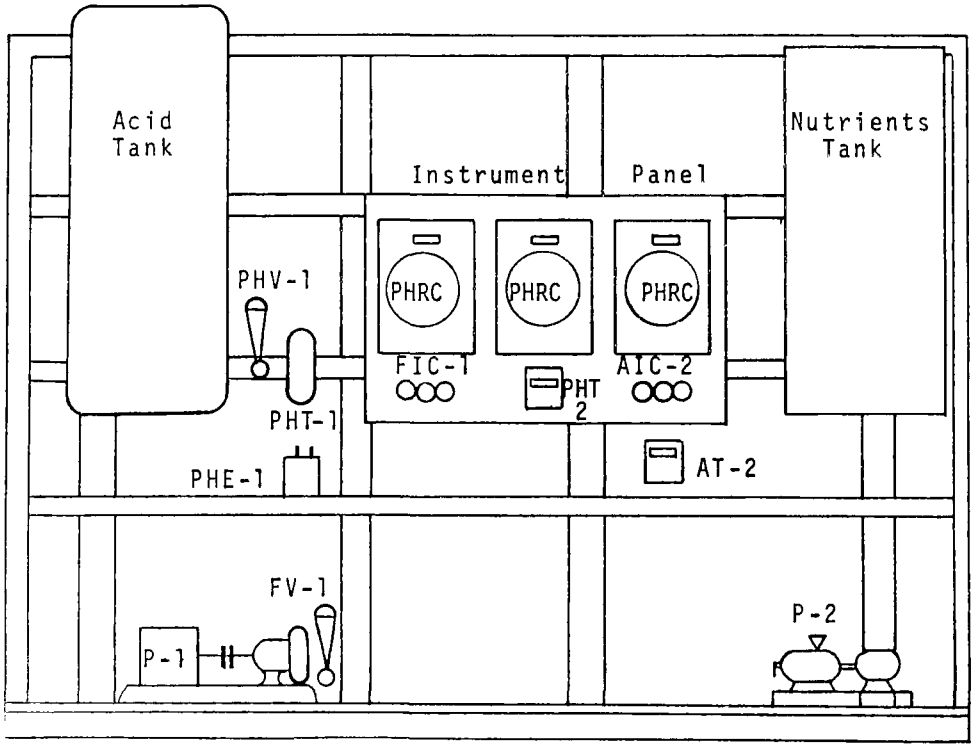


Figure 3.

INFLUENT FLOW AND pH CONTROLS

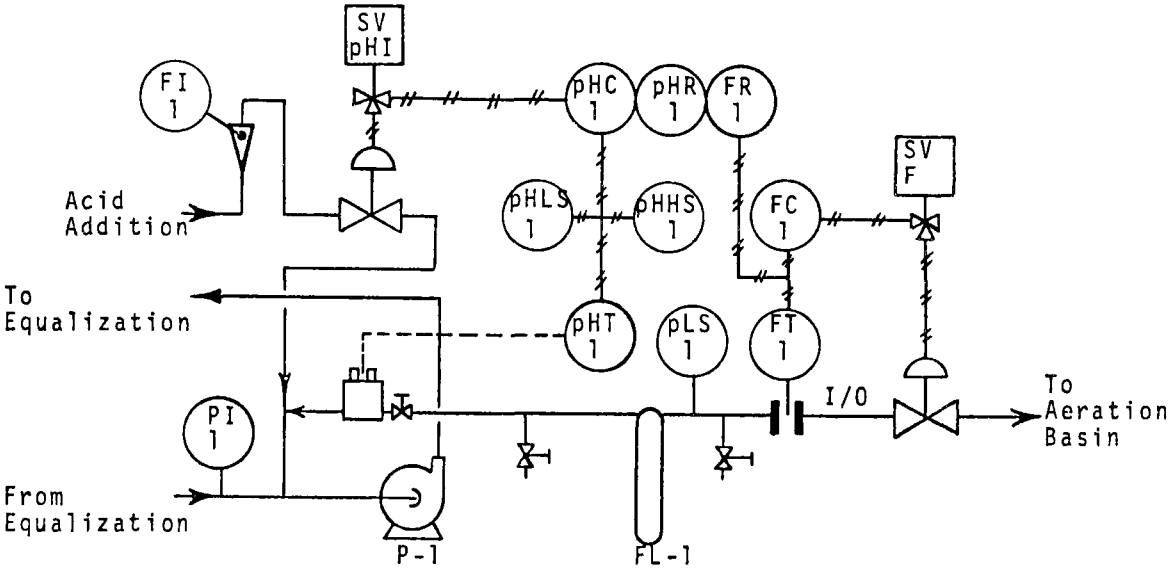


Figure 4.

ACTIVATED SLUDGE PILOT PLANT
Nutrients Control and F/M Control

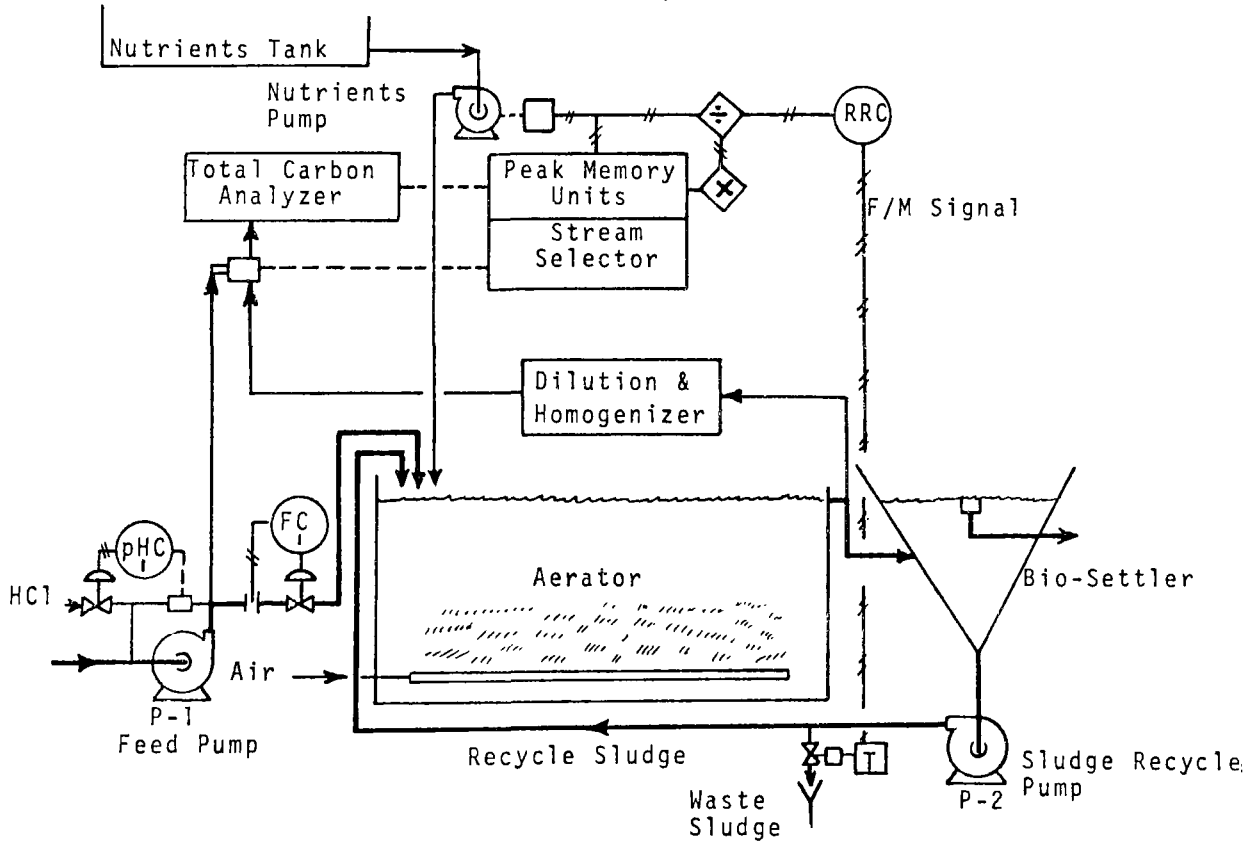


Figure 5.

F/M CONTROL SAMPLING SYSTEM

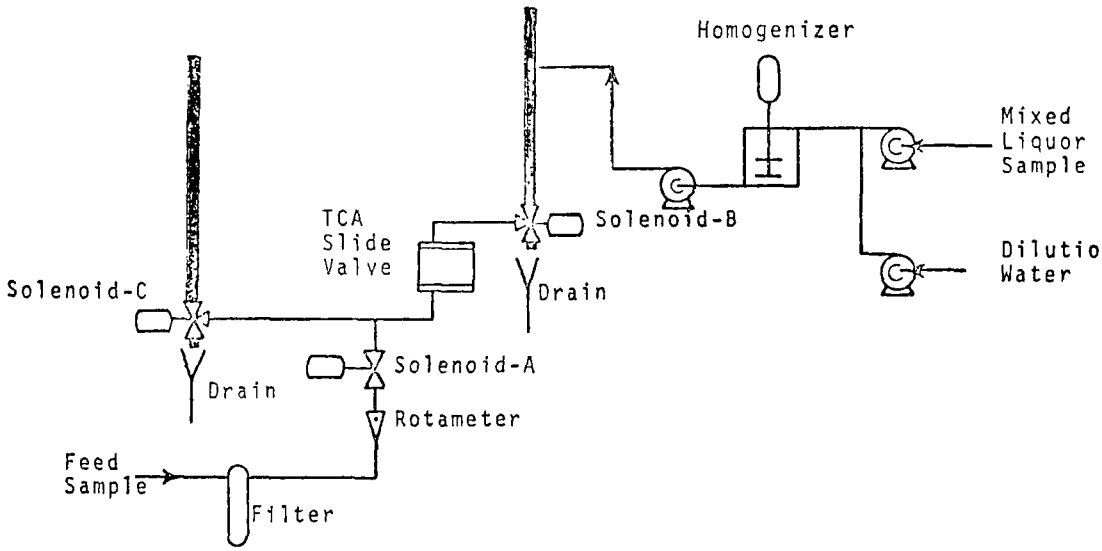


Figure 6.

AMMONIA CONSUMPTION BY MICROORGANISMS

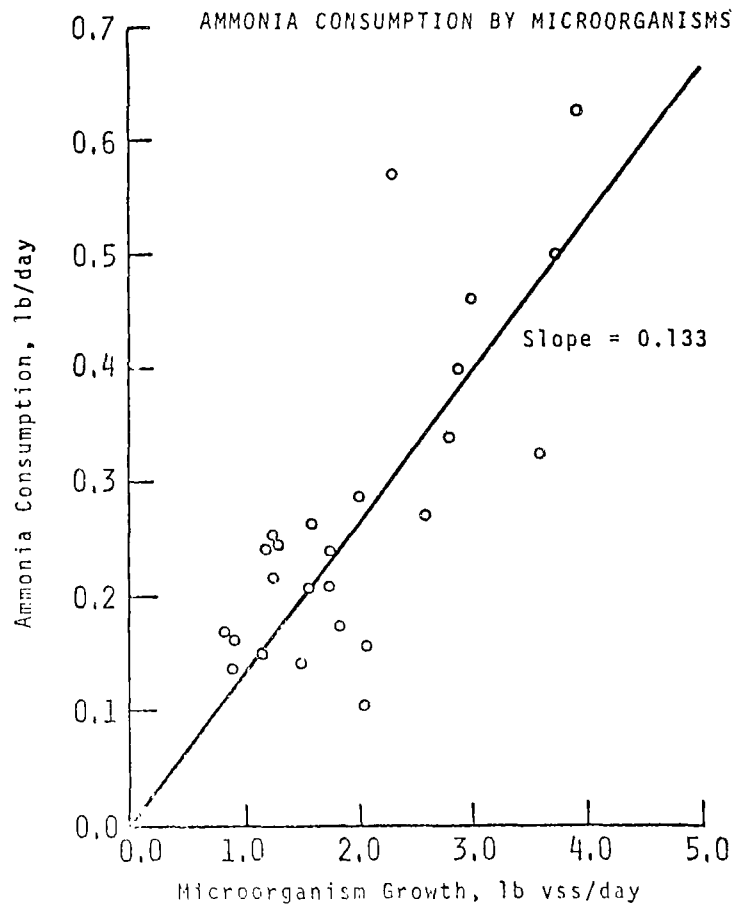


Figure 7

DETERMINATION OF AMMONIA REQUIREMENT

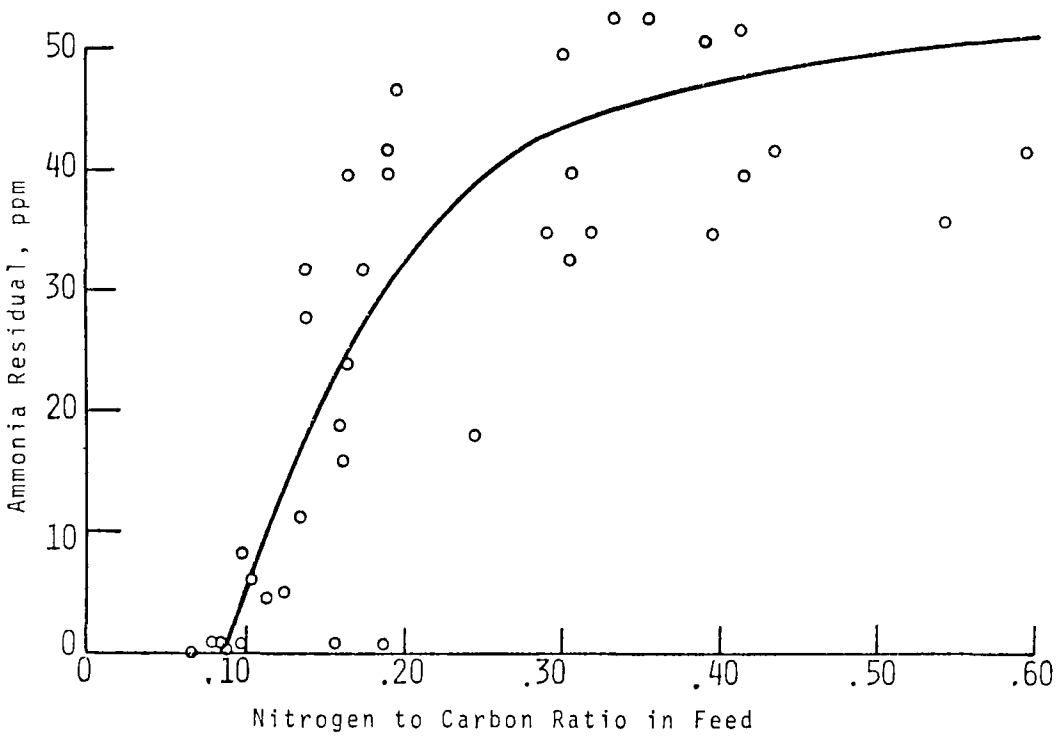


Figure 8.

UNSTEADY STATE VARIATION OF THE SLUDGE COMPACTION RATIO
(DATA FROM RUN C)

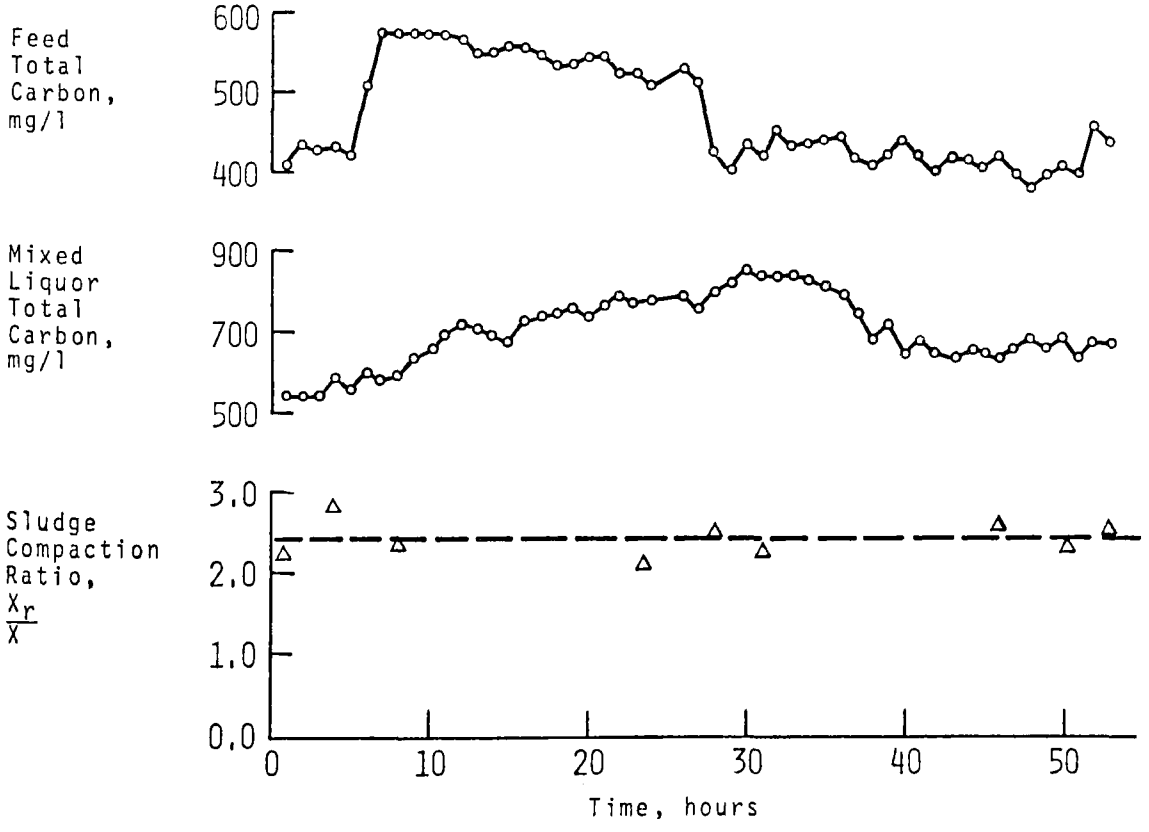


Figure 9.

F/M BLANK TEST - BACTERIA GROWTH
AND F/M RESPONSE
(Constant Recycle Flow) Run A

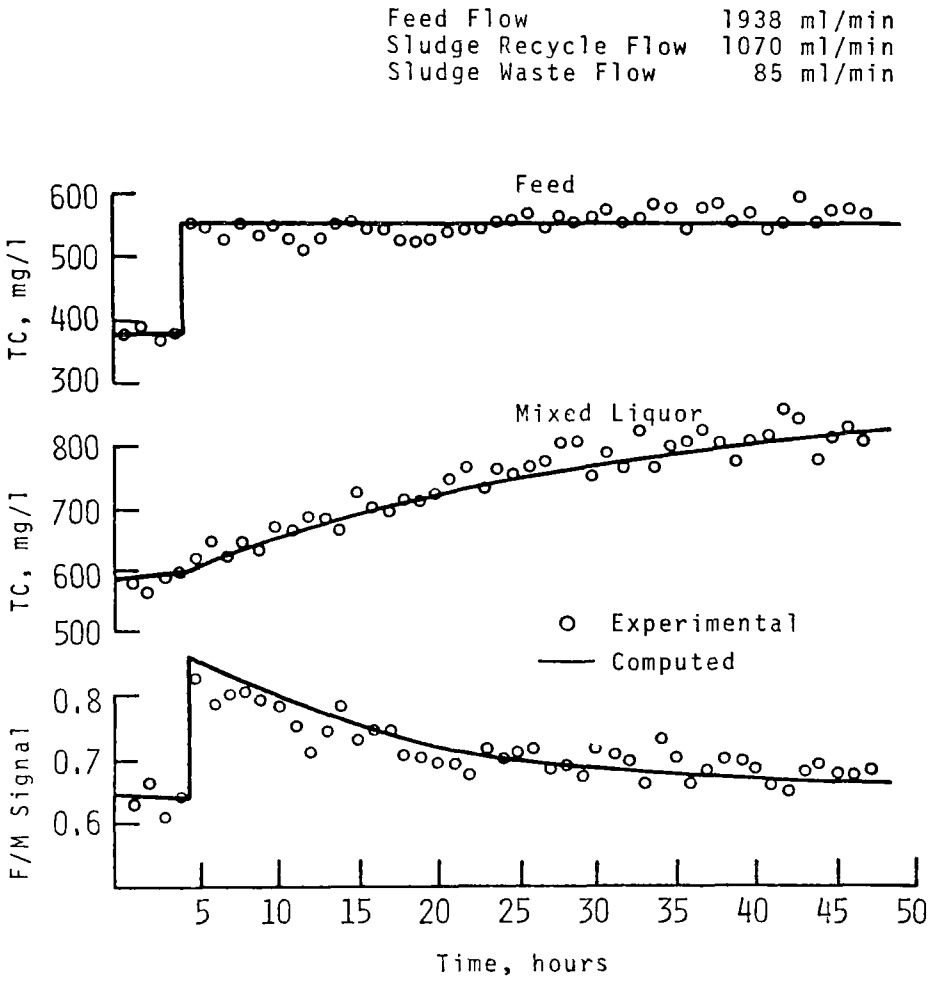


Figure 10.

F/M CONTROL TEST - BACTERIA GROWTH AND F/M RESPONSE
RUN C

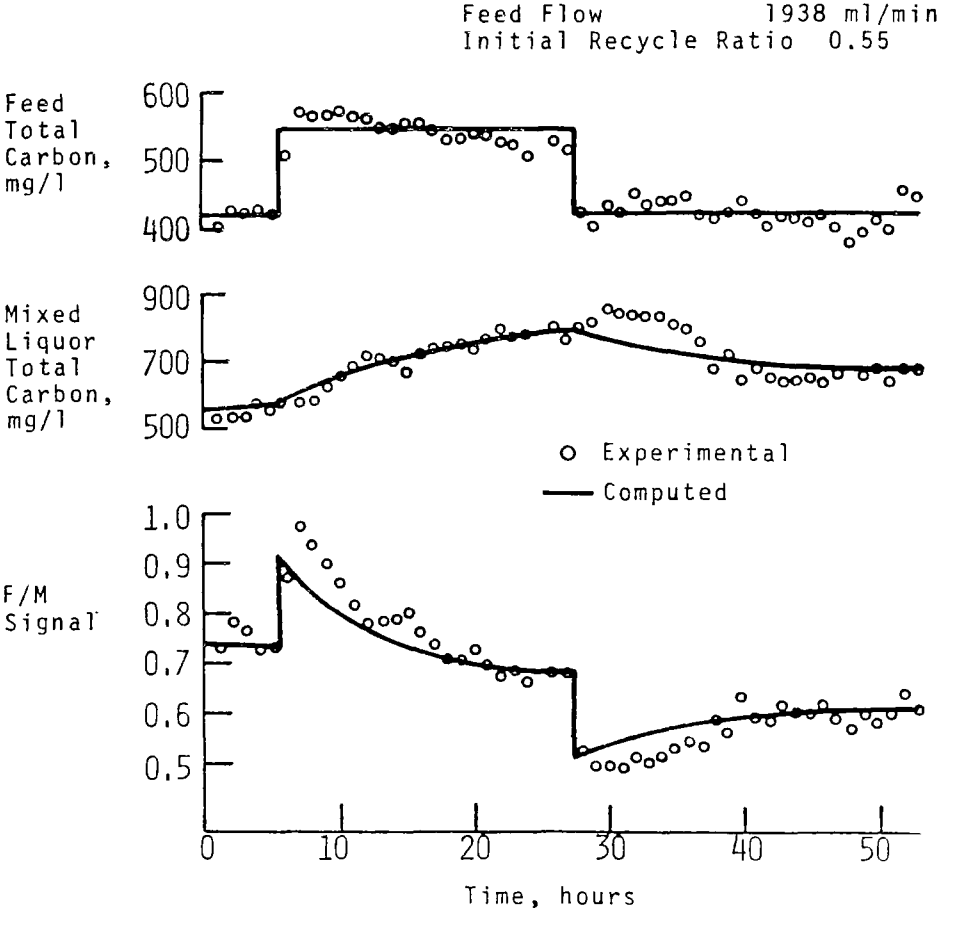


Figure 11.

F/M CONTROL TEST - RECYCLE AND WASTE RESPONSE
RUN C

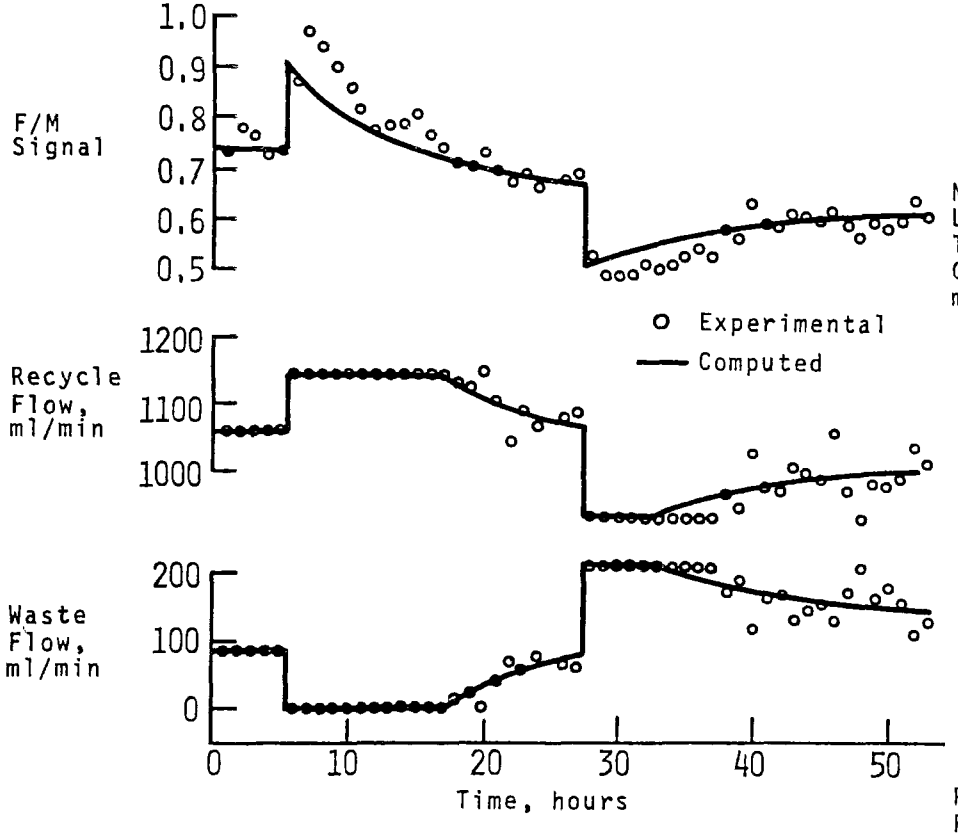


Figure 12.

RESPONSE CHARACTERISTICS WITH AND
WITHOUT F/M CONTROL - LOW LOADING

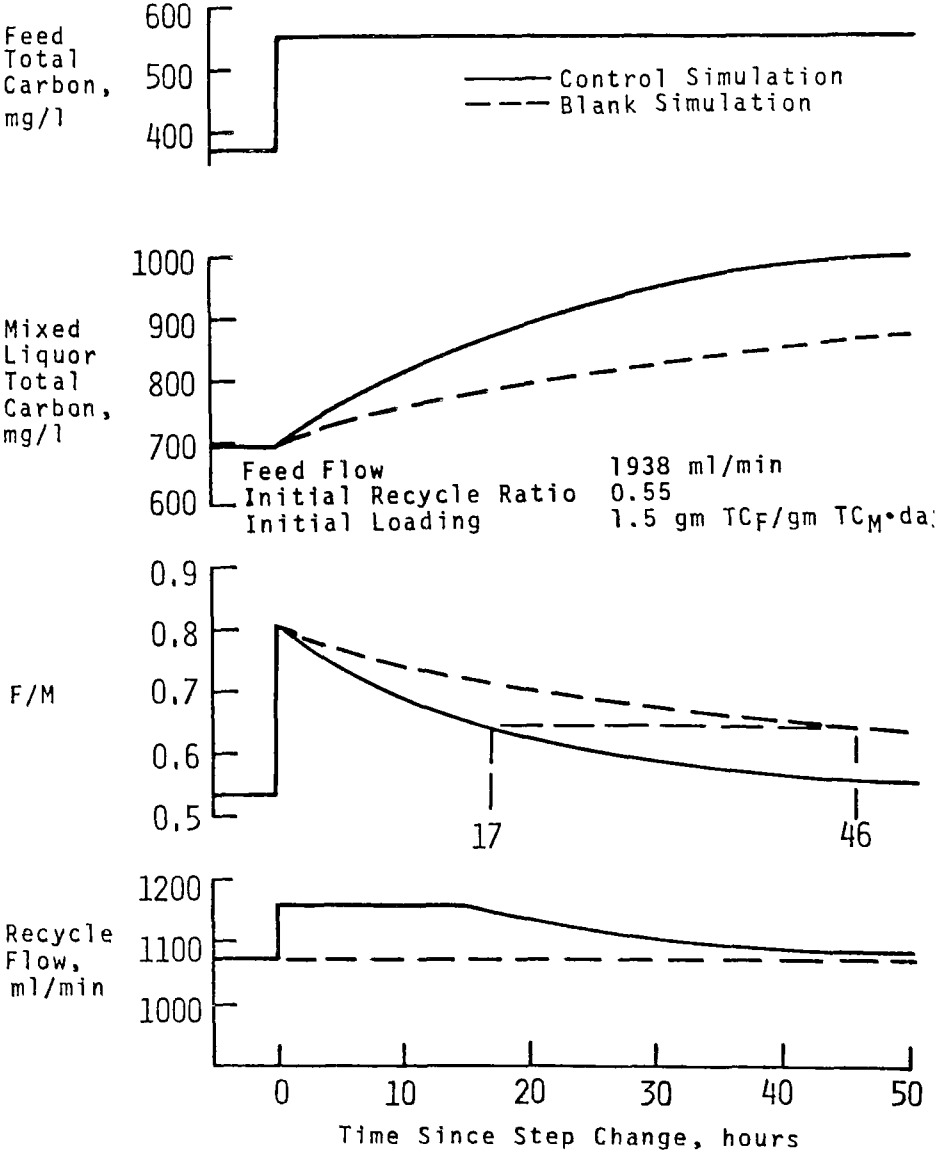


Figure 13.

RESPONSE CHARACTERISTICS WITH AND WITHOUT F/M CONTROL - HIGH LOADING

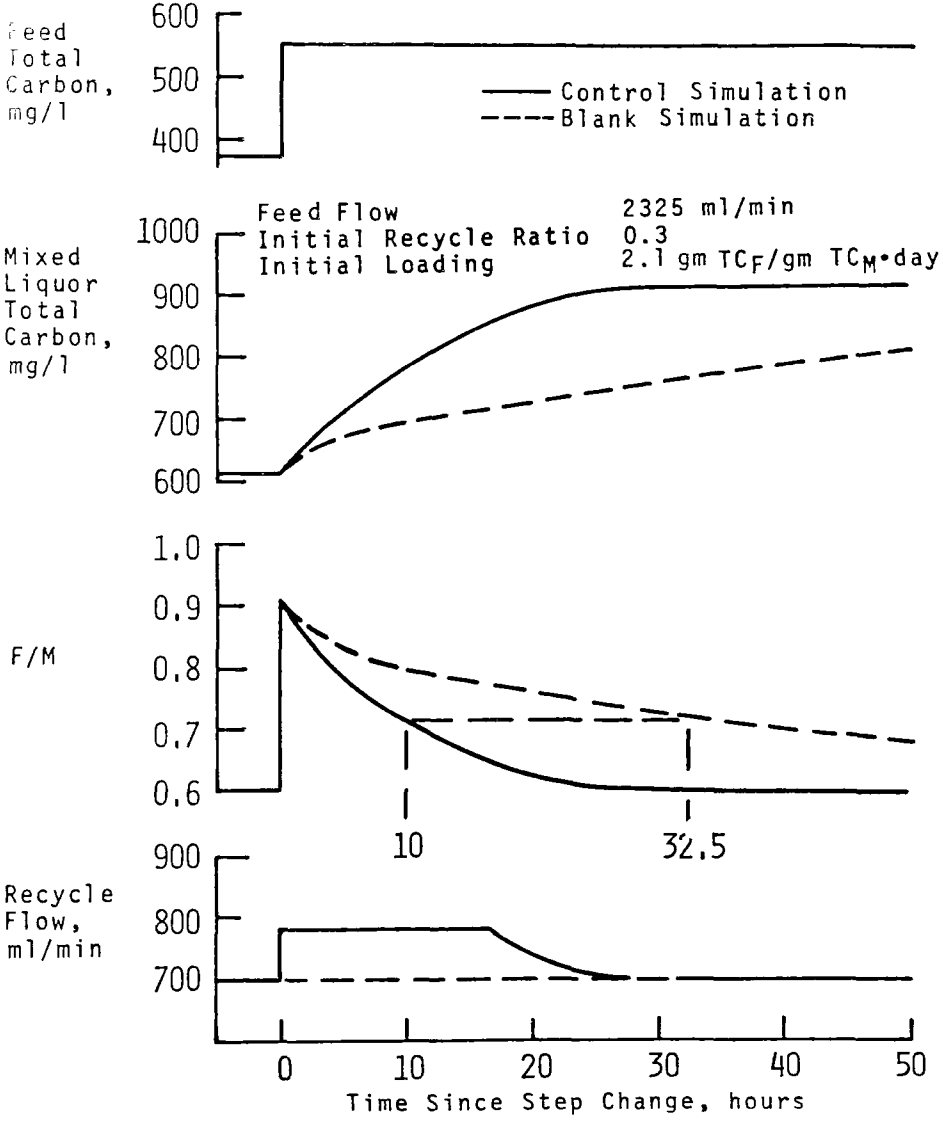


Figure 14.

COMPARISON OF AERATION BASIN SUBSTRATE CONCENTRATION WITH AND WITHOUT F/M CONTROL

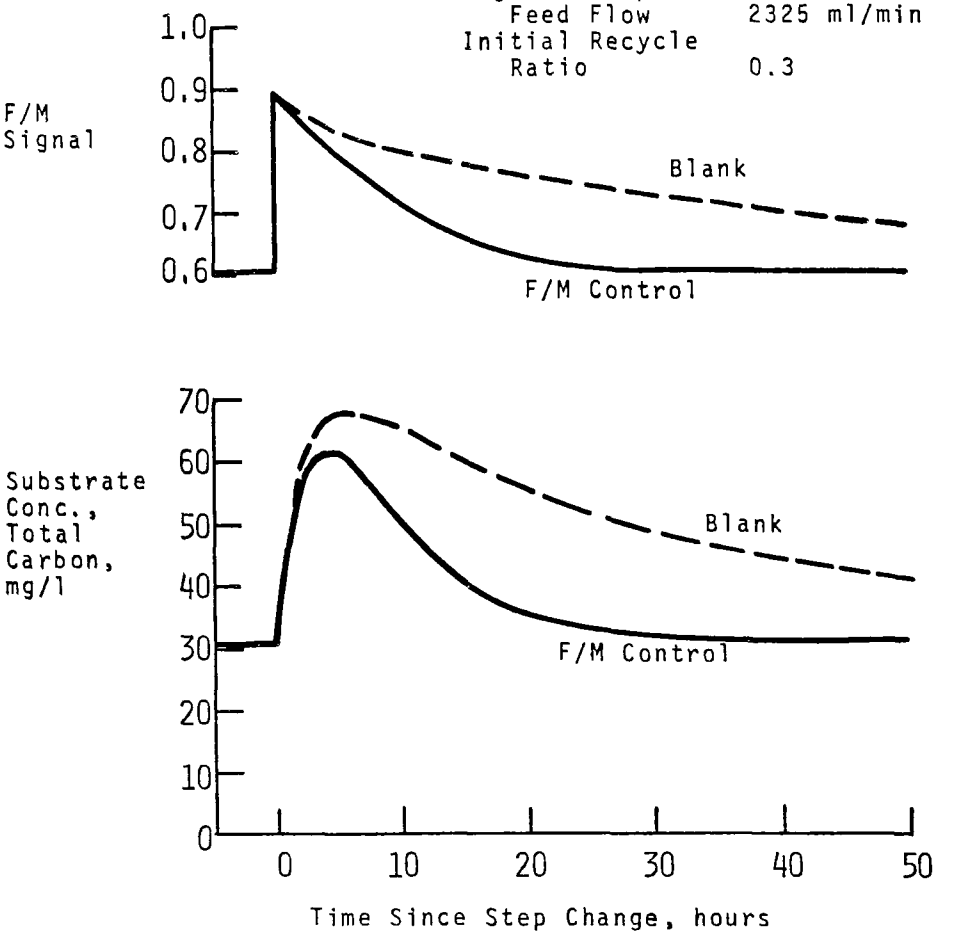


Figure 15.

RESPONSE CHARACTERISTICS WITH AND WITHOUT F/M CONTROL

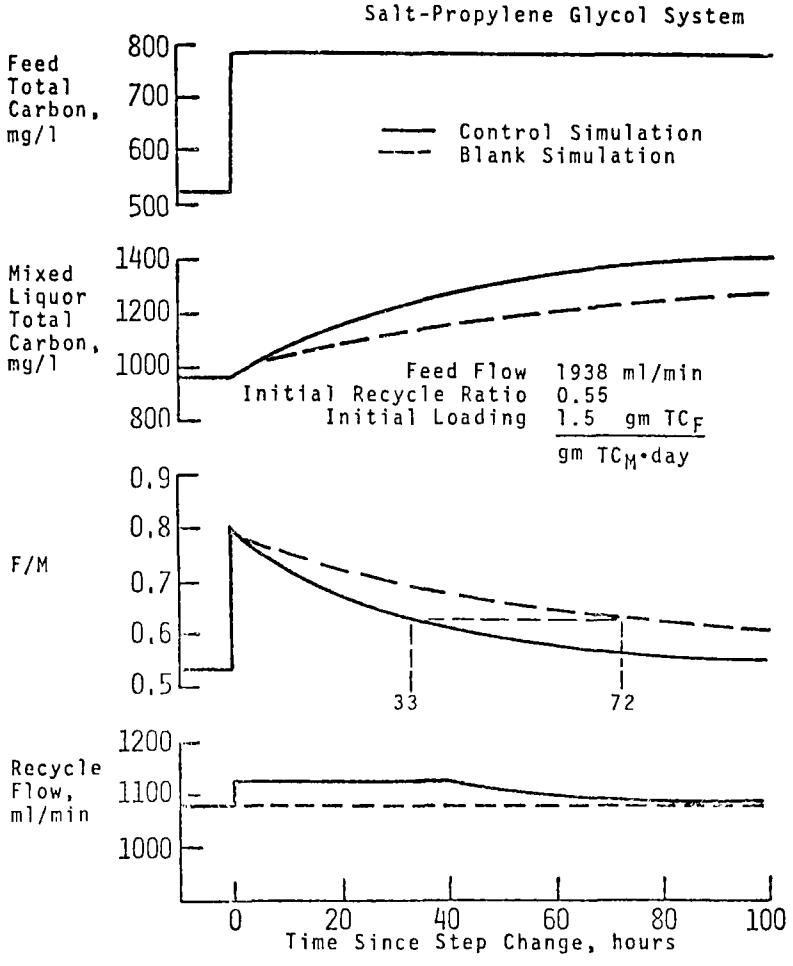


Figure 16.

FLOCCULATION CONTROLS

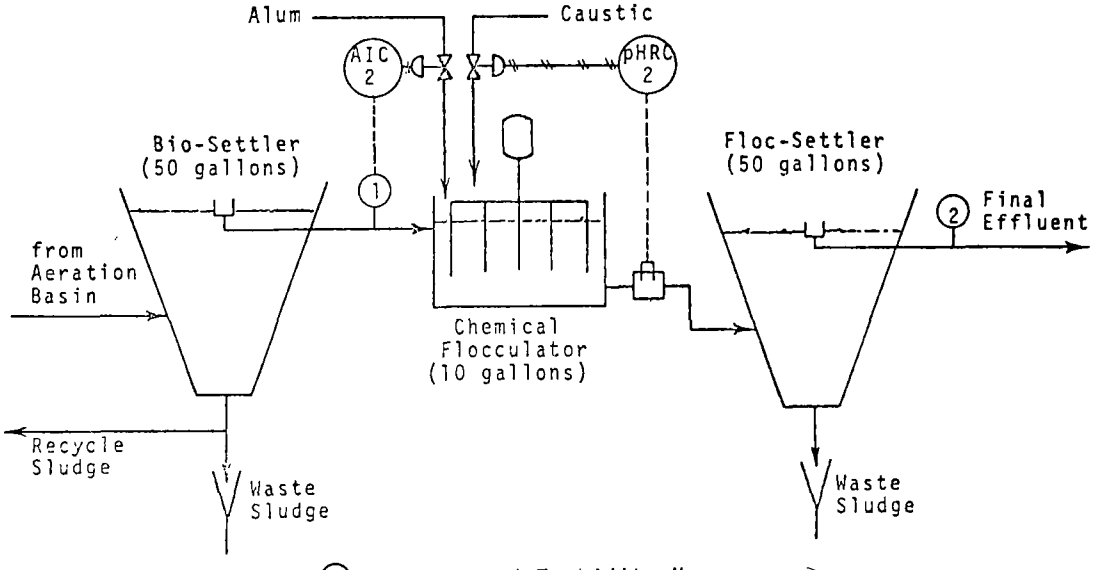


Figure 17.

OPTIMUM ALUM DOSE AS A FUNCTION OF INITIAL TURBIDITY

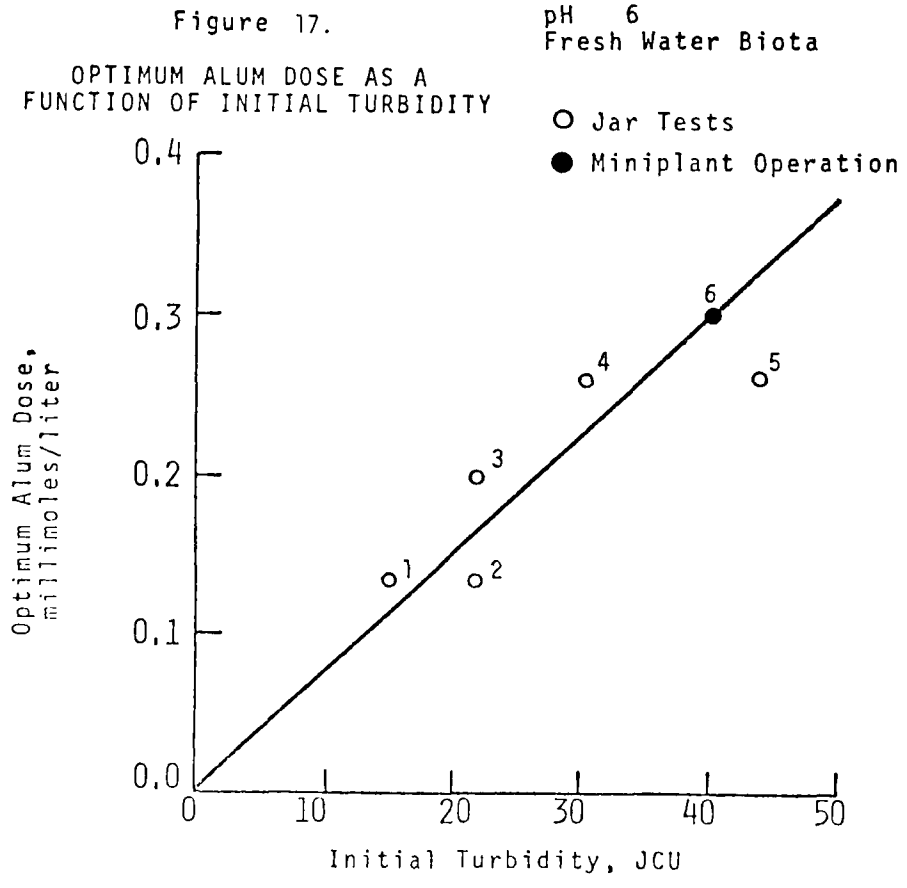


Figure 18.

BIOLOGICAL INHIBITOR DETECTOR
SCHEMATIC OF MEASUREMENT CYCLE WITH NO TOXIN IN FEED

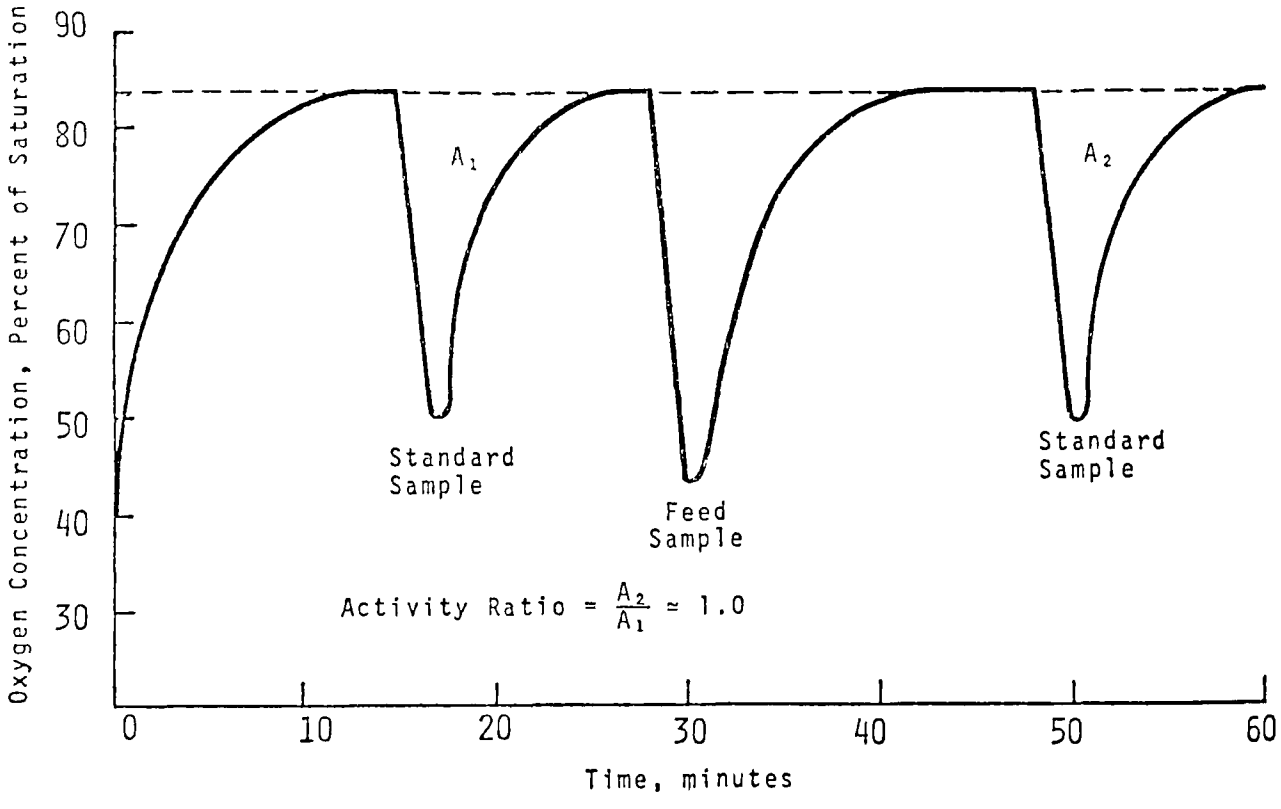


Figure 19.

BIOLOGICAL INHIBITOR DETECTOR
SCHEMATIC OF MEASUREMENT CYCLE WITH TOXIN IN FEED

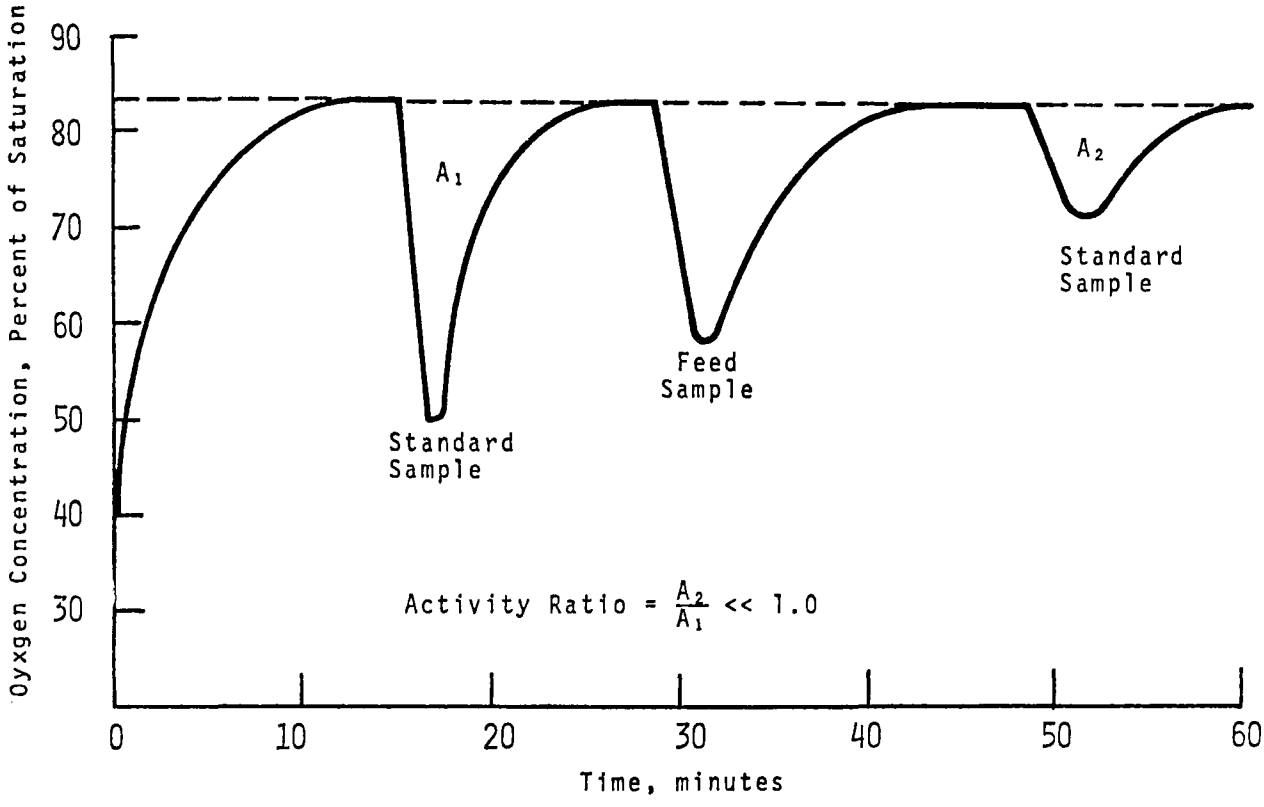
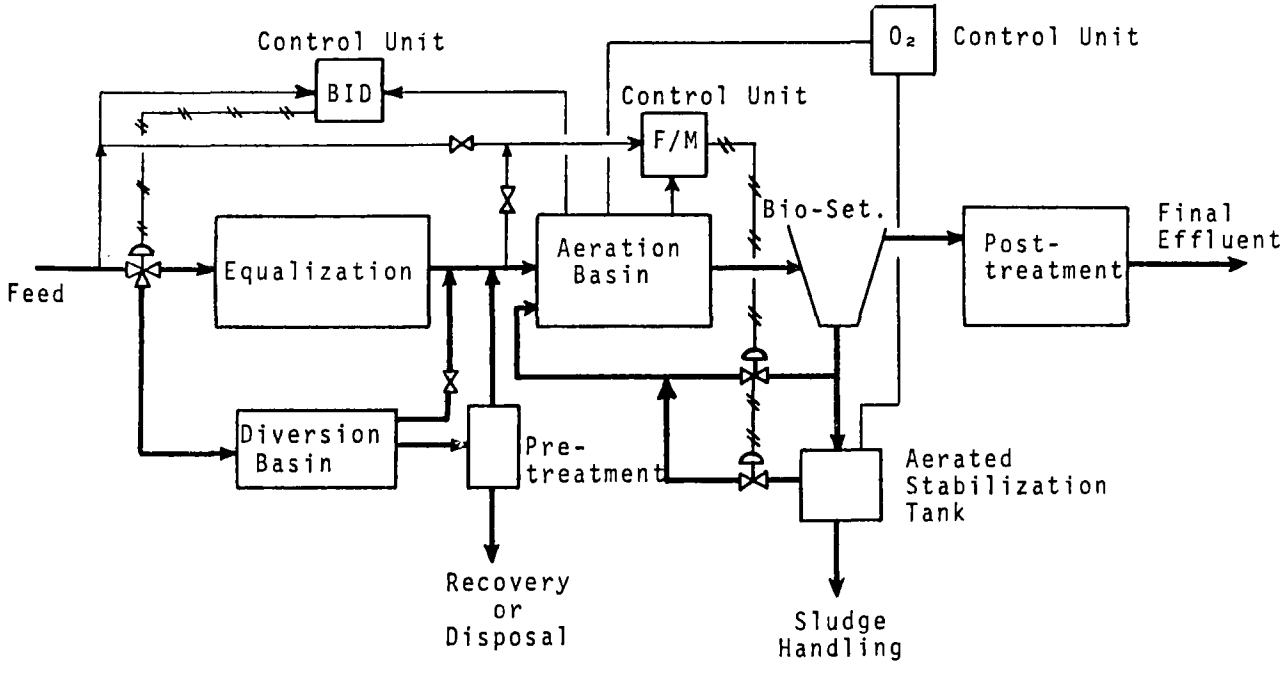


Figure 20.

CONTROLLED ACTIVATED SLUDGE TREATMENT



THE NATIONAL PETROLEUM REFINERY WASTEWATER CHARACTERIZATION STUDY

Leon H. Myers, Fred M. Pfeffer, and Marvin L. Wood
U. S. Environmental Protection Agency
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

ABSTRACT

The EPA and API jointly conducted an investigation to provide a verifiable data base under actual operating conditions in the treatment of petroleum refinery wastewater. This data base consisted of raw waste loadings and activated sludge treatment efficiencies. Industrial participation in the raw waste load phase accounted for 84 percent of the U.S. petroleum refining capacity.

INTRODUCTION

In 1965, with the passage of amendments to the Federal Water Pollution Control Act, the API Committee on Air and Water Conservation instigated a project to secure representative data on wastewater treatment and control practices in domestic refineries of the petroleum industry (1). The response to this project represented 93 percent of the industry's crude processing capacity. From this response, a profile of wastewater effluent quality was prepared reflecting the various types of operation in 1967.

The Refuse Act Permit Program and the impending legislation which became the Federal Water Pollution Control Act Amendments of 1972 (2) necessitated that the Environmental Protection Agency acquire a scientific characterization of various wastewater streams and a factual determination of the efficiencies of available wastewater treatment processes so as to ensure protection of the environment from any adverse effects caused by wastewater discharged under a permit system. In January of 1971, a series of contracts was let by EPA's Office of Water Programs to assemble available information and to utilize consultant expertise as a base from which effluent limitations might be prepared. At that time, the prevailing concept was to determine "standard raw waste loads" coming from the various unit processes, apply the optimum contaminant removal efficiencies afforded by available wastewater treatment processes, and then determine allowable effluent characteristics. There were limitations, however, in the usefulness and adequacy of the available and current technical data. The API offered to cooperate with EPA in conducting a survey of the petroleum refining industry to update the 1967 data. Following Agency acceptance of the offer, a planning committee was formed consisting of representatives from EPA's Office of Research and Monitoring, EPA's Water Quality and Refuse Act Permit Section, State water quality offices in Texas and California, the API, and the consulting field.

The committee agreed that the refining classification scheme used in the 1967 API survey should be incorporated into the plan of a joint API/EPA study. This classification assumes that the extent of processing complexity of oil refining would have a parallel impact on the character and quantity of contaminants entering a given refinery wastewater

system. The five refinery classifications were and are:

A. Crude topping (Atmospheric and vacuum distillation)
B. Topping and catalytic cracking
C. Topping, cracking, and petrochemicals
D. Integrated (Topping, cracking, and lube oil processing)
E. Integrated plus petrochemicals

Applying this fundamental refinery classification scheme to the nation's refineries, Class A represents about 5 percent of the domestic crude capacity, while Classes B, C, D, and E account for 36, 23, 26, and 10 percent, respectively (3).

The survey objectives agreed to by the committee were:

1. To determine the refinery raw waste load;
2. To verify analytical results from representative refineries;
3. To determine the contaminant removal efficiency of selected refinery wastewater treatment systems; and,
4. To evaluate and update interim reference guides for the petroleum refining industry.

The results of the raw waste load survey have been reported by the API (4). This presentation today concerns the second and third objectives: analytical validation and treatment efficiency. A draft report on the study is under consideration for publication (5).

ANALYTICAL VERIFICATION SURVEY

For the purpose of validating data obtained in the questionnaire portion of the raw waste load survey, EPA conducted a study of 17 of the 150 refineries which submitted the questionnaires. Selection of refineries to be monitored by EPA was made by the joint API/EPA Committee from the list of participating refineries by use of a random number table. Code numbers for plant identification were used to insure confidentiality. Validation consisted of a statistical comparison of results obtained when refinery and EPA personnel conducted thorough monitoring and sample-splitting programs at each of the 17 refinery locations. Responsibilities during the study were shared. The refineries' personnel documented flows and operating conditions, collected, composited, split, and preserved the samples for independent laboratory analyses within 24 hours of sampling under observation by EPA personnel.

Refinery Selection. Table 1 shows the number of refineries by class and crude capacity which were monitored by EPA. Also included are the questionnaires received from each refinery class, showing that for purposes of validation, EPA monitored 10 percent of the respondees in each class. Nominally, a 10 percent random sampling of a total population constitutes a statistically sufficient sample, and the results of many polls or surveys are based on much less data than such a sampling. Thus, the survey proposed by API in actuality approximated a study of the entire population, i.e., the petroleum refining industry. This conformity to strict scientific and statistical procedures continued during survey sampling, analysis, and interpretation of the data.

Analytical Procedures. Selection and implementation of laboratory methods are critical decisions for any survey. Analytical methods must be reliable; that is, they should

have widespread usage among water quality laboratories, compensate for interferences in samples, and be precise and accurate. In addition, the methods must conform to the equipment, skills, and analytical time limitations of the laboratory and the survey plan. The procedure for each method must be clearly described, including references and any modifications necessary because of interferences.

The joint API/EPA task group selected the 22 parameters for the study as shown in Table 2. A complete wastewater characterization of any industrial effluent would require analyses of every known wastewater parameter. The wastewater characteristics evaluated during this study do not reflect all known parameters but do represent the major constituents expected in this industry's wastewater.

In addition to these 22 parameters, EPA's sample splits were subjected to further analyses. A comparison was made of the hexane and freon gravimetric procedures for "oil and grease"; and additional parameters were measured: color, turbidity, volatile suspended solids, specific conductance, nitrite nitrogen, and acute fish toxicity. All participating refinery laboratories were instructed to adhere to the EPA's approved methods (6), as modified slightly in 1972; copies of these methods were distributed accordingly.

Analytical Quality Control. A host of determinate errors inherent to any survey of this nature dictated the incorporation of an analytical quality control program. Beginning with the planning phase, emphasis was placed on such laboratory variables as selection and sensitivity of instruments, glassware cleaning, and reagents. Control of performance was accomplished by following the EPA's approved methods of analytical quality control developed at the Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma. A systematic program of accuracy and precision testing was implemented. Initially, a sample of API separator effluent was examined by each of the methods in order to ascertain problem interferences as evidenced by comparison of duplicate results for precision and spike recovery results for accuracy.

Factors such as the number of samples received and time limitations for completion of analyses precluded duplicating and spiking each sample. The laboratory quality control program involved running a blank, standard, sample duplicate, and spiked sample --for every eight samples received. Success in duplication and spike recovery indicated that the results obtained for the corresponding eight-sample set were correct with a high degree of confidence. Failure presented two alternatives: rerun the set of eight samples, or disregard the results entirely.

The EPA's quality control results are summarized in Table 3 for the more important parameters. In all but three instances our Laboratory met the frequency requirement of $\geq$ 1.0 per eight-sample set. With the exception of sulfide, we achieved $\geq$ 95 percent accuracy (or spike recovery).

Results and Interpretation. In anticipation of a monumental task of interpreting the field and analytical data generated during the studies, it was decided to utilize RSKERL's Computer and Statistical Section for data accumulation. Verified analytical data were keypunched and machine verified by Computer Section personnel. Uniform rules for

rounding off decimal points and not reporting zero values were established for the data. Negative values were reported as negative values. Toxicities encountered in BOD_5 analytical data were treated uniformly by selection of the highest consistent values. Statistical techniques for data evaluation, interlaboratory and intralaboratory deviation, frequency distribution of parameters, quality control regression analysis, student "t" testing, and plotting were paramount to the studies.

Distribution analyses were performed on the raw waste loads per 1,000 barrels of crude throughout for each of the 22 parameters and each of the five refining classes. Median values were selected as the best measure of central tendency on all parameters because of the highly skewed frequency distribution (Figure 1) which is a common occurance in water quality data. The difference between the average (62) and median (37) in this figure is quite apparent.

Comparison of the 22 parametric results from 17 refineries with the EPA results was made. A summary of the difference in median values (mg/l) between EPA and API analyses and the student "t" values is shown in Table 4. The "t" value relates to statistically significant differences of analytical results at the 95 percent level. When the calculated absolute value of "t" at the 95 percent confidence level is ≥ 2.0, the medians are significantly different. The parameters for which this occurred are oil and grease, phenolics, sulfide, total chromium, ammonia nitrogen, cyanide, iron, copper, lead, and zinc. Note that BOD was a border line case. This observation of value differences between the same sample points is further justification for a strict quality control program.

ACTIVATED SLUDGE TREATMENT EFFICIENCY SURVEY

The activated sludge treatment process had previously been recognized by the joint API/EPA committee to be representative of the best level of treatment currently used by the refining industry. Consequently, this treatment system concept was selected for the efficiency studies.

Unlike the net raw waste load survey where the sampling was done by refinery personnel, the activated sludge efficiency survey required all sampling to be accomplished by EPA staff, with scheduled analysis at RSKERL in Ada. Field sampling work was planned to extend over fourteen 24-hour periods as compared to a one-day period (24 hours) for the net raw waste load survey; therefore, the EPA manpower impact would be somewhat extensive from both the field and the laboratory standpoint. The efficiency study was managed and coordinated by EPA's RSKERL, with aid in actual field sampling provided by EPA Region VI representatives from Surveillance and Analysis and Enforcement staffs.

Refinery Selection. In the selection of the participating refineries, significant consideration was given to the choosing of those refineries with treatment systems of adequate design. Through discussions with the respective refinery personnel concerning their operating and control procedures, a selection of treatment systems was made to meet this criteria. In order to study the maximum number of refineries with the EPA personnel available and still provide data in a quantifiable manner, five activated sludge systems were chosen from a list of 14 existing facilities provided by the API.

Refinery location selection was made so that distribution would approximate the geographic distribution of the refining industry as shown in Figure 2. Hence, two were located in EPA Region VI (southwest); two in Region V (Great Lakes); and one in Region X (west coast). An important aspect of a national study of this nature was to receive the samples at the laboratory as rapidly as possible; therefore, consideration was given to the relation between refinery location and airline schedules. Since not all classes of refineries use activated sludge as their biological treatment system, it was decided to study three Class B and two Class C systems. The initial plans included a specific Class D refinery; however, limited time and funds forced the EPA to eliminate this plant from the five-refinery list. The parent refining company voluntarily submitted 10-day survey data collected and analyzed in a manner identical to the five-plant investigation for use as an addendum to the final report.

Efficiency values were calculated from data obtained at two points in the treatment process: primary settling effluent and final clarifier effluent. No accounting was made for once through cooling, intake, and bypass waters, for domestic wastes, nor for the finishing systems following final clarification of the activated sludge treatment process. This was because the study objective was activated sludge treatment data; not discharge data.

The systems sampled for activated sludge efficiency employed separation or treatment ranging from API separators through equalization and intermediate treatment steps to final detention ponds. Schematic flow diagrams of the treatment systems are shown in Figure 3. In addition to primary separation, the systems included various combinations of the following individual processes: activated sludge, trickling filters, air flotation, chemical coagulation, aeration basins, and clarification. Further, most plant systems included sludge ponds, detention ponds, and lagoons. This diversity of treatment allowed the evaluation of treatment steps other than the activated sludge process.

Daily samples were composited on a two-hour basis; sample preservation, fixing, analyses, etc., were conducted as in the RWL procedures. Sample splitting between the EPA and the refiner was done on an irregular basis, at the discretion of the refiner.

Results The data base for the efficiency survey was obtained by analyzing 70 total samples from the five refineries. A summary of the range of influent and effluent concentrations and the median treatment efficiencies is shown in Table 5.

Median effluent loads from the five systems studied and the standard deviation of loading expressed as percent of the median are shown in Table 6. Although the refinery daily crude throughput and gallons of water discharged remained nearly constant it was observed that the pollutant load varied with daily samples, reflecting apparent operational differences within each refinery from one day to the next.

A summary of the median final clarifier loads for 13 parameters is found in Table 7.

CONCLUSION

This study represents the first industry-wide investigation of its type attempted by

the EPA or its predecessor agencies. It resulted in a valid data base of raw waste loading and contaminant removal efficiencies, and it was planned and conducted with the cooperation of the petroleum refining industry. There were problems encountered: interlaboratory analytical variability and interferences in analytical methods, particularly cyanide, sulfide, and oil and grease.

The survey supported our opinion that several needs deserve further consideration. Variability and interferences in methods require assessment and resolution through extensive round-robin testing. Also needed are the identification of major organics treatable by and refractory to the activated sludge process; the measurement of the fate and effects of these refractories; the study of metals adsorption on sludges; and additional characterization, especially of unit process streams such as catalytic cracking and sour waters.

We in EPA at the RSKERL would like to recognize the technical cooperation of the refining industry in our research endeavors and the many courtesies extended to us. We look forward to a continued coordinated approach to solving the many problems remaining in the management of refinery wastewaters.

REFERENCES

(1) "1967 Domestic Refinery Effluent Profile," Committee for Air and Water Conservation, API, 1968.
(2) "Federal Water Pollution Control Act of 1972," Public Law 92-500, 92nd Congress S-2770, October 18, 1972.
(3) "Annual Refining Report," The Oil & Gas Journal 70:13, 136, March 27, 1972.
(4) "Petroleum Industry Raw Waste Load Survey," Committee on Environmental Affairs, API, December, 1972.
(5) "National Petroleum Refining Wastewater Characterization Studies," U.S. EPA Project No. 12050 CNI (Report in preparation).
(6) "Methods for Chemical Analysis of Water and Wastes, 1971," U.S. EPA Report 16020---07/71.
(7) "Laboratory Quality Control Manual," 2nd Ed., 1972, U.S. EPA, Ada, Oklahoma.

DISCUSSION

J. J. Chavez: I understand that cationic polyelectrolytes are widely used flotation schemes in the United States. To your knowledge, have there been studies or surveys of the toxic effects of using polyelectrolytes?

Fred M. Pfeffer: I am not aware of any such studies.

Robert Farnham: I assume that the data you collected would allow you to calculate variabilities in the activated sludge process.

Fred M. Pfeffer: Our data at each of the five plants which were studied for treatment efficiency were collected for 14 continuous days and included measurements of flow and 27 parameters. The raw data depicted variations in flow and concentrations as it was collected. Mathematically, we have expressed the effluent variability (Table 6) in terms of the median loadings from the final clarifier and the standard deviation of these loadings expressed as a percentage of the median.

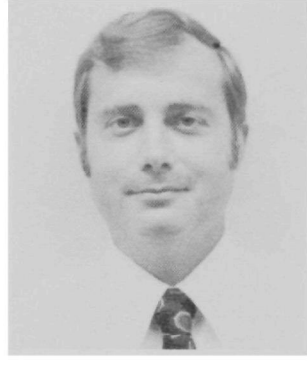
Robert Farnham: Did you take one sample from each plant, or more than one?

Fred M. Pfeffer: Each sample was a two-hour composite. We collected 14 samples from four of the plants studies, and 13 samples from the remaining plant.

BIOGRAPHIES



Leon H. Myers holds a BS in chemistry/biology from Southwestern Oklahoma State University and a MS in sanitary science from Oklahoma University. He is currently Chief, Industrial Section of the Source Management Branch at the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.



Fred M. Pfeffer holds the BA and MS degrees in chemistry from the University of Cincinnati. He is currently a Research Chemist at the EPA's Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma.

Marvin L. Wood holds a BS in chemical engineering from the University of Arkansas and an MS in instrumental science from the Graduate Institute of Technology of the University of Arkansas at Little Rock. He is currently Deputy Director and Chief of the Source Management Branch of the EPA's Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma.



TABLE 1 "REFINERIES MONITORED BY EPA"

REFINERY CLASS	QUESTIONNAIRES RECEIVED	REFINERIES MONITORED NO.	REFINERIES MONITORED CRUDE CAPACITY BPSD
A	14	2	13,200
B	79	8	424,400
C	31	3	388,500
D	12	2	397,300
E	14	2	702,000
	150	17	1,925,400

TABLE 2 "ANALYTICAL PARAMETERS"

BOD_5	AMMONIA N
COD^5	KJELDAHL N
TOC	NITRATE N
PHENOL	CHLORIDE
SUSPENDED SOLIDS	CYANIDE
DISSOLVED SOLIDS	SULFIDE
pH	T. CHROMIUM
ALKALINITY	IRON
ACIDITY	COPPER
OIL & GREASE	LEAD
T. PHOSPHORUS	ZINC

TABLE 3 "QUALITY CONTROL RESULTS"

	FREQUENCY PER 8 SAMPLES				AVG. SPIKE
	BLANK	STANDARD	DUPLICATE	SPIKE	RECOVERY %
BOD_5	1.8	0.7	4.9	-	-
COD^5	2.9	1.7	2.4	1.8	98
OIL & GREASE	0.7	-	-	-	
PHENOL	1.9	3.0	2.8	1.9	98
TSS	-	-	3.0		-
SULFIDE	0.8	2.3	2.2	3.3	85
AMMONIA N	3.3	9.8	1.6	1.2	98
KJELDAHL N	1.6	1.9	1.9	1.7	100
CYANIDE	1.7	5.2	1.7	2.7	98
pH	-	-	0.7		-

TABLE 4 "COMPARISON OF EPA & API DATA"

	MEDIAN DIFFERENCE (EPA MINUS API)	"t" STATISTIC	SIGNIFICANT DIFFERENCE
BOD_5	1.0	1.9	
COD	0.5	0.4	-
OIL & GREASE	8.4	3.9	YES
PHENOL	0.02	4.0	YES
TSS	-10.0	0.4	-
SULFIDE	0.5	5.6	YES
AMMONIA N	0.2	3.8	YES
CYANIDE	0.02	3.8	YES
T. CHROMIUM	0.03	4.8	YES
IRON	0.28	5.1	YES
COPPER	0.02	4.7	YES
LEAD	0.04	7.4	YES
ZINC	0.04	3.4	YES
pH (Units)	0.0	0.4	
FLOW (GPM)	0.0	1.3	

TABLE 5 "TREATMENT EFFICIENCY"

	INFLUENT (mg/l)			EFFLUENT (mg/l)			MEDIAN
	MAX.	MIN.	MEDIAN	MAX.	MIN.	MEDIAN	REMOVAL (%)
BOD_5	288.0	27.0	85.0	53.0	5.0	8.0	89.2
COD	583.0	93.0	213.0	201.0	46.0	70.0	54.6
OIL & GREASE	89.0	8.0	29.0	37.0	4.0	11.0	60.0
PHENOL	16.0	0.26	3.4	4.2	0.01	0.01	99.6
TSS	261.0	15.0	36.0	83.0	5.0	25.0	23.8
SULFIDE	43.0	0.10	2.9	1.7	0.0	0.3	90.0
pH (units)	11.5	6.2	8.8	8.7	5.0	7.3	--
AMMONIA N	160.0	6.0	12.0	124.0	0.05	11.0	16.2
KJELDAHL N	194.0	8.0	17.0	134.0	3.0	15.0	17.2
CYANIDE	2.5	0.02	0.2	0.03	0.02	0.1	30.9
T. CHROMIUM	4.25	0.03	1.43	1.45	0.02	0.26	58.2
IRON	44.0	0.50	1.02	0.50	0.18	0.78	37.1
COPPER	0.88	0.02	0.14	0.11	0.02	0.05	57.7
LEAD	1.73	0.00	0.10	1.04	0.10	0.11	0.0
ZINC	1.23	0.07	0.22	1.84	0.04	0.16	22.0

TABLE 6 "STANDARD DEVIATIONS OF EFFLUENT LOADINGS"

	MEDIAN LOADINGS (lb/1000 bbl)	STANDARD DEVIATION OF LOADINGS (% of median)
BOD_5	3.9	55
COD	23.0	21
OIL & GREASE	2.9	41
PHENOL	0.006	1100
TSS	7.9	44
SULFIDE	0.10	97
AMMONIA N	5.7	31
KJELDAHL N	7.6	25
CYANIDE	0.04	24
T. CHROME	0.083	29
IRON	0.330	29
COPPER	0.015	26
LEAD	0.046	20
ZINC	0.059	55

TABLE 7 "EFFLUENT LOADING FROM FINAL CLARIFIER"

	MEDIAN LOADING (lb/1000 bbl)				
	9973	2115	0288	6512	6693
BOD_5	5.5	3.1	3.9	4.0	1.5
COD	42.0	22.0	49.0	16.0	23.0
OIL & GREASE	9.2	2.8	7.1	2.9	2.4
PHENOL	0.006	0.006	0.006	0.003	0.002
TSS	17.0	4.0	14.0	7.9	6.4
SULFIDE	0.10	0.05	0.32	0.13	0.04
AMMONIA N	4.1	17.0	7.5	0.1	5.8
CYANIDE	0.06	0.01	-	-	-
T. CHROME	0.025	0.078	0.136	0.085	0.210
IRON	0.480	0.148	0.330	0.083	0.650
COPPER	0.032	0.005	0.015	0.014	0.030
LEAD	0.397	0.018	0.064	0.030	0.046
ZINC	0.086	0.027	0.036	0.059	0.089

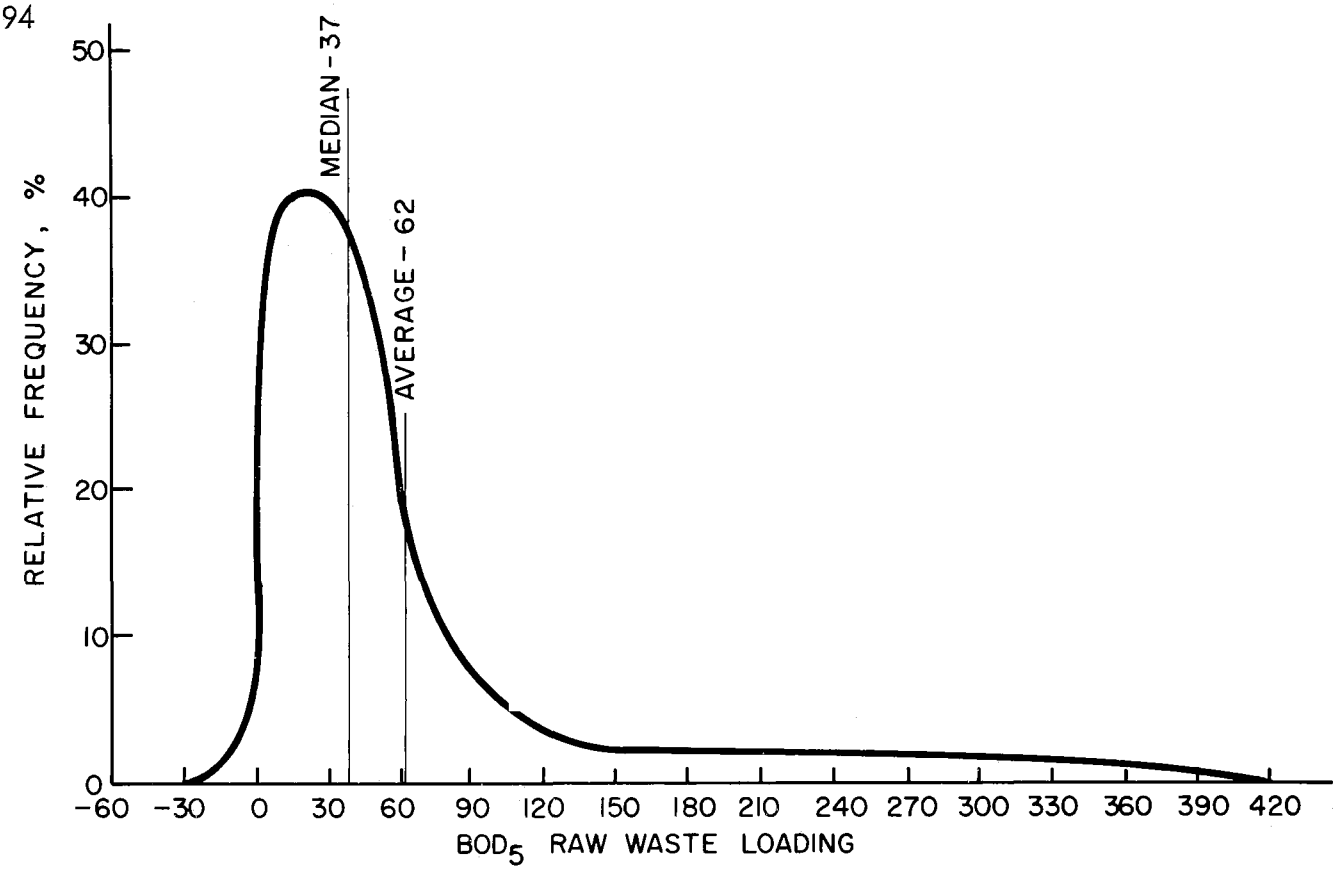


Fig. 1. RELATIVE FREQUENCY DISTRIBUTION OF BOD_5 RAW WASTE LOADING FOR CLASS B REFINERY

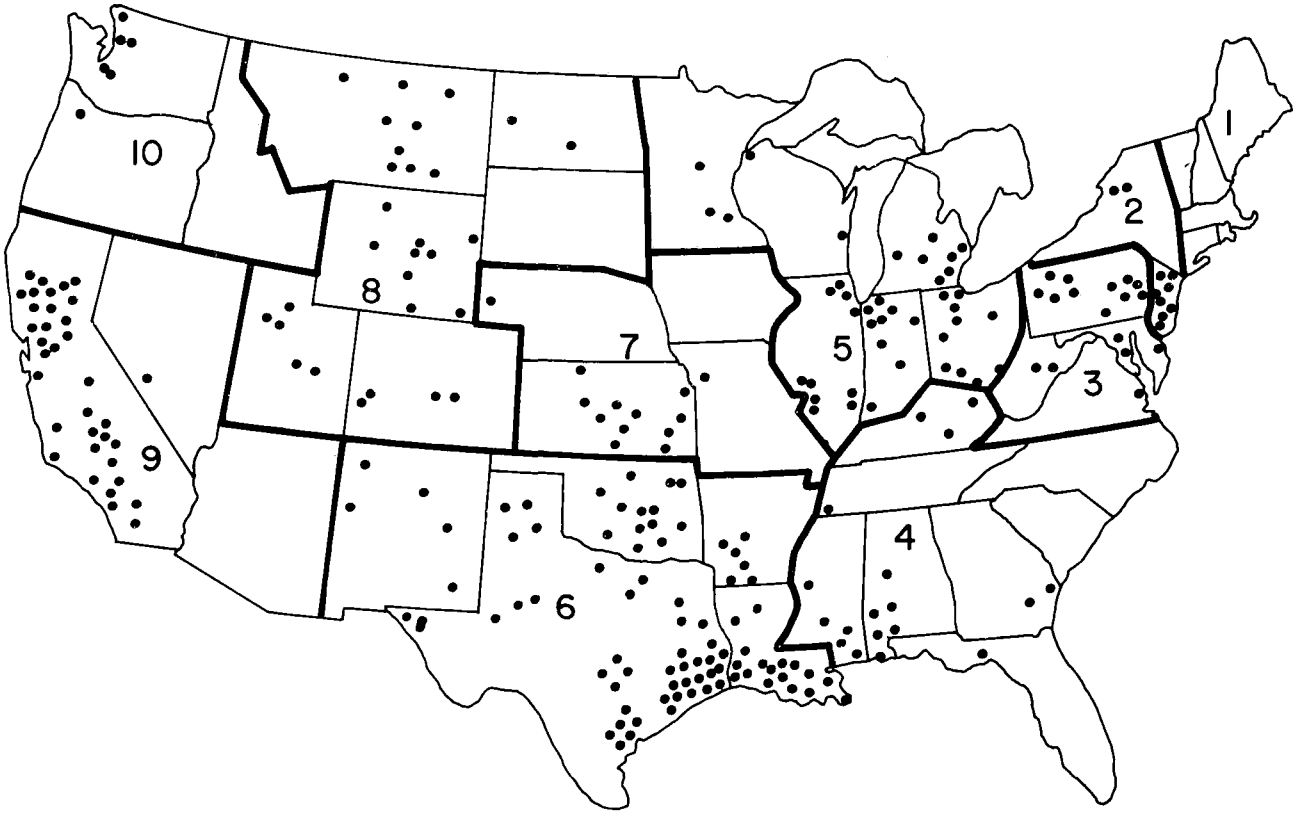


Fig. 2. DISTRIBUTION OF THE PETROLEUM REFINING INDUSTRY

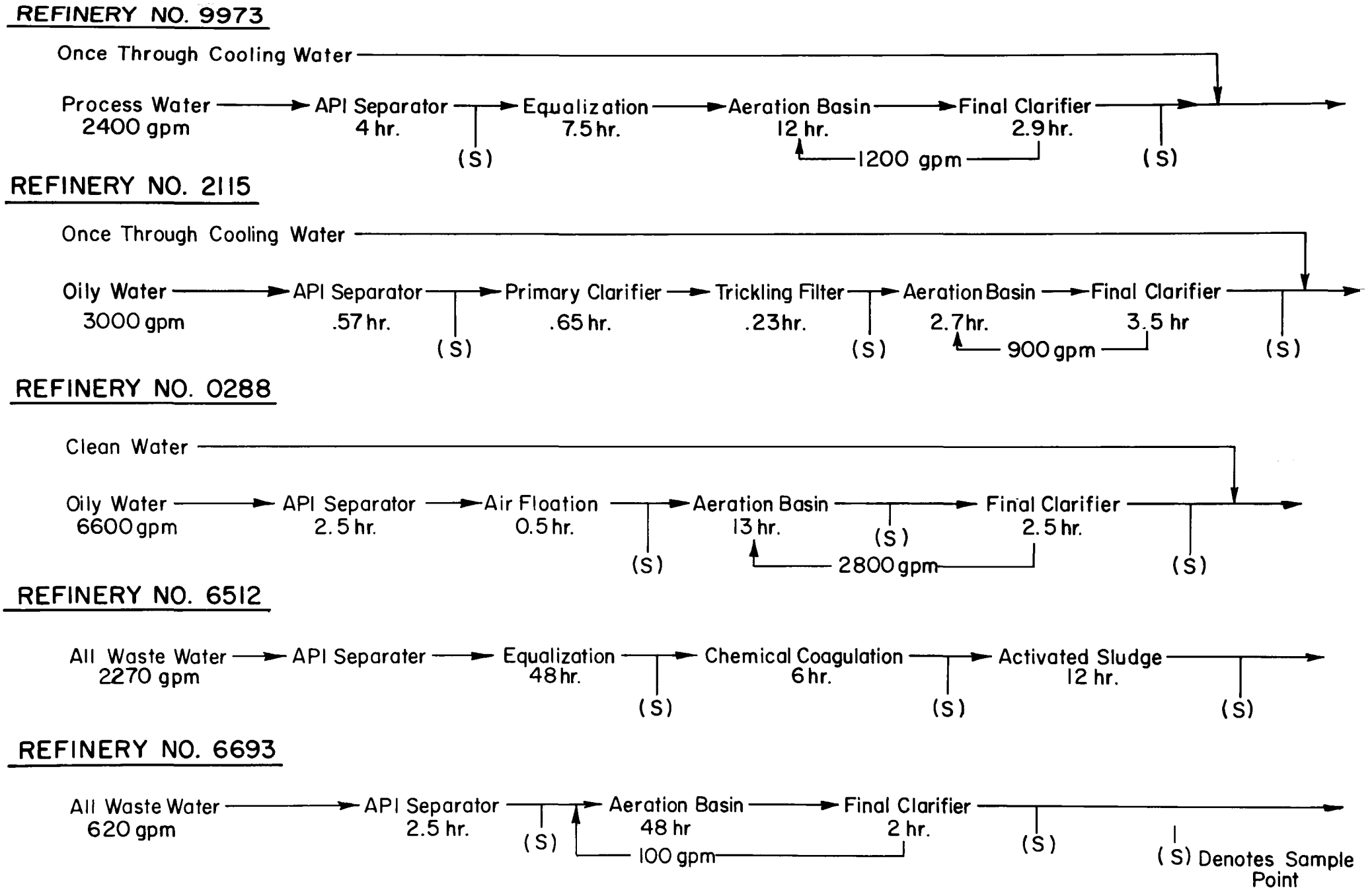


Fig. 3. REFINERY WASTE WATER SYSTEMS CHOSEN FOR THE ACTIVATED SLUDGE EFFICIENCY STUDY

SESSION IV

"SLUDGE MANAGEMENT"

Chairman

Milton Beychok

Consulting Engineer, Irvine, California

Speakers

Carl E. Adams, Jr.

"Sludge Handling Methodology For Refinery Sludges"

Jacoby A. Scher

"Processing of Waste Oily Sludges"

C.B. Kincannon

"Oily Waste Disposal by Soil Cultivation"

R.L. Huddleston

"The Disposal of Oily Wastes by Land Farming"

"SLUDGE HANDLING METHODOLOGY FOR REFINERY SLUDGES"

Carl E. Adams, Jr., President

and

Robert M. Stein,
Director of Operational Services

Associated Water and Air Resources Engineers, Inc.
Nashville, Tennessee

SOURCES OF REFINERY SLUDGES

There are several major sources of sludges generated from normal refinery operations. These sludges can be classified as storage tank bottoms, bottoms from API separators, crude desalting sludges, catalytic solids, spent clays, coking fines, and solids from the utilities and the biological wastewater treatment system. The basic source of many of the solids is the crude oils which contain materials that originate either in the well or result during transportation and storage of the crude oil. The solids generally associated with the crude oil include iron rust, rust sulfides, clay, sand, salt crystals, wax, and paraffin. These solids will settle out either in the tank bottoms or gravity API separators. A delineation of types and characteristics of refinery solids are given in Tables 1 and 2. Estimates of quantities of some of these sludges are given in Table 3. The waste sludge from API separators plus usual secondary treatment facilities will contain approximately 1,500 to 2,000 lb. of dry solids per million gallons of effluent treated.

Tank Bottoms. A summary of the tank bottom sludge characteristics is presented in Table 4. The tank bottoms can be divided into two basic types of solids: leaded and non-leaded. The leaded solids are generated from those processes which have been in contact with tetra-ethyl lead, e.g., gasoline and related products or the slop oil. These solids must be handled carefully because of their contact with the tetra-ethyl lead (TEL). TEL sludge from storage tanks will contain about 0.12 percent by weight TEL or 120 mg/l. A procedure recommended for handling TEL sludges is as follow (9):

> Manually remove the sludge and transport it to a drying bed area where it should be spread in a layer of 3-in. thickness or less. The sludge layer should be "weatered" for at least 4 weeks at ambient temperatures of above 32°F (if the temperature falls below 32°F for part of the time, the drying period should be correspondingly increased). Protective clothing should be used during the transporting and spreading of the sludge but face masks should not be necessary. At the end of 4 weeks, the sludge should have weathered down to a TEL content of 20 ppm wt. which Ball states to be a non-hazardous level.

The non-leaded solids originate from those processes which have not been in contact with tetra ethyl lead. These sludges result from the crude oil storage, lube oil, specialty oils and oil intermediates, gas oils, furnace oils, and injection gas oil or from asphalt. These solids range in concentration from about 10 to 30 percent solids by weight, averaging about 20 percent. The principal method of removing this sludge from the tanks is to add water to transfer by pump or vacuum truck. There are some problems experienced in the removal of the residual waxy crude tank bottoms because this material is extremely viscous and difficult to handle. It has been found that the heat addition minimizes pumping transfer problems.

Crude Desalting Sludges. The crude desalting process is another source of solids. Crude desalting is employed to separate the salts from the oil by the use of an emulsifier and settling tank. Sludges produced from this process include free and emulsified oils and suspended solids. These solids are usually discharged directly to the treatment system in the main waste flow.

Catalytic Solids. The catalytic processes may or may not provide a major sludge problem. The noble metal catalysts used in reforming and hydroprocessing are usually extremely valuable and should be completely recovered and reprocessed. The non-noble catalysts can be recovered and sold to a chemical processor for metal salts recovery. The remainder of the catalysts are not usually reprocessed, since they are inert, but they can be disposed of in a landfill operation. Many times the catalytic fines which are discharged from fluid beds catalytic crackers can be collected in the electrostatic precipitator system. These fines might have value as a sludge conditioner.

Spent Clays. Clay or acid treatment can be used to remove color froming and other undesirable materials from solvent refining and dewaxed lube oil stock. The acid treatment produces high concentrations of suspended solids, sludges and stable oil emulsions. The clay treatment results in a sludge which contains clay, fuel oil, and emulsified oils.

Coking Fines. The coking operation produces a sludge which consists of finely divided coke particles and waxy materials. These sludges can be land-filled or may possible have some reclamation value.

Utilities and Wastewater Treatment Sludges. The other major sources of sludge are from the utilities and wastewater treatment system. The utilities solids are usually sludges generated from the addition of lime or alum to treat raw water for use in the plant. Since these solids are inert and have no heat content, they should be dewatered and landfilled. Sludges generated by the wastewater treatment fcailities include oily sludges from API separators and air flotation systems and biological sludges from trickling filter and activated sludge processes. These solids can be dewatered and incinerated with other combustible solids, or disposed of in combination with the utilities and other inorganic solids.

The materials from a refinery which are readily combustible (See Table 1) include the waxy bottoms, oil sludges, coke fines, and waxy tailings. The non-com-

bustible sludges are sand, rust, silt, TEL-sludge, salt, spent catalyst, and lime sludge. The excess biological sludge, although not readily combustible, can be dewatered to a combustible state.

Both in-plant recovery and reclamation of amenable solids combined with final sludge handling and ultimate disposal are required in order to implement a successful sludge management program in a refinery. In-plant management consists of tight operational control, preventive maintenance for leak control and the location of separators at critical points to capture materials before they become contaminated and, thus uneconomical to recover. Sludge handling methods consist of gravity or air flotation thickening, dewatering by vacuum, pressure or centrifugation, and final disposal by incineration, landfill, landfarming, and barging to sea.

IN-PLANT CONTROL, RECOVERY, AND RECLAMATION

An important element in a refinery sludge handling program should be a good in-house control program. This program should include the reduction of oil leakage by preventive maintenance of pipe lines and equipment and the repairing of leaks as soon as possible after detection. The refinery should avoid discharges of oils by the necessary elimination of the water from process units, proper dispostion of solids and spent chemicals, careful handling of emulsions and awareness by all personnel that waste treatment begins at the process unit. It has been reported that a refinery can expect total oil losses of 0.1 to 2.0 percent by volume of throughput; however, losses in excess of 0.4 percent indicate the need for improved housekeeping.

The control system should be designed to allow for good housekeeping and should be equipped with adequate sampling and monitoring facilities to indicate problems immediately. The system design should provide facilities for cleaning up after charging new catalysts so that materials do not have to be flushed into the sewers. Adequate installation of both oil-water separators and coke-water separators at crucial locations is important to a good housekeeping program.

Proper attention should be given to the prevention of the formation of oil emulsions or, when these emulsions do exist, the system should be capable of isolation and separate treatment of these materials. API separators for removal of floating oils should be located as close to the source as possible.

Acidification of caustic wastes with sulfuric acid breaks some emulsions for oil recovery. Acid wastes may be reused as a source of fuel or to produce by-products, such as oils, tars, asphalts, resins, fatty acids and chemicals. Many refineries sell or trade these spent acids and acid sludges to acid manufacturers. Sometimes the spent acids are sold to other industries, where they may be used directly or fortified with acid of full strength. Hydrochloric acid alkalation and spent aluminum chloride sludges are sometimes burned in special incinerators. Additionally, the burning of oil sludges and salt-bearing sludges in power station furnaces has been practiced. However, air pollution considerations must be considered in these cases.

A well-planned slop oil and oil solids program is also important to the solids management program. An emulsion-breaking system can be used to recover oils which

can be reused within the refinery. The water from the emulsion breaking steps can be sent to the wastewater treatment plant, and the oily solids sent to the sludge recovery system. A summary of the slop-oil emulsion composition is presented in Table 5.

SLUDGE HANDLING AND DISPOSAL

There are basically three types of sludges which must be handled by a refinery wastewater treatment and sludge handling system. These are: recoverable oils, oily sludges, and excess biological sludges. Figure 1 indicates the sludges from a typical refinery waste treatment system. Although many refineries handle the oily sludges in combination with the biological sludges, the handling will be discussed separately for purposes of this paper.

Recoverable Oils. There are a number of processes utilized for recovery of oils from gravity separators. The API Manual on Refinery Wasts (12) provides an extensive review of these alternatives. Basically, the recoverable oily sludges are heated with steam to 150 to 180°F with and without chemical additions and are broken into three phases as shown in Figure 2: oil, water, and sludge. The oils are usually recovered, the water is sent to the water treatment system, and the sludges are discharged into the oily sludge handling system.

Separator skimmings, which are generally referred to as slop oils, require treatment before they can be reused, because they contain an excess of solids and water. Solids and water contents in excess of 1.0 percent generally interfere with processing.

In most cases, slop oils are easily treated by heating to 190°F, retained at this temperature for 4 to 6 hrs, then settled for 12 to 24 hr. At the end of the settling, three definite layers exist: a top layer of clean oil, a middle layer of secondary emulsions, and a bottom layer of water containing soluble components, suspended solids and oils. In some cases, it is advantageous or even necessary to use acid or a specific chemical to destabilize slop oil emulsions. The water layer resulting from acid and heat treatment has high levels of BOD and COD and a high pH and must be treated through the biological system before being discharged. Slop oils can also be successfully treated by precoat filtration. Table 6 presents operating conditions of filters during filtration of slop-oil emulsions.

Oily Sludges. Oil sludges are derived from oil-water separators, tank bottoms or cleanings, air flotation treatment of wastewaters, and cleaning or dredging from lagoons or oxidation ponds. The composition of API separator bottoms is presented in Table 7. After pumping from the API separators, etc., these sludges usually have an average composition of 97 percent water, 1 percent oils and 2 percent solids. There are several alternatives available for the dewatering and disposal of these sludges as shown in Figure 1. These sludges can be directly applied to land, or thickened and dewatered prior to ultimate disposal.

A problem with oil sludges is that these sludges are generated from various sources and are discharged at irregular intervals. Consequently, the sludge composi-

tion is highly variable from day to day. Sometimes tank bottoms contain heavy emulsions which require special treatment, and often the sludge and skimmings from air flotation systems can present special difficulties in handling. In many cases, the skimmings from air flotation are sent to a skimmed oil tank from which they can be taken to landfill or pumped to an oil recovery unit for subsequent reuse of the oils in the refinery. Chemical treatment is usually required for oil recovery

Thickening. Gravity thickening methods are successfully utilized for oily sludges. The performance of gravity-type thickeners varies considerably depending on the nature of the oily sludges being treated. Solids loading rates in the range of 5 to 30 lb/sq ft-day are reported. The range of thickened solids concentrations is from 3 to 10 percent. Normally, 3 to 7 percent solids can be obtained from a gravity thickener.

Studies which have been conducted on gravity thickening of oil sludges indicate that there is no significant correlation of surface solids loading and solids recovery (10). Surface hydraulic loadings above 400 gal/sq ft-day appeared to cause significantly decreased solids recovery; however, there is a wide scatter of data. The effluent from the gravity thickener would be unsatisfactory for direct release due to the high oil, solids and COD concentration. Basically, solids and oil recovery are low from gravity thickeners.

Another alternative for thickening of oily sludges is by use of dissolved air flotation. A number of studies have been conducted on dissolved air flotation and the results of some bench-scale evaluations with oily sludges are presented in Table 8. Flotation thickening of some types of oily sludges was unsuccessful. Tests with heavy particles indicated some dispersion after setting for 10 minutes. Thus, removal of heavy particles by partial gravity settling should improve air flotation thickening.

Facilities for chemical addition should be included in any flotation thickener for use when necessary. The results of tests indicated that dissolved air flotation would be successful for thickening of froth flotation sludges, but flotation thickening of other refinery oily sludges is not practical.

Dewatering. Dewatering alternatives for oil sludges include centrifugation, vacuum filtration, and pressure filtration.

Centrifugation

There have been a number of reports on the use of centrifugal dewatering for refinery sludges. A schematic of a system that is being utilized for a number of oily sludges is presented in Figure 3. This consists of a two-stage system whereby the first stage is used to dewater the thickened sludge and the second stage is utilized to separate oil from the centrate. In the first stage, a horizontal solid bowl centrifudge is employed and in the second stage a disc-type cetrifuge is utilized. In this process the sludge is heated to 180 to 200°F prior to centrifugation.

The results of tests on an oily sludge with a Sharple's P600 centrifuge are presented in Figure 4. Note that the total suspended solids recovery is relatively flat

as compared to the volatile suspended solids recovery. The volatile suspended solids are indicative of waxes and heavy tars. Consequently, most of the heavy organic materials go into the oil phase at high feed rates. Since it is desired to separate most of the solids from the oil, centrifuge selection should be based on the relatively flat portions of the recovery curve to maintain a high solids recovery in the cake. The results of another test for dewatering oily sludges on a solid bowl centrifuge is presented in Figure 5.

After using the solid bowl centrifuge as a first-stage, a second-stage disc-type centrifuge should be utilized. The function of a second-stage nozzle-type centrifuge is to remove the fine solids from the solids-stabilized emulsions and thus separate the oil phase from the solids. The results of a test using the disc-type centrifuge are shown in Figure 6 and indicate that successful operation was obtained for all feed rates studied.

The performance of a full-scale centrifuge system treating an oily sludge is presented in Table 9. An internal inspection of the scroll centrifuge following 9 months of operation revealed that the hard surface coating on the internal flights had worn away exposing the stainless steel. Layered deposits 0.5 in. thick of carbon fines and grit were found inside the scroll (8).

The maximum period that the disc centrifuge has been on-stream without plugging has been 25 days. The downtime required for removal of the disc stack and cleaning can extend to three days.

The results of centrifuge testing and experience can be summarized as follows:

1. A vertical solid bowl centrifuge is not recommended for dewatering most oily wastes.
2. A horizontal solid bowl centrifuge followed by a high-speed nozzle or disc centrifuge is best suited for dewatering mixtures of contaminated API bottoms, sludge decant pit material and truck bottoms.
3. A super decanter centrifuge dewatering oily sludges is anticipated to recover 75 to 90 percent of the solids in the cake when charged with heated oily sludges. The oily phase will consist of 1 to 5 percent solids and the cake will contain approximately 50 to 60 percent solids.
4. A nozzle ejector centrifuge separates 95 to 98 percent of the feed oil in the oily phase and 2 to 5 percent in the ringdam nozzle and nozzle water. Thirty to 50 percent of the nozzle ejector feed solids will be removed with the oily phase with the remainder being in the two water phases.

Vacuum Filtration

A significant number of refineries use vacuum filtration for dewatering oily sludges. If properly implemented, vacuum filtration of oil sludges renders the solids suitable for direct landfill or subsequent incineration. In order to accommodate oily solids, a precoat vacuum filter should be used and the incoming solids should be heated to temperatures greater than 170°F. Many variables affect the performance of filtration processes; however, the relative filterability of various sludges and estimates

of vacuum filter loading rates can be made using standard Buchner funnel and filter leaf tests.

The results of some filter resistance tests (7) using oily sludges are presented in Table 10. These tests indicate that oily sludges quickly blind the filter cloth when a precoat was not used. These data indicate that heating of oily sludges to 165°F decreased specific resistance and improved the characteristics of the cake. The effect of chemical addition on filterability is also indicated in Table 10. The addition of lime and ferric chloride did not improve the filterability of oil sludges.

A vacuum filtration filter leaf test was conducted on the oily sludges in the same study. The design filter loading rate for precoat vacuum filters for various types of oil sludges is presented in Table 11. Using an operating temperature of 160 to 180°F improves the vacuum filter performance in terms of oil recovery, filtration loading, and cake solids concentration. Several noteworthy observations can be made concerning the effect of clay addition on vacuum filtration performance. First, the oil recovery decreases with increased clay addition. Secondly, the effective filtration rate decreases with clay addition. However, the effective filtration rate is based on solids, excluding the clay, therefore, the total solids filtration rate may not be decreasing as rapidly as it might seem. The major conclusions regarding vacuum filtration of oil sludges are:

1. Increased feed temperature greatly improves vacuum solids performance.
2. Addition of spent clay decreases oil recovery and solids filtration rate on a clay-free basis.
3. The measured filtration loadings of 0.8 to 3.0 lb/sq ft-hr were required for oil recovery.

Pressure Filtration

A fixed plate, high pressure filter press may be used to dewater many types of oily sludges. Sludge is applied to a cloth covered filter plate at high pressure and water and oil are passed through the cloth media while solids are retained. Parameters which are important in evaluating the process are feed temperature, lime addition, spent clay addition, cycle time, cake characteristics, and filtrate characteristics.

The results of filter press tests on an oily sludge are presented in Table 12. The feed to the pressure filter consisted of a base mixture of refinery oily sludges which contained API separator bottoms, sludge decant pit material, and tank bottoms. These tests indicated that heating the feed was required to obtain satisfactory filtration. Effective breaking of solids-stablilized emulsions is obtained. Cake solids in excess of 50 percent can be obtained on pressure filtration with oil concentrations in the range of 5 to 20 percent.

The filter press cake solids concentration correlated with average filtrate temperature as shown in Figure 7. It is apparent that filtration temperature has a dramatic effect on cake solids and cake oil concentrations at constant cycle times. The addition of lime improved filtration somewhat, although the effect is not conclusive;

however, experience at other refineries indicates that a definite increase in filtration efficiency can be obtained by adding lime. A significant decrease in cake oil content can be obtained by washing the cake with hot water. The filtrate is usually readily separable into an oil and water phase. Test results indicate that the oil will probably require processing through the high chloride slop system. The water phase has not been found to create any problems in the wastewater system.

Disposal. The ultimate disposal of oily sludges can be by barging to sea, landfill, land farming, and incineration with landfill of the ash. However, sea disposal of oily materials is viewed as a short-term alternative and will eventually be eliminated as an option. The disposal of the oily sludges on soil is acceptable if it can be shown that such disposal will not contaminate groundwaters or contribute to contaminated storm runoff, and will not create a potential seepage problem. A proper land farming operation using soil bacteria for degradation of oils would satisfy the above requirements. The utilization of a lined landfill with leachate treatment would also meet these requirements.

Land farming of oily sludges has been successfully practiced by refineries where sufficient land area is available for proper decomposition of the oil-containing solids. Land farming involves spreading the sludge in 4 to 6-in. layers, allowing the sludge to dry about one week, adding nutrients, and then discing the sludge into the soil. A Texas refinery land farms crude oil tank bottoms containing high molecular weight, oil-containing olefinic or aromatic components and waxy raffinate containing high paraffinic components. Decomposition rates were found to be approximately 0.5 lb/mo-cu ft without nitrogen and phosphorus addition and 1.0 lb/mo-cu ft with nutrient addition. Disposal costs were estimated at $7 per barrel of oil including the cost of nutriel addition. The species of microorganisms which were found to remove the oils were pseudomonas, flavobacterium, nocardia, corynebacterium, and artherobacterium.

Incineration of oily sludges and landfilling of the ash should provide an acceptable means of final disposal. Important factors in disposal by incineration sould include the following:

1. Selection and cost of the incineration equipment.
2. Operating costs.
3. Potential air problems by particulates, sulfur dioxide and other pollutants.

Table 13 presents the results of an economic evaluation of flow and optimum solids concentration to incineration. The fuel costs associated with evaporation of excess water in an incineration system are presented in Figure 8. Oil and volatile matter in the contaminated sludges can be destroyed by incineration. The type of incinerator which is most applicable to a particular waste depends on the nature of the waste. Sludges and solids of high solids contents are conventionally handled by multiple-hearth incinerators.

A fluid bed incinerator operates with a bed of ash and sand particles fluidized by forced air feed. The fluidized bed incinerator is best suited for feeds that are partially liquid so that the incinerator can be fed by pumps and screw conveyers.

While feeding dry solids to a fluid bed incinerator is possible, the multi-hearth incinerator will be more economical if most of the feed is in the form of cake of non-pumpable solids.

Rabb indicates "suitable" incinerators as follows:

2-10 wt. % solids feed - fluid sand bed
5-70 wt. % solids feed - rotary kilm
40-70 wt. % solids feed - multiple-hearth

Biological Sludges. Basically, the sludge handling methodology employed for processing biological sludges is similar to that previously described for oily sludges. However, due to the putrescible potential of biological sludge, stabilization is required prior to disposal by sea or land. The basic process alternatives are depicted in Figure 9 with the most feasible alternatives having been summarized in Figure 1. Consequently, the process sequency for biological sludge handling consists of stabilization, thickening, dewatering, and final disposal. Oftentimes, the thickening step will precede stabilization in order to reduce the stabilization costs which are highly dependent on hydraulic flow. Detailed design procedures and examples for these processes are given elsewhere (1) and will not be described herein.

Biological Sludge Stabilization. Stabilization of excess biological solids is required because of the degradable nature of the microbial sludge. There are three basic methods of sludge stabilization which are technically available: aerobic digestion, anaerobic digestion, and wet air oxidation. Because of the complexity of anaerobic digestion and the problems experienced in operating the process, this method is not being utilized in new refinery sludge stabilization systems. However, there are several older treatment systems which have used anaerobic digestion. There have been considerable operational and materials problems experienced with wet air oxidation and, to date, this method has not received acceptance in the refinery industry.

The most common method of stabilizing water biological sludge in the refining industry is by utilization of aerobic digestion. Aerobic digestion is used chiefly to stabilize the sludge and render it suitable for land disposal. Additionally, the overall sludge quantity may be somewhat reduced and the dewatering characteristics improved slightly. Aerobic digestion is an extension of aerobic biological oxidation in the absence of an external food supply. Thus, the microbes digest each other due to endogenous respiration and autooxidation. A simplified summary of the aerobic conversion of organic materials into cellular materials and the subsequent breakdown into by-products and residue is shown in Figure 10.

The results of aerobic digestion on various biological sludges are shown in Figure 11. Approximately 10 to 15 days detention are required on an annual average to achieve 50 to 60 percent reduction of the volatile content of the sludge. This reduction represents about 80 to 90 percent reduction of the degradable content and is generally suitable for land application. Tests on refinery sludges (3) have indicated that about 0.5 to 1.2 lb of oxygen are required per lb of VSS destroyed per day.

Thickening of Biological Sludges. There appear to be three alternatives by which refineries can concentrate biological sludges. These are flotation thickening, gravity thickening, and centrifugal thickening. The primary objective of a thickner is to reduce sludge volume by removing the bulk water and concentrating the sludge, thereby increasing the system effectiveness and lowering the cost of subsequent dewatering processes

Gravity Thickening

Gravity thickeners utilize gravity sedimentation and compression for sludge concentration. The key design parameters are hydraulic and solids loading rate. If the surface loading rate is excessive, poor solids recovery will result. If the solids loading (lb solids applied/sq ft-day) is too great, then there will also be poor solids recovery and low underflow solids concentration. Solids loading rates for gravity thickening of waste refinery sludges range from 2 to 15 lb/sq ft-day. Biological refinery sludges can be concentrated by gravity to a concentration of 2 to 4 percent solids by weight.

Gravity thickeners do not require much operator attention and will perform fairly consistently provided the influent hydraulic flow and solids loading do not vary substantially. In extremely warm climates, gravity thickeners may generate obnoxious biological odors if they precede the stabilization process.

Centrifugation

Centrifugation has been utilized sparingly for thickening waste biological sludges in the refinery industry. There is little information available on the application of disc centrifuges for thickening of refinery biological sludges. Basket centrifuges are capable of thickening waste activated sludge to levels of 5 to 6 percent concentration with 80 to 95 percent solids capture. One refinery has reported using basket centrifuge for thickening to a concentration of 8 percent. However, excessive maintenance was experienced because of vibrational problems.

Air Flotation

A third method of thickening is by air flotation whereby air bubbles are released from solution and attach themselves to the sludge flocs. The air-solids mixture than rises to the surface of the basin where it concentrates and is removed. The primary variables with regard to flotation thickening are recycle rate, feed solids concentration, air-to-solids ratio, and solids and hydraulic rates. Pressures between 50 and 60 psi are commonly employed for flotation thickening. Recycle rates on the order of 100 to 500 percent, solids loadings of 2 lb/sq ft-hr, and hydraulic loading rates (including recycle) in the range of 1 to 4 gpm/sq ft are common of flotation thickeners.

Results of tests on refinery sludges indicate that these sludges are quite amenable to flotation thickening (3). These results are summarized in Table 14 and Figure 11A. These data indicate that the optimum pressure was about 50 to 55 psig and that polymer polymer addition was not justified. The correlation of these data in Figure 12 shows the optimum air-to-solids ratio to be about 0.01 lb/lb to obtain a float solids of 3.5 percent.

Dewatering of Biological Sludges.

Vacuum Filtration

Vacuum filtration is one of the most common methods used to dewater wastewater sludges. Water is removed from the sludge under an applied vacuum through a porous media which retains the solids. Chemicals are usually required in order to decrease the specific resistance of the sludge, thereby allowing higher sludge loading rates (lb/sq ft-hr) and, thus, smaller, more economical filters. The results of several tests on refinery wastewaters indicate that ferric chloride or a combination of lime and ferric chloride usually provides the optimum coagulant from an economical and performance standpoint. The optimum ferric chloride dosage usually ranges from 200 to 400 lb/ton of dry solids. Tests conducted on waste activated sludge indicated that there is not significant advantage of a precoat filter based on overall economics. Tests indicate that vacuum filtration of refinery biological sludges is usually able to obtain solids concentrations in the range of 10 to 16 percent at filter loading rates ranging from 1 to 5 lb/sq ft-hr.

The results of filter leaf tests on both a raw and digested refinery waste activated sludge are presented in Table 15. This table indicates that the digested sludge presented better dewatering characteristics than the undigested sludge.

Centrifugation

Basket centrifuges have been found to be the best centrifugal method of concentrating waste biological solids. The tendency for solid particles to separate from the water portion of the slurry due to a slight difference in density is accelerated by the application of centrifugal force. In fact, by spinning the slurry at appoximately 1,500 rpm, a centrifugal force of over 1,000 times that of natural gravity is extended and the particulate matter is concentrated on the external wall of the revolving basket or bowl. A schematic of the internal components of the basket centrifuge is presented in Figure 13.

There are a number of applications of utilizing basket centrifuges in the refining industry. Normally, the centrifuges provide a cake solids ranging from 8 to 18 percent concentration with biological sludges. A correlation of the cake concentration and solids recovery and cake solids and distance from the wall is presented in Figure 14. It should be indicated that there have been some problems in the utilization of the basket centrifuge due to mechanical vibrations of the centrifuge.

Pressure Filtration

Pressure filtration is another alternative for the dewatering of the biological solids. This process usually can obtain a solids concentration approaching 50 percent with biological sludges, thus producing the driest cake for disposal. The pressure levels for the pressure filtration systems range from 50 to 225 psig. Normally, it has been found that the pressure filtration system requires higher chemical dosages than for the vacuum filter and centrifugation system; however, these produce a higher solids concentration. In order to obtain an acceptable cake, the manufacturers recommend a pressure specific resistance of less than 3×10^{12} cm $^{-2}$.

Heat Content of Sludge. The heat content of various samples of dewatered secondary refinery sludge has been determined in a bomb calorimeter (3). The average fuel value for the undigested secondary sludge was approximately 8,000 BTU's per lb of dry solids. This value is within the expected range of secondary waste activated sludge with 70 percent voatile content. Approximately 6,000 BTU's per lb of dry solids were found after aerobic digestion which indicates that part of the vlatile content matter is destroyed by aerobic digestion. It is obvious that stabilization would not be desirable if incineration were the means of final disposal.

Ultimate Disposal. The alternatives for ultimate disposal of the biological sludge are similar to those for the waste oily sludge with the expection of land farming. In many cases, a thick slurry of activated sludge can be placed in 4 to 8 in. layers and utilized as a limited nutrient and soil conditioner. In this case, additional water is removed by natural evaproation and infiltration into the underlying soil. Following initial periods of drying, the sludge layer can be disced to encourage the activity of aerobic soil bacteria. The soil bacteria working in conjunction with plant growth will further stabilize the waste solids and transform them into a hemocyte material suitable for agricultural use as a soil conditioner.

SUMMARY

A design summary table for the thickening and dewatering alternatives of oily sludges is presented in Table 16. A summary on biological sludges is presented in Table 17.

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DISCUSSION

John Smith: You spoke of the rules-of-thumb reference to air oxygen input rates and sludge concentrations on bio-sludges. Does this also refer to those sludges generating on the rotating bio-disk units or have you found a difference?

Carl Adams: We have not conducted much sludge handling on bio-disk sludge, although we have performed about six pilot studies with the bio-disk. One was on a very large scale and we are presently evaluating the bio-disk at Cranston, Rhode Island on a fairly large scale. We are not far enough along into the study to comment on sludge handling. I would assume that the sludges dewater as well or better than conventional activated sludge. I say this because the material sluffs off in chunks. Most of the wastes we have evaluated have been high-strength, difficult-to-settle wastes using the activated sludge process. Consequently, we examined the bio-disk in order to establish a fixed medium. Thus, these wastes are bad examples for me to quote as representative of bio-disk performance. However, with the pulp and paper industry the sludge from a bio-disk settled very well. We did pilot a large 3-meter unit, with a pulp and paper waste, and observed very good settling.

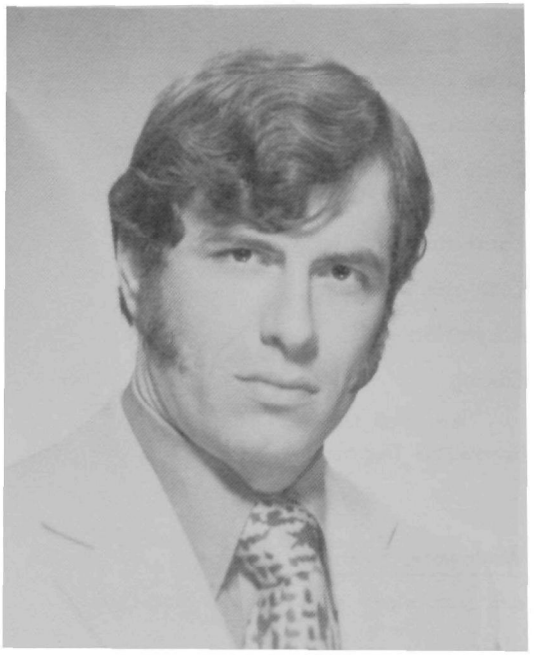
John Smith: The work we have done to-date indicates the settling is quite good but the oxygen input required for digestion is considerably higher?

W.C. McCarthy: From a leaching point of view, what criteria are used to decide

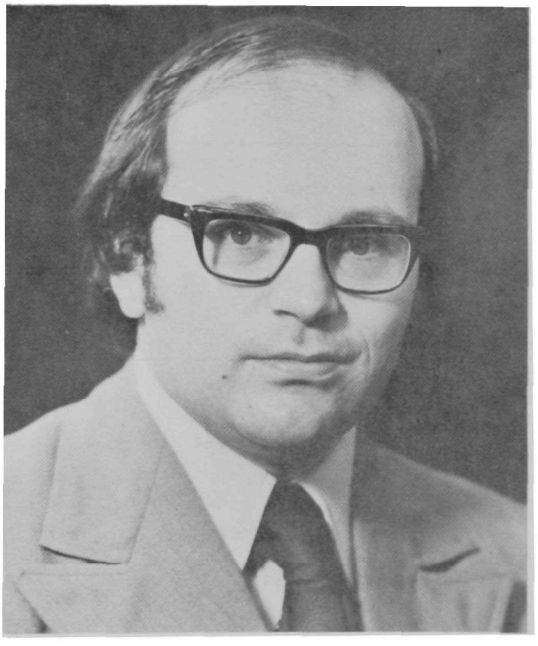
if a treated oily sludge would be suitable for landfill?

Carl Adams: I can get out of this one easily by referring this question to the next apeaker. Genrally, you are required to contruct a monitoring well if you can get permission from the authorities. The easy way for the regulatory authorities is to require you to line the area and treat the runoff. If you do not want to do that, you generally have to convince the authorities that you do not have heavy metals which will leach out. You can genrally do this; however, ash from incinerators, boilers and so on contain quite a bit of heavy metals from the coal that was burned. We usually argue that the rain water won't leach these metals because pH is sufficiently high that you will not get leaching. The only way you can resolve it if there is an argument is generally to construct monitoring wells. If a leaching problem then is observed to develop, you may have to line the pond and treat the storm water runoff from the landfill. We argue against it generally and hope we are not filling the pond with anything that would cause leaching and problems.

BIOGRAPHY



Carl E. Adams, Jr. is President of Associated Water and Air Resources Engineers, Inc. (AWARE) located in Nashville, Tennessee, and President of AWARE Engineering in Houston, Texas, and has consulted to over 200 United States and foreign industries. He holds the following degrees: B.E., Civil Engineering, Vanderbilt University; M.S., Environmental Engineering, University of Texas. He is a professional engineer, registered in 18 states. Dr. Adams serves as an Adjunct Professor in the Department of Environmental Water and Resources Engineering of Vanderbilt University. He holds membership in more than six professional societies, has authored and presented more than 50 technical papers, and edited and co-authored three books dealing with industrial wastewater treatment technology.



Robert M. Stein is Director of Operational Services for Associated Water and Air Resources Engineers, Inc. (AWARE) of Nashville, Tennessee. He holds the following degrees: B.A., Applied Science, Memphis State University, Memphis, Tennessee; and M.S., Environmental Engineering, Vanderbilt University Nashville, Tennessee. He is a professional engineer, registered in the State of Tennessee. Mr. Stein was associated for several years with the State of New York in the Department of Transportation.

TABLE 1 TYPE OF REFINERY SOLID WASTE

Source	Combustible	Non-Combustible	Biodegradable
Crude Oil Storage	Waxy Bottoms	Sand, Rust, Silt	
Product Storage		TEL Sludge	
Crude Processing		Sand, Rust, Silt, Salt	
Catalytic Cracking		Catalyst	
Catalytic Reforming		Catalyst	
Alkylation	Sludge	Corrosion Products	
Coking	Coke, Waxy Tailings		
Feedwater Treatment		Lime Sludge	
Wastewater Pollution Control			
API Separators	Slop Oils	Sand, Silt	
Flotation Separators	Float Solids		
Secondary Clarifiers			Bio Sludge
Sludge Thickeners		Lime Sludge	

TABLE 2
CHARACTERISTICS OF REFINERY SOLIDS WASTES (REF.5)

Waste Type	Typical Composition, Percent: Oil or Hydrocarbon	Water	Volatile Solids	Inert S Solids	Characteristics
API Separator Sludge	15	66	6	13	Fluid slurry of oil, water and sand
Tank Bottoms	48	40	4	8	Oil-water mixture
Chemical Treatment Sludge	5	90		5	Slightly viscous fluid.
Air Flotation Froth	22	75		3	Thick, oily fluid
Precoat Vacuum Filter Sludges	22	29		49	Temperatures
Biological Treatment Sludges					
Raw	0	98	1.5	0.5	Water Consistency
Mechanically Thickened	0	94	4	2	Thick, but pumpable
Centrifuged	0	85	10	5	Viscous-peanut butter consistency
Vacuum Filtered	0	75	15	10	Wet crumbly solid.
Screw Pressed	0	40	40		Intact, solid cake.
Water Treatment Sludge	00	95		5	Pumpable Fluid, sometimes gelatinous

TABLE 3

ESTIMATES OF REFINERY SOLID WASTE QUANITIES

Waste Types	Unit Loads
API Separator Sludge	200 mg/l Suspended Solids
Chemical Treatment (API Separator Effluent)	50 mg/l Suspended Solids Removed Only
Biological Sludges	0.7 lb Dry Solids per lb BOD Removed
Water Treatment Sludge	
A. Lime Soda Ash	2 parts Dry Sludge per 1 part Hardness Removed
B. Ion Exchange	0.4 lb Salt per 1,000 Grains Hardness
Office Wastes	1.0 cu yd per Employee per month
Cafeteria	0.6 lb per Meal

TABLE 4

SUMMARY OF TANK BOTTOMS SLUDGE CHARACTERISTICS (REF.11)

ANALYSIS (PERCENT BY WEIGHT)

	Average	Maximum	Minimum
Water	39.4	98.0	5.0
Oil	47.9	95.0	1.3
Volatile Solids	4.4	13.0	0.0
Ash	8.3	55.3	0.0
Total	100.0		

TABLE 5

COMPOSITION OF SLOP-OIL EMULSION (REF. 11)

	Percent by Weight		
	Maximum	Minimum	Average
Oil	80.9	13.2	40.2
Water	81.0	18.0	54.8
Sediment	8.0	11.1	5.0

TABLE 6
OPERATING CONDITIONS FOR PRECOAT FILTERS
(Treating Slop-Oil Emulsions, Separator Bottom Sediment, and Acid Oil)

Precoat Medium = Medium-grade diatomaceous earth

Temperature, F°	180
Vacuum, in. of mercury	18 to 20
Knife-cut depth, in. per revolution	0.0040
Drum speed, min per revolution	3 to 4

TABLE 7
COMPOSITION OF API SEPARATOR BOTTOMS (REF.11)

	Analysis as Taken from the Separator (Percent by Weight)		
	Average	Maximum	Minimum
Water	82.4	98.3	61.2
Oil	10.9	20.7	1.1
Volatile Solids	1.4	2.3	0.5
Ash	5.3	15.8	0.4
Total	100.0		

TABLE 8
BENCH SCALE FLOTATION THICKENING (REF. 10)

Sludge Mixture	Untreated Sludge TSS (mg/1)	Water Phase TSS (mg/1)	Float Solids Volume (ml)	Float Solids Solids (%)	Sludge Volume (ml)	Recovery (%)	Comments
WEMCO Float Solids	730	73	15	4.4	0	90	Water Phase COD = 270 mg/l BOD_5 = 140 mg/l
WEMCO Float Solids	1,136	96	30	3.5	0	92	
WEMCO Float Solids	420	66	10	5.5	Trace	84	Some of the float was dispersed after 10 min.
WEMCO Float Solids	2,260	830	40	5.2	Trace	93	Some of the float was dispersed after 10 min.
Contaminated API Btms = 10% Tank Bottoms = 20% Decant Pit Sludge = 10% Water = 60%	--	--	100	--	100	--	Solids dispersed rapidly.
Contaminated API Btms = 20% Water = 80%	--	--	100	--	Trace	--	Solids dispersed during 10 min.
Tank Bottoms = 50% Water = 50%	--	--	10	--	170	--	Most of solids sank. Float dispersed rapidly

Test conditions: 1) 100 percent Recycled Based on Sludge Volume. 2.) 50 psig Saturation Pressure

TABLE 9
FULL-SCALE CENTRIFUGE PERFORMANCE

	Percent Solids	Percent Oil
Scroll Centrifuge Feed[a]	1.6	6.9
Scroll Centrifuge Centrate	0.7	5.9
Scroll Centrifuge Sludge	59	2.5
Disc Centrifuge Water Discharge[b]	0.01	0.5
Disc Centrifuge Solids Discharge	0.1	0.1

[a] Scroll Centrifuge = 30 gpm

[b] Disc Centrifuge = 30 gpm

TABLE 10
FILTERABILITY OF OILY SLUDGES (REF.7)

Test Sample	Special Test Conditions	Specific Resistance $sec^2/gm \times 10^{-8}$	Comments
Composite of Plant Oily Sludges-Thickened	Precoated Filter	0.35	Recovered 36,900 mg/1 of oil from sludge
Composite of Plant Oily Sludges-Thickened	Precoated Filter-165°F	0.16	Recovered 40,000 mg/1 of oil from sludges
Thickened Oily Sludge	Cloth Media	-	Blinded Filter Badly
Composite of Plant Oily Sludges-Thickened	Precoated Filter-Heated to 165°F	0.19	Recovered 74,000 mg/1 of oil from sludge
Composite of Plant Oily Sludges-Thickened	Precoated Filter-0.67 mg Spent Water Treating Lime/1.0 mg of oily solids heated to 165°F		Recovered 85,000 mg/1 of oil from sludge
Composite of Plant Oily Sludges Thickened	Precoated Filter-2,600 mg/1 of $FeCl_3$ Heated to 165°F	0.48	Recovered 31,000 mg/1 of oil from sludge

TABLE 11
AVERAGES OF VACUUM FILTER RATES AND PERCENT OF FILTER TIME REQUIRED

Service	Average Charge to Filters (Barrels/day)	Average Filter Rate (gal/hr-sq ft)	Filter Time Required (%)
Slop-oil emulsion	427	1.7	37.8
Separator sediment	377	2.8	20.1
Flocculation sludge	627	8.6	10.7
Acid Oil	129	2.4	7.8
Precoating	--	--	8.5
Downtime	--	--	15.1

TABLE 12

SUMMARY OF RESULTS FROM FILTER PRESS PILOT UNIT (REF. 10)

Run[a] No.	Feed Mixture	Admix Added	Chemicals Added	Feed Temp (°F)	Average Filtrate Temp (°F)	Total Cycle Time (hr)	Feed TSS (%)	Feed Oil (%)	Cake TSS (%)	Cake Oil (%)	Comments
6	Base Mixture[b]	Clay @ 0.6 lb/lb D.S.	Lime @ 0.12 lb/gal	175	100	2	12.0	8.5	49.7	17.5	Cake heat value = 4,710 BUT/lb.
7	Base Mixture[b]	Clay @ 0.6 lb/lb D.S.	Lime @ 0.12 lb/gal	58	58	2	12.0	8.5	40.0	20.0	
8	Base Mixture[b]	Clay @ 0.6 lb/lb D.S.	--	175	94	2	22.7	12.3	54.0	13.0	
9	Base Mixture[b]	Clay @ 0.6 lb/lb D.S.	Spent Caustic @ 0.6 lb/gal	140	77	2	22.7	12.8	46.2	15.3	
10	Base Mixture[b]	Clay @ 0.6 lb/lb D.S.	Spent Caustic @ 0.6 lb/gal	180	85	2	22.7	5.9	61.4	6.4	
11	Base Mixture[b]	Clay @ 0.56 lb/lb D.S.	Lime @ 0.07 lb/gal	180	98	2	18.9	--	57.3	8.7	Cake heat value = 3,030 BTU/lb. Water free cake heat value = 4,590 BTU/lb.
12	Base Mixture[b]	Clay @ 0.56 lb/lb D.S.	Lime @ 0.07 lb/gal	180	110	1	16.3	--	57.9	10.1	Cake heat value = 2,900 BTU/lb.
13	Base Mixture[b]	Clay @ 0.56 lb/lb D.S.	Lime @ 0.07 lb/gal	180	119	2	16.8	--	60.5	4.9	Cycle time includes 1 hr of water wash.
14	Non-Contaminated API Separator Sludge	10-4 Catalyst @ 2.5 lb/lb D.S.	Lime @ 0.10 lb/gal	60	60	2	15.7	--	71.1	--	
15	Thickened WEMCO = 78% Base Mixture[b] = 22%	Clay @ 0.57 lb/lb D.S.	Lime @ 0.065 lb/gal	178	124	2	15.0	16.4	58.0	7.1	Cake heat value = 3,290 BTU/lb
16	Base Mixture[b]	Clay @ 3.2 lb/lb D.S.	--	180	82	2	38.5	22.7	60.5	11.9	Cake heat value = 3,270 BTU/lb. Crushed bulk density = 0.86 gm/cc.

[a] Runs one through five were incomplete due to filter press gasket and hose failures.

[b] Base refinery oily sludge mixture consisted of:
1. Contaminated API Separator Sludge - 28%
2. Sludge Decant Pit Material - 36%
3. Tank Bottoms - 36%

TABLE 13
INCINERATOR CONSIDERATIONS OF FLOW AND SOLIDS CONCENTRATION (REF. 4)

Effluent flow (gpm)[a]	2 wt. % lean sludge (gpm)	Optimum Sludge[c] Concentration to incinerator (wt. %)
50	1	3
100	2	7
200	4	17
500	10	50
1,500	30	70[b]

[a] Effluent flow assumes the 2 wt. % lean sludge is 2 vol. % of the effluent flow.

[b] This is the maximum practical concentration that achievable with a filter.

[c] Based on capital investment for dewatering equipment plus suitable incinerator, and operating costs for 5 years at the following unit rates:

Power	$0.0125 per kWh
Fuel Oil	$15 per ton
Labor	$8,000 per man-year

TABLE 14
FLOTATION THICKENING RESULTS (REF.3)

Influent Solids (%)	Pressure (psi)	Recycle (%)	Cake Solids (%)	Filtrate Solids (mg/1)	Polymer	Polymer Dosage (lb/tn)
0.9	40	100	2.6	324	--	--
0.9	40	230	3.6	217	--	--
0.44	40	100	319	153	--	--
0.44	40	100	4.0	191	Atlasep 105-C	3
0.6	40	100	3.2	243	--	--
0.7	50	230	3.8	250	--	--
0.7	50	230	4.0	187	Atlasep 105-C	3
0.6	50	100	3.1	146	Atlasep 105-C	5
0.6	50	100	2.8	215	--	--
0.7	60	230	3.9	272	--	--

TABLE 15
FILTER LEAF TESTS RESULTS (REF.3)

Sludge	Run No.	Feed Solids (%)	Vacuum (in. Hg)	Time Form (min)	Time Dry (min)	Cake Solids (%)	Cake Thickness (in.)	Loading (lb/sq ft-hr)
Raw[a]	1[b]	1.04	15	2.00	3.00	8.9	1/64	0.16
	2[c]	1.04	15	2.00	3.00	9.3	1/8	0.73
	3[c]	1.48	15	2.00	3.00	9.2	1/8	0.96
	4[c]	1.48	10	2.00	3.00	8.6	1/8	0.92
	5[c]	1.48	18	2.00	3.00	7.9	3/16	0.99
	6[c]	1.48	15	1.00	1.50	7.2	3/16	2.31
	7[c]	1.48	10	1.50	2.25	7.5	3/16	1.54
	8[c]	1.48	15	3.00	4.50	7.9	1/4	0.88
	9[c]	2.29	15	2.00	3.00	7.1	5/16	2.05
	10[c]	2.44	15	2.00	3,00	7.0	3/8	1.98
Digested[d]	1[b]	1.73	15	2.00	3.00	13.1	3/16	2.24
	2[b]	1.73	18	2.00	3.00	13.6	1/4	2.57
	3[b]	1.73	10	2.00	3,00	12.1	5/16	3.13
	4[b]	1.73	15	1.00	1.50	11.5	1/4	5.08
	5[b]	1.73	15	3.00	4.50	12.3	7/16	3.00
	6[b]	1.73	15	1.50	2.25	10.8	3/8	4.62
	7[b]	2.74	15	2.00	3.00	11.0	7/16	4.63
	8[b]	3.19	15	2.00	3.00	11.0	7/16	4.65
	9[b]	2.18	15	2.00	3.00	15.9	3/16	1.95

[a] Chemical dosage = 20% $FeCl_3 \cdot 6H_2O$ + 5% CaO.

[b] Media No. POPR-873, polypropylene from Eimco Envirotech

[c] Media No. POPR-929, polypropylene from Eimco Envirotech

[d] Chemical Dosage = 15% $FeCl_3 \cdot 6H_2O$ + 5% CaO

TABLE 16
SUMMARY FOR THE THICKENING AND DEWATERING ALTERNATIVE OF OILY SLUDGES

Type of Sludge	Process	Average Performance	Design Parameters	Comments
Oily Sludge	Thickening			
	Gravity	3-7 percent solids 50% recovery	5-30 lb/sq ft-day	Low solids and oil recovery
	Flotation	84-93% solids recovery 3.5-5.5% float solids	Untreated sludge 420-2,200 mg/l TSS, 100% recycle 50 psig saturation pressure	Sucessful for froth flotation sludges but impractical for other oily sludges
	Dewatering			
	Centrifugation	75-90% solids recovery when charged with heated oil sludges Oily phase will consist of 1-5% solids and cake will contain 50-60% solids. Nozzle ejector centrifuge separates 95-98% of oil in oily phase and 2-5% in the nozzle and nozzle water. 30-50% of nozzle ejector feed solids will be removed with oily phase.	Flow rate 50-350 gal/hr	A vertical solid bowl type not recommended for dewatering most oily sludges.
Oily Sludge (Cont'd)	Vacuum Filtration		Avg. Filter Rates gal/hr-ft^2 slop-oil emulsion-1.7 separator sediment-2.8 flocculation sludge-8.6 acid oil-2.4 Filter Time Required, per cent, slop-oil emulsion-37.8 separator sediment-20.1, flocculation sludge-10.7, acid oil-7.8 precoating-8.5, downtime-15.1	To dewater oily sludges, a precoat vacuum filter should be used and solids should be heated above 170°F. Solids should be suitable for landfill following vacuum filtration. Increased temperature for feed improves performance. Addition of Spent clays decreases oil recovery and solids F.H. rate
	Pressure	5-20% oil, 40-70% solids cake	2-hr cycle time, feed contents 12-38.5% TSS, 6-23% oil. Temperature of feed 58-180°F.	Heating of feed required for satisfactory filtration. Lime or spent caustic added.

TABLE 17
SUMMARY OF BIOLOGICAL SLUDGES

Type of Sludge	Process	Average Performance	Design Parameter	Comments
Biological Sludges				Similar to oily sludges but should be stabilized due to putrescible nature
	Thickening			
	Gravity	2-4% solids concentration by weight	Loading rate 2-15 lb/ft^2 day	If surface loading rate is excessive poor solids recovery results
	Centrifugation	5-6% with basket centrifuges, 80-95% solids capture	Feed rate 6-200 gpm	There is little information avaiable
	Flotation	Cake solids 2.6-4.0%	50-60psi, 100-500% recycle. Solids loading 216 sq ft-hr, hydraulic 1-4 gpm/ft^2	Sludges quite amenable to flotation thickening
	Dewatering			
	Vacuum Filtration	Solids concentration 10-16%	Loading rate 1-5 lb/sq ft-hr	Chemical usually required to decrease specific resistance. $FeCl_3$ or lime and $FeCl_3$ usually. Optimum $FeCl_3$ 200-400lb/ton of solids
Biological Sludges	Centrifugation	8-18% cake solids Solids recovery 20-90%	Feed rate 4-90 gpm	Basket type found to be best. There have been problems due to mechanical vibrations in the centrifuge
	Pressure Filtration	50% solids	Pressure levels 50-255 psig	Normally requires higher chemical dosages than for vacuum filters or centrifuges.

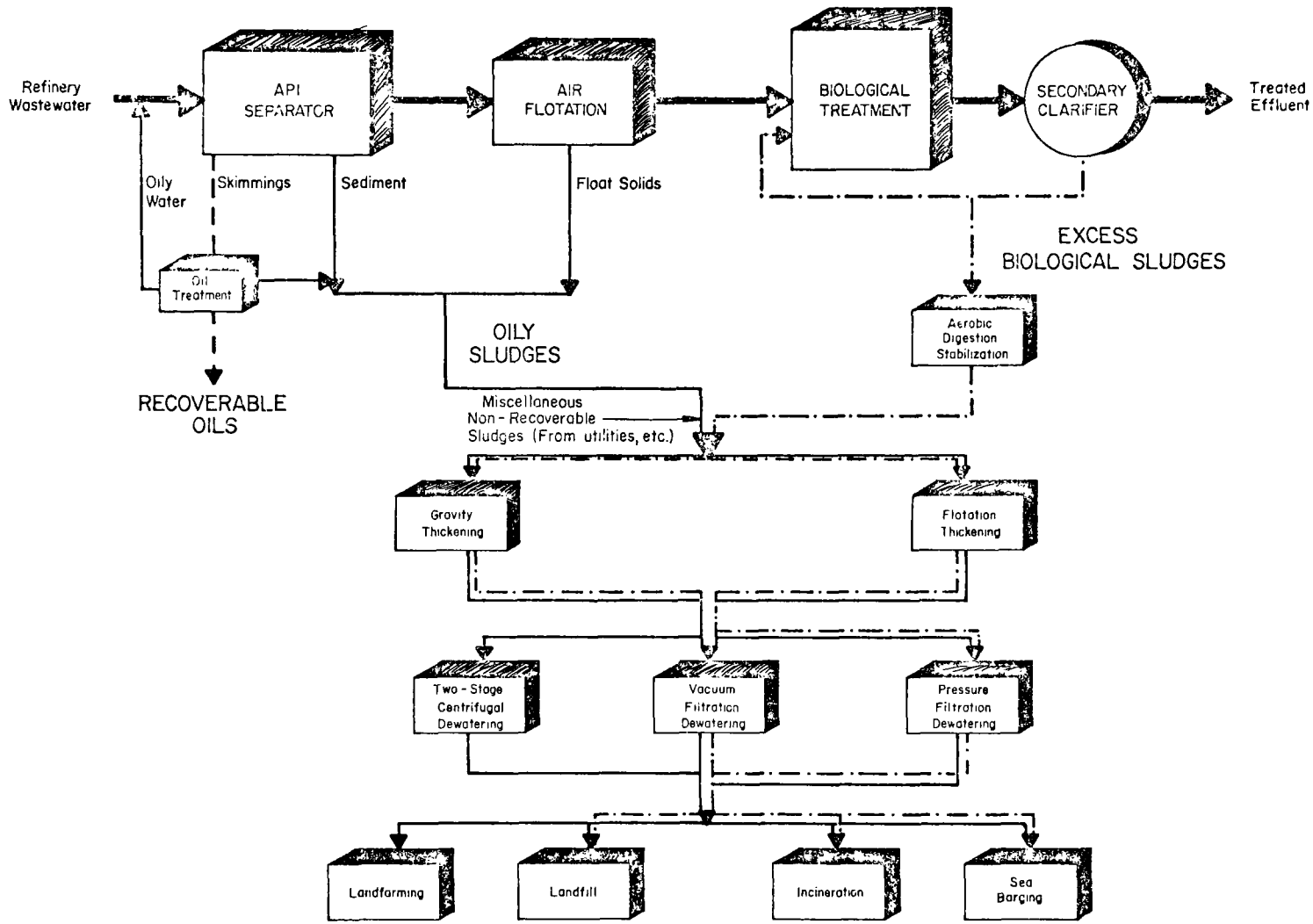


FIG. 1. SLUDGE HANDLING AND DISPOSAL OPTIONS FOR REFINERY SLUDGES

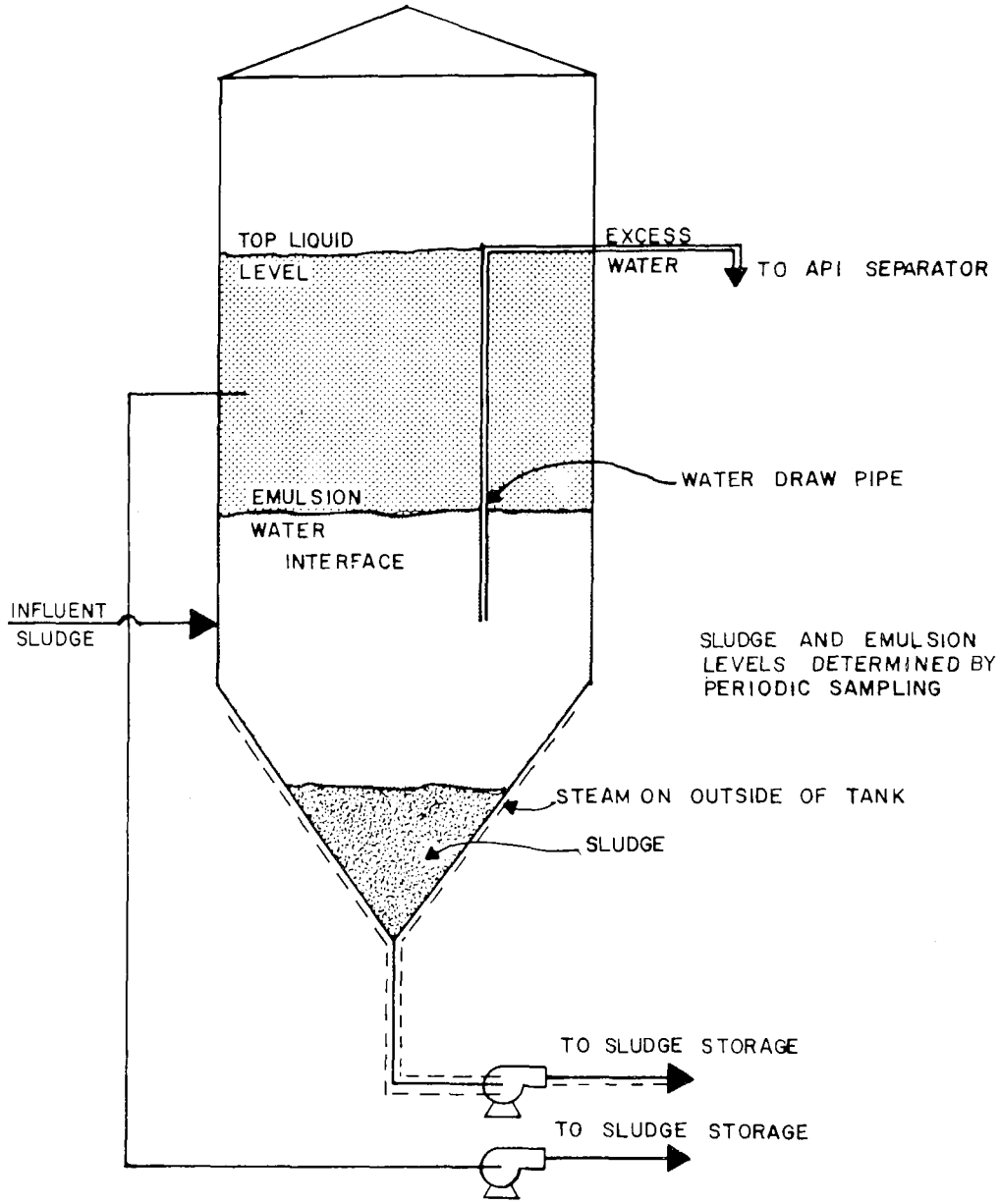


FIG. 2. PRIMARY OILY SLUDGE DECANT TANK

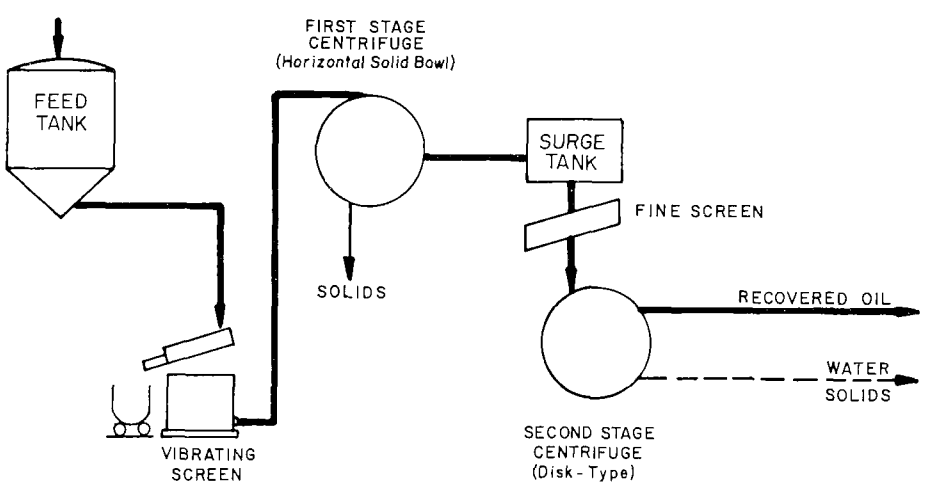


FIG. 3. TYPICAL OIL RECOVERY AND SOLIDS REMOVEL SYSTEM FOR OILY SLUDGE

CHARGE MIXTURE

CONTAMINATED API SEPARATOR BOTTOMS	28 %
SLUDGE DECANT PIT SLUDGE	36 %
398 TANK BOTTOMS	12 %
209 TANK BOTTOMS	12 %
253 TANK BOTTOMS	12 %

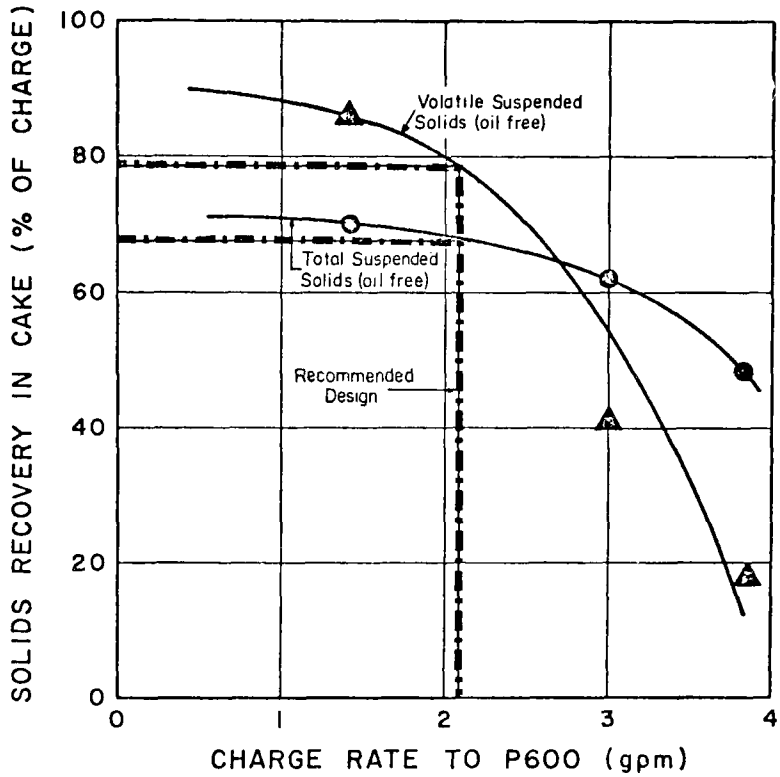


FIG. 4. SOLIDS RECOVERY FROM OILY SLUDGE (REF 10)

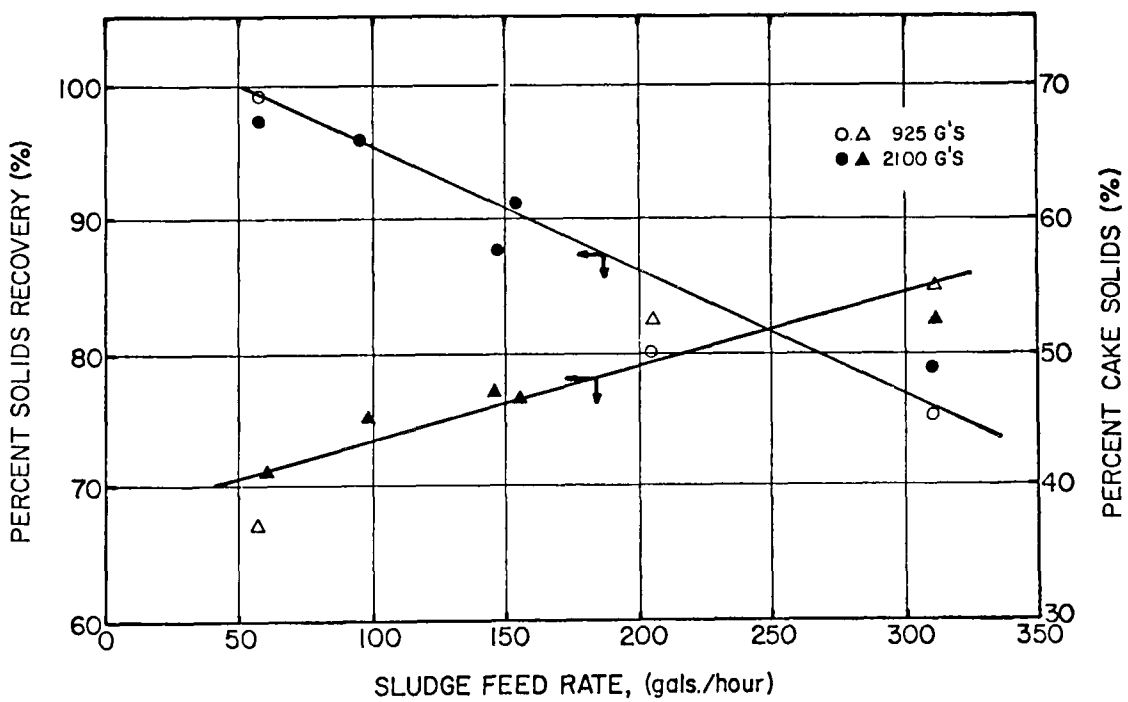


FIG. 5. PERFORMANCE OF PILOT SOLID-BOWL CENTRIFUGE (REF. 9)

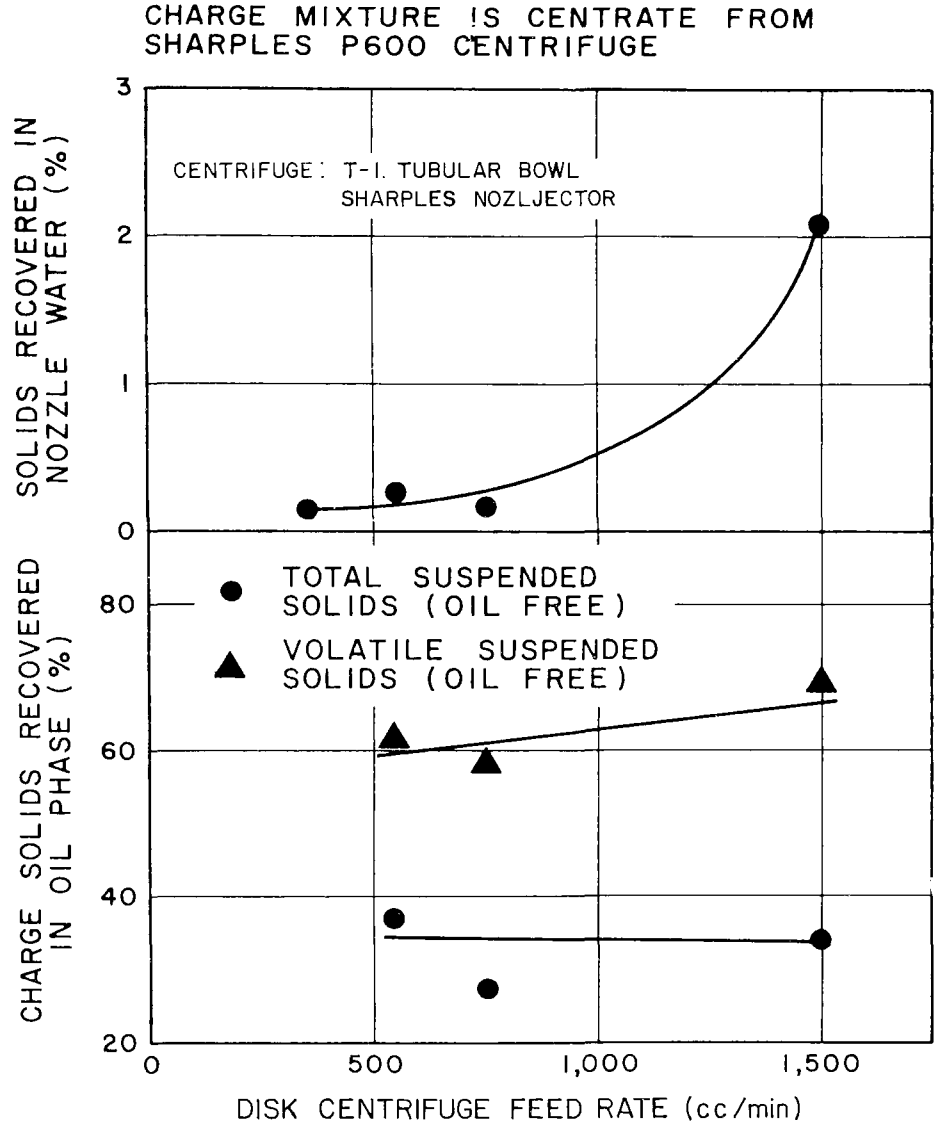


FIG. 6. SOLIDS RECOVERY FROM A SECOND-STAGE DISK CENTRIFUGE (REF. 10)

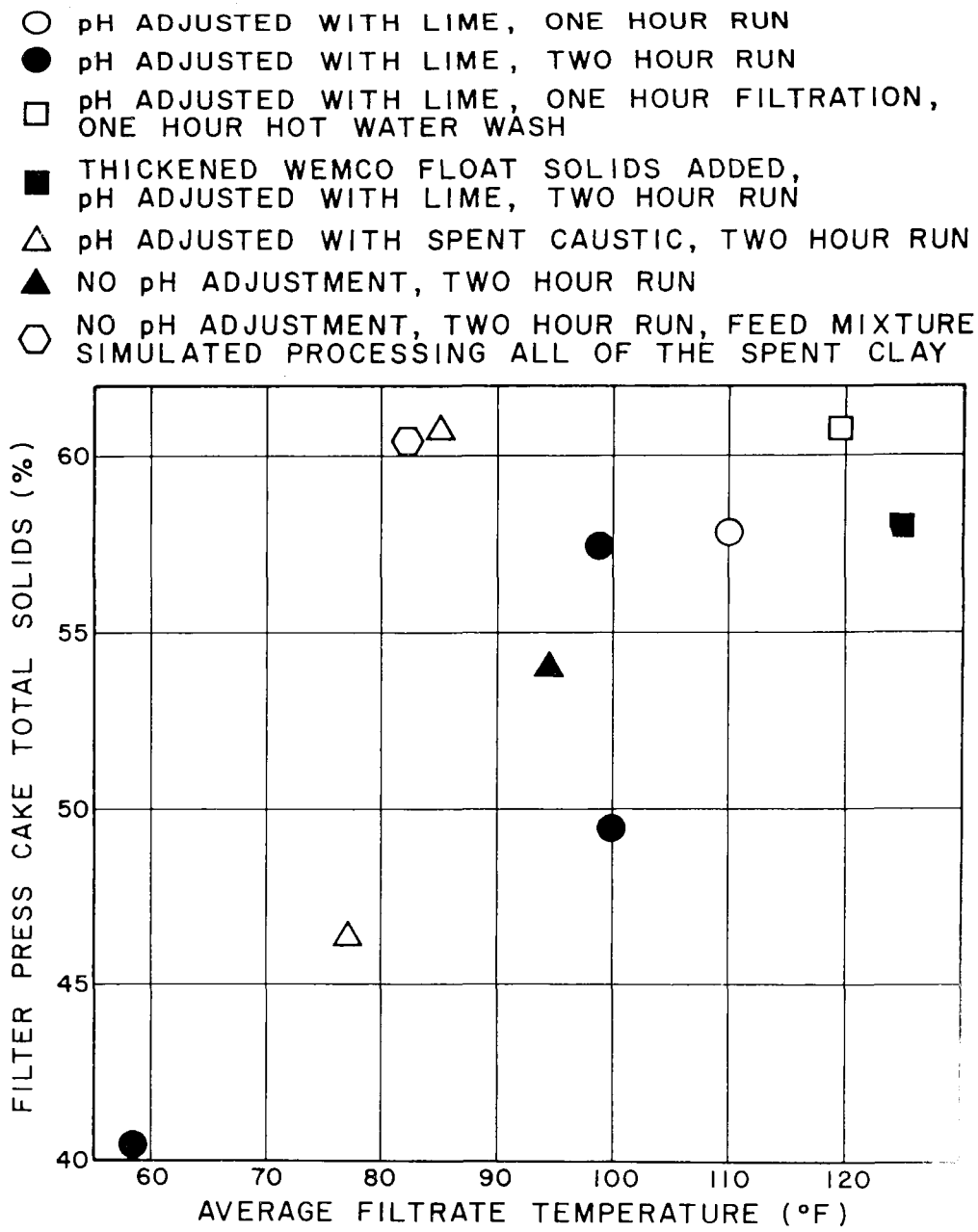


FIG. 7. EFFECT OF FILTER PRESS OPERATING CONDITIONS ON CAKE SOLIDS (REF. 10)

BASIS: FUEL OIL COST = $ 3.60 / F.O.E. BBL
GROSS HEATING VALUE OF OIL = 18,500 BTU / lb
DENSITY OF FUEL OIL = 7.35 lbs / gal.
STACK TEMPERATURE = 800°F AND EXCESS AIR = 100 %
GROSS HEAT REQUIRED FOR WATER EVAPORATION = 2400 BTU/lb

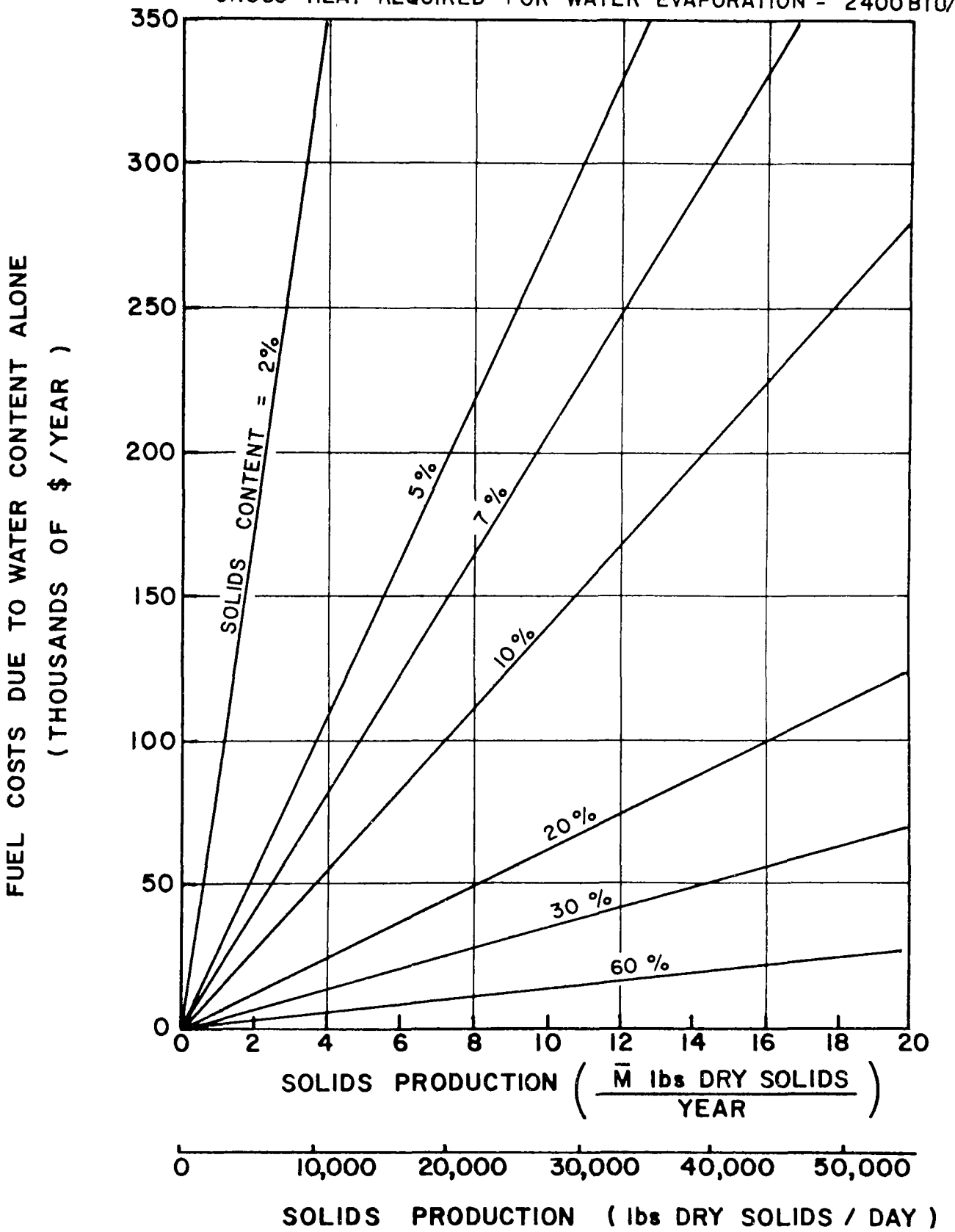


FIG. 8. INCINERATOR FUEL COSTS DUE TO SLUDGE WATER CONTENT ALONE (REF. 10)

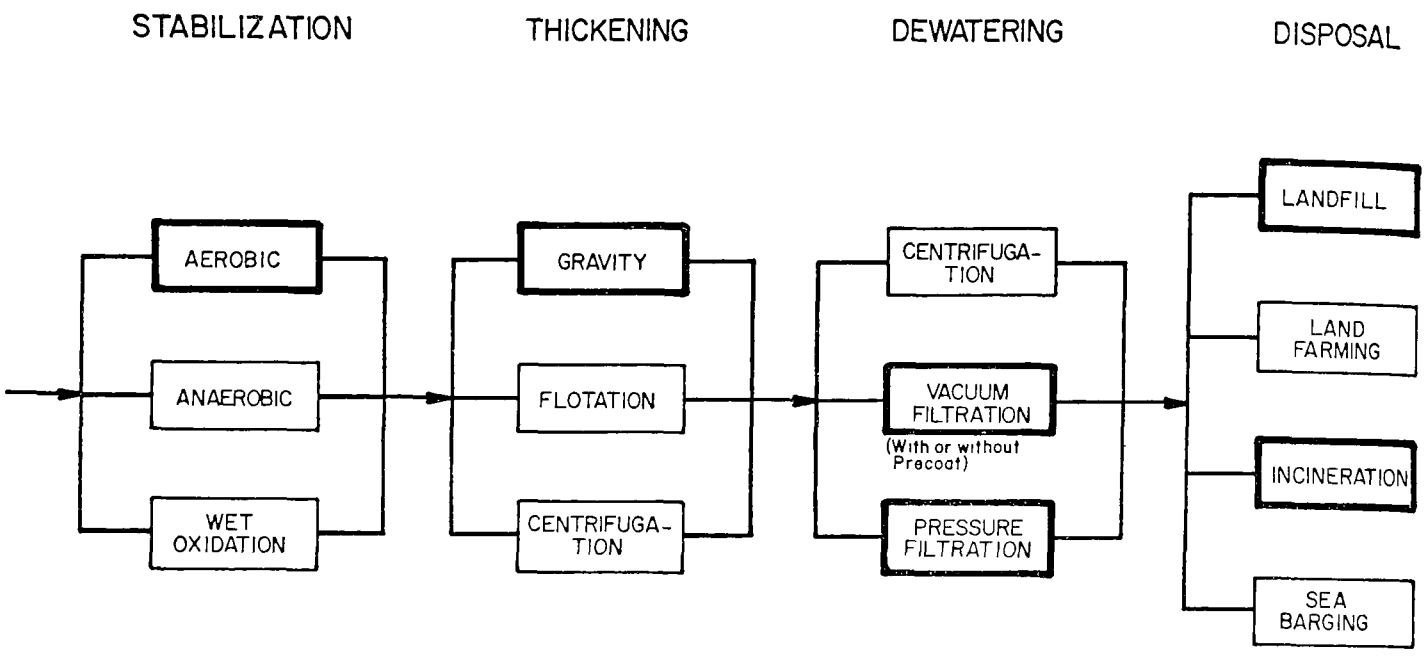


FIG. 9. BIOLOGICAL SLUDGE HANDLING ALTERNATIVES

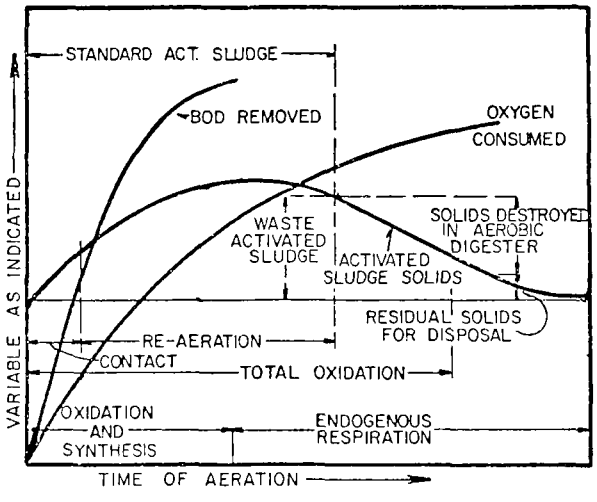


FIG. 10. SCHEMATIC DEPICTION OF AEROBIC BIOLOGICAL TREATMENT

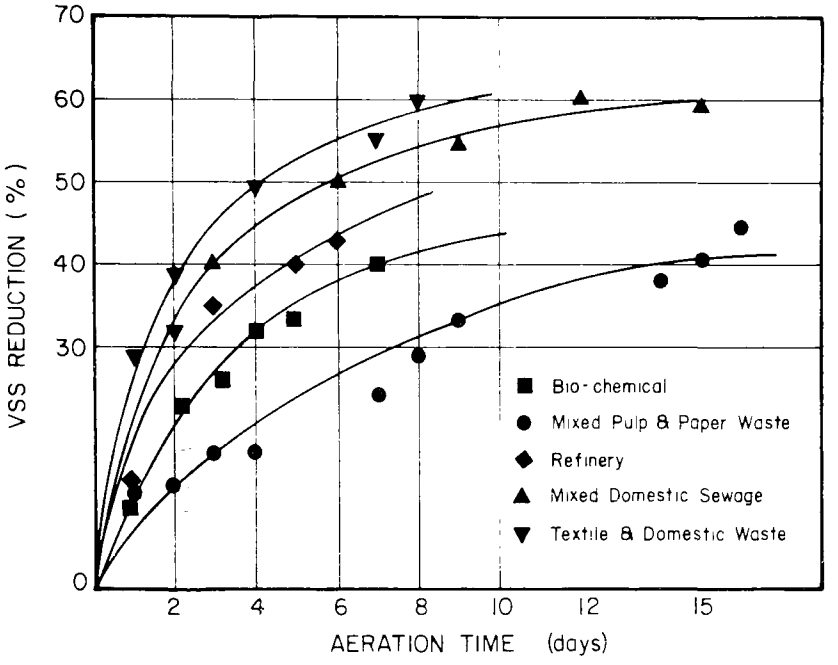


FIG. 11. TYPICAL VOLATILE SOLIDS REDUCTIONS BY AEROBIC DIGESTION

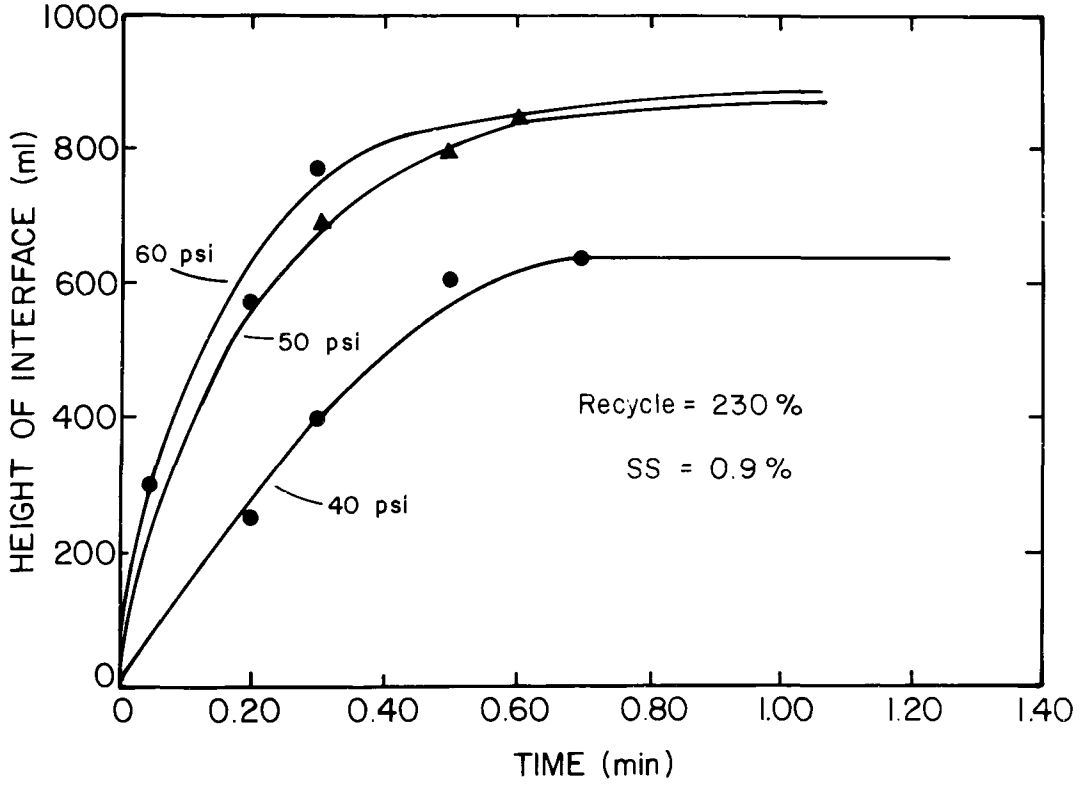


FIG. 12. RISE OF SLUDGE INTERFACE WITH TIME

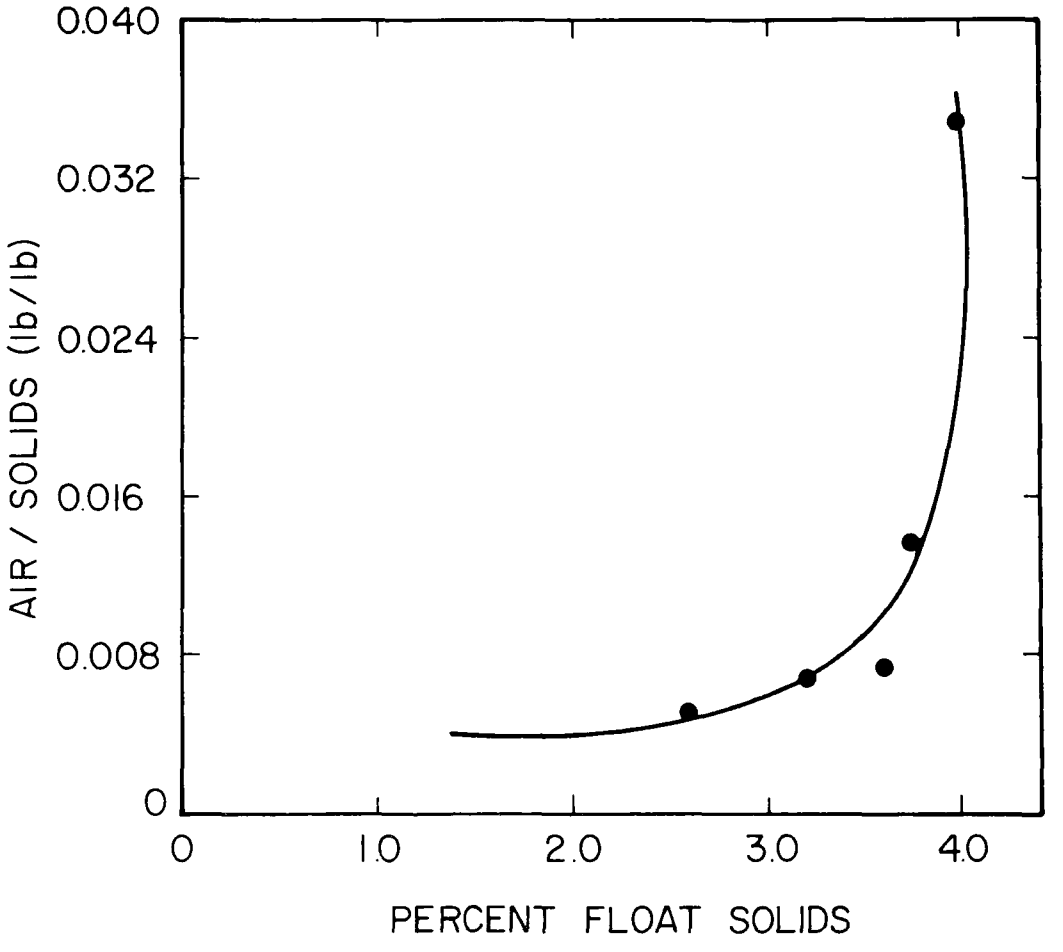


FIG. 13. DETERMINATION OF OPTIMUM AIR/SOLIDS RATIO (REF. 3)

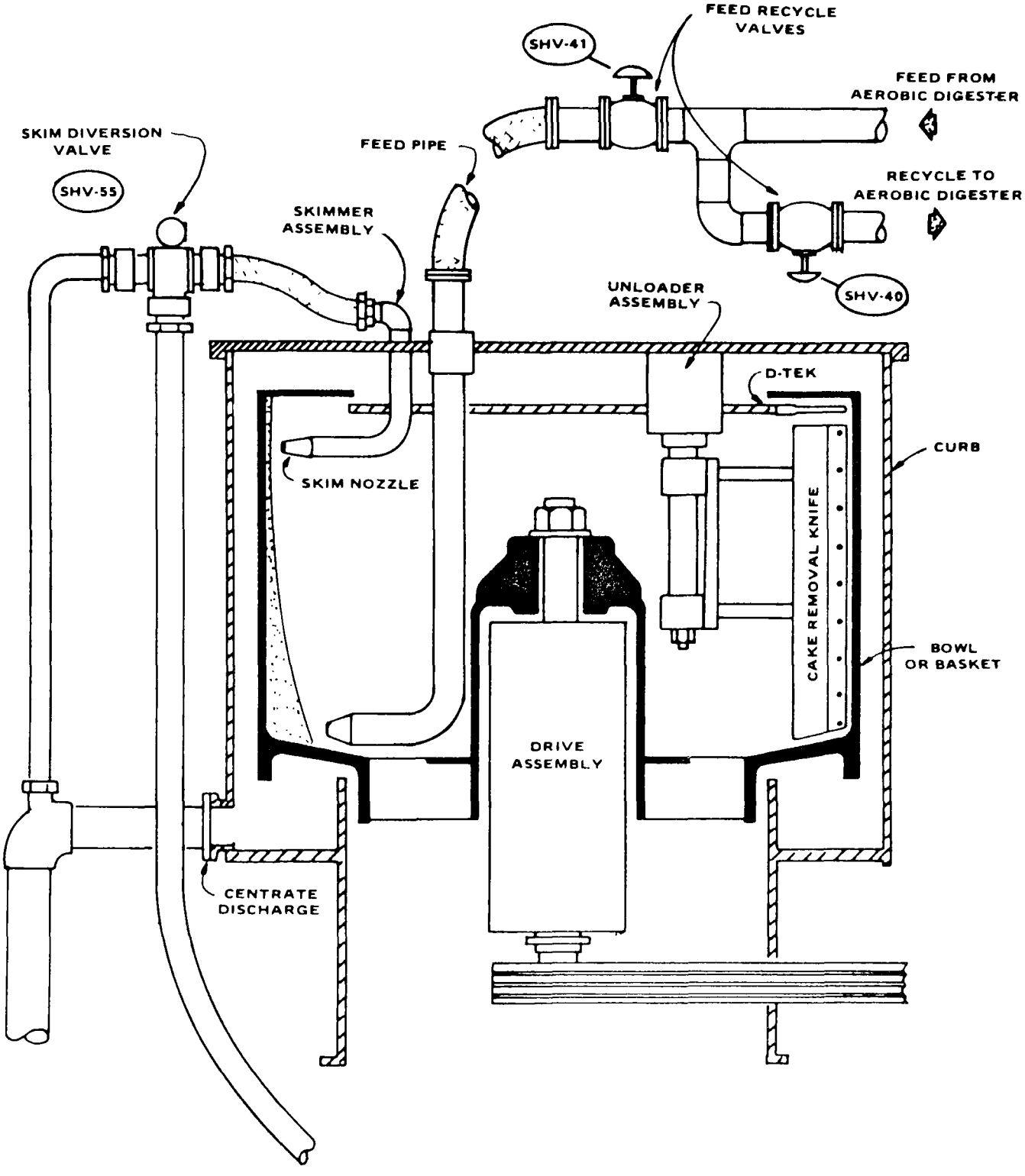


FIG. 14. INTERNAL COMPONENTS OF BASKET CENTRIFUGE

FIGURE A.

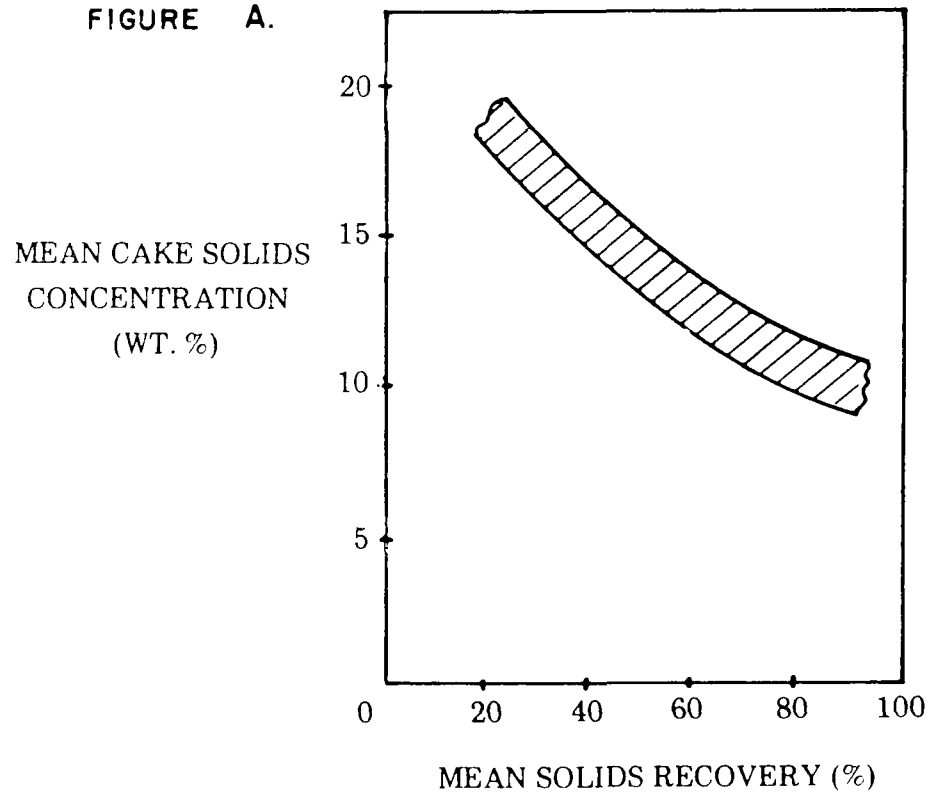


FIGURE B.

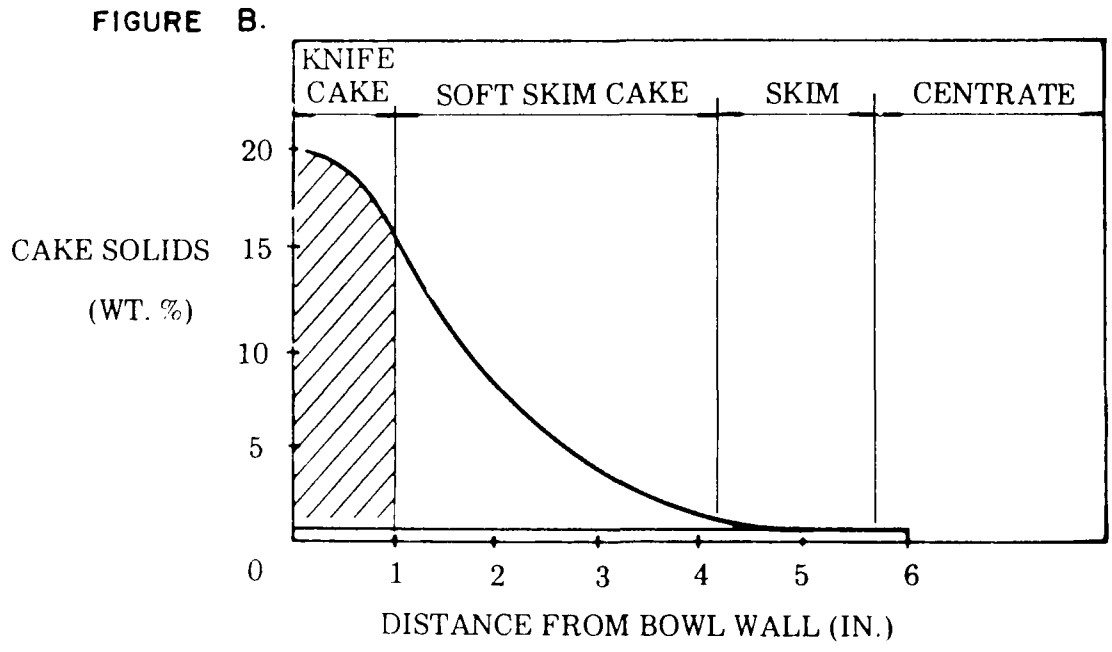


FIG. 15. PERFORMANCE OF BASKET CENTRIFUGE ON REFINERY BIOLOGICAL SOLIDS (REF 6)

PROCESSING OF WASTE OILY SLUDGES

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INTRODUCTION

Petroleum crude oil, fuels, and lubricants become waste components when emulsified with water, solids, and/or debris and are potential contaminants of surface and subsurface waters. The volume of oily waste is potentially large due to large quantities of petroleum oils handled and used. Sources of the waste are from spillage of crude oil and refined products and from petroleum refinery operations. This paper deals with the refinery operation, but the findings are expected to be applicable for most petroleum sludges. The title of this paper needs some clarification because the use of the word "sludges" is all-inclusive-oils, emulsions and sludges will all be treated as an umbrella topic.

SOURCES

Almost all operations of the petroleum industry, including exploring, producing (extracting), storing, transporting, and refining of crude oil and the storing, distributing, and handling of products are potential sources of oily sludges.

Accidental spills of crude oil and petroleum products during the handling, storing, and transporting operations are the principal cause for the formation of oily sludges in large quantities. At refineries, accidents seldom cause oily sludge production. Common sources are incoming crude oil, ship ballast water, tank and vessel cleanings, oil-water separators, and numerous miscellaneous sources such as sewer boxes and emulsion breaking facilities (demulsifier). The quantity of oil sludge for disposal at a refinery does not depend only upon the nature of the crude and processing units. Oily sludge formation can be minimized by prudent operating practices, sensitive attitudes and suitable control methods. Generally, most of the oily sludges accumulate in oil-water separators and in tank bottoms.

Crude oil shipped to the refinery contains emulsified material which is commonly referred to as bulk, sediment, and water (BS&W). The BS&W concentration in the crude oil ranges from about 0.01 to 0.1 percent by volume (%v). This BS&W fraction contains about 30%v oil, 50%v water, 10%v carbonaceous matter, and inorganic salts equivalent to about 10%v. The carbonaceous material which is the part of BS&W that could eventually become oily sludge for disposal, amounts to about 0.005 percent of the incoming crude oil to the refinery. However, in the refining steps, much of this carbonaceous material is utilized into fuels. The quantity of waste sludge from crude oil is small for the following reasons: 1) Crude oil receipts at a refinery are often stored in tanks for a few days before being fed to processing units. During quiescent periods, most of the BS&W material settles out as tank bottoms and is removed during tank cleanings at three to five-year intervals. Fortunately, tank bottoms have been in demand for oil and wax recoveries by independent operators and for road bed additives. When crude tank bottoms must be handled at the refinery, a concentration step is possible with conventional slop oil

demulsifying facilities. The BS&W emulsion is broken and some of the carbonaceous material is included with the recovered oil phase and some with the water phase. The recovered oil phase is fed to a refining unit and the water phase flows into an oil-water separator. 2) In the event a settling time is not possible, the crude oil containing BS&W material is fed to a crude distilling unit. The BS&W material is removed in the pretreatment (heater and desalter) section of the distilling unit. The oil fraction of the BS&W remains in the crude. Water fraction in the desalter effluent flows into the feedwater stream of an oil-water separator. Emulsified materials in the oil-water separator will either enter the recovered oil stream, settle with the bottom sludge inside the separator box, or remain in the water phase flowing to secondary treating facilities.

Ship ballast water-handling facilities vary at different refineries as does the quantity and quality of both the water and oil phases of the incoming ballast water. Ballast water may be fresh water, salt water, or a mixture of the two. Salt water is usually clean with respect to suspended solids, whereas fresh water of the surface category, such as that obtained from a large river, may contain large amounts of silt that will become deposited in the tanks of vessels. In addition to silt, ballast water may contain finely divided rust and precipitated chemicals used in tank cleaning. The oil contained in ballast water will range from gasoline to heavy cracked fuel oils.

Ballast water that is discharged from gasoline or light-distillate oil tanks will contain little oil until almost all the water has been pumped out. On the other hand, ballast water that is discharged from a tank that contained heavy fuel oil may have oil dispersed throughout the entire volume. This is also true of the emulsion from tank cleaning.

Tank bottoms obtained during cleaning of tanks vary in composition and the residual oil content can usually be recovered or at least reduced with emulsion breaking facilities. However, the real bottoms and final washings from a tank are often oily sludges not suitable for feed to a demulsified unit and are potential feed for the soil cultivation process.

Oily sludge from oil-water separator and holding pond cleanings is usually low in oil content. The sludge cleanings from the water box or pond usually contains about two percent carbonaceous material. Oil box cleanings which are mostly oil can be fed to the demulsifying unit, but sometimes mixtures of oil, straw, grass, and dirt make this material suitable only for disposal.

Solids and oily waste at the demulsifying unit usually accumulate in tanks which must be cleaned occasionally, and these cleanings cannot be further improved with additional treatment in demulsification facilities.

Process unit shutdowns include complete cleaning of a piece of equipment and/or vessel before maintenance work begins. In the shutting down of a process unit, oil is returned to storage. Immediately after shutdown and where possible, the equipment is washed with water which removes residual traces of oil and carbonaceous material. This material is sent to an oil sewer which connects to an oil-water separator.

Many refineries will require additional oil and suspended solids removal by pretreatment processes in order to meet process requirements of subsequent treatment stages. The quantity of additional oily sludge produced can be estimated based on material balances for the suspended solids removal process such as air flotation. The additional oil solids production as shown in Table I was estimated based upon median TSS removals by the air flotation process at median flow rates. Median suspended solids removal for all classes of refineries was indicated to be 15.3 pounds per thousand barrels of crude. The total oily sludge production was estimated based on the sum of the oily sludge production without additional oil and TSS removal equipment and the oily sludge production anticipated for dissolved air flotation. Total oily sludge production as a function or refinery size is indicated in Figure I.

Stating the sludge production in another fashion, it can be expected that the waste sludge from API separators plus the usual secondary treatment facilities will contain 1,500-6,000 pounds of dry solids per million gallons of effluent treated. The wet sludge composition will be approximately 1-3 wt.% dry solids, 10-30 wt. % oil, and 65-90 wt. % water.

On an average sludge composition basis of 2 wt. % dry solids, the flow or accumulation of wet sludge will therefore by 75,000-300,000 pounds per million gallons of effluent, or about 0.9-3.6 vol. % of the effluent (Rabb states the range to be 1.5-4.0 vol. % of the effluent).

Weston, Merman, and De Mann report 1,500 pounds of dry solids per million gallons of effluent from API separation plus chemical coagulation. They also report a range of 120-710 for API separation along.

For an existing refinery, the quantities and compositions of oily sludge are attainable by records and measurement. For the design of a new grass roots facility, these items must be estimated. As long as reasonable allowances are made for conservative design, the exact compositions are not very critical. It is highly unlikely that any such estimate would be duplicated precisely in real life.

The compositions shown in Tables II-V are from the API Manual on Dispoal of Refinery Wastes, Volume VI, Solid Wastes, 1963.

There are other oily sludges generated in refineries which may be classified as oily but usually require special consideration in handling and disposal. Typical among these are sludges generated in Tetraethyl Lead Gasoline Blending Operations and Hydrofluoric Acid Alkylation Processing. Oily sludges generated from these and other exotic operations must of necessity be segregated and handled separately because of their toxicity and other environmental hazards.

TRANSPORT AND HANDLING

Precaution should be taken in any wastewater collection and treatment plant design to minimize pumping where both oil and water are present together. One of the most difficult processes to run successfully is the breaking of oil-water emulsions.

Care should be taken during the design phase of a project to minimize pumping before the one constituent (oil or water) is removed by gravity or other separation.

If at all feasible, process wastewaters containing oil should drain by gravity into the API or other type oil-water separators. This will preclude the possibility of creating excessive amounts of emulsion. Oily water, if it must be pumped at all, should be pumped utilizing screw type lift pumps or low RPM open-impeller centrifugal pumps. Any mixing of chemicals with oily water should be accomplished using the lowest RPM mixing speed which will perform the task. An example of this concept is the chemical addition of alum and/or polymer before dissolved air flotation.

Oily sludges from separators, tanks and other sources are frequently quite viscous and can contain sand, gravel and other large particles. Screw pumps or positive displacement pumps are to be preferred for this type of service.

PROCESSING METHODOLOGY

Oily sludge processing techniques include emulsion breaking, gravity, separation, centrifugation, filtration, and incineration as shown in Figure 2.

Emulsion Breaking

Refinery emulsions may be defined as intimate, two-phase mixtures of oil and water with one phase dispersed as minute globules in the other phase. The minute globules are stabilized by an interfacial film or stabilizing agent such that the globules do not coalesce and do not respond to gravity settling.

Emulsions usually are complex, and emulsion technology is, at best, only quasi-scientific. Generalizations are risky, and trial-and-error experimentation is essential. For a systematic approach to emulsion problems, emulsions may be characterized by:

a. Dispersed phase, as oil-in water (O-W) or water-in-oil (W-O).
b. Dual O-W and W-O emulsions.
c. Stability, as measured by change with time of the dispersed phase particle size analysis and/or a time-separation study.
d. Type of interfacial film:
   Anionic - acid stable or acid sensitive.
   Cationic - alkali stable or alkali sensitive.
   Nonionic - hot-alkali stable or hot-alkali sensitive.
e. Degree of success in emulsion breaking according to process, e.g., physical methods - heating, distillation, centrifuging, or filtration.

Improper treatment of either O-W or W-O emulsions may invert the emulsion to the opposite type.

The most satisfactory theory of emulsions, which can also account for dual emulsions, inversion of phases, and effects of a wide range of emulsifiying agents,

is one which emphasizes the nature of the interface between oil and water. An interfacial film, which is a complex mixture of dissolved and colloidal matter and suspended solids, generally is understood to exist. Such an interfacial film may be highly viscous, gelatinous, and/or possess an electrical charge. Some experimenters consider the interfacial film as a third phase. Generally, the stability of an emulsion is not a function of the degree of dispersion; rather, it is a function of the stabilizing agents and properties of the interfacial film, such as film viscosity and electrical charges. This is illustrated by the following major factors which affect emulsion stability - four out of five of these factors being directly related to the interfacial film:

a. A coherent, mechanically strong interfacial film.
b. An oriented unimolecular layer of emulsifying agent or tightly packed solid particles at the interface.
c. Viscosity of the continuous phase and of the emulsion.
d. Nature and amount of emulsifying agents.
e. Physical storage or historical conditions, such as temperature, agitation, and dilution.

Properties of emulsions of refinery waste control are best approached by understanding what generally contributes to the stability of an emulsion and, therefore, what can be done to cause an emulsion to become unstable and separate or "break". Treating from this point of view requires an understanding of causative emulsifying and stabilizing agents.

Substances which cause or stabilize emulsions may be classified as ionic or nonionic and, generally, are of a colloidal nature or consist of solid particles which are surface active. Hydrated gels or gums, soaps, sulfonated oils, asphaltic residues, waxes, silt, finely divided coke, and sanitary sewage solids typify the range of emulsifying agents encountered. Colloidal matter may be further classified as hydrophilic (waterside active) or hydrophobic (oilside active).

The important ionic emulsifiers are chemically active because of the active carboxyl, sulfonic, amine, of hydroxyl groups. Such compounds, singly or in combination with electrolytes, may readily result in a stable emulsion. When there is no chemical reaction between the electrolyte and emulsifying agent, the electrical charge that may exist on the dispersed globules in an emulsion has little significance in regard to stability or to type of emulsion.

The following rules generally apply for emulsion formation:

a. O-W emulsions are formed when soaps are colloidal in the water phase (hydrophilic).
b. W-O emulsions are formed when soaps are salted or precipitated from the aqueous phase.
c. Soaps partially salted out may form and stabilize either type emulsion.
d. Electrolytes favoring O-W emulsions are salts of univalent cations and salts of di- and trivalent anions.

e. Electrolytes favoring W-O emulsions are salts of di- and trivalent cations.

One approach to emulsion breaking is to counter-balance emulsifying agents of one type of emulsion (W-O or O-W) with one of the opposite type.

Methods for emulsion breaking can be grouped into physical, electrical and chemical. Each is briefly described below. Frequently, the system used in any particular refinery will include more than one combination of these methods.

Physical Methods

Heating

The process of heating emulsions to obtain a break is the simplest and most economical approach available; the use of heat is nearly always advantageous. Heat markedly reduces the viscosity of the oil phase, melts interfacial waxy films, and, in some instances, weakens the interfacial films of various emulsifying agents. Coalescence and separation of the oil and water phases can then take place.

For W-O emulsions, heat increases the vapor pressure of the water which tends to rupture the films around the globules. The formation of steam within the globule generally will break a W-O emulsion, but the rate of steam generation must be controlled to avoid excessive foaming.

A heat-and-pressure system may be used to break many types of emulsions. The emulsion is heated in a suitable pressure vessel wherein water and sediment are precipitated. Adjustment of the pH by addition of acustic or acid may help facilitate the breaking of an emulsion with heat. There appears to be no general rule to serve as a guide in determining optimum pH. This is a situation where trial by experiment is the best solution.

Distillation

Distillation methods for breaking emulsions are effective in that they involve the use of heat as described previously. In addition, water and light ends of the oil are removed as overhead products, and the emulsifying agent remains with the residue.

Centrifuging

Comparatively stable mixtures sometimes may be separated by centrifuging. If there is a difference in specific gravity between the oil and water, centrifugal force may be used to accelerate separation. Loosely occluded water is readily separated from oil or emulsion by centrifuging.

Precoat Filtration

Stable W-O emulsions, particularly those stabilized by finally divided solids, can be resolved by filtration. Rotary vacuum precoat filters are commonly used for this purpose. In this operation, the emulsion is filtered through a layer of diatomaceous earth deposited on a continuously rotating drum filter. The suspended solid material and as a result of removing the stabilizing of the precoat layer during that portion of the cycle in which the drum is submerged in the material being filtered. During the

remainder of the cycle the filter cake and precoat are dried. A knife edge advances automatically into the precoat layer to a predetermined depth for each revolution of the filter drum, thereby removing the sediment deposited on the precoat layer along with a very thin layer of the precoat material.

The breaking of eumlsions occurs as a result of rupturing the globules in the dispersed phase when passing through the interstices of the filter cake and precoat material and as a result of removing the stabilizing solids. The oil and water phases of the filtrate readily separate by gravity difference. These phases may still contain dissolved emulsifiers. If so, care should be taken to prevent the re-formation of the emulsions by excessive turbulence or mixing before separation of the oil and water layers.

Electrical Methods

Some emulsions can be broken under the influence of a strong electrical field by application of the principle of the Cottrell precipitator. The emulsion is passed between two electrodes and subjected to a high-potential pulsating current. The water globules are attracted electrically and coalesce until the masses are of sufficient size to settle by gravity. This method is used in the dehydration and desalting of crude oil.

Where electrical desalting is used for treating crude oil feeds, some emulsions may be blended along with the regular crude oil charge. Emulsions can sometimes be blended at rates ranging from 1 to 10 percent of the crude oil charge if the water and sediment contents of the combined mixture are not too high. Before attempting to dispose of emulsions through a crude oil desalter, consideration should be given to the possibility of cracked material in the slop oil throwing virgin products from the crude oil unit off specifications. Equally important for consideration are emulsifiers in the slop oil that might throw the oil or water from the desalter off specification.

A combination of electrical and chemical methods is frequently successful where neither method alone is effective.

Chemical Methods

Emulsions can be broken by chemicals which will balance or reverse the interfacial surface tension on each side of the interfacial film, neutralize stabilizing electrical charges, or precipitate emulsifying agents.

Anionic and cationic surface-active agents are not compatible and will tend to neutralize each other. Rules for breaking emulsions stablizied with electrolytes are:

a. Reactive anions, such as OH^- and PO_4^{-2}, will break W-O emulsions.
b. Reactive cations, such as H^+, Al^{+3}, and Fe^{+3}, will break W-O emulsions.

The use of a heavy metal salt to form a flocculent precipitate of a heavy metal hydroxide to break dilute O-W emulsions is typified by the flocculation process. The resulting clarification or emulstion breaking is believed to result from

destruction of the emulsifying agents by neutralizing or reversing interfacial-film electrical charges and, in turn, by agglomeration of the precipitated floc and adsorption of suspended oil matter on the floc surface.

Any wetting agent will break a W-O emulsion provided the agent is effectively surface-active on the waterside of the interfacial film and a certain critical amount is not exceeded. An example of the use of a surface-active chemical to break an emulsion is the use of a detergent to break an asphaltic, solids-stabilized W-O emulsion by causing water to wet the solid preferentially - thereby displacing the loosely adsorbed asphaltic emulsifying agent.

Effective organic chemicals for breaking W-O emulsions generally have either an inorganic group (phosphate) or a reactive group (such as OH^- or $-NH_2$) and have at least three focuses of polarity occurring in different terminal groups.

Organic chemicals used in breaking W-O emulsions should:

a. Be soluble in both phases, i.e., the treating chemical contains both hydrophilic and hydrophobic groups.
b. Form an adsorption complex with the predominantly hydrophobic emulsifying agent present thereby creating a hydrophilic complex that can be wetted by water.
c. Contain one or more radicals able to react with calcium (Ca) or magnesium (Mg) salts in the aqueous phase and result in insoluble salts that are wetted by water.

In general, the dewatering of recovered oil or breaking of recovered oil emulsions in refinery practice is a series of batch operations involving several stages of water and solids removal. The simplest system consists of holding tanks operated on a batch basis, usually with the addition of heat and use of recirculation. However, both cold and hot settling are used, with cold settling time varying from one day to four weeks, and hot settling time usually varying from one to three days at temperatures in the range of 150 F to 200 F.

At the end of each stage of treatment, substantially oil-free water is drawn off and returned to the refinery separators and low-water-content oil is decanted and returned to the refinery for reprocessing. In most cases, a layer of emulsion remains after these separations. This emulsion is generally given further treatment. The methods used vary widely and are usually adaptations of the mthods described earlier in this chapter.

The dewatered oil may be charged to crude oil units, with or without desalters; to thermal or catalytic cracking units; to coking units; to visebreakers; or to separate distillation units. Water content of recovered oils fed to crude oil units or separate distillation units may run as high as 2 percent, but the water content of recovered oil fed to the other types of units is generally limited to 0.3 to 0.5 percent.

The following figures 3 and 4 illustrate a rather simple continuous process for breaking emulsions emanating from storage tanks and a rather sophisticated process for de-emulsifying all refinery-wide sources.

Gravity Sedimentation and Phase Separation

The processes of gravity sedimentation and phase separation combine the effects of specific gravity, viscosity, and time to provide for the separation of substances of different densities. Conical bottom vessels are utilized for most applications, especially where a continuous drawoff or a concentrating effect is desired.

Centrifugation

The use of centrifugation permits the mechanical dewatering of sludges through centrifugal force. Dewatering by this method may be defined as sedimentation under the influence of forces greater than gravity. Within a centrifuge, centrifugal force acts on a suspended particle in the sludge, causing it to settle through the liquid. It would seem logical to design machines for maximum centrifugal force, but this is not the only consideration. While additional centrifugal force helps settle solids, it also increases the difficulty of discharging the settled solids. Thus, for maximum efficiency, a compromise must be made.

Several variables which affect gravity sedimentation also effect sedimentation within centrifuges; these variables are:

1. Particle size and shape,
2. Density differential between solid particles and the liquid,
3. Concentration of the particles, and,
4. Liquid viscosity.

Sludge solids in suspension are a combination of granular, fibrous and flocculent particles. Granular particles in dilute solution are generally considered to settle at terminal velocity, independent of one another, and without change in size or shape. When the particles become concentrated however, volumetric considerations predominate and the observed settling velocity appraoches zero. Flocculent and fibrous particles do not settle at a constant velocity since they tend to cluster during sedimentation, bringing about a continuous change in size, shape, and relative density. Extremely fine particles which may not settle under normal gravity separation can be made to settle by increased gravitational forces. In general those sludges which spearate most readily and concentrate to the greatest degree by sedimentation are also those which are dewatered most efficiently by centrifuges.

Two of the major types of centrifuges in industrial use today are the solid bowl and the basket type. These two types may be used singly or in combination to remove solids from solution. When used together, flow is first directed to the solid bowl centrifuge where the large solids are removed and then to the basket type centrifuge where finer solids are removed and emulsions broken due to the higher centrifugal forces in this unit. The solid bowl sludge dewatering centrifuge assembly consists of an outer horizontal cone (bowl) and an inner screw conveyer, each rotating at slightly different speeds. Sludge is fed to the centrifuge through the central screw and enters the bowl about halfway along the side of the cone.

Centrifugal action forces both liquid and solid phases to the walls of the cone and down the cone to the large end, where water in the top layer of the liquid pool is drawn off. The solids, which accumulate closer to the wall, are conveyed by the screw to the small end of the cone where they are discharged. Turbulence due to the screw, limits the solids concentration obtained, and maximum solids concentrations from this type centrifuge are normally in the range of 5-10 percent.

As opposed to the continuous operation of solid bowl centrifuges, basket type centrifuges operate on a timed cycle. The units resemble the rotating tub of a spin dryer used in home laundering with the exception that the tub has a hopper at the bottom. Slurry is fed to the tub (basket) during the first portion of the cycle, and the spin of the basket creates centrifugal action up to 13,000 times the force of gravity which forces liquid and solids against the outer walls. Part of the liquid travels up the wall and solids layer and out over the top lip of the basket and into a discharge trough. According to a timed cycle, remaining liquid is then drawn off by a pipe which slowly moves toward the wall from the center of the basket. As the pipe approaches the wall, it begins picking up a concentrated solids slurry, and a valving change routes these to the bottom hopper. A new cycle then begins. After several such cycles, a hard solids layer accumulates near the wall and this layer is then removed with a knife edge at a slower rpm and these solids fall to the bottom of the hopper where they combine with the other concentrated slurry and are discharged. Using this type of centrifuge, overall sludge concentrations of 8-15 percent are possible.

The introduction of flocculation aids, such as polymers, has increased the range of materials that can be dewatered satisfactorily by centrifuges. The degree of solids removed can be regulated over a wide range depending on the amount of chemical coagulant used. Wetter sludges result from chemical aids because of the increased capture of fines.

Rotary Drum Vacuum Filtration

Vacuum filters are the most widely used type of mechanical sludge dewatering device. The filtration process is used to separate the solids from the liquid by means of a porous media which retains the solids but allows the liquid to pass through. Filter media employed include Nylon, Dacron, and Polyethylene cloth; steel mesh; or tightly wound steel coils. The types of rotary drum vacuum filters currently in use differ primarily in the way cake is removed from the drum. The filtration process is accomplished by means of a horizontal drum covered with the filter media. The drum is rotated in a tank with approximately one quarter or more of the drum submerged in wet sludge. Valves and piping are arranged so that as the drum rotates a vacuum applied on the inner side of the filter media draws water from the sludge and holds the layer of sludge to the drum. The application of a vacuum is continued as the drum rotates out of the slurry. This pulls additional water from the sludge, leaving a moist cake of sludge on the outer surface which is removed prior to re-entering the tank. Cake is removed by a knife that moves on the filter drum as it rotates.

Precoats and filter aids are often used to speed filtration rates or collect more of the fine particles in the slurry. The precoat, usually diatomaceous earth, is a

finely divided, hard-structured solid that forms an open, noncompressible cake. When applied on the filter cloth, the precoat acts as the primary filter medium and permits high removal of fine particles from the slurry. A filter aid may also be mixed with the slurry where it becomes distributed throughout the cake, thereby keeping the cake relatively open for flow and continuously supplying a large surface for adhesion of finely divided solids. This method is particularly good when filtering colloidal solids that are not to be recovered from the cake.

Filter media may consist of cloth, paper, or woven or porous metal as mentioned before. Criteria on which a filter medium is selected must include the ability to remove the solid phase, high liquid throughput for a given pressure drop, mechanical strength, and chemical inertness to the slurry or any wash fluids. In operation, some filter cake solids usually penetrate the filter medium and fill some of the pores. In normal cases, five to 25 percent of the pore volume of the filter medium if filled with solids. As a result, resistance to flow through the medium increases greatly - in some cases to such an extent that the filtration rate is seriously reduced.

Properties which affect the vacuum filtration dewatering process include:

1. Solids feed concentration,
2. Sludge and filtrate viscosity,
3. Sludge compressibility,
4. Chemical and physical characteristics of the sludge,
5. Operating vacuum,
6. Drum rotational speed,
7. Drum submergence,
8. Type and porosity of the filter media, and
9. Effect of chemical additions.

Pressure Filtration

The filter press is the simplest of all pressure filters with the most widely used type being the plate-and-frame press. As the name implies, the plate-and-frame is an assembly of alternate solid plates, the faces of which are grooved to permit drainage. Between these plates are hollow spaces in which the cake collects during filtration. A filter medium, usually some sort of a fabric, covers both faces of each plate. As filtration proceeds, cake builds up on the filter cloths until the cakes being formed on each face of the frame meet in the center. When this happens, the flow of filtrate which has been decreasing continuously as the cake thickness increases, drops off rapidly. Usually, filtration is stopped well before this occurs. After the filtration sequence, the press is disassembled and the solids are collected either manually or mechanically and discarded.

Filter presses can be built for high pressures and can handle the filtration of either heavy or light slurries. The filter press has many advantages, the greatest of which are its simplicity, flexibility, and ability to operate at high pressures. A filter press, with proper operation, will produce a denser, drier cake (up to 60 percent solids) than any other type of filter. The sludge and filtrate properties which

affect the filter press dewatering process are the same as those for vacuum dewatering. The operation of separating waste oil from oily emulsion by means of a filter press opearated at elevated temperatures is being practiced. A process in which oily sludges are subjected to high pressure filtration enabled the oil to be removed in the form of a separable phase. This process produced a cake with a high concentration of solids and low concentration of oil which would be suitable for land farming. The cake produced by high pressure filtration contained very little volatile material which could be removed by incineration. Significant oil recovery in the process reduces the overall cost of the disposal. The economic incentive of recovering oil from oily sludges will increase as crude oil supplies become less available.

Incineration

A properly designed and controlled incinerator is satisfactory for burning combustible waste provided air pollution standards can be met. A high control temperature is needed for efficiency, prevention of excess air pollution, and odor control. Incinerators are readily adaptable to the disposal of virtually all oxidizable wastes, including streams which contain inorganic or other non-combustible materials. Combustible wastes which contain 10,000 BTU per pound or more can usually be incinerated without the requirement of an auxiliary combustion chamber. In some instances, where the heat value is less than 10,000 BTU per pound, it is possible to enrich the liquid waste with another fuel. Incineration is being used at many large plants where final disposal of the solid waste is a problem. It has the advantage of freedom from most odors, independence of weather conditions, and high reduction of the volume and weight of the end product to be disposed of. There is a minimum size of treatment plant below which incineration is not considered economical since there must be enough waste solids to warrant reasonable use of the expensive equipment involved.

CASE HISTORY

A major Gulf Coast Refinery is presently in the midst of a major process expansion program to essentially double their throughput and increase their ability and flexibility in processing a wider slate of crude oil, including high sulfur mid-eastern crudes. New facilities to be installed include Crude and Vacuum unit with Electrostatic Desalting, FCC, Hydrotreater, Gas Plant, Product Treating Plants and Sulfur Plant. Inherent in the design of new, additional processing facilities was an examination and evaluation of existing offsite facilities such as raw water and waste treating, steam generation and tankage. In conjunction with a consultant, a major program for modification of and addition to the waste treatment facilities was undertaken in order to assure compliance with both State and Federal discharge requirements. Concurrent with and as a part of this operation, an evaluation of the "oily sludge" sector of the plant operation was also performed. The following describes the history of this evaluation.

Old Facilities (Figure 5)

All oily wastes plus cooling tower blowdown water, boiler blowdown water, lime softener blowdown, and zeolite regenerant water were discharged to the oily sewer. The oily waste sewer discharged to an API Separator where gravity separation

of free oil and water was accomplished, followed by an air flotation unit, employing a cationic polymer as the sole chemical feed. The API effluent was sprayed to the atmosphere to accomplish cooling and was collected in a basin and discharged to two aeration basins connected in series. Aeration was supplied by a 15 hp aerator in each basin. The waste was discharged to a settling basis and thence to a lagoon. The lagoon discharged through a measurement weir to the ship channel.

All storm waters were collected and discharged to the second aeration basin for treatment prior to discharge to the lagoon.

Ballast water was pumped to a ballast water tank where oil was separated by gravity and discharged to ballast water holding basins and thence to the second aeration basin for further treatment prior to discharge to the lagoon.

Recovered oil from the API separator was sent to an emulsion breaking process and the resultant sludge from recovery was discharged to a sludge pond. The float from the air flotation unit consisting of sludge and some oil was also discharged to the sludge pond. Efforts have been made to recover this oil in the emulsion breaking process but the inclusion of the air float sludge rendered the process inoperable, probably due to the presence of calcium and magnesium salts in the air float sludge.

The sludge ponds did not dewater readily and removal and subsequent land disposal of the sludge had become a problem.

Due to the inclusion of highly alkaline boiler blowdown, filter backwash water, lime softener blowdown and softener regenerant waste, the pH of the API influent averaged 9.0. The average total steam load was 304,000 lbs/hr and at 10% blowdown, the discharge, at an average pH of 11.5, to the oily water sewer was 60 gpm, or 17% of the average volume input to the API Separator. In addition, the discharges from the lime softener, filter backwash, zeolite regenerant wastes as well as some spent caustics from the refinery process contributed to the high pH.

Since it is well known that high pH conditions tend to cause oil/water emulsions, the efficiency of gravity separation of free oil at the API Separator was impaired, reducing the quantity of recoverable oil at that point.

The inclusion of boiler water blowdown in the oily waste stream produced a softening effect within the oily waste system, resulting in a rather heavy precipitate. The average blowdown flow of 60 gpm or 715,000 lbs. per day was the equivalent to 114 lbs. of soda ash, 175 lbs. of caustic, and 44 lbs. of tri-sodium phosphate per day. The precipitate formed was removed as float in the air flotation unit contributing to the excessive sludge problem at this point, and prohibiting further recovery of oil. In addition, the oil adsorbed on the floc particles carrying over from the air flotation unit contributed to the oil content of the final effluent as did the emulsified oil due to the pH.

The emulsion breaking process operated very satisfactorily upon recovered oil from the API separator but could not handle the float from the air flotation unit due to precipitated calcium and magnesium salts.

Sludge from the emulsion breaking process and the float was discharged to the sludge ponds where after a period of dewatering it was mechanically removed and sent to land disposal. The sludge was very difficult to dewater due primarily to the air float sludge and the amount of rainfall and presented a difficult problem.

INITIAL RECOMMENDATIONS AND SYSTEM UPGRADING

The most economical and feasible point to accomplish more efficient oil removal and recovery was at the API separator. This could be accomplished by diverting high alkaline wastes from the oily waste stream to lower the pH of the stream entering the API separator to prevent emulsification of oil and achieve more efficient gravity separation of oil.

The diversion of boiler blowdown alone, which represented 17% of the flow volume to the API separator, would increase the retention time considerably to accomplish better gravity separation of oil.

A second beneficial effect of diverting alkaline waste streams was the elimination of precipitated calcium and magnesium salts which constitute the greatest part of the sludge volume discharged to the sludge ponds by way of float from the air flotation unit. Thirdly, the float, with the absence of precipitated matter, could be discharged to the emulsion breaking process for additional oil recovery. Of course, a prime benefit of diversion of the alkaline wastes would be the reduction of emulsified oil content of the discharge to final waste treatment facilities and final outfall to the ship channel.

The reduction in sludge volume discharged to the sludge ponds would facilitate dewatering and ultimate final disposal.

The water treatment plant blowdown was diverted from the main process sewer and pumped into a holding pond. It was apparent immediately that oil recovery was more efficient and sludge and emulsion formation less severe. However, due to the project timing and financial considerations, it was decided not to try to recover oil from either the API sludge or DAF float. This would be attempted when the expansion was complete and more permanent facilities installed.

NEW REFINERY SYSTEM

Waste Oil

The refinery has been treating waste slop oils and emulsions in the following manner - that is, place the slop oils into 500 BBL tanks, heat, add a chemical, and cool. Emulsions were easily broken and oil and water were separated. The oil was returned to the crude units and the water was recycled to the waste treating unit.

This method was very successful excep that during the hot summer months the two existing 500 BBL tanks were sometimes overloaded due to insufficient cooling. The operating cycle was as follows:

1. Fill tank and heat to 130-160°F - this required 4 to 7 days.
2. Cool tank - 4 to 5 days (Atmospheric Cooling.)

With only two tanks and periods of high oil loadings, a tank that has not sufficiently cooled may need to be drained so that it can be refilled. The warmed drainage was usually not completely demulsified.

For the expanded refinery, the following treatment of the waste slop oil was proposed.

1. Results of the tests by local waste water treatment chemical vendors indicated that cold settling of oily water emulsions did not result in demulsification.
2. Add four 500 BBL tanks with mixers, heating/cooling coils and sloped bottom for treating slop oil. Separated oil from these tanks could be pumped to existing slop oil tanks for surging prior to pumping the oil back to the crude unit feed tanks.
3. During periods in which excessive amounts of slop oils were collected, the existing slop oil tanks could be converted back into demulsification treating service.

Oil Sludges

The refinery was treating their sludges in the following manner. Both API bottom sludges and air flotation skimmed material were sent to sludge pits where the oily solids settled. The oil and water overflowed to second and third pits. The water was recycled to the air flotation unit and oil routed to slop oil treating. The thickened sludge was pumped to another pit for drying. This method worked satisfactorily. However, the new waste water treating facilities would be constructed in the same area that the existing sludge pits are now located, therefore an intermin and permanent solution to the disposal of waste solids was required.

Two disposal alternatives for oily solids were compared in order to determine the most cost effective method of waste solids disposal. The projected waste oily sludge inventory is shown in Table 6 and a mass balance diagram for oily solids is given in Figure 6.

Alternate No. 1 - Contract Disposal

The bottoms from both gravity oil separators would be combined in a cone bottom 500 barrel tank with the air flotation skimmings being stored in another identical tank. The separator bottoms will concentrate to approximately 15% solids and the skimmings will concentrate to approximately 3%. After emulsion breaking decant oil from the tanks would be routed to the slop oil system, oily water to the old area API, and sludge to contract disposal.

Contract Disposal Site: A 60 barrel vacuum truck would be needed at approximately two week intervals, to haul sludge to a disposal site. Since tank bottoms and oily sediment will be removed intermittently, it was assumed that a 110 barrel vacuum truck would be used for hauling direct to a disposal site. Current

vacuum truck rates are $17.50 to $23.00 per hour, and 4 hours per load was used to estimate hauling costs. The estimated capital cost and yearly operating cost is indicated in Figure 7 based on the project waste solids volumes given earlier.

Alternate No. 2 - Incineration and Landfill

The separator bottoms, air flotation skimmings, oily sediment, and tank bottoms would be stored in a 1000 barrel tank before being charged to the incinerator. Although variation in the oil content is expected, an oil content of 10% was used for estimating purposes. An average solids concentration of 4% was used for the estimate. The cost considerations of incineration can significantly influence the processing steps required. The major factors are fuel costs, loss of oil recovery potential, and the capital cost of the incinerator. The principal parameters which determine the above costs are solids production rate, water concentration, and oil concentration. Due to the complexity of incinerator design and the absence of data, the cost for incineration was based on data from similar systems at other refineries. The capital and operating costs are shown in Figure 7.

On the basis of the preceding discussion and preliminary cost estimates the most cost effective temporary solution to solid waste disposal at the refinery is to continue the practice of contract disposal of oily solids following thickening. It must be recognized that the proposed system is not the ultimate solution to the refinery's waste solids problems. However, the proposed system is a prerequisite for most future ultimate solids dispoal systems.

The future of contract disposal sites is presently in doubt as is future regulations governing landfill and land farming operations. In order to determine the magnitude of the waste solids disposal problem at the refinery, the suggestion is made that the refinery initiate an investigation to determine the feasibility of combining the oily and biological solids and either incinerating the wastes or dewatering them prior to land farming or contract disposal. Also to be considered and, in fact, in progress is a program to reclaim oil from the sludge prior to dewatering and ultimate disposal. The study should commence after the expanded refinery is in operation and should encompass all solid wastes generated within the refinery. This recommendation is made on the basis of limited available land area. The fact that contract disposal costs will continue to increase must be recognized. It is suggested that it would be in the refinery's best interest to minimize dependence on off-site disposal facilities.

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DISCUSSION

Morris Wiley: You mentioned the problem of sludges from ballast reception. The 1973 IMCO convention is ultimately going to require shore reception facilities for all kinds of wastes from ships and from tankers in particular. There are really about four major categories of wastes. One of these is clean ballast from tanks that have been cleaned at sea with the Load-on-Top procedure, one is dirty ballast from tanks which haven't been cleaned, and one is the slop oil residue which is carried on board from Load-on-Top, and another is that some refineries accept the total tank washings without any overboard discharge from the vessel while at sea. But then the most troublesome kind of waste arises when the ship has to go into ship repair port. They have to get in and muck out the bottom of the tank and for a very large tanker this can run at a huge volume of unpumpable tank cleanings. Do you have a recommendation as to what to do with that type of sludge?

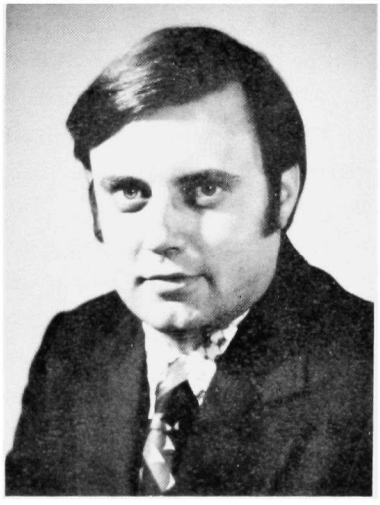
J. A. Scher: That is a difficult question for me to answer. I recognize the problem, in fact, even a lot of refineries don't have the proper facilities for handling the quantitites of sludge that are involved. I think you will find in the long run, in conjunction with the whole toxic material system sludges are going to be handled more or less on a regional basis. I think, and I am really speculating here, that the government is interested in handling these in a more uniform system. Of course, you are familiar with the toxic and hazardous materials legislation that is being generated and I understand there is a very strong possibility of regional waste management for sludges, etc. In the long run I think you will see a regional approach to taking these sludges to a central area for processing rather than trying to do them on individual basis, because it is very expensive and it is very difficult to do. As far as an individual facility like you describe it would be a very expensive proposition for them to put in a complete dewatering, oil handling, oil removal, sludge disposal system at a shipyard.

Morris Wiley: I think I would agree with that point but then there is a subsidiary question. If you are going to consider Baltimore harbor, for example, or New York or Philadelphia, there probably should be a regional sludge disposal facility, but the question would be should that facility be operated in conjunction with some other petroleum industry facility such as a refinery which would have a way of getting rid of any recovered oils from processing of this sludge or should it be a separate

authority which has no connection with the petroleum industry? The marine people would like to give it to the refineries and the refineries don't really want it. It is really an oil industry problem because they are carrying our materials.

J. A. Scher: This gets into the political sphere. I am not so sure the oil industry is going to operate these kinds of facilities, I don't think they want to operate these kind of facilities. I really don't know what the answer to that is. I don't know whether I can answer it and give you a very good answer but it is something I think is going to be approached on that type of a scale and who the operators and who the contractors are I don't know, I could speculate but I am just guessing.

Morris Wiley: I guess it is an open question, I am asking the question, but not really expecting an answer at this time.



BIOGRAPHY

Jacoby A. Scher is a Principal Environmental Engineer with Fluor Engineers and Constructors, Inc. in Houston, Texas. He holds a B.A. in Chemistry from Rice University and an M.S. in Environmental Engineering from the University of Houston. He is a Registered Professional Engineer in the State of Texas. Mr. Scher has been involved in the Industrial Waste Treatment Field for ten years and has been with Fluor since 1973.

TABLE 1 ESTIMATED OILY SLUDGE PRODUCTION FROM AIR FLOTATION TREATMENT

Refinery Class Class	Air Flotation Influent TSS (mg/1)	Air Flotation Effluent TSS (mg/1)	TSS Removal (mg/1)	Flow (gal/bbl)	TSS Removal (lbs/mbbl)
A	29.5	8.8	20.7	18.0	3.1
B	35.2	10.6	29.6	38.0	9.4
C	52.2	15.6	36.6	42.7	13.0
D	99.3	29.8	69.5	47.3	27.5
E	29.9	8.9	21.0	87.0	15.3
				MEDIAN	15.3

* Economics of Refinery Wastewater Treatment, American Petroleum Institute, 1973.

TABLE 2 COMPOSITION OF SLUDGE WITHDRAWN FROM OIL-WATER SEPARATORS

	API Units with Removal Equipment		All Survey Samples	
	Average (Percent by Weight)	Range (Percent by Weight)	Average (Percent by Weight)	Range (Percent by Weight)
Water	82.4	61.2 to 98.3	66.5	8.9 to 99.5
Oil	10.9	1.1 to 20.7	15.0	0.1 to 59.0
Volatile Solids	1.4	0.5 to 2.3	5.5	0.0 to 49.4
Ash	5.3	0.4 to 15.8	13.0	0.3 to 56.2

TABLE 3 COMPOSITION OF OIL-WATER SEPARATOR SLUDGES

(Water-Free Basis)

	Average (Percent by Weight)	Range (Percent by Weight)
Oil	46.0	9.4 to 81.5
Volatile Solids	14.7	0.0 to 54.3
Ash	39.3	2.3 to 85.3

TABLE 4 COMPOSITION OF AIR FLOTATION SLUDGE

(Alum Used as a Coagulant)

	Average	Range
Water removed by settling 1 hr, percent by weight	15	2.5 to 42.0
Froth analysis, percent by weight:		
Oil-free solids	3	1.0 to 5.2
Oil (by difference)	22	
Water (after settling 1 hr.)	75	60.8 to 90.1
Ash, percent by weight of solids	27	3.1 to 43.8

TABLE 5 COMPOSITION OF TANK BOTTOM SLUDGES

	Average (Percent by Weight)	Range (Percent by Weight)
Water	39.4	5.0 to 98.0
Oil	47.9	1.3 to 95.0
Volatile Solids	4.4	0.0 to 13.0
Ash	8.3	0.0 to 55.3

TABLE 6 PROJECTED WASTE SOLIDS INVENTORY*

Solid Waste	Dry Solids lbs/day	% Solids wt/wt	Volume gal/day	Characteristics	Remarks
1. Gravity Oil Separator Sludge					
a. Oil Area	95	1.2	1,200	Oily Sludge Containing up to 10% Oil & 16% Solids After Settling	Potential Oil Recovery
b. New Area	79	1.2	1,000		
2. DAF Skimmings					
a. Old Area	68	0.5	1,700	Oil, Solids & Emulsion Breaking Chemicals	Potential Oil Recovery by Chemical & Heat Treatment
3. Oily Sediment	1,600	up to 20	Approx. 1,000	Oily Sediment Containing Clay, Sand, & Carbonate Precipitates and up to 10% Oil	
4. Tank Bottoms	2,500	up to 20	1,500	Up to 50% Oil	Potential Oil Recovery if Leaded & Non-Leaded Sludges are Segregated

* Excluding Tar and CBM from the HF Alkylation Unit

FIGURE 1. OILY SLUDGE PRODUCTION VERSUS REFINERY CAPACITY

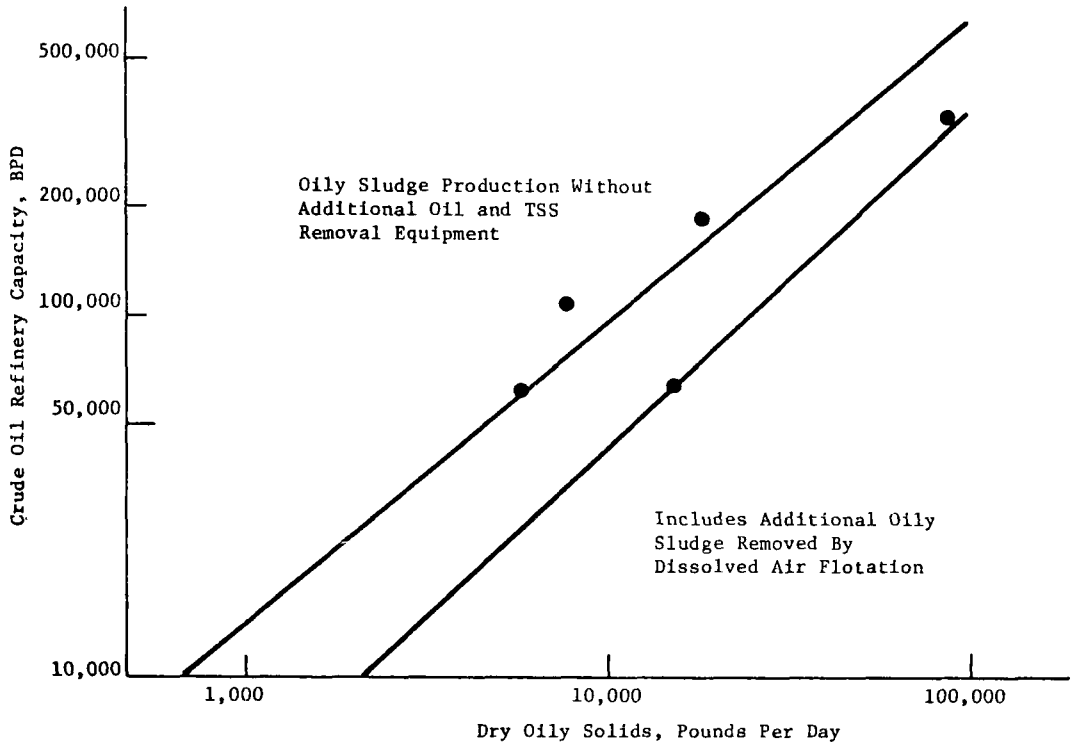


FIGURE 2

SOLIDS HANDLING AND DISPOSAL ALTERNATIVES

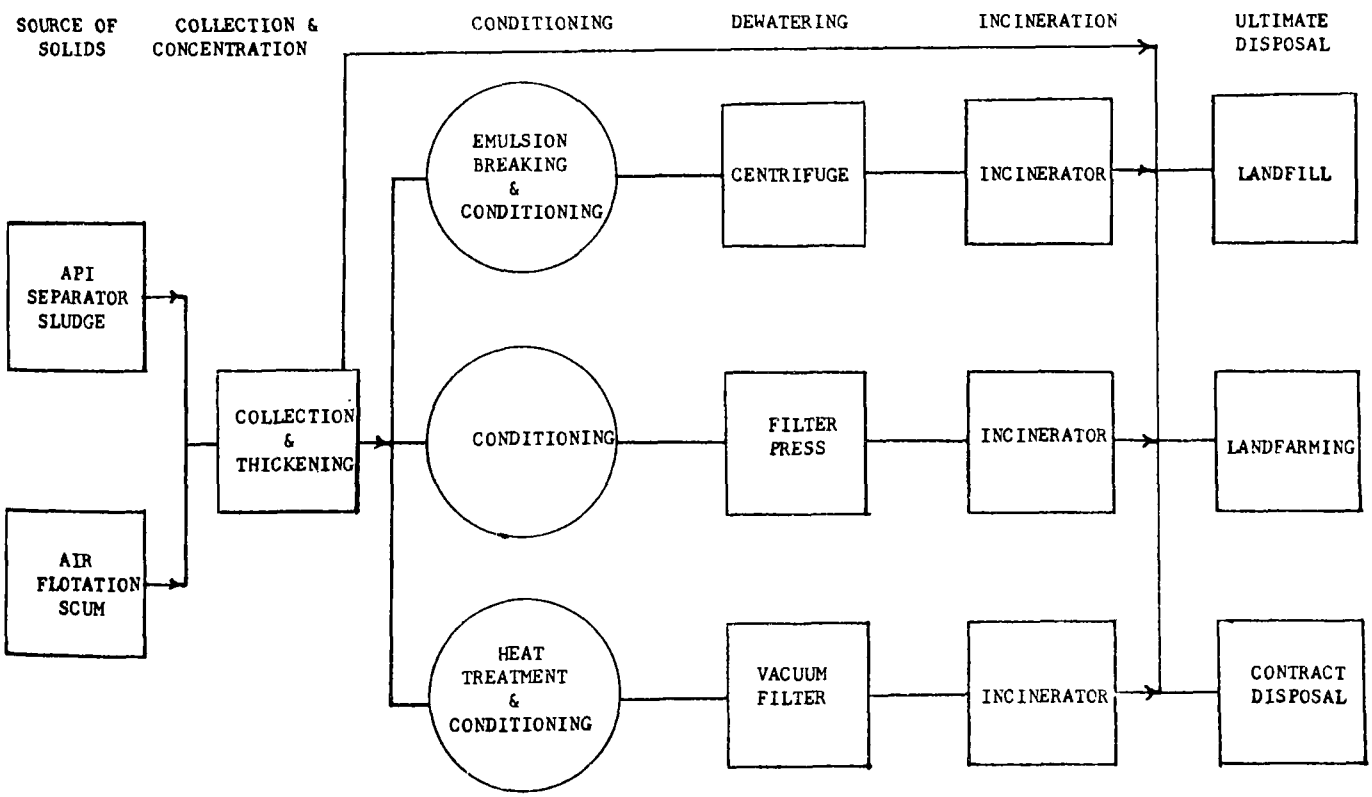


FIGURE 3

TYPICAL AUTOMATIC WATER DRAW-OFF SYSTEM

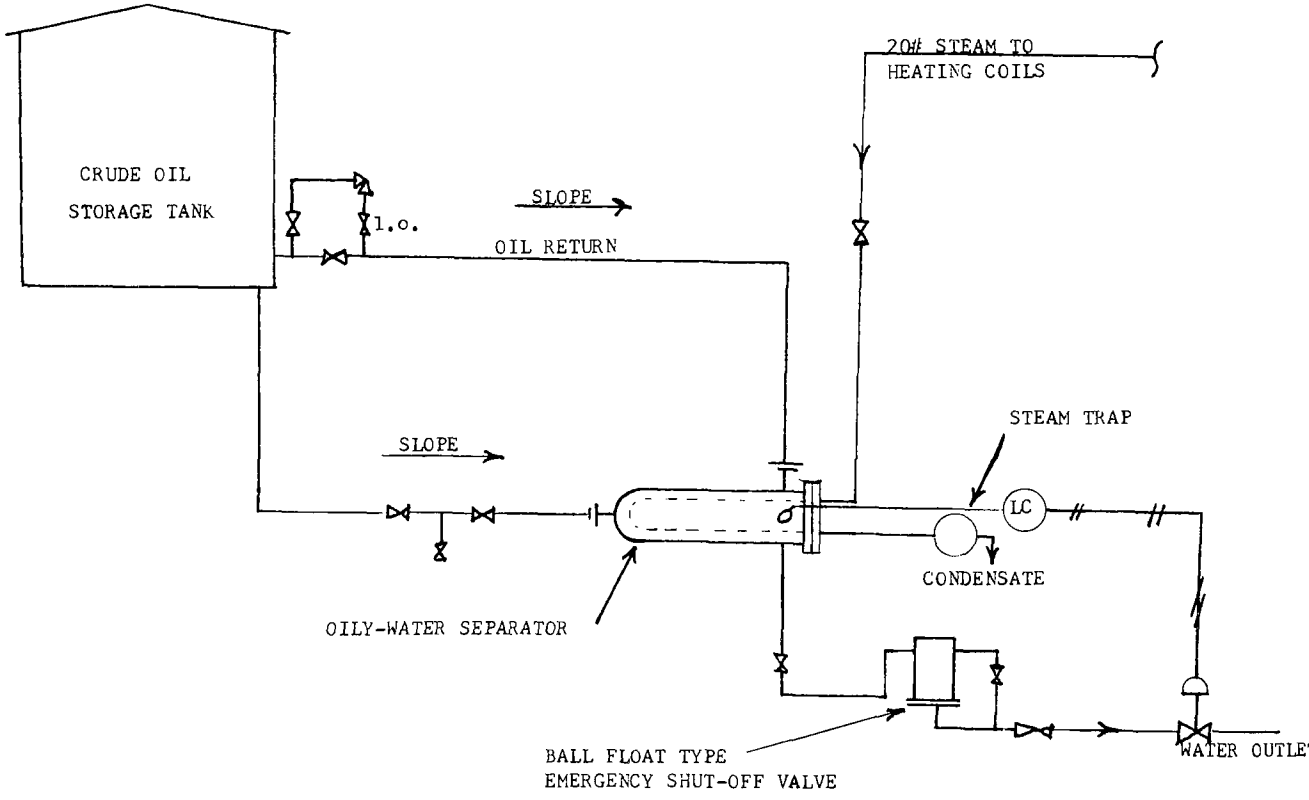


FIGURE 4

RECOVERED OIL TREATMENT

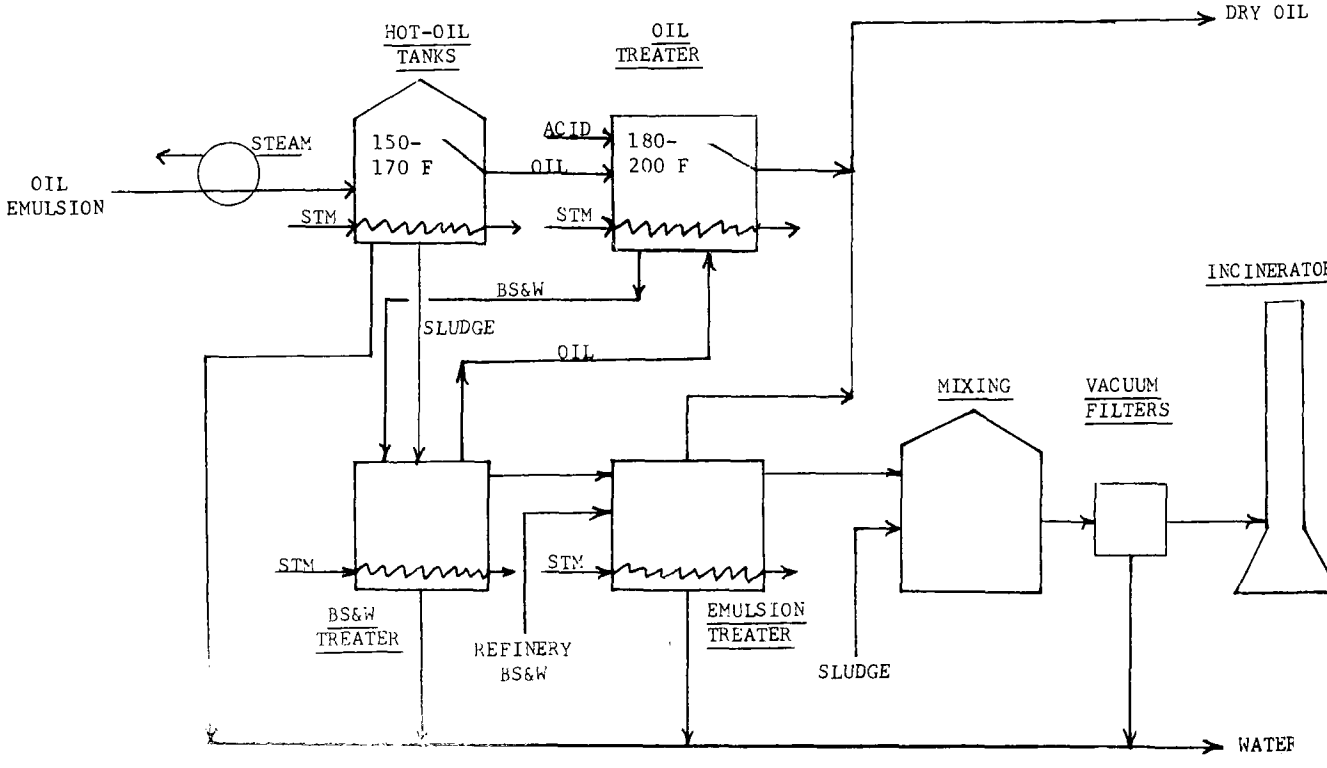


FIGURE 5

REFINERY WASTEWATER TREATMENT SYSTEM

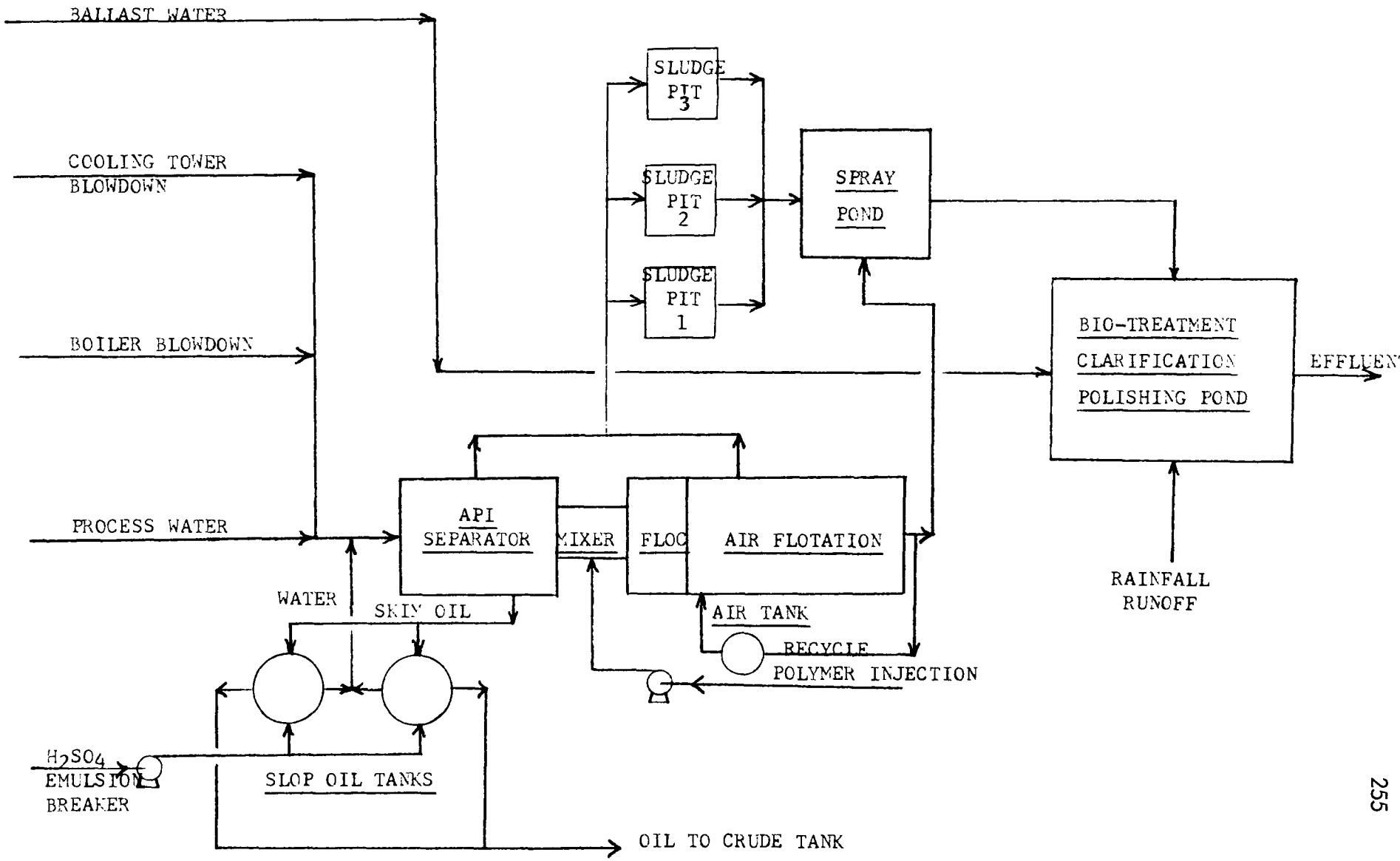


FIGURE 6

MASS BALANCE DIAGRAM

OILY WASTE SOLIDS DISPOSAL SYSTEMS

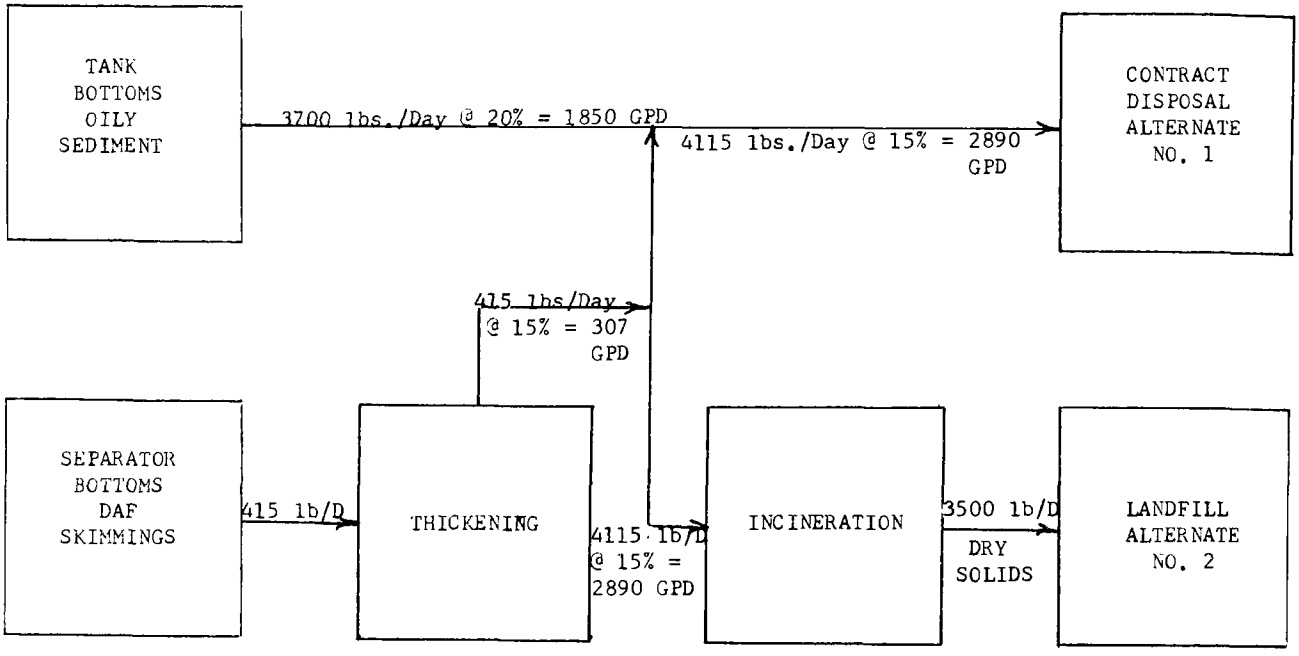
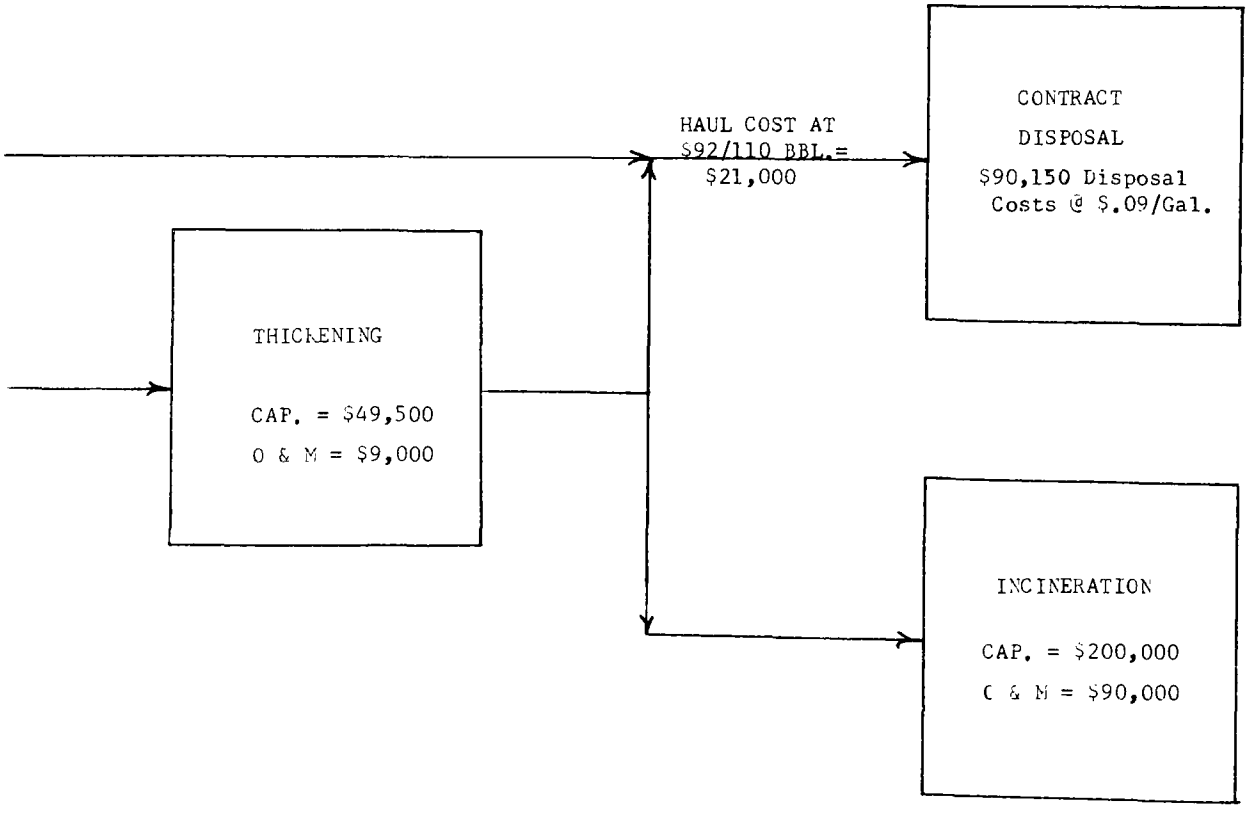


FIGURE 7

OILY WASTE SOLIDS DISPOSAL SYSTEMS

ESTIMATED COSTS



"OILY WASTE DISPOSAL BY SOIL CULTIVATION"

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INTRODUCTION

Numerous companies dispose of oily waste materials by adding the sludge to land areas. This method of disposal may be referred to as land disposal, land treatment, land spreading or land farming.

Sources of oily sludges include petroleum refinery wastes, oil spills and pipe line ruptures. Also, numerous waste materials from industrial chemical and petrochemical plants contain oil. The quantity, quality and type or types of oil in oily sludges may vary widely and often the oil exists as mixtures with solids. Determination of the optimum disposal method for each batch of sludge based upon chemical and physical composition of the sludge is not practical. Generally, the disposal of oily waste sludges on land areas has been done on a trial and error basis. The control of the disposal site may have been based solely upon visual observations, with a minimal of attention toward the quality of surface water runoff or the effects on the soil or on the subsurface groundwater.

The purpose of this paper is to review a study using a soil cultivation process for disposal of known oil materials made in 1971 under the partial sponsorship of the Environmental Protection Agency (1). In this study oily materials were spread over the soil, then mixed with the soil using a roto-tiller type cultivator. Soil microorganisms were utilized to decompose the oil at prevailing soil and climatic conditions. Experimentally determined oil decomposition rates and other findings during the study suggest that the process can be controlled and is one method for disposal of oily sludges at the plant site.

OILY MATERIALS USED

Since the oil present in oily sludges from a plant may vary widely in composition and properties, the selection of representative oils to use in a study may be somewhat arbitrary, but should include oils similar to those which may be present in the plant waste sludges. For the cultivation process study, oil feed materials were selected to represent different combinations of hydrocarbon types. The properties and composition of three oils used in the experiment are given in Table 1. The oils include the following:

crude oil tank bottoms containing a natural balance of hydrocarbon types.
bunker C (No. 6 fuel oil), a residual fuel oil containing olefinic and aromatic components.
waxy oil, an intermediate refined product containing highly paraffinic components.

Differences in pour points, viscosity and hydrocarbon types are shown in Table 1 for the three oil materials.

TEST PLOTS

The study included three parallel experiments with each oil material. A total of nine test plots were used. A sketch of the experimental plots is shown in Figure 1. Test plots were treated identically except for soil nutrient additions. Plot No. 1 was fertilized heavily, Plot No. 2 was fertilized moderately and Plot No. 3 was not fertilized.

Each of the nine plots was 12 x 125 feet; i.e., 1,500 square feet. Plots were separated by levees designed so that rainfall runoff from each plot drained through a pipe to a ditch. A plug in the pipe was used to control the runoff. The levees prevented crossflow of water from one plot to another and kept oil within the plot area.

Space between the plots permitted vacuum truck passage for convenience in spreading oil evenly over the soil. The roto-tiller was cleaned after working each plot to prevent mixing of oil, soil and fertilizer from one plot to another.

The experimental plots were located in an area which had been used previously for oily waste disposal. Residual oil in the soil at the start of the experiment was approximately ten percent by weight. Rainfall runoff was accumulated in a holding pond. The depth of soil mixed with the roto-tiller was approximately six inches. The six inch depth was used in calculating the volume of the soil in the test plot.

FERTILIZERS

In agricultural crop production, nitrogen and phosphorus are removed from the soil with the harvested grain or forage. Replenishing of the nutrients is required. For a waste disposal system such as the soil cultivation process, there should be an equilibrium condition established which would minimize the need for supplementing the nutrients. Endogenous metabolism, autoxidation of cellular protoplasm, results in the release of nitrogen and phosphorus previously used for synthesis. The released nutrients are made available for reuse in biological waste treatment systems (2). No reference information was found to use as a guide in selection of appropriate quantities of nitrogen and phosphorus which should be added to the biological system. Instead, the selection of fertilizer quantities was based upon agricultural-oriented experience. Warnings that 1) excess nitrogen fertilizer elements hinder (poison) bacterial action and 2) excessive total soluble salts may cause unfavorable osmotic conditions for bacterial growth, were considered in the selection of the quantities of nutrient additive. Excess phosphate was not considered toxic except for its contribution to the total soluble salt content.

Urea and calcium hydrogen phosphate were added initially as fertilizers. Plots numbered 1, heavily fertilized, received 1,000 pounds of nitrogen (N) and 200 pounds of Phosphate (P_2O_5) per acre compared to 500 pounds of nitrogen and 100 pounds of (P_2O_5) for the moderately fertilized plots numbered 2. No supplemental nutrient was added to plots numbered 3.

Fertilizer materials added during the course of the experiment to plots number 1 and number 2 were based upon the results of periodic analysis of nitrogen and phosphorus in the

soil. After about 6 months, loss of ammonia to the atmosphere was noted and a change in the type of nitrogen fertilizer material appeared warranted. About midway of the project, ammonia nitrate (NH_4NO_3) was used instead of urea and relatively small doses applied frequently.

EXPERIMENTAL PROCEDURE

Each plot was cultivated with a roto-tiller type plow. Fertilizer materials were added by manually spreading solid granular fertilizer over the surface of plots No. 1 and 2. After spreading fertilizer and before adding oily sludge materials, the plots were again roto-tilled to mix fertilizer and soil.

Oily feed materials were transported to the test plot area with a vacuum tank truck, and distributed over the soil surface by manual direction of a discharge hose. After cultivating with the roto-tiller, the oil-soil mixture appeared uniform and presented no problem at the ambient May temperature of 80 degrees F. The initial schedule for roto-tilling was once each two weeks, weather permitting. After six months of cultivation, the soil was friable, had lost its oily appearance, and based upon test results was suitable for a second addition of the oily sludge. Differences in the plots were apparent. The color of the unfertilized No. 3 plots was darker than for fertilized Plots No. 1 and 2.

The date for the second addition of oils was in early February when the temperature was in the low 40 degrees F range. Congealing and solidification of the oils was apparent. Mixing of the viscous oily matter into the soil was not successful until the ambient temperature had increased to about 80 degrees F.

At the end of the 18-month experiment, the soil had again returned to the friable condition with the appearance of normal agricultural soil.

Although no attempt was made to grow vegetation on soils previously used for oil decomposition during this experiment, native grass and plants did sprout and grow on top of the levee. The soil in the levees was the same as the starting test plots, which contained about ten percent by weight (10%w) of oily material.

SAMPLING AND TESTING

Oil and nutrient contents were used as controls for the experimental work. Generally, oil determinations were made once every two weeks and nutrients were determined once per month. Microbial analyses were made monthly, hydrocarbon types of oil added and extracted from the soil were made for each new addition of sludge to the soil, and oil content of core soil samples were made at the start, midway and at the end of the 18-month experiment.

Obtaining representative samples was a recognized problem from the start of the project. The sampling procedure included combining portions of soil from three sampling points to form subsamples a, b, and c, as shown in Figure 2. Subsamples a, b, and c were composited to represent the whole test plot.

EXPERIMENTAL RESULTS

The experimental results when using the three oily materials as feed were similar. The relationships of the percent weight (%w) oil in the soil with time are shown in Figure 3 for the waxy oil test plots and these results are representative of the other two oily material test results. From the first addition of oil in May to about November 1970, the oil content of the soil decreased markedly. During the period November 1970 to February 1971, a reduction of oil was not apparent. From February, when a second dosage of oil was added to October 1971, the oil content again decreased. The reason or reasons for the period of inactivity, November 1970 to February 1971, may have been due to one, two or all of the following reasons: During this period, the concentration of oil in the soil was near the starting content and this residual oil may be nonreactive or slowly reactive with soil microorganisms. Another reason may have been the lack of available nitrogen and a third reason may have been the relatively low temperatures during this period.

The relationship of the nitrogen concentration and oil removal rate is shown in Figure 4 and the relationship of temperature and oil removal rate is shown in Figure 5. The oil removal rate was expressed as pounds of oil removed per cubic foot of soil (lbs/ft^3). During the period November 1970 to February 1971, the ammonia concentration was 20 mg/l or less for waxy oil experiments and the nitrate content was nil indicating a possible lack of the nitrogen nutrient. Also, during this period, the soil temperature, shown in Figure 5, was less than 40 degrees F and may have been too low for favorable bacterial growth. The reason or reasons for the period of inactivity was not further determined.

Oil decomposition rates expressed in pounds of oil per month per cubic foot of soil ($lbs/mo/ft^3$) are given in Table 2. For the periods May to November 1970, and February to October 1971, the oil decomposition rate averaged 0.9, 0.9 and 0.7 $lbs/ft^3/mo$ for Plots 1, 2 and 3 for crude oil; 1.8, 1.7 and 0.8 $lbs/ft^3/mo$ for Plots 1, 2 and 3 for Bunker C; and 1.7, 1.3 and 0.7 $lbs/ft^3/mo$ for Plots 1, 2, and 3 for waxy oil feed. For a three month period of November 1970 to February 1971, the oil decomposition rate was minimum. The average decomposition rate per year at these test conditions was 1.1, 1.0 and 0.6 $lbs/ft^3/mo$ for heavily fertilized No. 1, medium fertilized No. 2 and unfertilized No. 3 plots, respectively.

The general conclusion was that the oil decomposition rates were approximately 0.5 lbs/ft^3 of soil per month without fertilizer and 1.0 $lbs/ft^3/month$ when fertilized. Items for consideration in developing the cost of the process using fertilizer are given in Table 3. The fertilizer requirement may be assumed to be 1,000 pounds of nitrogen and 500 pounds of phosphorus per acre per year. The cost for spreading oil and fertilizer and cultivating the soil likely would vary with location. An oil decomposition rate of 1.0 $lb/ft^3/mo$ is equal to 21,780 lbs/acre/mo or about 70 barrels (bbls)/acre/mo. The cost for delivering the oil to the area and distributing the oil over the surface of the soil was about $1/bbl or $70/acre/mo in 1971. The fertilizer material and labor for spreading costs prorated on a monthly basis was estimated to be about $23/mo. Cultivation (plowing) would require about 8 hours (hrs)/acre at $25/hr and two plowings/mo totals $400/mo. The total cost/acre/mo was estimated to be $493 or about $7 per barrel of oil at conditions prevailing in 1971. The cost for disposal of oily sludge containing 33 percent oil was estimated to be

about $3 per barrel in 1971. The cost of disposal of oily sludge would depend upon the oil content of the sludge. Current costs for a specific entity or industrial plant would of course require an independent evaluation.

MICROBIAL ACTION

Microorganisms in the soil decompose nitrogenous and carbonaceous materials into microbial cellular matter. When oil or hydrocarbon is the only source of carbon, oil degrading microorganisms survive and become the predominant species. Results of monthly determinations of the total aerobic count indicate that the addition of fertilizer affected the total aerobic count. The relationship of total aerobic and oil removal rate and the effect of fertilizer are shown in Figure 6 for the waxy oil experiments. The No. 1 plot (heavily fertilized) generally was higher in total aerobic count than No. 2 (medium fertilized) and No. 3 (not fertilized) plots. Also, the microbial count was found to be sensitive to change in the oil content of the soil as shown in Figure 7. The addition of oil in May 1970 and February 1971 appeared to upset the soil microbial equilibrium and caused the total aerobic count to be low.

The predominant species given in Table 4 included Arthrobacter, Corynebacterium, Flavobacterium, Nocardia, and Pseudomonas. Since the area where the experimental plots were located had been used previously for oily waste disposal, the presence of a variety of oil consuming microorganisms might be expected in the soil. Flavobacterium and Pseudomonas species were present but the microbial population was different on all plots. Distribution of the microorganism species were not greatly different for the three oils used in the experiment.

OIL EXTRACTED FROM THE SOIL

Oils added to and extracted from soil plots were quantitatively analyzed for hydrocarbon types, qualitatively analyzed by infrared for "fingerprint" differences and qualitatively analyzed by gas chromatography for boiling point profile. Detailed description and results of the analysis have been reported previously (1). Some of the more pertinent procedures and results follow.

Adsorbents of clay and silica gel were used to separate the oils into total saturates, resins (asphaltenes, organic acid, etc.) and aromatics. The hydrocarbon content of the fertilized plots related with time are shown on Figure 8. Generally, the saturate and aromatic contents are shown to decrease and the resin content remained unchanged or increased. This may indicate the saturate and aromatic materials to be decomposed and the resinous material to be relatively nonreactive with soil microorganisms. Also shown is the hydrocarbon content of the oil originally in the soil.

Generally from the three parallel experiments, more changes in composition for the No. 1 and No. 2 plots were noted than for the No. 3, indicating an effect of fertilizer. Further, differences were noted from infrared analyses.

The oil originally in the soil contained saturate groups, small amount of organic acids

and a substantial amount of condensed multi-ring aromatic structures.

Infrared spectra for crude added to the soil and after eight months in the soil are shown on Figure 9. Some observations follow:

1. The crude oil feed contained saturates and simple aromatics.
2. The oil extracted from the unfertilized plot was similar to the original oil in the soil. The aromatic were more representative of the polyaromatic groups, and saturates were present.
3. The oil extracted from the fertilized plot still contained polyaromatic types and some saturates but contained organic acids, also.
4. Organic acid contents are significantly different in the fertilized and unfertilized samples. Saturate peak intensities are related to quantity and are higher in the unfertilized sample.

In general, oils from plots that were fertilized showed higher concentrations of organic acids and the concentration appeared to be greatest in the heavily fertilized plots.

INFILTRATION

Oil and nutrient concentrations at depths of 2, 4, and 6 feet, determined at the start, middle, and end of the project, indicated that these constituents did not infiltrate the soil under the conditions of the project.

RAINFALL RUNOFF

Analysis of accumulated rainwater for oil, ammonia, nitrate, and phosphate contents indicated that little, if any, of these constituents were present when drained immediately after a rain. Long standing appeared to cause higher oil contents.

The oil content ranged from 30 to 100 mg/l and infrared examination of these extracted oils indicated the soluble oil to be essentially organic acids with characteristics quite similar with spectra for naphthenic acids.

Each plot was drained about 36 times during the project and the quantity of oil discharged with the water was equal to about 0.03 lbs/ft^3 of oil in the soil.

The ammonia content of the water varied with the soil nutrient level. During periods when the ammonia was excessive on the No. 1 plots, discharge water contained up to 150 mg/l ammonia as N. Nitrates and phosphates were generally absent in the discharge.

APPLICATION OF THE PROCESS

This study demonstrated that soil microorganisms decompose petroleum oily waste and that oil and fertilizer chemicals did not penetrate the soil at the location and conditions of the test. However, numerous factors are left unresolved and future experiments should gain knowledge concerning the following uncertainties:

1. The residual oil in the soil after the 18-month project contained organic acids, and those soluble in rainfall runoff water were primarily naphthenic acids. Since most organic acids are water soluble, this suggests that naphthenic acids do not decompose in the soil as rapidly as aliphatic acids or that naphthenic acids are formed from aliphatic or aromatic materials at the soil conditions. Speculatively, large concentrations of naphthenic acids may inhibit microbial growth in the soil, and water washing of these organic acids from the soil to a separate biotreatment system might improve the oil decomposition rate in the soil.
2. Residual oil extracted from the soil was characterized by infrared to be poly-aromatic oils, suggesting this hydrocarbon group to have a slow reaction or to be nonreactive for microbial decomposition at the prevailing conditions. Certain, and yet unknown, environmental conditions might improve the decomposition rate of the polyaromatics.
3. Accumulation and buildup of metals or salts contents with long-range usage may affect the microorganism activity. The acidity or alkalinity range, optimum for microbial action, may vary with the soil contents.
4. The time required for native soil bacteria to become acclimated oil decomposers likely depends upon the soil composition and temperature.

For application of the process, one should follow the suggested action items given in Table 5.

CONCLUSIONS

The decomposition rate of oily sludges (hydrocarbons) by microbial action in cultivated soil averaged about 0.5 lbs/ft^3/mo without fertilizers and about 1.0 lb/ft^3/mo when fertilizers were added.

Major bacterial species included Pseudomonas, Nocardia, Flavobacterium, Corynebacterium, and Arthrobacter.

Organic acids are produced and water solubles appear to be naphthenic acids.

Oil and fertilizer did not infiltrate.

Rainfall runoff water contained organic acids (and possibly fertilizer).

The soil cultivation process is one method which can be used to dispose of oily waste materials.

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DISCUSSION

Banks: Has this soil been returned to cultivation and if so, what were the crop yields?

C. B. Kincannon: This experiment did not include agricultural crop production. In the study, the soil was utilized as a bacterial bed for the decomposition of oils. I cannot answer your question concerning the current use of the experimental area because I am no longer associated with Shell Oil Company where the work was done. I refer you to Shell Oil Company, Deerpark, Texas for further information along these lines.

Morris Wiley: We have used an alternate method which does not involve cultivation whereby you put 0.5 cm of oil sludge over, say 1 square mile and find that not much happens during the cold season in say New York. During the summer and certainly by September, the oil is weathed completely into little "pebbles" which the earth worms cover up. You can put 5,000 cubic meters per square kilometer which is a much lower application than you are discussing. The difference is to eliminate the cost of having to cultivate, till, fertilize, etc. Would you care to comment on the potential savings of such a method?

C. B. Kincannon: I believe we should know more about the material put on the soil.

Morris Wiley: I should have described that. It was a refinery disposal pit sludge stabilized for some years leaving principally the heavy ends - 20% oil, 20% water, the rest primarily solids.

C. B. Kincannon: With my limited knowledge, I would say if that works - power to you - I'd do it.

Morris Wiley: Do you think that would be cheaper if the land area were available?

C. B. Kincannon: If you can place the waste on the land area, not fertilize, till, etc. and the waste will disappear without damage to the receiving water or create an air pollution problem, the disposal cost should be a minimal cost.

Morris Wiley: Would you think that you would have to collect the land run-off in an impoundment?

C. B. Kincannon: I would recommend that.

R. A. Farnham: Could you explain the meaning of that No. 9 you had up there - the 25 milligrams per liter, I thought we were about in the 30% oil range?

C. B. Kincannon: As I pointed out, we found from exploratory experiments in the laboratory that concentrations in excess of 30 percent weight oil caused the oil decomposition reaction rate to become slow or nil. When the soil particle becomes completely enclosed with oil globules, water is prevented from getting into the soil and water is a necessary element for the bacteria.

BIOGRAPHY

C. B. Kincannon is an engineer in the Central Operations Division of the Texas Water Quality Board (TWQB). He obtained a B.S. degree from Panhandle A and M College (now Panhandle State University) and was an employee of Shell Oil Company for 30 years before joining the TWQB staff. He is a certified Grade A sewage works operator and a professional engineer registered in the State of Texas.

TABLE 1 "OIL PROPERTIES"

	Crude Oil	Bunker C	Waxy Oil
Lb/Gal	7.12	8.52	7.08
Pour Point (^{o}F)	-5	40	95
Viscosity			
SU 60^{o}F	60	19000	
SF 122^{o}F		120	59
HC Type (Wt%)			
Saturates	36	18	90
Resins	8	26	0
Aromatics	56	56	10

TABLE 2 "OIL DECOMPOSITION RATE LB/MONTH/CU FT OF SOIL"

Feed	Plot	May to Nov 70	Feb to Oct 71	Avg	Nov 70 to Feb 71	Yearly Avg
Crude Oil	1	0.7	1.1	0.9	Min	0.7
	2	0.5	1.4	0.9	Min	0.7
	3	0.2	1.3	0.7	Min	0.5
Bunker C	1	1.8	1.8	1.8	Min	1.3
	2	1.2	1.5	1.7	Min	1.3
	3	1.8	0.5	0.8	Min	0.6
Waxy Oil	1	1.8	1.6	1.7	Min	1.3
	2	1.5	1.0	1.3	Min	0.9
	3	0.8	0.5	0.7	Min	0.5
Average	1					1.1
	2					1.0
	3					0.6

TABLE 3 "ITEMS FOR ESTIMATING COST"

	Quantity
Oil Spreading/Month	1
Lb/Cu Ft	70
Fertilizer	
Nitrogen Lb/Year	1000
Phosphorus	500
Cultivation	

TABLE 4 "MICROBIAL ANALYSES"

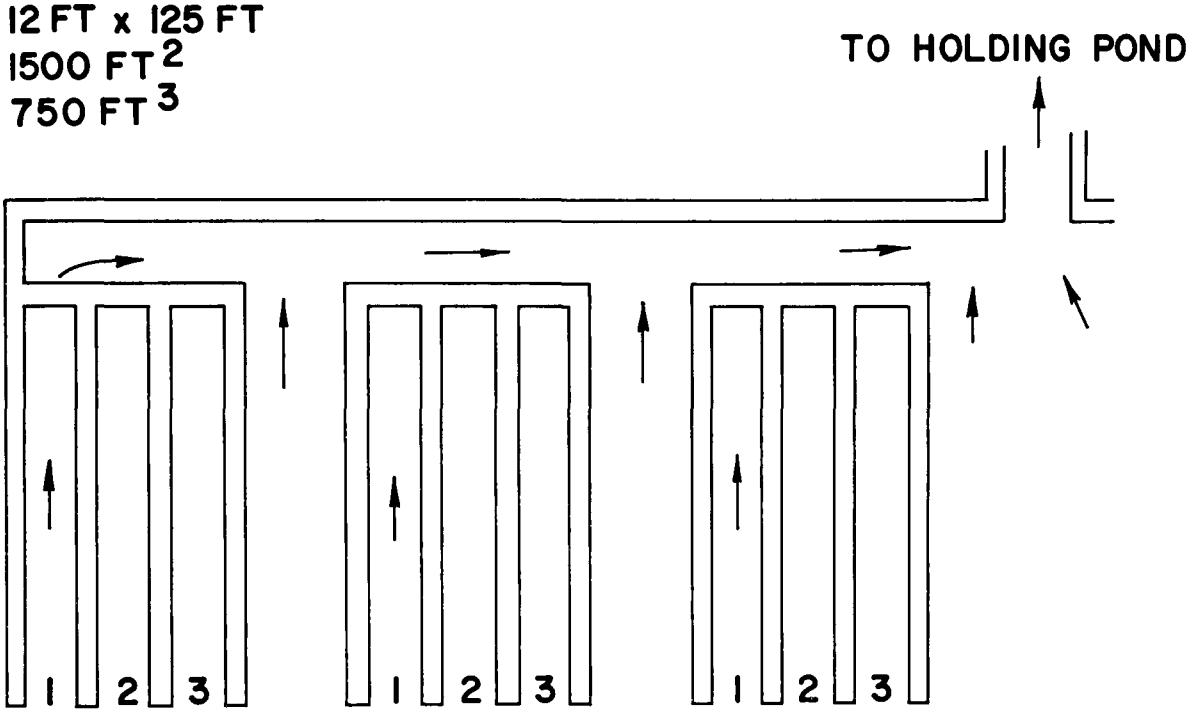
Predominant Species
Arthrobacter
Corynebacterium
Flavobacterium
Nocardia
Pseudomonas

TABLE 5 "FOR APPLICATION OF THE PROCESS"

1. Prepare Area
2. Provide Treatment Facilities For Rainfall Runoff
3. Obtain Samples To Determine Background Level
4. Add Fertilizer Material
5. Cultivate
6. Distribute Oil Over Surface
7. Cultivate, Analyze For Oil
8. At Regular Intervals, Cultivate and Analyze
9. Oil Content Of Soil Should Not Exceed 25% wt.
10. Determine Oil Penetration Rate Into Soil

FIGURE 1
EXPERIMENTAL PLOTS

EACH PLOT
12 FT x 125 FT
1500 FT^2
750 FT^3



CRUDE OIL

BUNKER C
(NO 6 FUEL OIL)

WAXY OIL

FIGURE 2
TYPICAL SAMPLING POINTS

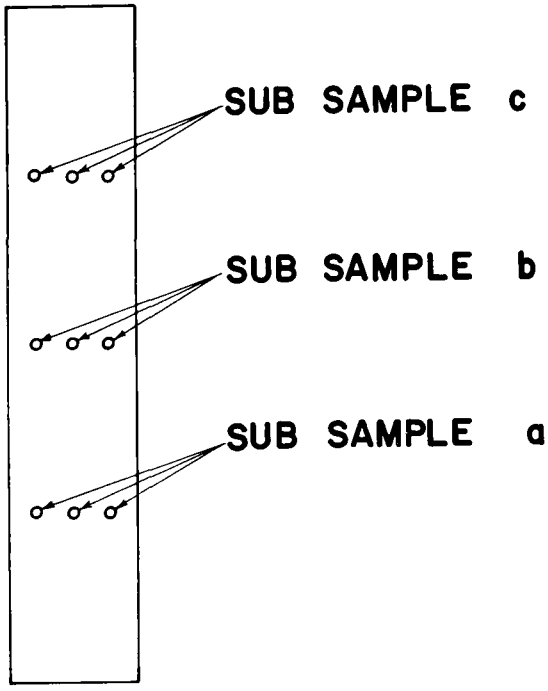


FIGURE 3
OIL IN SOIL

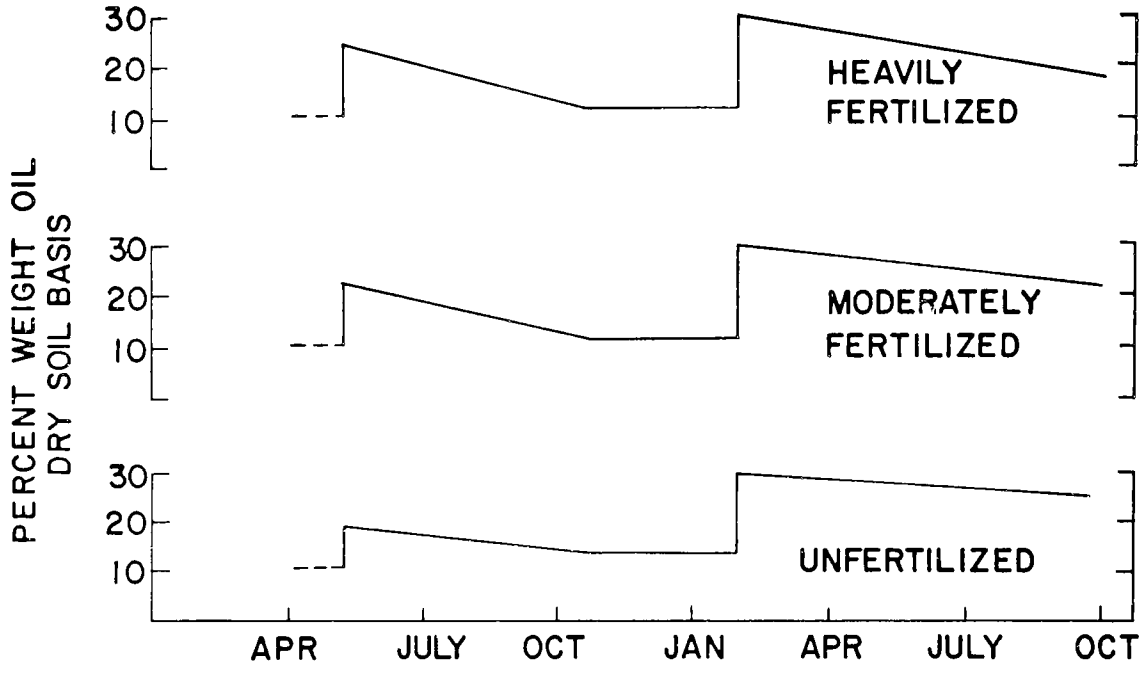
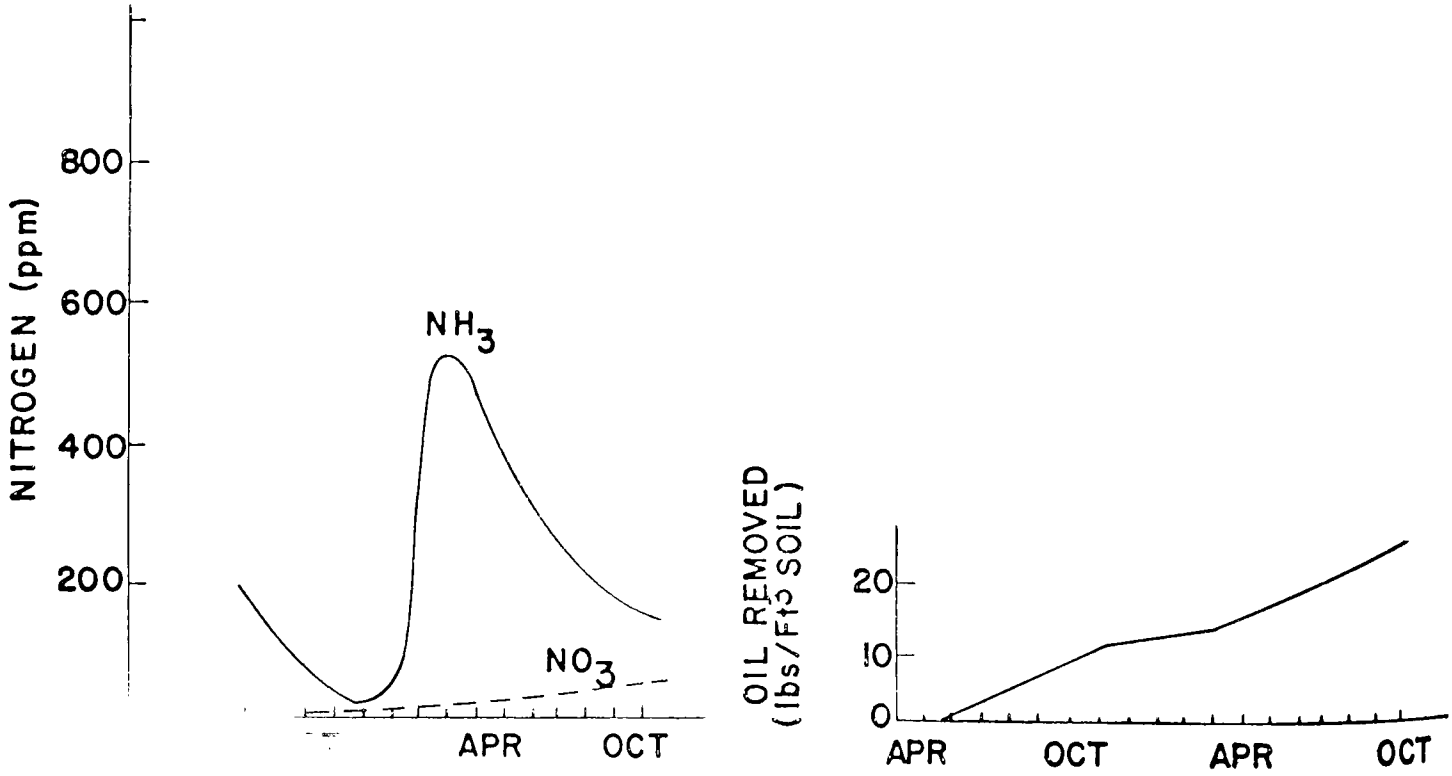


FIGURE 4
EFFECT OF FERTILIZER



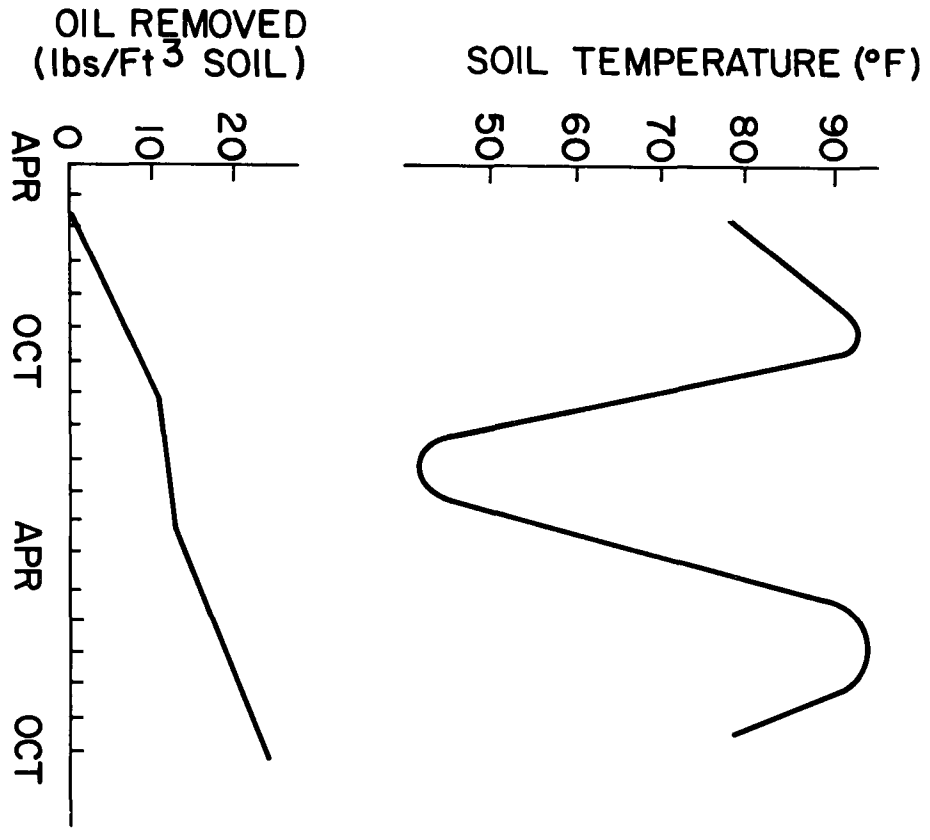


FIGURE 5
EFFECT OF TEMPERATURE

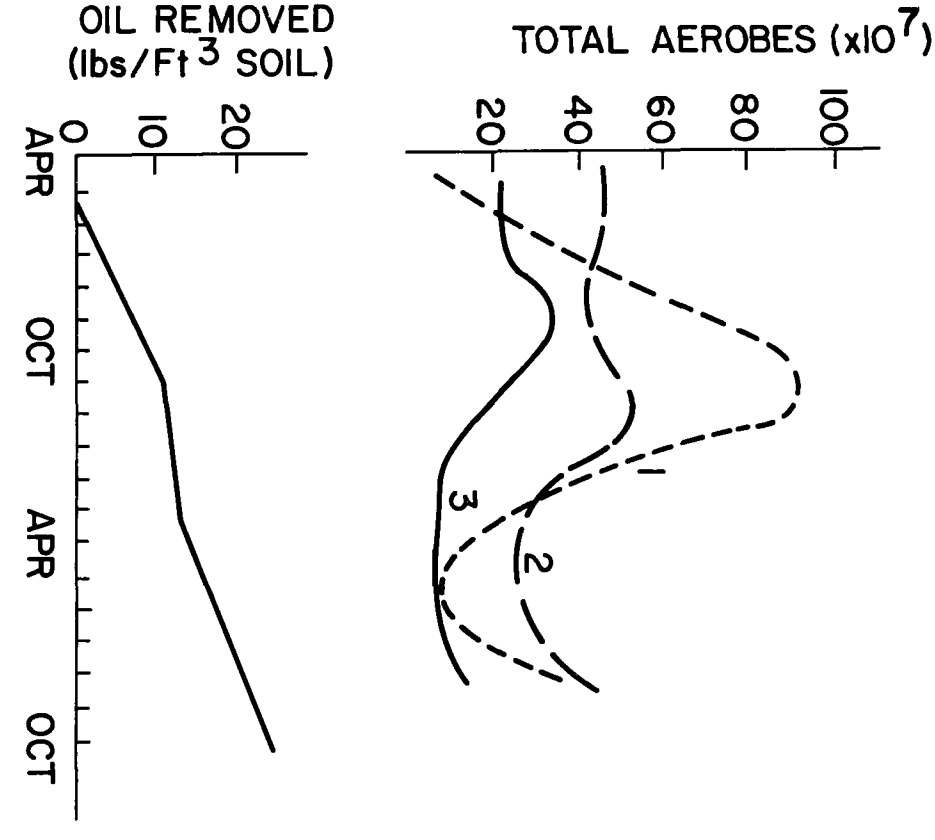


FIGURE 6
MICROBIAL COUNT

FIGURE 7
EFFECT OF OIL ADDITION ON MICROBIAL COUNT

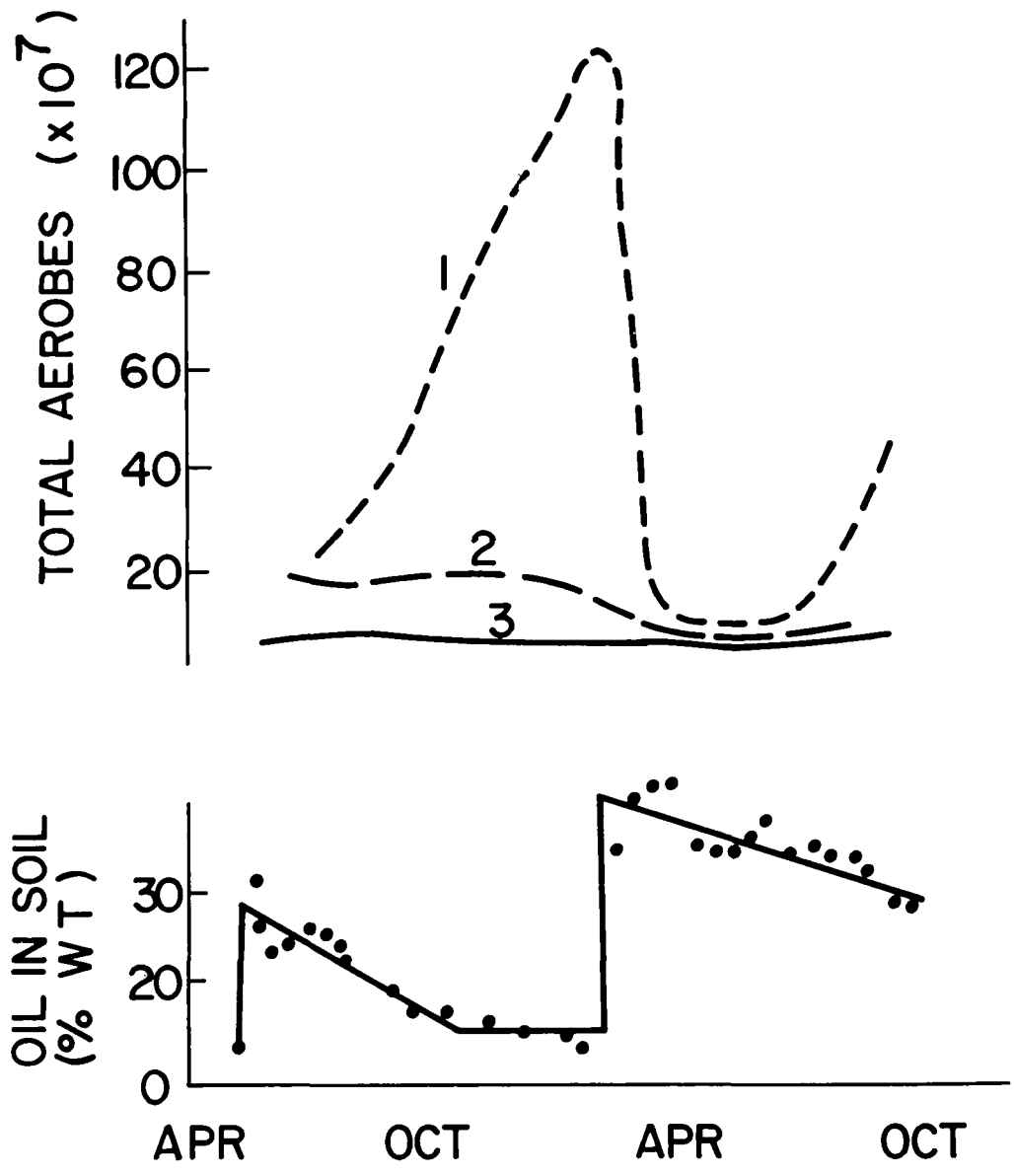


FIGURE 8
HYDROCARBON TYPES

S-SATURATES
R-RESINS
A-AROMATICS

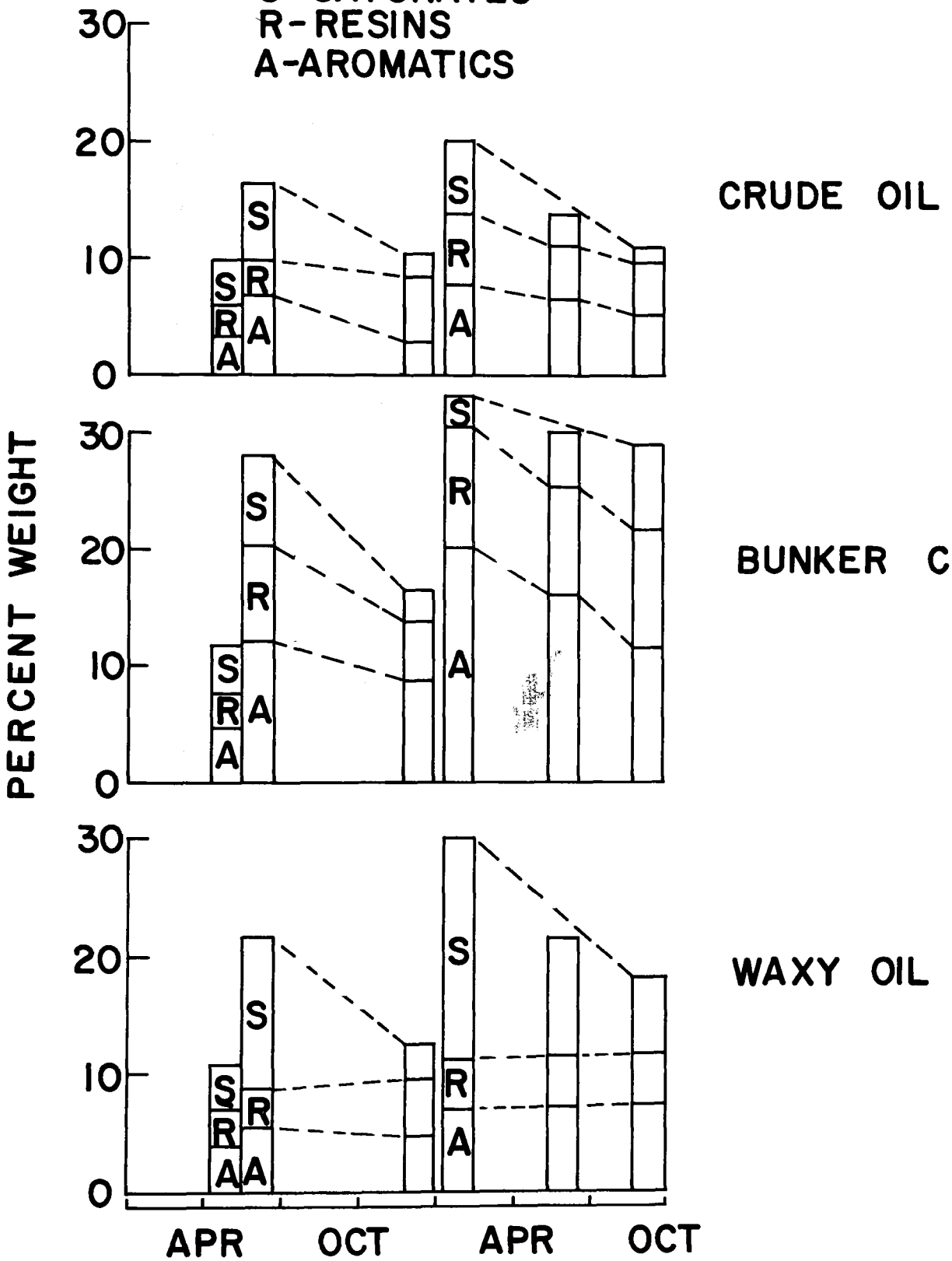
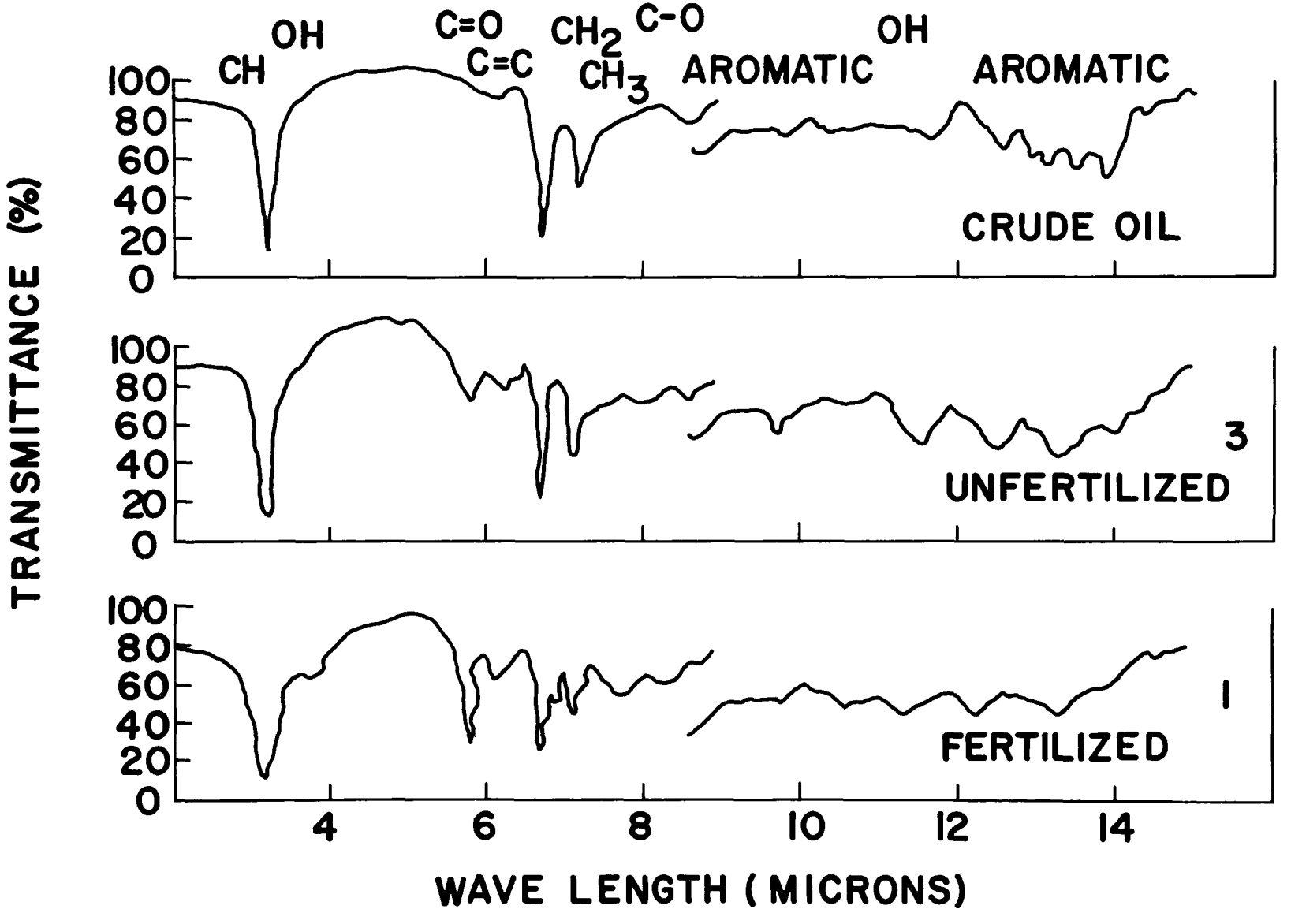


FIGURE 9
INFRA-RED SPECTRA



THE DISPOSAL OF OILY WASTES BY LAND FARMING

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and
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At CONOCO we have been studying the disposal of oily wastes by land farming for about three years. By "land farming" we mean the use of the soil environment for the planned, orderly treatment of waste. The work has been strictly experimental in nature, but has been conducted in field plots out-of-doors using actual waste materials. In this presentation we will describe the need for land farming as an oily waste disposal method, the results of our studies to date, and our view of factors that must yet be addressed before land farming can be used routinely on an environmentally safe basis for oily wastes disposal.

SOURCES AND CHARACTERISTICS OF OILY WASTES

Oily wastes are generated by numerous routine refinery operations. Examples of such wastes and their compositions are shown in Table 1. Amounts of these wastes generated are not well defined and vary widely from refinery to refinery and from time to time within a given refinery. However, it is probable that a 100,000 BPD refinery generates from 5,000 to 100,000 bbl/year of such wastes. As increasingly better jobs are done in waste water treatment and air pollution control, the amount of oily wastes that are generated will inevitably increase.

Some oil can be recovered from these wastes by chemical and physical means, and it is very important that we learn how to more effectively and economically deoil such wastes. It is unlikely, however, that we will ever be able to economically deoil all wastes of these types.

The characteristics of waste oil prevent its decomposition in conventional waste treatment systems. Some disposal methods used in the past are shown in Table 2. For various reasons these methods are rarely used today, and we obviously need suitable alternatives.

At present, it appears that incineration and land farming may be the only safe and possibly economic ways to dispose of oily waste. Although incineration is expensive, a fire hazard, poses air pollution problems, and is difficult to adapt to wastes containing non-combustible solids and high water content, it may have to be used at locations where land is economically unavailable. An alternative and less expensive disposal method may be land farming.

THE CONCEPT OF LAND FARMING

It is well known that many microorganisms can decompose numerous petroleum components. We must also recognize, however, that petroleum is an extremely complex blend of tens of thousands of chemical structures. Our knowledge of how, and to what extent, this complex blend is biodegradable, is quite small indeed. Nevertheless, many workers have

shown that the bulk of at least some crude oils is biodegradable (1,2,3).

Soil contains an enormous microbial population as shown in Table 3. Many of these organisms can decompose hydrocarbons (4). Although the water insolubility of petroleum constituents (see Table 4) adversely affects biodegradation rate, this property helps to "fix" oily wastes in place when they are added to the soil. The extremely large surface area offered by the soil environment (see Table 5) helps spread added oil into thin films making the oil more vulnerable to microbial attack.

A simplistic scheme of oily wastes disposal by land farming is shown in Table 6. We must quickly point out that the mechanism shown represents what we "hope" will occur and has not been proven as yet. Exceptions may be waste oil constituents that are not completely mineralized and others that may prove to be recalcitrant to degradation.

At present we need the answers to a number of questions to define the suitability of land farming for oily wastes disposal. Some of these questions are posed in Table 7. At present, we have partial answers to several, and there is almost certainly justification for using land farming prior to having complete answers to all of these questions. If we are diligent in providing sufficient data to show that oily wastes land farming is reasonably safe from an environmental standpoint, we can logically expect little valid opposition to its use in the near future. More complete answers and answers to some of the less urgent questions can be ascertained as land farming is practiced.

CONOCO'S EXPERIMENTAL LAND FARMING STUDIES

Billings, Montana. At a site near Billings, Montana, we have studied the land farming disposal of oily pond bottoms. A view of the area prior to preparation is shown in Figure 1. The test site and surrounding area was examined to assess the plant and animal life, soil microbial populations and soil composition. Numerous $4\frac{1}{2}$ foot cores were taken to document subsurface soil characteristics. The surface soil was found to be a sandy clay containing a low humus level and very small amounts of nitrogen and phosphate. The Billings climate is arid, warm in the summer and very cold in the winter.

The test area was diked with subsoil, plowed and disked. The oily waste, described in Table 8, was spread as evenly as possible on the soil surface using a vacuum truck. We later found that by using a large diameter hose instead of a truck to spread the waste, we could prevent the heavy trucks from compacting and generally disturbing the test plot soil and get more even waste distribution.

After application, the waste was allowed to dry and weather for three weeks. This step changed the waste to a crumbly consistency, making it much easier to work into the soil. Even during this period no significant odor problem was evident. The waste was then blended into the upper 6-inches of soil with a tractor-mounted rototiller. The appearance of the area at this point is shown in Figures 2 and 3. A description of the cultivation, fertilization and sampling pattern used is shown in Table 9.

The test plots were fertilized with nitrogen and phosphate. This was done because the soil and waste contained very small amounts of these nutrients, and we did not want to limit

rate of oil degradation by these controllable factors. An increased soil microbial population must be preceded not only by available carbon, but also by available nitrogen and phosphate. These nutrients were added as a mixture of urea and 15-15-15, the only fertilizers available at the time.

Thus, the soil at the start of this land farm study contained the waste constituents as shown in Table 10.

During the course of the study, oil contents were measured using a benzene-methanol soxhlet gravimetric technique. A Leco combustion furnace method was used to determine total organic carbon content. Paraffin, aromatic and resin-asphaltene contents of oil extracts were estimated by taking the extracts up in tetrahydrofuran and subjecting them to thin layer chromatography.

Over an 18-month exposure period, we observed a 70% oil loss from the soil as shown in Figure 4. As also illustrated, the loss was apparently created by an 88% loss of the paraffins initially present in the oil, an 85% loss of the aromatics and only a 2.5% loss of the resin-asphaltenes fraction. The original oil contained 50% paraffins, 30% aromatics and 20% resin-asphaltenes. After 18-months of exposure in the soil, the residue contained only 20% paraffins and 15% aromatics, while the resin-asphaltenes fraction had increased to 65%.

Unfortunately, measurements of the organic carbon content of the soil samples produced very scattered results as shown in Figure 5. While the scatter is more pronounced than usual in this case, similar scatter is not uncommon when examining field soil analytical data. Sample differences are magnified by the difficulty in producing thorough soil-waste blending using only practical field cultivation techniques. Scatter can be minimized by compositing large numbers of samples, very careful composite blending and sub-sample taking. We have found it necessary to accept considerable data scatter to economically conduct our studies. In spite of the scatter, the TOC data does seem to confirm that the oil was not only degraded but that much of it was mineralized completely to CO_2.

Accompanying data over the 18-month period showed that the pH of the soil did not change, there was little nitrogen and phosphate loss, and the soil bacterial population increased about 10-fold.

As expected, climatic conditions over the 18-month period of soil exposure were not entirely conducive to good microbial activity. As can be seen from Figure 4, the air temperature during 10 of the 18-months of exposure was about 10°C or less. In addition, the soil moisture content ranged between only 9 and 18% over the 18-month interval. For optimum soil microbial activity, the soil moisture content should be at least 30% (5). It should also be emphasized that the oily waste studied came from a waste water treatment pond (bottoms). As a result, the waste had been exposed to microbial attack for an extended period prior to land farming. Undoubtedly, the most readily biodegradable substances had been removed from the waste prior to land farm exposure.

It should also be mentioned that crested wheat was grown on part of the test area.

Visual observations judged the plant growth to be normal and identical to the control (no waste oil) plot crop.

The average rate of waste oil loss in the Billings study is shown in Table 11. Losses are shown for the 18-month period and on an annualized basis.

Ponca City, Oklahoma. At Ponca City, we have been studying the land farming of an oily (crude petroleum) sand waste and, to a limited extent, the land farming of a refinery oily waste. Unfortunately, the refinery waste was inadvertently added to a soil that was later found to have been previously contaminated with oil and salts. This problem has complicated evaluation of certain portions of our studies.

Methods used for test site preparation, waste application and analytical work were similar or identical to those used in the Billings study. The oily sand was extremely viscous and could not be flowed onto the plots. Due to the small size of the oily sand test plots, we were able to manually distribute the waste over them.

Views of the oily sand and refinery waste plots are shown in Figures 6 through 9. Test plots were fertilized after waste weathering and soil waste blending.

The composition of the refinery oily waste is shown in Table 12. Addition of this waste to the soil produced the waste-in-soil levels shown in Table 13. The oil in the refinery waste was found to contain 21% paraffin, 49% aromatics and 30% resins-asphaltenes (Table 14). Amounts of nitrogen (as NH_4) in the fertilized test plots ranged from 50 mg/kg soil to 320 mg/kg soil and phosphorus (as PO_4) ranged from 10 to 50 mg/kg soil. To date we have noted no detectable effect of fertilizer level, within these concentration limits, on the rate of oil degradation. Even in the most heavy fertilized plots, we have not found over 20 ppm NO_3.

Over a 24-month exposure period, we have measured at 35% loss of oil from the test plots.

Composition of the oily sand that we have been investigating is shown in Table 15. In oily sand test plots ammonium nitrogen and phosphate phosphorus levels have been kept above 50 and 30 mg/kg, respectively. Soil water contents have stayed around 15% (about 30% of moisture holding capacity) during exposure and we have observed no difference in pH between test plots and control plots.

Soil core samples, 30 inches deep, were taken directly beneath test plots and in central areas one year after oily waste was applied to the test areas. Results of extractable oil and organic carbon measurements on these cores are shown in Table 16. As can be seen, these data indicate that the waste has been strictly held within the shallow soil zone in which it was originally placed. For these tests we selected plots to which we had added 8 and 10 weight % oil to the soil in order to examine most severe test conditions.

As may be seen in Figure 10, we have observed about 40% degradation of oil in these oily sand test plots over a 22-month period. Actually this expression is an average of what we observed over several plots. A plot that initially had 8% oil in the soil was found to

have experienced a 41% oil loss and several 5% oil plots showed an average of 45% oil loss. This small difference, of course, has a sizable effect on mass oil lost. This is illustrated in Table 17.

Oil composition measurements (see Figure 8) have shown that about 82% of the paraffins were lost along with 60% of the aromatics. Only 1% of the resin-asphaltenes fraction was lost. This oil initially contained 22% paraffins, 28% aromatics and 50% resin-asphaltenes. The 22-month residue consists of over 80% resin-asphaltenes.

OVERALL PERSPECTIVE OF LAND FARMING DISPOSAL OF OILY WASTES

Several companies have been practicing various forms of land farming as a means of oily waste disposal for many years. While most have relied on visual oil loss as evidence of success, several investigators have examined the technical aspects of land farming in recent years. Among those that have carried out such investigative studies are Shell Oil Company, Union Carbide and Sun Oil Company. A summary of oil and oily wastes studied and reported rates of oil degradation are shown in Table 18. We have taken the liberty of converting all reported rates into annualized figures and identical units of measure so they can be more easily compared.

All of these data support the contention reached long ago with little or no analytical data; crude petroleum and many of its components are biodegraded in the soil. Of course, we still don't know to what extent such materials are degraded in the soil. This we must learn. We have also some data now that oil in the soil can be degraded at reasonable rates in climates as cold and as arid as Montana, as well as in warmer and more humid climates such as Houston and Corpus Christi. We have also learned that if we can mechanically handle the presence of an initial oil addition of 10% in the soil, the rate of oil degradation is greater. Here at CONOCO, we found that 5% additions are much more manageable, especially during the initial stages of waste oil and soil blending. We now have data that indicates that as little as 50 ppm nitrogen and 20 ppm phosphorus (109 lb. and 44 lb. per acre, respectively) are sufficient to support the degradation of some oils at their maximum rates in some climates. We also have data that indicates oil in soil can be decomposed at reasonable rates even when the water content of the soil stays below 20%. We have evidence that waste oil tends to stay tightly bound in soil to which it is added while degradation is occurring. There is some data that indicates normal crops can be grown in soil where oily waste is being decomposed. All of these data are encouraging for those of us who hope we can prove the acceptability of land farming as an oily waste disposal technique.

There remains, however, a number of very important factors that must be more clearly established before we can safely recommend the full scale use of land farming for the disposal of oily wastes. These factors are listed in Table 19. We believe that until these factors are reasonably well established, the disposal of oily wastes by land farming must be very carefully controlled and safeguarded against any unforeseen environmental hazards.

ECONOMICS OF OILY WASTE DISPOSAL BY LAND FARMING

At present it appears that land farming represents a relatively inexpensive disposal method. An example of what costs might be are shown in Table 20. We are aware that costs will vary widely with land cost, labor costs, amount of analytical work required, type of oily waste applied and other factors. In this example we have used a land cost of $1,000/acre, costed borrowed capital at 10% for 10-years and assumed very small fertilizer requirements. It is obvious that we need more clearly defined bases for establishing oily wastes land farming costs.

In summary, we are encouraged by data that indicates land farming to be an effective, safe and economic disposal method for at least some oily wastes. We believe, however, that considerably more investigative effort must be expended before the concept can be safely used on a wide scale basis. Finally, it is imperative that sound data be utilized to construct reasonable but precise ground rules for the effective, safe and economic use of land farming for oily wastes disposal.

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(10) Francks, H. C., et al, "Disposal of Oil Wastes by Microbial Assimilation," NTIS, Y-1934, May (1974).

DISCUSSION

John Smith: This is not a particular question, but just a general comment concerning the solids wastes, the problem facing the petroleum industry. As most of you know the EPA has contracted a study for the potentially hazardous waste and that document is being prepared to reference the guidelines. They have now advertised for contractual bids another study in the same line reference to the investigation of various methods of elimination of these hazardous wastes. The first study was predicated on the incineration, land farming, etc. and now they are coming out asking contractors to look into other methods of waste disposal from petroleum operations. The point being here that EPA is very aware of and is going to be spending money reference to solids waste disposal so it is a very timely topic.

Robert Huddleston: I will speak for all of us - I hope they are successful in finding more economical and acceptable disposal methods.

R. A. Farnham: We have been doing some land farming experiments and you mention soil water contents. Now you are talking weight percent water rather than percent field capacity, are you?

Robert Huddleston: Yes, for the soils we have examined, the water holding capacities tend to average about 60 weight %. Thus, when these soils contain 30% moisture, the moisture content is condusive to good microbial activity.

R. A. Farnham: That's for clay?

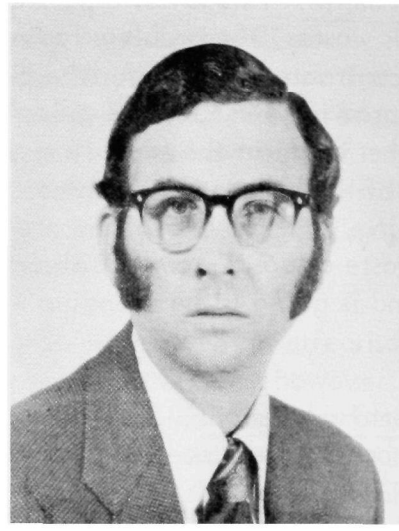
Robert Huddleston: Yes, clay type soils.

Anonymous: For those of us who have trouble with numbers, your number describing Shell's rate of oil degradation experience was 165 g oil lost per kg of soil per year. Was that fertilized or unfertilized?

Robert Huddleston: I used the fertilized rate in the table.

BIOGRAPHIES

Lewis W. Cresswell is a Research Scientist in the Environmental Group of Continental Oil Company's Research and Development Department. He has a B.S. degree in Chemical Engineering from Mississippi State University. Prior employment includes Continental's Process Engineering Environmental Group and the U.S. Environmental Protection Agency, Denver Region.



Robert L. Huddleston is supervisor of the Environmental Research Group in the Research and Development Department of Continental Oil Company, Ponca City, Oklahoma. He holds B.S. and M.S. degrees in Microbiology from the University of Oklahoma and has taken additional studies from Oklahoma University and Oklahoma State University in Microbiology and in Environmental Science. He is currently Vice President of the Society For Industrial Microbiology. Bob has been a member of Conoco R&D for almost 20 years and has authored more than 25 papers dealing with various aspects of industrial microbiology and waste treatment.



TABLE 1 "SOURCES OF OILY REFINERY WASTES"

	Typical Weight % Composition		
	Water	Solids	Oil
Crude Oil Tank Bottoms	15	45	40
Slop Tank Bottoms	64	4	32
API, CPI Separator Bottoms	36	47	17
Biotreatment Solids	96	4	0.4
Coker Blowdown Solids	20	40	40
Water Impoundment Pond Bottoms	40	40	20

TABLE 2 "HISTORICAL DISPOSAL OF OILY SOLIDS"

Burning	Road Surfacing
Landfill	Ocean Dumping
Surface Pitting	Burying

TABLE 3 "MICROBIAL DISTRIBUTION IN SOIL"

(TAKEN FROM ALEXANDER, 1961) (5)

	Organisms Per Gram of Soil				
Depth (cm)	Aerobic Bacteria	Anaerobic Bacteria	Actinomycetes	Fungi	Algae
3-8	7,800,000	1,950,000	2,080,000	119,000	25,000
20-25	1,800,000	379,000	245,000	50,000	5,000
35-40	472,000	98,000	49,000	14,000	500
67-75	10,000	1,000	5,000	6,000	100
135-145	1,000	400	-	3,000	-

TABLE 4 "HYDROCARBON SOLUBILITY IN WATER"

(TAKEN FROM MING, 1974, AND "FATE OF OIL SPILT AT SEA," 1973) (6,7)

	PPM in Distilled Water
Benzene	1800
Xylene	175
Octane	1
Anthracene	0.075
C_{30} Paraffin	0.002
Chrysene	0.002
Gas Oil	0.0003 - 0.00000008
Kerosene	0.0001 - 0.2
Bitumen	10^{-14}

TABLE 5 "SOIL PARTICLE SIZE AND SURFACE AREA"

(TAKEN FROM ALEXANDER, 1961) (5)

	Diameter mm	No. Particles Per g Soil	Surface Area sq cm/g
Fine Gravel	2.00 - 1.00	90	11.3
Sand	1.00 - 0.05	722 - 722,000	22.7 - 227
Silt	0.05 - 0.002	5,780,000	454
Clay	0.002	90,300,000,000	11,300

*Based on spherical shapes and maximum diameters

TABLE 6 "LAND FARMING OILY WASTE"

Waste Analysis
Land Selection and Preparation
Waste Application
Fertilizer Application
Cultivation and Other Care

$$\text{Oil} + O_2 + N + PO_4 \xrightarrow[\text{Activity}]{\text{Microbial}} \text{Microbial Cells} + CO_2 + H_2O$$

TABLE 7 "QUESTIONS ABOUT LAND FARMING OILY WASTE SOLIDS"

1. What type of waste can be applied?
2. How long does it take for the oil to be decomposed?
3. Is there any oil residual? How much? What is it?
4. Are there any environmentally harmful materials formed?
5. Will the oil or other waste components migrate through the soil?
6. Mechanically, how is the waste best applied and blended with the soil?
7. How much fertilizer must be added?
8. Is subsequent cultivation required?
9. Should plant growth be established on the site?
10. How do different climatic conditions affect the process?

TABLE 8 "BILLINGS REFINERY WASTE POND BOTTOMS"

Analysis	WT %	Metal Content	mg/kg	Metal Content	mg/kg
Extractable Oil	15	Silicon	12,900	Iron	12,000
Water	72	Calcium	10,900	Aluminum	4,300
Solids	13	Chromium	1,900	Magnesium	890
Total Organic Carbon	10	Sodium	810	Zinc	690
		Barium	370	Copper	360
		Lead	50	Nickel	10
		Vanadium	10		

TABLE 9 "TREATMENT OF BILLINGS LAND FARM TEST PLOTS"

	Months of Exposure											
	0	1	2	3	4	7	12	13	14	15	17	18
Cultivation	R (1)	R	R					D (2)			D	D
Fertilization			1									
Sampling (3)	1	1	5	4	2	1	1		4	4	1	3

(1) R = Rototiller
(2) D = Disc
(3) Numbers refer to samplings per month

TABLE 10 "INITIAL BILLINGS LAND FARM SOIL-WASTE COMPOSITION DUE TO WASTE ADDITION"

Analysis	WT %	Analysis	mg/kg	Analysis	mg/kg
Extractable Oil	0.93	Nitrogen	130	Phosphate	20
TOC	1.2	Iron	720	Calcium	650
		Chromium	115	Sodium	50
		Zinc	41	Copper	22
		Lead	3		

TABLE 11 "OIL LOSS - BILLINGS LAND FARM"

18 Months	Annualized
15,840 lb/Acre Soil	10,560 lb/Acre Soil
7.2 g/kg Soil	4.8 g/kg Soil

TABLE 12 "PONCA CITY REFINERY TEST OILY WASTE"

Analysis	WT%	Metal Content	mg/kg	Metal Content	mg/kg
Extractable Oil	39	Silicon	21,000	Calcium	13,000
Water	24	Aluminum	3,200	Iron	3,000
Solids	37	Lead	1,400	Magnesium	880
Total Organic Carbon	53	Sodium	870	Potassium	480
		Zinc	400	Chromium	370
		Barium	240	Strontium	180
		Copper	150	Titanium	150
		Manganese	130	Nickel	21
		Vanadium	21	Cadmium	3

TABLE 13 "PONCA CITY REFINERY WASTE IN SOIL"

Analysis	WT% of Soil	Metal Content	mg/kg of Soil	Metal Content	mg/kg of Soil
Extractable Oil	4.8	Silicon	2,600	Calcium	1,600
Water	3.0	Aluminum	390	Iron	370
Solids	4.6	Lead	170	Magnesium	108
Total Organic Carbon	6.5	Sodium	107	Potassium	60
		Zinc	50	Chromium	46
		Barium	30	Strontium	22
		Copper	18	Titanium	18
		Manganese	16	Nickel	3
		Vanadium	3	Cadmium	0.4

TABLE 14 "OIL COMPOSITION IN PONCA CITY REFINERY WASTE SUBJECTED TO LAND FARM STUDY"

Analysis	WT %
Paraffins	21
Aromatics	49
Resins-asphaltenes	30

TABLE 15 "PONCA CITY OILY SAND WASTE"

Analysis	WT %
Extractable Oil	27
Water	4
Solids (sand)	69
Total Organic Carbon	10

Metal Content	mg/kg	Metal Content	mg/kg
Sodium	2,000	Calcium	1,000
Magnesium	260	Chromium	90
Copper	90	Lead	90
Vanadium	90	Nickel	130

TABLE 16 "CORE ANALYSES - OILY SAND LAND FARM TEST PLOT AND CONTROL AREAS"

		Sampling A		Sampling B	
	Core Depth	Control	Test Area	Control	Test Area
Extractable Oil (Wt. %)	0 - 6"	0.15	4.79	0.11	6.35
	6 - 9"	0.20	0.19	0.05	0.10
	9 - 12"	0.09	0.17	0.02	0.05
	12 - 15"	0.09	0.08	0.03	0.05
	15 - 18"	0.11	0.18	0.03	0.05
	18 - 24"		0.14	0.05	0.05
	24 - 30"		0.06		
Organic Carbon (Wt. %)	0 - 6"	1.90	5.74	1.48	6.15
	6 - 9"	0.79	0.79	0.87	1.53
	9 - 12"	0.26	0.31	0.93	1.04
	12 - 15"	0.29	0.37	0.81	0.91
	15 - 18"	0.25	0.60	0.62	0.79
	18 - 24"		0.78	0.52	0.60
	24 - 30"		0.61		0.56

TABLE 17 "OIL LOSS % AND RATE - PONCA CITY OILY SAND LAND FARM STUDY"

Initial % Oil In Soil	% Oil Loss Per Year	Mass of Oil Lost Per Year
5	25	27,500 lb/acre soil (12 g/kg soil)
8	22	38,720 lb/acre soil (18 g/kg soil)

TABLE 18 "REPORTED RATES OF OIL LOSS DURING LAND FARM STUDIES"

(TAKEN FROM SUN, SHELL, UNION CARBIDE, NEW ZEALAND DATA) (8,9,10)

		Gm Oil Lost Per kg/soil/year	Approximate Initial Oil in Soil Concentration (wt. %)
Refinery Oily Waste			
CONOCO -	Billings	7	1
	Ponca City	9	5
Shell -	Houston	165	10
Petroleum Crude Oil			
CONOCO -	Ponca City	17	5
Sun -	Marcus Hook, Tulsa, Corpus Christi	14 ± 2	1
Lube Oil Waste			
Sun -	Marcus Hook, Tulsa, Corpus Christi	18 ± 5	5
New Zealand		27	2
		38	5
		69	7
		454	9
Waste Vacuum Pump Oil			
Union Carbide -	Oak Ridge	171	7
#6 Fuel Oil			
Shell -	Houston	311	10
Sun -	Marcus Hook, Tulsa, Corpus Christi	20 ± 7	2

TABLE 19 "FACTORS TO ESTABLISH PROPER USE OF LAND FARMING"

1. Firm establishment that oily waste is not mobile with respect to waste composition, soil composition and climate.

2. Final extent of waste oil decomposition in the soil as related to oil composition.

3. Demonstration that no dangerous substances are present or produced when oily wastes are land farmed.

4. What types of vegetation can be grown on oily waste land farms and what effects does such growth have on rate and extent of oil degradation.

5. Need precise nitrogen and phosphate requirements for oily wastes land farming.

6. Establishment of ground rules for safe and economic application of land farming for oily wastes disposal.

TABLE 20 "ESTIMATED COST OF LAND FARMING OILY WASTES"

100 tons of waste
25% oil
Application limited by oil degradation
Oil degradation rate - 15 g/kg soil/yr.
Farm life - 10 years

	Annual Cost ($)	% of Total
Land	355	16
Site Preparation	540	24
Diking, Fencing, Cultivation		
Waste Hauling (5 miles)	275	13
Waste Spreading	160	7
Fertilizer, Spreading	115	5
Cultivation of Soil-waste (4/yr)	160	7
Samples - Analytical Support	600	27
TOTAL COST	$2,205	

Cost per ton of waste: $22.05

FIGURE 1

Photograph of Billings' Land Farm Area Prior to Waste Spreading

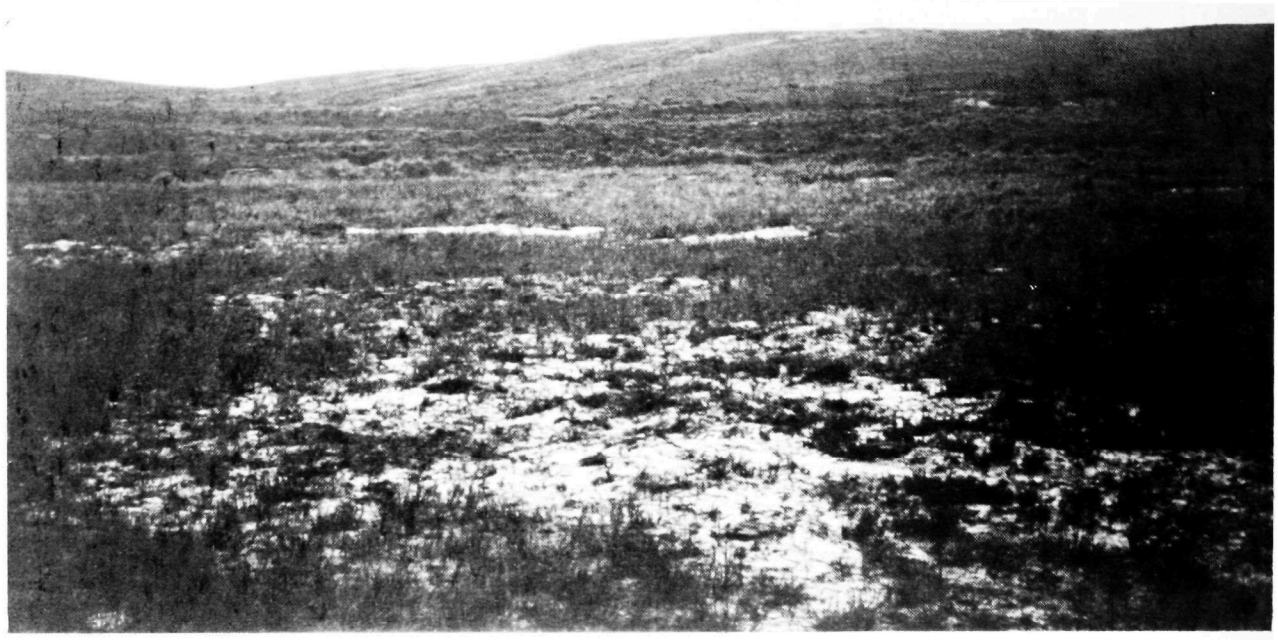


FIGURE 2

Photograph of Billings' Land Farm Area After Waste Tilled In



FIGURE 3

Photograph of Billings' Land Farm Area After Waste Tilled In - Close up



FIGURE 4

BILLINGS WASTE OIL LAND-FARM STUDY

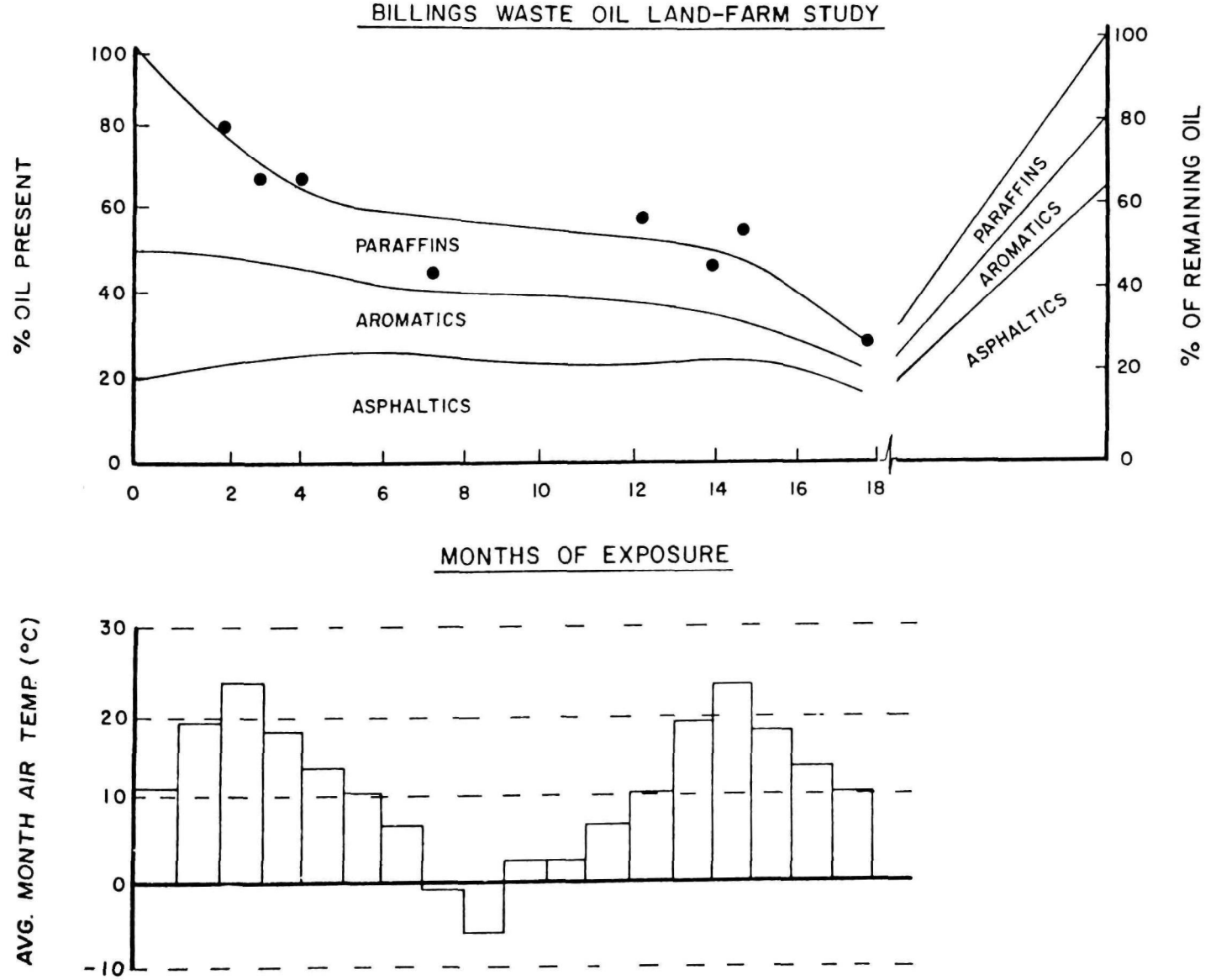


FIGURE 5

TOO - BILLINGS LAND FARM

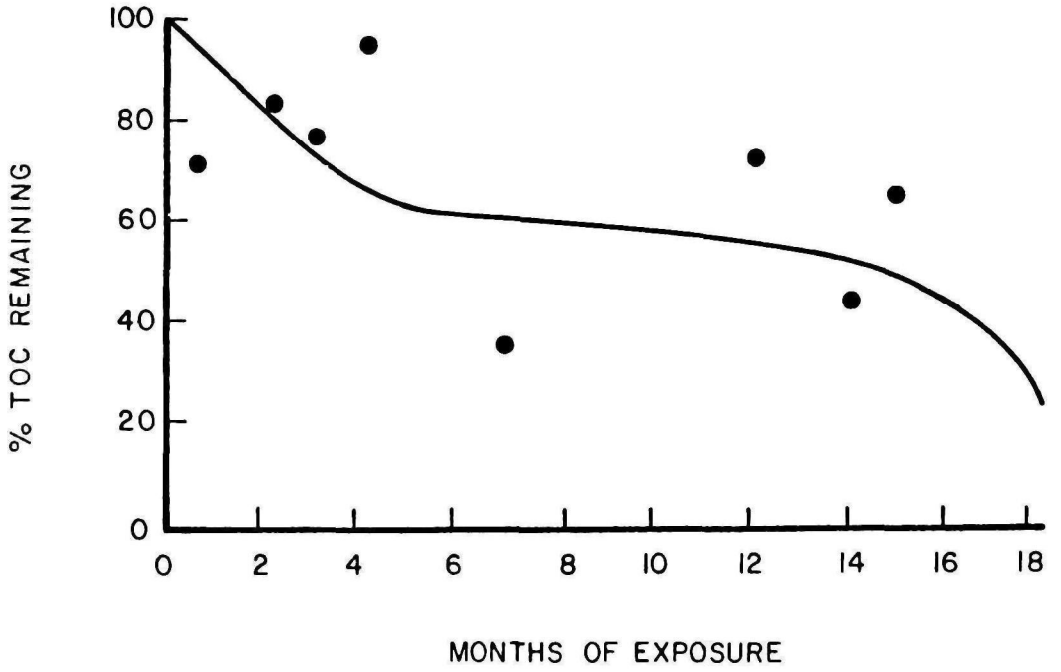


FIGURE 6
Photograph of Ponca City Refinery Waste Land Farm Area
Prior to Preparation



FIGURE 7

Photograph of Ponca City Refinery Waste Land Farm Area
After Waste Addition



FIGURE 8

Photograph of Ponca City Refinery Waste Land Farm Test
Area - Wheat Growth

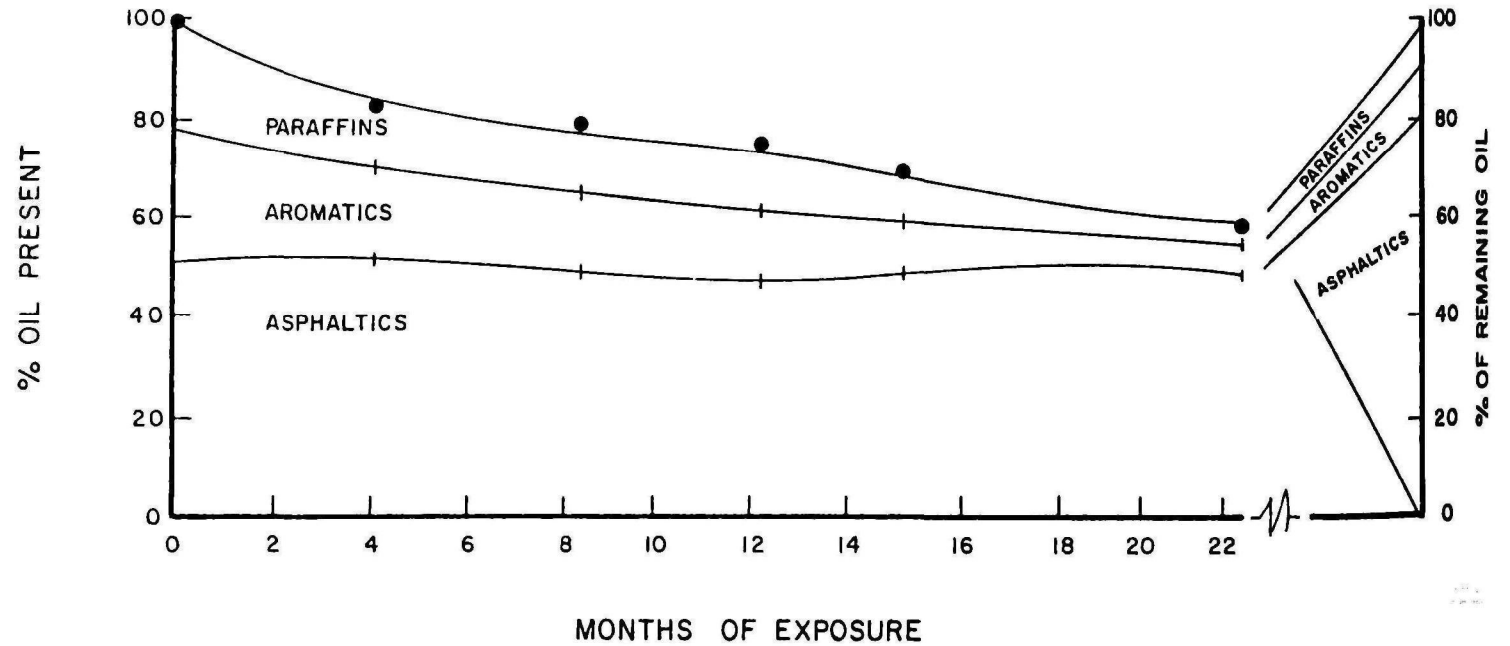


FIGURE 9
Photograph of Ponca City Oily Sand Land Farm Test System

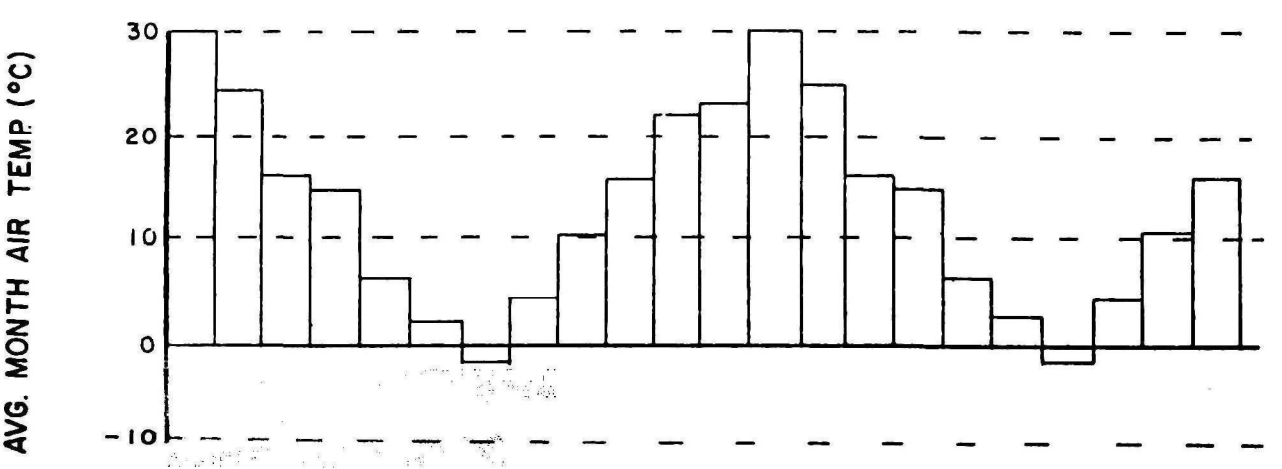


FIGURE 10

PONCA CITY CRUDE OIL LAND-FARM STUDY



MONTHS OF EXPOSURE



SESSION V

"ACTIVATED CARBON TREATMENT"

Chairman:

Nicholas D. Sylvester

Professor of Chemical Engineering

University of Tulsa, Tulsa, Oklahoma

Speakers

Davis L. Ford

"Current State of the Art of Activated Carbon Treatment"

C.T. Lawson

"Cautions and Limitations on the Applications of Activated Carbon Adsorption to Organic Chemical Wastewaters"

Joyce A. Rizzo

"Case History: Use of Powdered Activated Carbon in an Activated Sludge System"

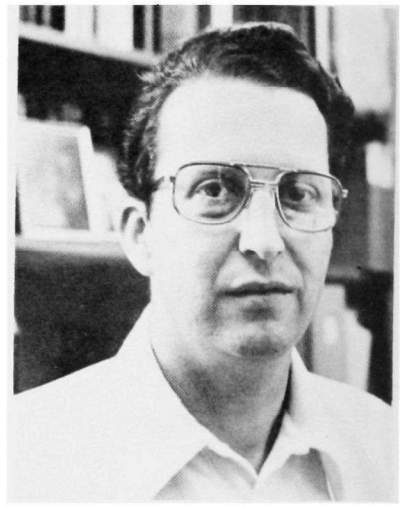
Leon H. Myers

"Pilot Plant Activated Carbon Treatment of Petroleum Refinery Wastewater"

M.A. Prosche

"Activated Carbon Treatment of Combined Storm and Process Waters"

BIOGRAPHY Nicholas D. Sylvester



Nicholas D. Sylvester is Professor of Chemical Engineering and Director of the Environmental Protection Projects program at the University of Tulsa. Dr. Sylvester received his B.S. degree from Ohio University, and his Ph.D. from Carnegie-Mellon University both in Chemical Engineering. Before coming to the University of Tulsa he taught at the University of Notre Dame. Nick is a member of the American Institute of Chemical Engineers, Society of Petroleum Engineers, American Chemical Society, Society of Plastics Engineers, Society of Rheology and the American Society of Engineering Education.

Professor Sylvester is currently conducting research in the following areas: two-phase flow, drag reduction, environmental protection, chemical reaction engineering and improved oil recovery. Dr. Sylvester has more than 50 technical publications and has been principal investigator of funded research totalling nearly $600,000.

In addition to his professional interests, Nick is active in youth athletic programs, having coached junior high basketball and elementary school baseball and soccer. He is also an avid, though, inept, golfer.

"CURRENT STATE OF THE ART OF ACTIVATED CARBON TREATMENT"

Davis L. Ford, Ph.D., P.E.
Senior Vice President
Engineering-Science, Inc., Austin, Texas

The treatment of wastewaters using activated carbon has received wide attention for several years - more recently catalyzed by the development of effluent quality guidelines pursuant to Public Law 92-500. These effluent quality criteria and the accompanying development documents prominently mention carbon as an applicable and attractive treatment concept, particularly in the Best Available Treatment Economically Achievable (BATEA) process mode currently stated as necessary to produce the 1983 quality level objective. Until recently, most of the literature has dealt with exploring theoretical concepts and documenting experimental results. As more information on full-scale operations is becoming available, however, it is considered appropriate to review the current state of the art of activated carbon treatment - both in municipal and industrial sectors. It is the purpose of this treatise, therefore, to present pertinent and current information relative to the activated carbon treatment of municipal and industrial wastewaters. A brief discussion of adsorption concepts and carbon characteristics also is included.

ADSORPTION CONCEPTS AND THEORY

Molecules are held together by cohesive forces ranging from strong valence bonds to the weaker van Der Waals forces of attraction. These attractive forces are satisfied in the solid phase interior molecules, having the ability to capture certain fluid molecules as they contact the surface. van Der Waals forces are the bases for the adsorption of wastewater constituents onto carbon which has been activated to maximize this interphase accumulation of liquid constituents at the surface or interphase of the solid phase.

The rate at which substances are removed from the liquid phase (adsorbate) to the solid phase (adsorbent) is of paramount importance when evaluating the efficacy of activated carbon as a wastewater treatment process. Unfortunately, the task of quantifying the many forces acting at the solid-liquid interface is a formidable one. Developing a mathematical expression which describes the dynamic phenomenon occurring in a continuous-flow/fixed-bed reactor has been difficult because of multi-variable influences. The overall adsorption rate represents the combined effects of diffusion through a laminar layer of fluid surrounding the constituent, surface diffusion, and adsorption on the internal pore surfaces. Most mathematical solutions for equations which describe concentration/time profiles are limited to the special case in which only one of these phenomena controls the overall rate of adsorption (1).

One expression for the continuous-flow regime assumes the diffusion of the constituent through the liquid phase and through the pores of the carbon (which are rate-limiting), then combining these resistances in an overall mass coefficient term. Using this rationale:

$$q\frac{dC}{dD} = k_2 r(C_s - C) \qquad \text{(Eq. 1)}$$

where:

q	=	flow rate
C_s	=	concentration of the adsorbate
D	=	adsorbent bed depth
C	=	equilibrium adsorbate concentration
k_2r	=	overall mass transfer coefficient

A more convenient expression of Equation 1 is in terms of the adsorbate rate with respect to the weight of the carbon in the columns:

$$q\, dC/dM = k_2r/X\ (C_s-C) \qquad \text{(Eq. 2)}$$

where:

M	=	weight of the carbon in the column
X	=	packed density of the carbon in the column

Another proposed model predicts four successively decreasing adsorption rates would be observed as the adsorption proceeds to equilibrium. The initial rate would be limited by the rate of adsorbate transfer across the film layer, film diffusion, or, if sufficient turbulence existed, control would be exerted by the combined rate of external surface adsorption and macropore filling. After the external surface adsorption capacity was exhausted, there would exist three secondary adsorption rates controlled, respectively, by the filling of the macropore (an effective radius of 5,000 to 20,000 A°), the transitional pore (20 to 100 A°), and the micropore (10 to 20 A° effective radius). This model is illustrated in Figure 1 (2). It is inherent in this model that the intraparticle transport occurs as a series of adsorption/desorption steps, each linear with respect to time, and their summation resulting in a time/linear function.

The development of adsorbate removal kinetics on a batch basis can be used to approximate carbon effectiveness and predict organic residual levels. The adsorption isotherm is used for this purpose and is defined as a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at a constant temperature. The isotherm is expressed in terms of removal of an impurity - such as BOD, COD, and color - per unit weight of carbon as a function of the equilibrium impurity remaining in solution. Linear plots as shown in Figure 2 can be expressed in terms of the empirical Freundlich equation. This expression relates the amount of impurity in the adsorbed phase to that in solution:

$$\frac{X}{M} = KC^{1/n} \qquad \text{(Eq. 3)}$$

where:

X	=	amount of impurity adsorbed
M	=	weight of carbon
C	=	equilibrium concentration of impurity in solution
K, n	=	constants

The Freundlich isotherm is valid within the context of a batch test for pure substances and some dilute wastewaters. As shown in Figure 2, its application is limited in certain

cases when a significant portion of the organic impurities are not amenable to sorption, resulting in a constant residual, regardless of the carbon dosage.

The constants "n" and "K" can be used to define both the nature of the carbon and the adsorbate. A high "K" and "n" value, for example, indicate good adsorption throughout the concentration range studied. A low "K" and "n" value would infer low adsorption at dilute concentrations with high adsorption at the more concentrated levels. Variations of the constants for selected wastewaters are shown in Table 1 (3).

FACTORS WHICH INFLUENCE ADSORPTION

There are many factors which influence both the rate and magnitude of adsorption - underscoring the difficulty in developing predictive models which would apply to all complex wastewaters. A brief discussion of the more important factors is presented herein.

Molecular Structure. The molecular structure, or nature of the adsorbate, is particularly important in dictating the degree of adsorption that can actually occur. As a rule, branched-chain compounds are more sorbable than straight-chain compounds, the type and location of the substituent (functional) group affects adsorbability, and molecules which are low in polarity and solubility tend to be preferentially adsorbed. Unless the screening action of the carbon pores actually impedes, large molecules are more sorbable than small molecules of similar chemical nature. This is attributable to more solute chemical bonds being formed, making desorption more difficult.

Inorganic compounds demonstrate a wide range of adsorbability. Disassociated salts - such as potassium chloride and sodium sulfate - are essentially nonsorbable. Mercuric chloride and ferric chloride are relatively sorbable, and iodine is one of the most adsorbable substances known. Generally, however, a significant reduction in inorganic materials is not expected in carbon systems.

Organic compound sorbability can be classified to some extent. Primary alcohols and sugars, for example, are resistant to adsorption, while ethers and certain organic acids are highly sorbable. Recently published experimental data presented in Table 2 are indicative of the sorbability of many organic compounds (4). Additional sorbability data conducted independently are presented in Table 3.

Solubility. An increase in solubility acts to oppose the attraction of the adsorbate to carbon. Thus, polar groups which have a high affinity for water usually diminish adsorption from aqueous solutions. Conversely, the greater adsorption of the higher aliphatic acids and alcohols is attributed in part of their relatively lower solubility in an aqueous solution. There are exceptions to this, as in the case of the highly soluble chloracetic acid (5).

Ionization. Ionization is generally adverse to adsorption by carbon as strongly-ionized materials are poorly adsorbed. Hydrogen ions, which are significantly adsorbed under some conditions, would be an exception to this. Some negative ions, therefore, are more sorbable when associated with hydrogen ions. For this reason, mineral acids - such as sulfuric acid - are sorbable at higher concentrations.

A change in ionization can drastically affect adsorption. A low pH, for example, promotes the adsorption of organic acids whereas a high pH would favor the adsorption of organic bases. Phenol adsorbs strongly at neutral or low pH while the adsorption of the phenolate salt at a high pH is poor. The optimum pH is therefore solute-specific and must be determined for each wastewater.

Temperature. As adsorption reactions are generally exothermic and high temperatures usually slow or retard the adsorption process, lower temperatures have been reported to favor adsorption (1,5). Very little information has been presented, however, which documents significant shifts in adsorbability within the temperature range of 65°F to 90°F (typical of most wastewaters). Lower temperatures should increase adsorption, but the effect in aqueous solutions is very small.

Adsorption of Mixed Solutes. Most wastewaters contain a myriad of compounds which may mutually enhance, interfere, or act independently in the adsorption process. Factors which affect overall adsorption of multiple adsorbates include the relative molecular size and configuration, the relative adsorptive affinities, and the relative concentrations of the solutes (1). Predictive models obviously require validation for complex wastewaters, as extrapolation from investigations using synthesized wastes containing controlled concentrations of selected adsorbates may not reflect all of the interactions occurring in the waste.

A summary of the factors which potentially influence adsorbability is presented in Table 4.

PROPERTIES OF ACTIVATED CARBON

Activated carbons are made from a variety of materials including weed, peat, lignin, bituminous coal, lignite, and petroleum residues. Granular carbons produced from medium volatile bituminous coal or lignite have been most widely applied in the treatment of wastewater as they are relatively inexpensive and readily available. The activation of carbon is essentially a two-phase process which includes burning off the amorphous decomposition products and enlarging the pores in the carbonized material (6). The burn-off, or carbonization, phase involves drying the carbon at approximately 170°C, heating the material to 270°C to 280°C with the evolution of carbon monoxide, carbon dioxide, and acetic acid, and, finally, completing the carbonization process at a temperature of 400°C to 600°C. The yield following carbonization is approximately 80 percent. The intermediate product is then activated by using carbon dioxide or steam at a temperature of 750°C to 950°C, burning off decomposition products, exposing and widening the pores in the development of macroporous structure. In the activation process, the kind of adsorptive powers developed are determined by:

1. the chemical nature and concentration of the oxidizing gas;
2. the extent to which the activation is conducted;
3. the temperature of the reaction; and
4. the amount and kind of mineral ingredients in the char (5).

The proper activation conditions provide an oxidation which selectively erodes the surface so as to increase the surface area, develop greater porosity, and leave the remaining

atoms arranged in configurations that have specific affinities.

Activated carbons from coke, coal, or lignite have specific properties, depending on the material source and the mode of activation. Property standards are therefore helpful in specifying carbons to perform a specific task.

As a rule, granular carbons made from calcined petroleum coke have the smallest pore size, the largest surface area, and the highest bulk density. Lignite carbon has the largest pore size, least surface area, and the lowest bulk density. Bituminous coal has a bulk density equal to that of petroleum coke and an average pore size and surface area somewhere between those of petroleum coke and lignite-based carbons (7). A brief description of carbon properties follows:

Total Surface Area: This is the surface area of carbon expressed in square meters per gram, normally measured by the adsorption of nitrogen gas by the BET method (8).

Carbon Density: Apparent density is the weight in grams of one ml of carbon in air. Bulk density, backwashed and drained, is often used and is usually expressed in pounds per cubic foot.

Particle Size Distribution: The particle size distribution is critical in terms of hydraulic loading and backwash rates. Commonly manufactured particle size ranges for granular activated carbons expressed in limiting U.S. Standard Sieve Sizes include 8 x 16, 8 x 30, 10 x 30, 12 x 40, and 20 x 40. Effective sizes (sieve opening at which 10 percent of the material passes) range from 0.55 mm to 1.30 mm. In general, the uniformity coefficient (the millimeter opening at which 60 percent of the material passes divided by the millimeter opening at which 10 percent of the material passes) for granular activated carbon should not exceed 2.1.

Adsorptive Capacity: The best measure of adsorptive capacity is the effectiveness of the carbon in removing the critical constituents (BOD, COD, color, etc.) from the wastewater in question. Various tests, however, have been developed to give relative removal capacities of activated carbon under specific conditions. Phenol number is used as an index of a carbon's ability to remove taste and odor compounds; tannin is representative of organic compounds added to water by decayed vegetation; and iodine and molasses numbers are used to show if a carbon is activated. The iodine number, defined as the milligrams of iodine adsorbed by one gram of carbon (with an iodine concentration in the residual filtrate is 0.03) is probably the most widely used method of expressing carbon capacities. It generally can be correlated to the ability of an activated carbon to adsorb low molecular weight substances while the molasses number correlates the carbon's ability to adsorb higher molecular weight substances. The iodine number measures the micropores having an effective radius of less than 20 angstroms and the molasses number measures the transitional pores ranging from 20 to 500 angstroms.

These are the principal general parameters used in specifying carbons, the objective being the selected carbon

1. has the adsorption capability to meet the effluent requirements;
2. incurs minimal losses occurring during carbon transport and regeneration;
3. has good hydraulic characteristics with respect to head loss or pressure drop; and
4. represents the most cost-effective media to accomplish the prescribed task.

These, of course, represent general parameters of specification and should be augmented by test data and process requirements developed from bench- or pilot-scale evaluation using representative wastewater samples and selected carbons.

Comparative properties of the most widely used carbons in wastewater treatment - those from lignite and bituminous coals - are shown in Table 5 (6); a broader presentation of properties from commercial carbon manufacturers also is tabulated in this Table (9). Typical properties of a petroleum-base powdered carbon developed but not yet marketed by AMOCO are shown in Table 6.

REGENERATION

Because of economic and solid waste disposal considerations, it is generally more feasible to regenerate spent carbon for subsequent reuse than to dispose of it. In the regeneration process, the objective is to remove from the carbon porous structure the previously-adsorbed materials, thus reinstituting its ability to adsorb impurities. There are several modes of regeneration which can be applied including thermal, steam treatment, solvent extraction, acid or base treatment, and chemical oxidation. Of these, only thermal regeneration using a multiple-hearth or rotary-tube furnace is widely applied in wastewater treatment. The discussion on regeneration therefore centers around thermal treatment.

Thermal regeneration refers to the process of drying, thermal desorption, and high temperature (1,200°F to 1,800°F) heat treatment in the presence of limited quantities of oxidizing gases such as water vapor, flue gas, and oxygen (10). Multiple-hearth furnaces are the most commonly used, although rotary kilns or fluidized-bed furnaces are occasionally applied.

The sequential stages in thermal regeneration are shown in Table 7. Of these steps, the gasification stage is the most critical. The system should be controlled in order to selectively gasify the sorbed organic material while minimizing the gasification of the carbon structure. Basically, there are three major variables involved in thermal regeneration. These include furnace temperature, residence time, and the carbon loading. Of these three, furnace temperature is controllable, although it may take several hours to adjust, the residence time can be changed by varying the rabble-arm speed in a multiple-hearth furnace, or the rotation rate and slope of the tube in a rotary kiln. Very little can be done to change the carbon loading, which affects the severity of regeneration required.

The multiple-hearth furnace is the most commonly used system for granular carbon regeneration. A schematic diagram of a typically-designed multiple-hearth furnace is shown in Figure 3. The wet spent carbon is added at the top of the furnace and drops from hearth to hearth, being raked along by the rabble arms. The temperatures shown for the various hearths are typical gas temperatures for granular carbon regeneration. It was

found that the addition of steam on hearths four and six gave a more uniform distribution of temperatures throughout the furnace. The effect of steam is to reduce the apparent density and increase the iodine number of the regenerated carbon (6). Normally, about one pound of steam per pound of carbon is used. Natural gas or fuel oil is usually added to supply the auxiliary heat. Although the fuel requirement varies, generally about 3,000 BTU/lb of carbon and 1,300 BTU/lb of steam generated is required.

Rotary kiln furnaces are not being installed in new facilities but many are still in use. The kilns are usually direct-fired, counter-current units with steam injection with up to 10 percent excess air. Again, natural gas or fuel oil is commonly used as auxiliary fuel. The heat efficiency of rotary kilns is less than that of multiple-hearths.

Fluidized-bed systems for powdered carbon regeneration have been evaluated on a pilot scale and appear to have promise (11, 12, 13). In this process a bed of inert granular material such as sand is fluidized by the upward flow of hot gases and the wet spent carbon is injected directly into the bed. The inert bed particles provide a reservoir of heat which is rapidly transferred to the spent carbon particles. The heat economy of the fluidized-bed furnace is less favorable than the multiple-hearth furnace or the rotary kiln - providing afterburners are not required.

There is considerable debate as to the effect of regeneration on carbon capacity, carbon losses during the regeneration cycle, and hydraulic characteristics of the regenerated carbon. Much of this is focused on the regeneration effects on lignite as compared to bituminous carbon. The manufacturers of lignite claim that, after a number of regeneration cycles, both carbons tend to become more like each other and perform the same (9). Specifically, lignite - while softer and lighter than bituminous - is less susceptible to change during regeneration and can be regenerated under less severe conditions (lower temperature and shorter residence time). The bituminous manufacturers note that lignite carbon losses per cycle are higher than bituminous, indicating a higher operating cost, and bituminous adsorption capacities based on molecular weights ranging from phenol at 94 to dextran at 10,000 are significantly higher than lignite (14). It is not the intent in this writing to favor one over the other, but simply to present information from manufacturers of both types. Based on discussions with independent evaluators of bituminous and lignite, several trends in thinking evolve. First, few full-scale plants using lignite are currently in operation, necessitating an evaluation based on pilot-plant studies. There appears to be little firm evidence that bituminous carbon capacities are higher than those of lignite, although screening tests should be conducted in any event to determine the optimum carbon to perform a specific task. Somewhat higher losses have been noted during regeneration of lignite as compared to bituminous (six to nine percent for lignite, and four to seven percent for bituminous over three cycles). Lignite requires lower temperature for its regeneration and more skilled regeneration operation and control. There has been little evidence to show significant hydraulic differences as demonstrated by head loss characteristics in the two carbons following regeneration. Carbon selection is therefore predicated on process test results, capital cost requirements, and an annualized cost evaluation.

EXPERIENCE IN CARBON TREATMENT OF MUNICIPAL WASTEWATERS

Treatment of municipal wastewaters using activated carbon has been practiced on a full scale for over 10 years. For this reason, ample performance records are presently available for a realistic evaluation of this application, both in the physical/chemical and biological effluent polishing modes of treatment. A summary of these systems has been tabulated elsewhere, but it is the intent in this section to document selected municipal facilities and discuss salient features of these systems which are pertinent to this overall discussion on carbon. The two effluent polishing systems selected for discussion are the South Lake Tahoe and Colorado Springs facilities. The physical/chemical discussion centers around the new plant being constructed for the Cleveland Regional Sewer District, with the Garland, Texas; Rosemount, Minnesota; and Pomona, California plants also included. A syllabus of these selected case histories is presented as follows.

South Tahoe Tertiary Treatment System. The first major and most widely publicized application of activated carbon in treating domestic wastewater was the system constructed for the South Tahoe Public Utility District in 1965. The plant was conceived to polish the effluent from an existing activated sludge facility to a quality level which would have little or no impact on the receiving waters in an ecologically-sensitive area.

The facility consists of a chemical mix-coagulation, precipitation, and clarification unit, an ammonia stripping tower (which has been used infrequently), a recarbonation and settling basin, mixed-media filters, carbon adsorption, and final chlorination. A simplified flow diagram is shown in Figure 4 (15). The water quality at various points in the process following 18 months of operation is presented in Table 8 (16). The more recently reported water quality at the various stages of treatment is presented in Table 9 (9). The carbon (bituminous) efficiency per regeneration period at the South Tahoe Plant is cited in Table 10 (6).

It should be recognized that this facility was a demonstration project, involving expensive capital and annual expenditures. With the possible exception of nitrogen, the effluent quality should represent the best level obtainable in treating a domestic wastewater effectively using maximum biological treatment polished by chemical treatment, filtration, and carbon adsorption.

Colorado Springs Tertiary Treatment System. As at Tahoe, the Colorado Springs treatment system involves chemical treatment, filtration, and carbon adsorption for polishing a slipstream of biologically treated effluent. There are basically two regimes of historical data from this facility. The first was when the slipstream was taken from an overloaded trickling filter effluent (the flow diagram schematically illustrated in Figure 5). The second regime follows the addition of a contact stabilization facility to the biological treating component of the system. This indicates that the influent to the polishing portion of the system, the design data for which are presented in Table 11, has a lower concentration of biodegradable organics in the second regime than in the first (17). This is detected in a general comparison of the effluent quality observed during the two periods. Effluent quality data from a three-month period in 1972 indicate an approximate level obtained during the first regime. The average quality values for the reactor-clarifier influent and effluent,

filter effluent, lead carbon column effluent, and polishing carbon effluent are tabulated in Table 12. The data averaged during the second regime of operation are shown in Table 13 (17). Considerable improvement is noted in the comparison, underscoring the need for adequate biological pretreatment if the tertiary system is to realize maximum performance. It is noted that the Tahoe and Colorado Springs (second regime) effluents are relatively similar - both plants have adequate biological pretreatment. The deterioration of effluent quality when this is not the case is evidenced in Table 12.

The Colorado Springs facility is using a bituminous coal activated carbon, using a multiple-hearth furnace regeneration system. As in the other carbon systems, there has been sulfide generation problems in the carbon vessel. This problem has been ameliorated by adding a copper sulfate solution (100 mg/l as $CuSO_4$) to the top of the carbon columns and altering the backwashing frequence to remove biological solids.

Cleveland Regional Sewer District Physical/Chemical System. A physical/chemical wastewater treatment plant of which activated carbon is an integral part is presently being constructed for the Cleveland Regional Sewer District (CRSD) at the Cleveland Westerly plant site. This system is designed to receive an average flow of 50 MGD with peak flows of 100 MGD. A flow diagram of this system is shown in Figure 6. Extensive pilot-plant treatability studies were conducted prior to finalizing the design as there is a significant industrial contribution in the raw waste load (18). Moreover, assurance of meeting the NPDES requirements of 20 mg/l BOD (30-day average) and 30 mg/l (seven-day average) was required. These studies, combined with those more recently conducted by CRSD, provided some interesting results with respect to carbon adsorption.

The raw waste load of the Westerly collection system documented during the two pilot studies (1970-71 and 1974-75) is shown in Table 14. The strength of this wastewater, combined with the organic nature of the industrial component, created some difficulty in meeting the required permit levels during the pilot-plant evaluation. Although these results could be overly-pessimistic for various reasons, CRSD evaluated several process alterations with the objective of improving process efficiency and effluent quality. Most of this investigation centered around the use of ozone injection - both as a post-carbon and as a precarbon mode of operation. The postozonation step was originally conceived as strictly a disinfection step, although some further reduction of BOD through ozone oxidation was anticipated. However, studies indicated the ozone requirement for disinfection to the required level of 200 fecal coliforms per 100 ml ranged from 2.6 to 10.9 mg/l (19). The higher doses were attributed to the ozone demand from the sulfides generated in the carbon columns and ferrous bicarbonate resulting from iron slugs in the influent. This ferrous species was solubilized in the recarbonation step and was not altered while passing through the carbon columns. As the higher demands of ozone are economically prohibitive, reducing the ozone-demanding constituents or looking closer at chlorine was merited. Moreover, postozonation did not improve organic effluent quality - as indicated in Table 15. Ozonation prior to the carbon columns was then applied by CRSD with encouraging results. This quality improvement in terms of a frequency analysis of carbon column effluent BOD is shown in Figure 7. The same trend in terms of COD is shown in Figure 8. These results infer that some nonsorbable compounds are converted to more sorbable intermediates through ozone transformations. This possibility

is substantiated in the literature, documenting ozone oxidation of aldehydes, ketones, and alcohols to carboxylic acids, the product being more sorbable than the reactants (20, 21). Based on these results, the possibility of injecting ozone prior to the carbon columns is being seriously considered because of the potential advantages of:

1. possibly transforming nonsorbable compounds to sorbable compounds, enhancing carbon adsorption efficiency;
2. reducing the bacterial load to the carbon columns through particle sterilization; and
3. increasing the dissolved oxygen level in the carbon column influent, reducing the possibility of sulfide production and anaerobic bacterial activity.

There may be problems concerning this approach, such as the technical problems involved with injecting ozone in the pressurized carbon influent line, the high decomposition rate of ozone, and enhancing corrosion potential in the carbon reactors. Moreover, disinfection following carbon adsorption still needs to be resolved. However, the advantages presently appear to outweigh the disadvantages and this approach is being seriously considered as a process modification.

Garland Physical/Chemical System. A physical/chemical treatment plant is presently being constructed at Garland, Texas. This 30 MGD plant is being designed to produce an effluent having less than 10 mg/l BOD and TSS. The raw wastewater quality used for design is presented in Table 16 (22). The flow diagram for this facility is shown in Figure 9. The carbon basins are common-wall concrete facilities, each having a surface area of 950 square feet and a depth of 10 feet. Nine basins can treat the 30 MGD, while the remaining basin is off-line for the backwashing or regeneration. The wastewater is in contact with the carbon for a minimum of 30 minutes and the upflow rate is 2.5 gpm/ft^2 at design flow. A 14.5 foot multiple-hearth furnace is designed to regenerate 80,000 pounds of carbon daily. Based on the treatability studies, an effluent quality of 15 mg/l COD and 10 mg/l BOD is predicted (22).

Rosemount Physical/Chemical System. The Rosemount, Minnesota physical/chemical facility has been in operation since 1974. The system receives between 0.3 and 0.6 MGD and consists of screening, chemical clarification using either lime or ferric chloride, prefiltration, upflow activated carbon adsorption, postfiltration, clinoptilolite ammonia exchangers, and disinfection. During the first year of operation, the average BOD removal was 90 percent, the average effluent BOD concentration being 23 mg/l. More recently, however, operating problems have been reduced and the reported effluent BOD has been in the range of five to 10 mg/l (23).

Pomona Physical/Chemical Pilot Plant. A pilot-scale physical/chemical system has been operating for 27 months in Pomona, California, under the auspices of the Los Angeles County Sanitation District and the Environmental Protection Agency. The objectives of this study included an evaluation of the long-term effectiveness of granular activated carbon in the removal of soluble organic matter from chemically-clarified municipal wastewater, controlling hydrogen sulfide generation in the carbon columns, and determining the effects of repeated thermal generations on carbon characteristics and performance.

A flow diagram of the pilot system is shown in Figure 10, the design data for which are presented in Table 17 (24). The primary organic control parameters used in these studies

were total chemical oxygen demand (TCOD) and the dissolved chemical oxygen demand (DCOD). A summary of the overall performance of the physical/chemical system is presented in Table 18. These quality levels represent average values observed during the 27 months of study. For comparative purposes, the effluent quality from an 8.0 MGD activated sludge system treating the same wastewater is also included. As noted in Table 18, the major portion of pollutants, with the exception of DCOD, was removed in the clarification phase.

The problems of excessive biological growths in the columns, particularly the biochemical reduction of sulfates, has persisted in many of the case histories cited. A review of this problem was therefore an integral part of the Pomona study. As microorganisms have the hydrogen acceptor preference of molecular oxygen, nitrate, sulfate, and oxidized organics, it follows that an environment having the presence of sulfates and organics and the absence of molecular oxygen and nitrates would favor the anaerobic sulfate reducers. The sulfide levels in the effluent approached as high as six mg/l. This was a major concern as sulfide production was correlated directly to net head loss in the column (head loss before the daily backwash minus the head loss after backwash). The fact that the column head loss was caused primarily by abundant biological growths in the column is underscored by the graphical relationship depicted in Figure 11 (24). Several methods of ameliorating the biological proliferation and sulfide production were undertaken. This concluded oxygen addition, intensive air/water backwash, chlorination, and sodium nitrate addition to the carbon column at an average dosage of 5.4 mg/l (as N) was determined to be the most effective in terms of retarding sulfide generation in the carbon column.

The spent carbon used in the regeneration studies was backwashed, dewatered to approximately 50 percent moisture, conveyed to a six-hearth furnace, and regenerated at temperatures ranging from 1,650°F to 1,790°F. Steam in the amount of 0.6 lb/lb of carbon was added to the lower two hearths to enhance the regeneration. The regeneration cycle normally took from 53 to 66 hours to complete. The effects of regeneration on the physical properties of the carbon are shown in Table 19 (24). A reduction in the iodine number (a measure of the extent to which the micropores have been cleared) is noted, although the molasses number (a measure of the extent of macropore clearing) is essentially unchanged. The ash content of the carbon, which measures the amount of calcium and other inorganic residues picked up by the carbon during service increased over 60 percent from the virgin level during the first regeneration. The ash increase during the second regeneration was less, however, with a decrease during the third regeneration. The overall carbon regeneration loss (bituminous coal) ranged from 2.5 to 6 percent with an average loss of 4.3 percent over three regenerations.

Summary. A summary of the municipal wastewater treatment using the tertiary applications of activated carbon has been published recently and is shown in Table 20 (6). A similar summary for a straight physical/chemical application of carbon is shown in Table 21 (6) and in Table 22 (25).

EXPERIENCE IN CARBON TREATMENT OF INDUSTRIAL WASTEWATERS

Although ample carbon treatment data from full-scale facilities are becoming available

from the municipal sector, much of the performance data in industrial applications evolves from pilot-plant studies. There are several full-scale carbon systems treating industrial wastewaters, however, and this section includes results from pilot studies and selected operational systems. Specifically, results from pilot-plant studies - primarily in the refinery and petrochemical sector - will be cited, as well as the full-scale systems at the ARCO Refinery near Wilmington, California, the Reichhold Chemicals system in Tuscaloosa, Alabama, and the British Petroleum Refinery in Marcus Hook, Pennsylvania.

Pilot Carbon Studies. There have been pilot studies conducted in the industrial sector evaluating activated carbon as both a total (physical/chemical) process and as an effluent polishing (tertiary) unit. Nine of these studies have been conducted by the author for various petrochemical and petroleum refining facilities (26). The efficiency ranged from 50 to 86 percent COD removal, as noted in Table 23. It should be recognized that these results were obtained using virgin carbon with controlled hydraulic and feed rate regimes. The attendant problems of full-scale operation and the effect of using regenerated carbon on process efficiency should be considered when translating these results to what might occur in an operating carbon treatment system.

A comprehensive pilot-plant study treating petroleum refinery effluents by activated carbon was conducted recently by the Environmental Protection Agency (27). Both API separator effluent and biologically-treated effluent were charged to the columns in order to obtain a comparative evaluation. The results of this study in terms of BOD and COD removal are plotted in Figures 12 and 13, respectively. It is apparent that, when operated in parallel, the biological system was more effective in removing BOD and COD - particularly the former. This is consistent with the results observed in pilot studies conducted by the author. It is also noted that carbon adsorption following biological treatment was particularly effective in reducing both the BOD and COD to low levels. The residual COD is in the same range as that cited in Table 23 when the carbon application mode and influent COD levels were similar. The complete results of this study are shown in Table 24. It is noted that there is no removal of cyanides or ammonia although there was a reduction of the cited organic constituents, particularly phenols. There was surprisingly good removal of chromium, copper, iron, and zinc although the exact mechanisms of removal were not determined. The carbon capacity observed in the columns was 0.31 lb TOC removed/lb of carbon, while the isotherm determined capacity was 0.12 lb/lb. This difference was attributed to biological activity observed in the column. The carbon regeneration activity analysis is reported in Table 25, the change in iodine and molasses numbers showing trends similar to those observed in previous studies. The investigators emphasized that these data were generated using virgin carbon in the columns, and cautioned that the pres ence of iron or aluminum salts present in the effluent could have a deleterious effect on the carbon through the regeneration cycle. They hypothesized that aluminum salts can remain on the surface of the carbon during regeneration, reducing the effective surface area of the carbon and reducing its adsorption capacity. Moreover, iron salts can catalyze oxidation reactions of the carbon and the gases during regeneration, thus permanently damaging the carbon structure (27).

Extensive pilot-plant studies have been conducted recently by Union Carbide evaluating activated carbon as a tertiary process treating effluent from an activated sludge plant

receiving petrochemical wastewaters (28). The objectives of this study were both to establish a basis of justification for applying activated carbon and to optimize its design. Controlled organic and hydraulic application rates were applied to pilot-scale carbon columns. The results of the various throughput rates are listed in Table 26. The first verity which can be deducted from this Table is the fact that, as the activated sludge improves in quality, the efficiency of the adsorber in terms of COD or soluble organic carbon (SOC) improves. The improved efficiency with decreasing hydraulic throughput rates is also apparent. There was still a 30 to 50 percent COD residual in the adsorber influent attributable to organic compounds which are neither biologically degradable nor sorbable on activated carbon. There was a high BOD residual at the same throughput rate, although this residual was reduced to 35 to 50 percent of the adsorber influent at the uneconomical throughput rate of 0.15 bed volumes per hour. This BOD residual includes low molecular weight-oxygenated organics such as aldehydes, ketones, alcohols, glycols, and other polar organics which are adsorbed to a very limited extent. Other observations from this study are cited as follows:

1. breakthrough curves for multi-component wastewaters tend to be poorly defined and sporadic rather than sharp sigmoidal wavefronts;
2. in multi-bed series adsorbers, the lead bed removes the more readily-adsorbable organics and has the highest adsorptive capacity - typical capacities through both beds ranged from 0.2 to 0.4 lb COD/lb of carbon and 0.1 to 0.3 lb BOD/lb of carbon (the observed capacities for the first bed generally were twice as high as those observed in the second); and
3. the maximum hydraulic application rate that appeared to be technically justifiable was 0.5 bed volumes per hour (through both columns of the series).

Full-scale Carbon Studies. There are currently several full-scale operational carbon treatment systems in the United States. Three systems from which data are available are cited here. These include the Atlantic Richfield (ARCO) system in California, the Reichhold system in Alabama, and the British Petroleum (BP) system in Pennsylvania.

ARCO Carbon Treatment System (Watson Refinery)

The first full-scale carbon treatment system in the petroleum refining industry was installed by ARCO at their Watson Refinery near Wilmington, California. This facility was necessitated by a resolution from the Los Angeles Regional Water Quality Control Board which limited the amount of COD that could be discharged by industry into the Dominguez Channel in Los Angeles County. At the time, process wastewaters could be treated in the County's primary treatment unit, but they could not accommodate storm runoff from the Refinery. This presented a problem as the storm water collection system and the process sewers were interconnected. Therefore, during periods of rainfall, the combined storm runoff and process flow could not be sent to the County nor could it be discharged to Dominguez Channel because of its COD concentration. A holding basin and a carbon treatment plant were therefore deemed to be the most efficacious way of treating this combined flow on an intermittent basis (29).

The treatment system, completed in 1971, is illustrated schematically in Figure 14. The process wastewater flows through an API separator and then through pH adjustment and chemical flocculation tanks. Following the addition of both coagulants and polyelectrolytes, the flow is routed to one of two circular dissolved air flotation units. At this

point, the oil and grease (O & G) levels are normally below 15 to 20 mg/l. Under dry weather conditions, the flow goes to the County for further treatment. During periods of rainfall, it is diverted to a 50 million gallon holding basin where it is surged and conveyed "as required" to the carbon treatment plant. The plant consists of 12 adsorber cells, the flow to which is controlled by a handwheel-operated slide gate. Each bed can be backwashed with treated water from a backwash sump, the backwash water being returned to the holding basin. The carbon handling and regeneration system includes storage hoppers for spent and regenerated carbon, a pump, eductor, piping, and controls to convey the carbon from any cell to the regeneration furnace and back, and the multiple-hearth furnace with gas scrubber. It is gas-fired and supplemental steam and air are added on two hearths. An afterburner section is separately gas-fired to raise the off-gas temperatures to approximately 1,450°F (necessary to combust the organic vapors in the exit gas).

The actual design criteria for the system are presented in Table 27. Based on a probability distribution of two typical runs presented in Figure 15, the effluent COD was in the range of the predicted level if the influent concentration did not exceed the design basis. Chlorination was attempted once the effluent COD exceeded the design level on the premise that the halogenated compounds would be more effectively adsorbed and the overall performance would be enhanced. There was no noticeable improvement in effluent COD when this step was concluded, however (29). Although oil and grease was not cited as a design parameter, the observed effluent concentration and its dependence on the influent level is shown in Figure 16. The performance of this full-scale system in terms of COD removal approximates the design basis and the observed reduction of COD and O & G is consistent with pilot studies using similar wastewaters. It was noted, however, that algal proliferation in the holding basin adversely affected the carbon plant performance. When excessive algal growths developed, a deterioration of effluent quality and more frequent backwashing was characteristic of the system. At one time, the algae became so concentrated that the carbon plant had to be shut down. Copper sulfate was added to the holding basin to minimize algal growth and ease this problem.

The most significant variance of observed performance from the basis of design was the carbon capacity. Although a precise determination was not possible, the loading based on several runs ranged from 0.30 to 0.35 lb COD removed/lb of carbon, rather than the 1.75 lb COD/lb carbon prediction cited in Table 27.

With the exception of carbon capacity, the carbon plant generally performed as expected. It is no longer in operation, however, primarily because the treatment requirements imposed by Los Angeles County have been changed.

Reichhold Carbon Treatment System (Tuscaloosa Plant)

The Reichhold Chemical Plant produces sulfuric acid, formaldehyde, pentaerythritol, sodium sulfate, sodium sulfite, orthophenylphenol, and a number of synthetic resins. A carbon adsorption system was designed to treat an effluent flow of 500,000 gpd having an average BOD concentration of 390 mg/l, a COD level of 650 mg/l, and a pH ranging from 5.4 to 12.3 (30). An agreement between the Company and the Alabama Water Improvement Commission established an organic removal objective of 90 percent.

A physical/chemical treatment plant using activated carbon was designed and constructed and Figure 17 presents a simplified flow diagram. The process streams are routed to a 2.5-day retention equalization basin where the water is pumped to an acid mixing chamber. Concentrated sulfuric acid is added to maintain a pH range of 6.5 to 8.5. A nonionic polymer is added prior to the flocculation chamber. Following gravity sedimentation, the water is pumped to one of two moving-bed adsorbers. Each adsorber contains 124,000 lb of granular activated carbon. At the design flow rate of 175 gpm/adsorber, the empty bed contact time is approximately three hours. Treated water is collected in a trough at the top of each adsorber where it flows to a final retention tank and then to the river. A conventional regeneration furnace with an afterburner and wet scrubber system is used for reactivation of the carbon.

In the first few months of operation, the results have been reported as meeting the effluent quality requirements. The effluent BOD has been in the 35 to 40 mg/l range, while a 90 percent removal of COD infers an effluent at the 65 to 70 mg/l level (30).

British Petroleum Carbon Treatment System (Marcus Hook, Pennsylvania)

The British Petroleum (BP) Refinery is a 105,000 barrel/day Class "B" refinery located in Marcus Hook, Pennsylvania. In order to comply with discharge standards prescribed by the Delaware River Basin Commission (DRBC), a preliminary engineering program and treatability study was undertaken by the Company. Based on these results, the decision to treat the effluent from the existing API separator to the required level using a filtration/carbon adsorption system was made.

The treatment system, placed into operation in March 1973, is shown in Figure 18 (31). The API separator effluent flows to an intermediate surge basin where it is pumped to three downflow filters, operated in parallel. The flow rate ranges from seven to 12 gpm/ft^2, depending on the operation, and the media consists of 2.5 ft of anthracite and 4.5 ft of sand. The filters are backwashed using filtered water, with provisions for air scouring at 7.1 scfm/ft^2. The design filter pressure is 47.5 psi and the maximum allowable pressure drop through the media is 6.5 psi. The backwash interval is 12 hours.

Three carbon adsorbers (10 ft diameter and 65 ft high) are operated in parallel. Each adsorber contains 92,000 pounds of granular activated carbon in a bed depth of 45 feet. An additional 8,000 pounds occupy the lower and upper cone areas. Flow to the three adsorbers is controlled by the level in the filtered water holding tank. The upward flow rate is 8.5 gpm/ft^2, which gives an empty bed contact time of 40 minutes. Spent carbon at the bottom of the adsorber is pulsed out at the rate of approximately 1,000 lb/day. Fresh carbon is then added to the top of the column from a feed hopper. The design criteria and activated carbon properties for the system are shown in Table 28 (32).

The regeneration facility is a five-foot diameter multiple-hearth furnace. The design feed rate to the six-hearth furnace is 125 lb/hr. In an atmosphere controlled by the addition of steam, the adsorbed organics are volatized and oxidized. In order to insure complete oxidation, all flue gases pass through an afterburner fired by refinery fuel gas and maintained at a temperature of 1,350°F. A wet scrubber is included for gas cooling and the removal of particulate matter. The design data for the thermal regeneration system is shown in

Table 29.

As the full-scale system has been in operation for over two years, performance data are available (31, 32). During the first months of operation while the adsorber still contained virgin carbon, the COD removals were determined to be independent of influent concentration but dependent on contact time. This relationship is shown in Figure 19. The oil and grease removal during this period, shown in Figure 20, followed two different regimes. Good removal was observed initially prior to the start of carbon pulsing. However, once the pulsing began, taking the pulsed bed out of operation, the adverse effect on the remaining two columns is reflected in terms of deteriorating effluent quality. The reduction of oil removal with increasing increasing influent concentrations is attributed to both the oil removal mechanism and pulse bed "off-line" mode of operation.

There have been four distinct phases of operation since the carbon system came on line. The first period of data reported herein occurred when virgin carbon was in the adsorbers and the foul water condensate stream from the Fluidized Catalytic Cracking Unit (FCCU) was not yet included in the raw wastewater stream. The second period included the FCCU stream, but virgin carbon was still present in the adsorbers as the wave front had not yet reached the top of the carbon bed. The third period encompassed a time following a complete turnover of the carbon bed and still included the FCCU stream. The fourth period excluded this stream and incorporated a modification to the column septum design, still following a complete carbon turnover. The average and maximum adsorber effluent concentrations for several parameters observed during each period is tabulated in Table 30. A significant deterioration in quality following the inclusion of the FCCU foul water condensate and complete carbon turnover in the reactor is noted in Figure 21. This has been attributed to inadequate pretreatment of the API separator effluent in terms of O & G and soluble organic removal as well as significant buildups of anaerobic biological growths and oily materials in the carbon media. A 40 percent decrease in adsorptive capacity of the regenerated carbon also has been observed. The iodine number of the regenerated carbon is 560 to 680, while the virgin carbon was in the range of 950 to 1,000 and the molasses number of the regenerated carbon was 280, or approximately 50 higher than the virgin carbon. This indicates u decrease in micropores and an increase in macropores during the regeneration cycle.

The Company is currently reviewing methods of improving process performance over that observed in the last three periods of operation, or possibly changing the system concept altogether. Particular emphasis is being placed on more adequate pretreatment, including biological oxidation, as steps necessary to effectively use the existing carbon system.

SUMMARY

Activated carbon treatment of industrial wastes, while promising, must be carefully evaluated before process decisions are made and capital funds are committed. As noted in the pilot- and full-scale case histories presented herein, breakthrough geometry and adsorption kinetics of multi-component wastewaters are difficult to define, many organic compounds are not amenable to carbon adsorption, and the effects of regeneration on carbon capacities are variable and unpredictable. For these and other reasons, comprehensive testing and technical reviews are a necessary prerequisite to process commitment.

Unfortunately, most of the literature regarding carbon treatment of industrial wastewaters centers around pilot-plant results. There are, however, sufficient data from pilot studies and the two full-scale systems in the petroleum refinery industry to draw general conclusions, at least within this industrial category. For example, a distribution of long-term average COD concentrations in effluents from carbon adsorbers treating refinery wastewaters is presented in Figure 22 (33). These levels are relatively consistent with those residuals reported in the petrochemical industry (28). A similar presentation of oil and grease effluent levels from a full-scale refinery carbon system is shown in Figure 23. Carbon adsorption capacities in terms of lbs of COD removed/lb of carbon exhausted have ranges from 0.2 to 0.4 in the petrochemical industry and from less than 0.1 to 0.55 in the petroleum refining industry. These are lower than reported carbon capacities for municipal wastewaters, as shown in Figure 24, emphasizing the inaccuracies which can occur by extrapolating results from the treatment of one wastewater and using them as the basis for predicting another.

SYNOPSIS

A review of the current state of the art of activated carbon treatment has been presented. Basic concepts of activated carbon treatment have been included, as well as pertinent municipal and industrial case histories with which the author is familiar. It is recognized that new truths pertaining to this subject become known on a continuing basis. However, in evaluating process concepts, developing design bases, predicting effluent quality, and finalizing management decisions in terms of constructing control systems with attendant capital commitments, one must base these judgments on the current state of the art. It is toward the objective of defining the art of activated carbon treatment that this information is presented.

In the pursuit of this definition, certain apparent verities emerge. Some of the more significant include the following:

1. Adsorption theory is rigorous for single solutes, but becomes less definitive when applied to wastewaters containing multiple components with varying molecular weights and chemical characteristics. A good example is the poorly-defined and erratic breakthrough geometry observed in the carbon treatment of complex industrial wastewaters.
2. Many classes of organic compounds are not amenable to carbon adsorption - particularly oxygenated organics - and show up as residual BOD, COD, or TOC in carbon column effluents. This limits the overall process efficiency of pure physical/chemical treatment systems. As many of these residual compounds are biodegradable, activated carbon as a polishing process is generally capable of producing a better quality of effluent than is the strict physical/chemical application.
3. Anaerobic conditions which prevail in carbon reactors have caused difficulty through the proliferation of biological growths on the carbon media. Sulfide generation has been particularly troublesome. Although biological activity in the column has the potential of increasing carbon capacities and is hypothesized to offer regeneration possibilities, full-scale experience has indicated that uncontrolled biological growth in carbon reactors has more negative features than

positive.

4. Ozonation of wastewaters prior to carbon adsorption has been demonstrated on a pilot scale to enhance adsorption in the columns. This is attributed to the ozone products being more sorbable than the reactants. Other possible attractions of this application are controlling biological densities on the carbon media through partial disinfection and maintaining an aerobic environment in the reactor column.
5. Carbon capacities used as design criteria generally have been overstated and have not been realized in full-scale experience. Breakthrough concentrations which force premature regeneration cycles in single-operated columns, and desorption phenomena which cause low capacities in series-operated polishing columns, are partially responsible for this.
6. Design criteria for carbon adsorption systems should be sensitive to:
   (a) wastewater constituents and their classification in terms of adsorbability, and the effluent residual potential; and
   (b) effect of the selected carbon media with respect to capacity, resistance to abrasion, regeneration impacts, and hydraulic characteristics; and
   (c) the biological growth potential with the associated effects on carbon capacity, backwash requirements, and hydraulic characteristics of the flow through the column; and
   (d) the necessary pretreatment requirements for control of suspended solids (organic and inorganic), oil and grease, dissolved oxygen, biological population, and other constituents which affect carbon adsorber performance.

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DISCUSSION

Ed Sebesta: Were these pilot plant data taken with regenerated carbon and equilibrated carbon?

Davis Ford: No. It was virgin carbon. That's a good point. Many of the pilot plants studies that we have run have been with virgin carbon. It is not that we don't recognize that it would be more applicable with regenerated carbon, it is just sometimes that it is hard to get that much regenerated carbon from the vendor and that has been our problem. One would think it would be more practical to run all these pilot studies with regenerated carbon.

Bob Huddleston: Do you have any data that indicates whether or not the effects of ozone were anything other than simply killing the microbes?

Davis Ford: Yes. They ran some GC work to identify the nature of the compounds after organization and I don't have the results in this paper. Just in talking with these people, it's what you really have done is gone from the ketones, aldehydes to carboxylic acids, there has been a shift and the carboxylic acids being more ameniable to carbon absorption, so its a combination of the biological growth but also the transformation of these oxygenated organics to carboxylic acids.

M. K. Hutton: Discuss if you will the cost of ozone. Do you have any figures on this? I expect it is quite expensive.

Davis Ford: I left cost completely out of the paper because that is almost another paper itself; but considering the concentration of ozone that we think we have to have, it is probably about 4 or 5 milligrams per liter is within the cost effective parameters that we have set to shis point. So we think it is cost effective.

Anonymous: Do you have some comments on phenol removal?

Davis Ford: No. Phenol is highly sorbable, most of the data we have seen on phenol removal has been excellent and the only exceptions to this was when we just had so many physical problems, the biological growths and oil and grease, that the phenol removal has gone down. I think that is shown in one table. If you don't have this constraint, phenol removal should be good, carbon is a good phenol remover.

Morris Wiley: The little village where I live has a new sewer system and biological treatment plant. It is an extended aeration without any primary treatment, then a second stage nitrification and finally a sand filter. They are able to do less than one part per million BOD and less than one part per million ammonia in the effluent. Now I should caution that it is only operating at one quarter of rated capacity. Thus, it appears that if one has to go to these very low organic and nitrogen contents in the effluent, that one can do it by a conventional biological system simply by spending a lot of money. I estimate that this is about $1,000 per family per year, total annualized cost for this system including the sewer connections which were put in. Have you done any economic studies to try to figure out which would really be preferable, an advanced biological reactor system versus an activated carbon where you need a very low concentration of pollutants in the effluent?

Davis Ford: Let me speak in general terms here. First, you have a good analytical chemist at that plant.

Morris Wiley: Well, I have some reservations about the precision of the tests. The plant operator is a Texaco employee running the plant in his spare time with his wife and his son, but it is a good quality effluent and the county is accepting their test reports.

Davis Ford: Let me say, from the cost studies that we have run, we have seen biological treatment is more cost effective than carbon, I don't think there is any question about that. When you get down to the fact that a biological system can't make a permit and you have to go to carbon, you know some people are not sympathetic with cost effectives, but if you can get to those levels biologically, it just intuitively has to be more cost effective than carbon. Carbon has gone up, it is 50-60¢ now for bituminous. When we started running these studies three or four years ago, it was 32¢ or 30¢ and just because of these lower carbon capacities I have stated, biological treatment has to be more cost effective. If we can make it with biological treatment, that is certainly the theology that I would like to see.

Morris Wiley: Then it looks as though our research should be concentrated on enhancing the effectiveness this biological treatment as Jim Grutsch pointed out earlier?

Davis Ford: I do not disagree with that. I also think we have got to be realistic, there are certain limitations to biological treatment. When you look at BAT, if and when it comes, it is going to take some real engineering to make those numbers biologically.

Neale Fugate: Do you have any data on the possible adsorption of heavy metals, or conversely desorption of heavy metals on carbon?

Davis Ford: Yes, sir. I have it, but it is not presented in the paper. I have just seen some data on that. There is slight reductions of some of the metallic ions probably as metallic hydroxides. I think in some literature absorption of some metallic ions has been reported. It has not been significant, something like 10-15% reduction of zinc, mercury, cadmium, some of these substances but percent removal is quite low, but some removal has been noted. I am not sure of the mechanism as a physical removal of zinc or sorption of zinc iron, but one of those two mechanisms.

Robert L. Wortman: It is my understanding that ozone is a very effective phenol remover, it removes the phenol quite effectively, it is probably even better than activated carbon (through oxidation). It would seem to me that may be secondary conventional treatment followed by ozonation may be as effective as secondary treatment followed by carbonation. My question is, have you had any experience on this in combination with carbon filtration and I am interested in treating each one individually, that is considering ozonization as a treatment method?

Davis Ford: Let me answer that two ways. First of all, I think I mentioned in the talk that we tried preozonation after carbon with bad results. However, there is a treatment plant, financed in part by EPA which goes on line in about two months and that is at Estes Park, Colorado, which is exactly the system you described. Other than that plant, I am not personally familiar with a real good biological treatment system including nitrification followed by ozone but that system is designed that way. That is the upper sanitation district in Estes Park, Colorado, the plant is completed and is probably going through shake down right now and we will get some good full scale information from that facility in the next few months.

Anonymous: I think there is also some work being done in Pomona, I don't know exactly what it was, but on a different combination of ozonation and various schemes; but to further explore the Estes Park, if you say you had a multimedia filter and then go in ozonation, this may be quite effective to work with.

Fred Gowdy: Davis, I wonder if you would give us some of the reasons you believe why the carbon capacities that we have realized in some of our full scale plants, haven't been anywhere close to those predicted by various pilot studies?

Davis Ford: I am not really sure that I know the answer to that, I can just hypothesize. First of all, I think Union Carbide has presented carbon capacities in lead columns as far as polishing columns were concerned, so that would indicate the operation has a lot to do with carbon capacity, in other words, how well you can operate the carbon utilization in a series mode of operation to get the operable capacity of the overall system. You can pretty well do that in a pilot scale. I am not sure you can do it in a full scale quite so easily. It is easier to operate that pilot scale, I assure you, than a full-scale plant. So I think part of the answer lies in the operation. Secondly, it is possible that you had more physical problems in terms of biological growth, influent constituents in the full scale that you don't perceive in a pilot scale. You might control the pilot scale a little better and for this reason are able to realize a better carbon capacity. Those are the two main reasons I think, I just can't prove it.

Ed Sager: I wondered if you would like to elaborate on the back washing features of these columns. Why is that required if you have adequate pretreatment, are you removing suspended solids build-up?

Davis Ford: I think the best case history to point to there is the BP, they have got some data on their filters, good filters which work quite well; but the effluent suspended solids are probably in the 10-15-20 milligram per liter range and these influent suspended solids to the carbon column are going to accumulate after a certain period of time, combined with the biological proliferation in the columns. I think you always have to have the flexibility operational flexibility of back washing columns as well as the filters. I think that has been the experience to date. You may not have to do it, but it is an operational flexibility that you should have. It seems like even if you go in with zero suspended solids, some point in time you are going to have to back wash the filters or the carbon columns.

Pat DeJohn: One of the things that one of the gentlemen asked about the loadings, most of the loadings that are reported are reported with virgin carbon and the properties of activated carbon change quite substantially when you regenerate carbon and I think that is part of the BP problem, they are not able to maintain their phenol standards because of the loss in capacity, adsorptive capacity and consequently, their system has been substantially under design. The other thing that you mentioned about why you should be back washing, that BP plant is a pulse bed unit and there are fines that are created due to the regeneration of the carbon and they have no way to remove those fines; consequently they recycle them back into the absorber and they pulse that unit a lot of times because of pressure drop problems and that is another thing about that particular plant.

Davis Ford: I agree with that. In the past, Pat, when we have had to use virgin carbon, we have just applied a factor on the capacity, reduced capacity, just an empirical factor and that is a less favorable way of doing it than using regenerated carbon; but we just haven't had that luxury a lot of times.

J. J. Chavez: I was just wondering if you could elaborate on the regeneration phase from the economic side by which a refinery could put in one regulation facility and the options open to him if he can't afford one?

Davis Ford: There again I didn't really get into cost. I believe the reported regeneration cost now is something like 15-20¢ per pound. Some manufacturers, I believe, are offering a regeneration service. If you have a small system, it doesn't make sense because of economy in scale to put in your own regeneration facility, to have a contractor regenerate it, if that's possible, but I think if you go into regeneration which in most areas you would have to for most size of plants, you have to count on about a 15-20¢ per pound regeneration cost.

BIOGRAPHY

Davis L. Ford holds a B.S. in Civil Engineering from Texas A & M University and M.S. and Ph.D. degrees in Environmental Health Engineering from the University of Texas at Austin. Dr. Ford is currently Senior Vice President and Member of the Board of Directors of Engineering Science, Inc., in Austin, Texas. Dr. Ford has written 4 books, 20 reports, 60 publications in the field of environmental engineering and has consulted for over 50 industries, the United Nations (WHO and PAHO), the EPA and various state and municipal agencies.

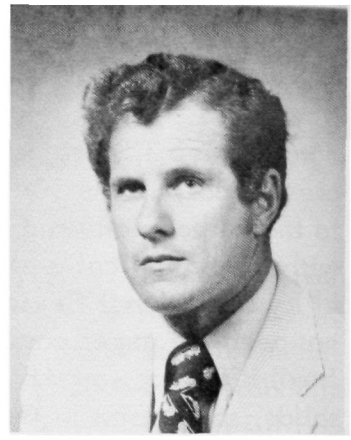


TABLE 1 "COMPARATIVE ANALYSIS OF BATCH ISOTHERM DATA - REFINERY & PETROCHEMICAL WASTEWATERS"

	K	n
OIL SEPARATOR (PRIMARY) EFFLUENT		
Refinery - Petrochemical Complex No. 1	0.0290	0.77
Refinery - Petrochemical Complex No. 2	0.0036	0.80
Refinery No. 3	0.0140	0.36
SECONDARY (ACTIVATED SLUDGE) EFFLUENT		
Refinery - Petrochemical Complex No. 1	0.0062	0.60
Refinery No. 3	0.0043	1.00
Refinery Secondary Effluent	0.0051	0.96
Refinery Secondary Effluent	0.0038	1.08
Refinery Secondary Effluent	0.0020	0.69
SINGLE ADSORBATE		
Phenol	0.1110	5.80
Dichlorethane (pH 4)	0.0045	1.82
(pH 6)	0.0038	1.67
(pH 10)	0.0041	1.49

TABLE 2

AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION [4]

Compound	Molecular Weight	Aqueous Solubility (%)	Concentration (mg/l) Initial (C_0)	Final (C_f)	Adsorbability* g compound/ g carbon	Percent Reduction
Alcohols						
Methanol	32 0	∞	1,000	964	0 007	3 6
Ethanol	46.1	∞	1,000	901	0 020	10 0
Propanol	60.1	∞	1,000	811	0 038	18 9
Butanol	74 1	7.7	1,000	466	0 107	53 4
n-Amyl alcohol	88.2	1.7	1,000	282	0 155	71.8
n-Hexanol	102 2	0.58	1,000	45	0.191	95 5
Isopropanol	60 1	∞	1,000	874	0 025	12.6
Allyl alcohol	58.1	∞	1,010	789	0.024	21 9
Isobutanol	74 1	8 5	1,000	581	0 084	41 9
t Butanol	74.1	∞	1,000	705	0.059	29 5
2 Ethyl butanol	102 2	0.43	1,000	145	0 170	85 5
2 Ethyl hexanol	130 2	0 07	700	10	0 138	98 5
Aldehydes						
Formaldehyde	30.0	∞	1,000	908	0.018	9.2
Acetaldehyde	44 1	∞	1,000	881	0 022	11.9
Propionaldehyde	58 1	22	1,000	723	0 057	27 7
Butyraldehyde	72 1	7 1	1,000	472	0 106	52.8
Acrolein	56.1	20 6	1,000	694	0 061	30 6
Crotonaldehyde	70 1	15 5	1,000	544	0 092	45 6
Benzaldehyde	106 1	0.33	1,000	60	0.188	94 0
Paraldehyde	132 2	10.5	1,000	261	0 148	73 9
Amines						
Di N Propylamine	101 2	∞	1,000	198	0.174	80 2
Butylamine	73 1	∞	1,000	480	0 103	52 0
Di N Butylamine	129 3	∞	1,000	130	0 174	87 0
Allylamine	57 1	∞	1,000	686	0 063	31 4
Ethylenediamine	60 1	∞	1,000	893	0 021	10 7
Diethylenetriamine	103 2	∞	1,000	706	0 062	29 4
Monethanolamine	61 1	∞	1,012	939	0 015	7 2
Diethanolamine	105 1	95 4	996	722	0 057	27 5
Triethanolamine	149 1	∞	1,000	670	0 067	33.0
Monoisopropanolamine	75 1	∞	1,000	800	0 040	20 0
Diisoprupanolamine	133 2	87	1,000	543	0 091	45 7
Pyridines & Morpholines						
Pyridine	79 1	∞	1,000	527	0 095	47 3
2 Methyl 5-Ethyl pyridine	121 2	sl.sol	1,000	107	0 179	89 3
N Methyl morpholine	101 2	∞	1,000	575	0 085	42 5
N Ethyl morpholine	115 2	∞	1,000	467	0 107	53.3
Aromatics						
Benzene	78.1	0 07	416	21	0 080	95 0
Toluene	92 1	0 047	317	66	0 050	79 2
Ethyl benzene	106 2	0 02	115	18	0 019	84 3
Phenol	94	6 7	1,000	194	0 161	80 6
Hydroquinone	110 1	6.0	1,000	167	0 167	83 3
Aniline	93 1	3 4	1,000	251	0 150	74 9
Styrene	104 2	0 03	180	18	0 028	88.8
Nitrobenzene	123 1	0 19	1,023	44	0 196	95.6
Esters						
Methyl acetate	74 1	31 9	1,030	760	0 054	26 2
Ethyl acetate	88 1	8 7	1,000	495	0 100	50 5
Propyl acetate	102 1	2	1,000	248	0 149	75 2
Butyl acetate	116 2	0 68	1,000	154	0 169	84 6
Primary amyl acetate	130 2	0 2	985	119	0 175	88 0
Esters						
Isopropyl acetate	102.1	2.9	1,000	319	0 137	68.1
Isobutyl acetate	116.2	0.63	1,000	180	0.164	82.0
Vinyl acetate	86.1	2.8	1,000	357	0.129	64.3
Ethylene glycol monoethyl ether acetate	132.2	22.9	1,000	342	0.132	65.8
Ethyl acrylate	100.1	2 0	1,015	226	0 157	77.7
Butyl acrylate	128.2	0 2	1,000	43	0 193	95.9
Ethers						
Isopropyl ether	102.2	1.2	1,023	203	0 162	80 0
Butyl ether	130.2	0.03	197	nil	0 039	100.0
Dichloroisopropyl ether	171.1	0.17	1,008	nil	0 200	100.0
Glycols & Glycol Ethers						
Ethylene glycol	62.1	∞	1,000	932	0 0136	6 8
Diethylene glycol	106 1	∞	1,000	738	0 053	26 2
Triethylene glycol	150.2	∞	1,000	477	0.105	52 3
Tetraethylene glycol	194.2	∞	1,000	419	0 116	58 1
Propylene glycol	76 1	∞	1,000	884	0 024	11 6
Dipropylene glycol	134.2	∞	1,000	835	0 033	16 5
Hexylene glycol	118 2	∞	1,000	386	0 122	61 4
Ethylene glycol monomethyl ether	76.1	∞	1,024	886	0 028	13 5
Ethylene glycol monoethyl ether	90 1	∞	1,022	705	0 063	31 0
Ethylene glycol monobutyl ether	118 2	∞	1,000	441	0 112	55 9
Ethylene glycol monohexyl ether	146 2	0 99	975	126	0.170	87 1
Diethylene glycol monoethyl ether	134 2	∞	1,010	570	0 087	43 6
Diethylene glycol monobutyl ether	162 2	∞	1,000	173	0 166	82 7
Ethoxytriglycol	178 2	∞	1,000	303	0 139	69 7
Halogenated						
Ethylene dichloride	99 0	0.81	1,000	189	0.163	81 1
Propylene dichloride	113.0	0.30	1,000	71	0.183	92.9
Ketones						
Acetone	58 1	∞	1,000	782	0 043	21 8
Methylethyl ketone	72 1	26 8	1,000	532	0.094	46 8
Methyl propyl ketone	86 1	4 3	1,000	305	0 139	69.5
Methyl butyl ketone	100 2	v sl sol.	988	191	0.159	80 7
Methyl isobutyl ketone	100.2	1 9	1,000	152	0 169	84 8
Methyl isoamyl ketone	114 2	0.54	986	146	0.169	85.2
Diisobutyl ketone	142 2	0.05	300	nil	0.060	100.0
Cyclohexanone	98 2	2.5	1,000	332	0.134	66.8
Acetophenone	120 1	0.55	1,000	28	0 194	97 2
Isophorone	138 2	1 2	1,000	34	0.193	96 6
Organic Acids						
Formic acid	46 0	∞	1,000	765	0 047	23 5
Acetic acid	60 1	∞	1,000	760	0.048	24 0
Propionic acid	74 1	∞	1,000	674	0 065	32 6
Butyric acid	88 1	∞	1,000	405	0 119	59 5
Valeric acid	102 1	2 4	1,000	203	0 159	79 7
Caproic acid	116 2	1.1	1,000	30	0.194	97 0
Acrylic acid	72 1	∞	1,000	355	0 129	64 5
Benzoic acid	122 1	0 29	1,000	89	0 183	91 1
Oxides						
Propylene oxide	58 1	40 5	1,000	739	0.052	26 1
Styrene oxide	120 2	0.3	1,000	47	0.190	95.3

Dosage 5 g Carbon C/l solution

TABLE 3 "RELATIVE AMENABILITY TO CARBON ADSORPTION OF TYPICAL PETROCHEMICAL WASTEWATER CONSTITUENTS"

Compound	% Adsorption	Compound	% Adsorption
Ethanol	10	Vinyl acetate	64
Isopropanol	13	Ethyl acrylate	78
Acetaldehyde	12	Ethylene glycol	7
Butyraldehyde	53	Propylene glycol	12
Di-N-propylamine	80	Propylene oxide	26
Monoethanolamine	7	Acetone	22
Pyridine	47	Methyl ethyl ketone	47
2-Methyl 5-ethyl pyridine	89	Methyl isobutyl ketone	85
Benzene	95	Acetic acid	24
Phenol	81	Proprionic acid	33
Nitrobenzene	96	Benzoic acid	91
Ethyl acetate	50		

Initial Compound Concentration = 1,000 mg/l Powdered Carbon Dosage = 5,000 mg/l

TABLE 4 "INFLUENCE OF MOLECULAR STRUCTURE AND OTHER FACTORS OF ADSORBABILITY"

1. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

2. Branched chains are usually more adsorbable than straight chains. An increasing length of the chain decreases solubility.

3. Substituent groups affect adsorbability:

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double Bonds	Variable effect as with carbonyl.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.
Aromatic Rings	Greatly increases adsorbability.

4. Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.

5. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

6. Unless the screening action of the carbon pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

7. Molecules with low polarity are more sorbable than highly polar ones.

TABLE 5

PROPERTIES OF SEVERAL COMMERCIALLY AVAILABLE CARBONS* [6]

	ICI AMERICA HYDRODARCO 3000 (LIGNITE)	CALGON FILTRASORB 300 (8x30) (BITUMINOUS)	WESTVACO NUCHAR WV-L (8x30) (BITUMINOUS)	WITCO 517 (12x30) (BITUMINOUS)
PHYSICAL PROPERTIES				
Surface area, m^2/gm (BET)	600-650	950-1050	1000	1050
Apparent density, gm/cc	0.43	0.48	0.48	0.48
Density, backwashed and drained, lb/cu. ft.	22	26	26	30
Real density, gm/cc	2.0	2.1	2.1	2.1
Particle density, gm/cc	1.4 1.5	1.3 1.4	1.4	0.92
Effective size, mm	0.8 0.9	0.8 0.9	0.85 1.05	0.89
Uniformity coefficient	1.7	1.9 or less	1.8 or less	1.44
Pore volume, cc/gm	0.95	0.85	0.85	0.60
Mean particle diameter, mm	1.6	1.5 1.7	1.5 1.7	1.2
SPECIFICATIONS				
Sieve size (U.S. std. series)				
Larger than No. 8 (max. %)	8	8	8	—
Larger than No. 12 (max. %)	—	—	—	5
Smaller than No. 30 (max. %)	5	5	5	5
Smaller than No. 40 (max. %)	—	—	—	—
Iodine No.	650	900	950	1000
Abrasion No., minimum	**	70	70	85
Ash (%)	**	8	7.5	0.5
Moisture as packed (max. %)	**	2	2	1

* Other sizes of carbon are available on request from the manufacturers.
** No available data from the manufacturer.
— Not applicable to this size carbon.

TYPICAL PROPERTIES OF 8 X 30-MESH CARBONS[9]

	LIGNITE CARBON	BITUMINOUS COAL CARBON
Total surface area, m^2/g	600-650	950-1,050
Iodine number, min	600	950
Bulk density, lb/ft^3 backwashed and drained	22	26
Particle density wetted in water, g/cm^3	1.3-1.4	1.3-1.4
Pore volume, cm^3/g	1.0	0.85
Effective size, mm	0.75-0.90	0.8-0.9
Uniformity coefficient	1.9 or less	1.9 or less
Mean-particle dia., mm	1.5	1.6
Pittsburgh abrasion number	50-60	70-80
Moisture as packed, max.	9%	2%
Molasses RE (relative efficiency)	100-120	40-60
Ash	12-18%	5-8%
Mean-pore radius	33 A	14 A

TABLE 6 "TYPICAL PROPERTIES OF POWDERED ACTIVATED CARBON (PETROLEUM BASE)"

Surface Area (BET m^2/gm)		2,300-2,600
Iodine No.		2,700-3,300
Methylene Blue Adsorption (mg/gm)		400-600
Phenol No.		10-12
Total Organic Carbon Index (TOCI)		400-800
Pore Distribution (Radius Angstrom)		15-60
Average Pore Size (Radius Angstrom)		20-30
Cumulative Pore Volume (cc/gm)		0.1-0.4
Bulk Density (gm/cc)		0.27-0.32
Particle Size Passes:	100 mesh (wt%)	97-100
	200 mesh (wt%)	93-98
	325 mesh (wt%)	85-95
Ash (wt%)		<1.5
Water Solubles (wt%)		<1.0
pH of Carbon		8-9

TABLE 7 "STAGES OF THERMAL REGENERATION"

Stage	Approximate Temperature (°F)	Processes
Drying	Ambient to 212	Water Evaporation
Thermal Desorption	212 to 500	Physical desorption of volatile adsorbed organics
Pyrolysis and Carbonization	400 to 1,200	Pyrolysis of nonvolatile organics and carbonization of the pyrolysis residue
Gasification	1,200 to 1,900	Gasification of pyrolytic residue through controlled chemical reaction with water vapor, vapor, carbon dioxide, or oxygen

TABLE 8 "WATER QUALITY AT VARIOUS POINTS IN PROCESS" (16)

Quality Parameter		Raw Wastewater	Secondary Effluent	Separation-Bed Effluent	Carbon-Column Effluent
BOD (mg/l)		200-400	20-100	<1	<1
COD (mg/l)		400-600	80-160	20-60	1-25
Total organic carbon (mg/l)		-	-	8-18	1-6
ABS (mg/l)		2.0-4.0	0.4-2.9	0.4-2.9	<0.01-0.5
PO_4 (mg/l as PO_4)		-	25-30	0.1-1	0.1-1
Color (units)		-	-	10-30	<5
Turbidity (units)		-	30-70	<0.5-3	<0.5-1
Nitrogen organic N (mg/l as N)		10-15	4-6	2-4	1-2
Ammonia N (mg/l as N)		25-35	25-32	25-32	25-32
NO_3 and NO_2 (mg/l as N)		0	0	0	0
Unchlorinated:	Coliforms (MPN/100 ml)	-	2,400,000	9,300	11,000
	Fecal coliforms (MPN/100 ml)		150,000	930	930
	Virus			Negative	Negative
Chlorinated:	Coliforms (MPN/100 ml)			8.6	<2.1
	Fecal coliforms (MPN/100 ml)			<2.1	<2.1

TABLE 9 "WATER QUALITY AT VARIOUS STAGES OF TREATMENT AT SOUTH LAKE TAHOE"

Quality Parameter	Raw Wastewater	Effluent					
		Primary	Secondary	Chemical Clarifier	Filter	Carbon	Chlorinated Final
BOD (mg/l)	140	100	30		3	1	0.7
COD (mg/l)	280	220	70		25	10	10
SS (mg/l)	230	100	26	10	0	0	0
Turbidity (JTU)	250	150	15	10	0.3	0.3	0.3
MBAS (mg/l)	7	6	2.0		0.5	0.1	0.1
Phosphorus (mg/l)	12	9	6	0.7	0.1	0.1	0.1
Coliform (MPN/100 ml)	50×10^6	15×10^6	2.5×10^6		50	50	<2

TABLE 10 "CARBON EFFICIENCY PER REGENERATION PERIOD AT SOUTH LAKE TAHOE" NOVEMBER 1968 THROUGH JANUARY 1971

Parameter		Average	Maximum	Minimum
Carbon Dosage (lb regenerated/million gallons treated)[1]		207	418	111
Iodine Number[2]	Spent Carbon	583	633	497
	Regenerated Carbon	802	852	743
Apparent Density (gm/ml)[2]	Spent Carbon	0.571	0.618	0.544
	Regenerated Carbon	0.487	0.491	0.478
Percent Ash[2]	Spent Carbon	6.4	7.0	5.8
	Regenerated Carbon	6.8	7.2	5.8
Chemical Oxygen Demand	Percent Removal	49.9	63.3	30.1
	lb COD applied	28,250	54,970	15,680
	lb COD applied/$\overline{M}$G	162	254	105
	lb COD removed/$\overline{M}$G	81	149	32
	lb COD applied/lb carbon regenerated[1]	0.78	1.56	0.52
	lb COD removed/lb carbon regenerated[1]	0.39	0.71	0.16
Methylene Blue Active Substances (Methylene Blue Active Substances (MBAS))	Percent removal	77	93	58
	lb MBAS applied	995	1,675	457
	lb MBAS applied/$\overline{M}$G	5.7	10.7	2.6
	lb MBAS removed/$\overline{M}$G	4.4	8.2	1.6
	lb MBAS applied/lb carbon regenerated[1]	0.027	0.045	0.012
	lb MBAS removed/lb carbon regenerated[1]	0.021	0.039	0.007

[1]Based on ft^3 of carbon fed to furnace at 30 lb/ft^3
[2]November 1968 through November 1970

TABLE 11 "COLORADO SPRINGS TERTIARY PLANT DESIGN DATA"

Solid Contact Clarifier	48 ft diameter, 11 ft 9 in sidewall, 2 ft cone depth 1,809 sq ft surface area 168,465 gallon capacity 2 hr detention time and 0.76 gpm/sq ft rise rate @ 2 MGD flow
Spent Lime Tank	14 ft diameter, 10 ft sidewall depth, 8 ft cone 1,948 cu ft 14,610 gallon capacity
New Lime Holding Tank	14 ft diameter, 10 ft sidewall depth, 8 ft cone 1,948 cu ft 14,610 gallon capacity
Recarbonization Tank	14 ft diameter, 14 ft sidewall depth, plus 2 ft freeboard - 154 sq ft 2,156 cu ft 16,160 gallon capacity - 12 minutes detention time @ 2 MGD flow
Activated Carbon Adsorbers	20 ft diameter, 14 ft sidewall depth, 10 ft of carbon media 314 sq ft surface area, 4,396 cu ft 32,970 gallon capacity total tower detention time is 24 minutes - 4.5 gpm/sq ft (@ 2 MGD flow) carbon bed detention time is 17 minutes 4.5 gpm/sq ft (@ 2 MGD flow) 3,140 cu ft of carbon @ 30 lb/cu ft 94,200 lbs carbon
Dual Media Sand Filters	12 ft diameter, 11 ft sidewall depth, 1 ft 6 in top cone 113 sq ft surface area 1,243 cu ft capacity 9,323 gallon capacity 3 ft of e.s. 1.5 mm sand 5 ft of e.s. 2.8 mm anthrafilt (#2)

TABLE 12 "TERTIARY TREATMENT PLANT DATA SUMMARY (FIRST REGIME)"

PARAMETER	R-C INF.	R-C EFF.	FILTER EFF.	LEAD CARBON EFF.	POLISH CARBON EFF.
BOD	106	46.9	48.0	44.0	33.0
COD	305	120	114	83	64
TOC	76	37.9	36.8	27.9	23.8
TSS	56	31.0	3.7	2.1	3.7
Turbidity	53	10.1	4.2	3.6	3.2
$O.PO_4$ (total)	32	2.2	1.7	2.2	1.9
$O.PO_4$ (soluble)	31	0.16	1.6	2.2	1.8
MBAS	5.32	3.22	-	1.36	0.51
pH	7.35	11.44	7.93	6.91	7.12
Alkalinity (total)	197	282	69	63	69
Hardness	163	210	250	240	253
C_a (as C_a^{++})	52	79	95	84	92
C^aC_a (as $^aC_aCO_3$)	130	197	237	209	231
Color	162	44	38	25	13
Sulfates	88	80	439	439	401
Sulfides	0.15	0.14	-	0.26	0.41
Flow (MGD)	1.93	1.93	1.93	1.70	1.70
Lime Dose (ppm Ca 0)		349			

NOTE: During this period, the reactor was operated with a deep sludge blanket of approximately six feet.

TABLE 13 "TERTIARY TREATMENT PLANT DATA SUMMARY (SECOND REGIME)"

PARAMETER	INFLUENT (mg/l)*	EFFLUENT (mg/l)*	REMOVAL (percent)
BOD	102	8.0	92.2
COD	258	15.7	93.9
TSS	62	2.2	96.5
Turbidity	54	2.2	96.3
O. Phosphate (total)	30	1.0	96.7
O. Phosphate (soluble)	26	1.0	96.2
MBAS	4.2	0.15	96.4
Fecal Coliform	5×10^5/100 ml	225/100 ml	99.96
Fecal Strep	6.5×10^5/100 ml	1150/100 ml	99.82
Average Flow (MGD)	-	1.5	-
Average Lime Dose		345 mg/l	-
Lead Tower	5 ft of twice-regenerated + 5 ft of virgin carbon		
Polish Tower	8 ft of twice-regenerated + 2 ft of virgin carbon		

*All units in mg/l unless indicated.
The "INFLUENT" is the secondary effluent going to the solids contact clarifier.
The "EFFLUENT" is the final polish carbon tower effluent.
Influent to tertiary plant is from a trickling filter plant with a flow of 23 to 25 MGD; trickling filter plant capacity is 13 MGD.

TABLE 14 "COMPARISON OF WASTEWATER STRENGTH BATTELLE AND CRSD TEST PROGRAMS"

	Probability (% of Occurrences)		
	10	50	90
Battelle Series (1970-71) BOD	180 mg/l	240 mg/l	320 mg/l
CRSD Series (1974-75) BOD	115 mg/l	170 mg/l	250 mg/l
Battelle Series (1970-71) COD	320 mg/l	500 mg/l	720 mg/l
CRSD Series (1974-75) COD	215 mg/l	350 mg/l	580 mg/l
Battelle Series (1970-71) BOD/COD	0.56	0.48	0.44
CRSD Series (1974-75) BOD/COD	0.53	0.48	0.43

TABLE 15 "EFFECT OF POST-OZONATION ON EFFLUENT ORGANIC QUALITY"

CRSD PILOT-PLANT TEST RESULTS*

Parameter	Before Ozonation	After Ozonation
BOD (unfiltered)	32 mg/l	31 mg/l
BOD (filtered)	25 mg/l	24 mg/l
COD (unfiltered)	72 mg/l	66 mg/l
COD (filtered)	59 mg/l	52 mg/l
TOC	31 mg/l	29 mg/l

*All data represent average values over an eleven day period. Ozone dosage ranges from 4 9 mg/l.

TABLE 16 "QUALITY OF RAW WASTEWATER"

GARLAND PHYSICAL/CHEMICAL TREATMENT FACILITY

Parameter	Results
Total BOD (mg/l)	266
Filtered BOD (mg/l)	236
Total COD (mg/l)	542
Filtered COD (mg/l)	240
Suspended Solids (mg/l)	233
Alkalinity (mg/l as $CaCO_3$)	200
pH	7.2 - 7.7
PO_4 (mg/l)	15

TABLE 17 "PCT SYSTEM DESIGN DATA" (24)

CHEMICAL TREATMENT SYSTEM			
1.	Flocculation: Detention Time, minutes		45
	Chemical Dosage	Alum, mg/l Al	22
		polymer, mg/l	0.25
2.	Sedimentation: Detention Time, hrs.		1.5
	Overflow Rate, gpd/sq ft		900
	Underflow, % of plant flow		1.25
	Underflow solids, % by weight		2
3.	Gravity Thickening: Solids Loading, lb/day-sq ft		12
	Underflow solids, % by weight		4
4.	Vacuum Filtration: Yield, lb/hr-sq ft		2
	Cake solids		18
5.	Sludge Incineration: Solids Loading, lb/hr-sq ft		2
CARBON TREATMENT SYSTEM			
1.	Carbon Contacting (8 x 30 mesh carbon) Empty-bed contact time		25
	Hydraulic surface Loading, gpm/sq ft		4
	Backwash volume, % of plant flow		5
	Sodium Nitrate dosage, mg/l N		5.5
	Carbon Dosage, lb/MG		250
	Carbon Regeneration loss, %		5

TABLE 18 "SUMMARY OF PHYSICAL/CHEMICAL TREATMENT SYSTEM PERFORMANCE" (24)

Parameters	Raw Sewage	Clarified Effluent	Carbon Effluent	Average Percent Removal: Chemical Treatment	Average Percent Removal: Carbon Treatment	Average Percent Removal: Overall	AS Effluent*
Suspended Solids (mg/l)	199	28.3	6.7	85.8	76.3	96.6	11.6
Turbidity (JTU)		22.9	6.3		72.5		7.7
TCOD (mg/l)	321	95.8	19.3	70.2	79.9	94.0	39.5
DCOD (mg/l)	49.4	48.6	13.5	1.6	72.2	72.7	25.7
BOD (mg/l)		36.2	7.8		78.5		8.0
Total Phosphate (mg/l P)	11.1	1.3	0.9	88.3	30.8	91.9	
Nitrate (mg/l N)		0.9	1.3				
Color		20	7.8		61.0		33.1
pH	7.7	6.8	6.8				

Notes: 1. Average alum dosage = 25 mg/l Al (275 mg/l alum)
2. Average polymer dosage = 0.3 mg/l Calgon WT-3,000
3. AS Effluent refers to Activated Sludge Plant Effluent (8 MGD, existing facility)

TABLE 19 "EFFECT OF REGENERATION ON THE PCT CARBON CHARACTERISTICS"

Carbon Characteristics	Virgin Carbon	Spent Carbon (Composite Sample): 1st Reg.	Spent Carbon (Composite Sample): 2nd Reg.	Spent Carbon (Composite Sample): 3rd Reg.	Regenerated Carbon (Composite Sample), Before Quenching: 1st Reg.	Before Quenching: 2nd Reg.	Before Quenching: 3rd Reg.	After Quenching: 1st Reg.	After Quenching: 2nd Reg.	After Quenching: 3rd Reg.
Iodine No. (mg/l)	1,040	402	572	570	805	722	773	751	727	721
Apparent Density (g/cm cu ft)	0.484	0.629	0.585	0.594	0.528	0.537	0.526	0.565	0.548	0.535
Molasses No.	222	120	168	154	213	233	230	189	221	204
Methylene Blue No. (mg/g)	259	147	153	153	223	243	246	227	239	245
Ash (%)	6.4	10.3	8.22	8.67	10.7	11.6	7.81	12.0	12.2	9.0
Mean Particle Dia. (mm)	1.44	1.46	1.58	1.48	1.57	1.50	1.54	1.55	1.50	1.43

TABLE 20

TERTIARY TREATMENT PLANTS

Site	Status 1973	Design Engineer	Average Plant Capacity (MDG)	Contactor Type	No. of Contactors In Series	Contact Time[1] (Min.)	Hydraulic Loading (gpm/ft^2)	Total Carbon Depth (ft)	Carbon Size	Effluent Requirements[2] (Oxygen Demand)
Arlington, Virginia	Design	Alexander Potter/ Engineering-Science	30	Downflow Gravity	1	38	2.9	15	8 x 30	BOD < 3 mg/l
Colorado Springs, Colo.	Operating Dec.'70 to Present	Arthur B. Chafet & Assoc.	3	Downflow	2	30	5	20	8 x 30	BOD < 2 mg/l
Dallas, Texas	Design	URS Forest & Cotton	100	Upflow Packed	1	10	8	10	8 x 30	BOD < 10 mg/l BOD < 5 mg/l (by 1980)
Fairfax County, Va.	Design	Alexander Potter/ Engineering-Science	36	Downflow Gravity	1	36	3	15	8 x 30	BOD < 3 mg/l
Los Angeles, Calif.	Design	City of Los Angeles	5[3]	Downflow Gravity	2	50	4	26	8 x 30	COD < 12 mg/l
Montgomery County, Md.	Design	CH_2M/Hill	60	Upflow Packed	1	30	6.5	26	8 x 30	BOD < 1 mg/l COD < 10 mg/l
Occoquan, Va.	Design	CH_2M/Hill	18	Upflow Packed	1	30	5.8	24	8 x 30	BOD < 1 mg/l COD < 10 mg/l
Orange County, Calif.	Construction	Orange County Water District	15	Upflow Packed	1	30	5.8	24	8 x 30	COD < 30 mg/l
Piscataway, Md.	Operating Mar.'73 to Present	Roy F. Weston	5	Downflow Pressure	2	37	6.5	32	8 x 30	BOD < 5 mg/l
St. Charles, Missouri	Construction	Moran and Cooke	5.5	Downflow Gravity	1	30	3.7	15	8 x 30	
South Lake Taho, Calif.	Operating Mar.'68 to Present	CH_2M/Hill	7.5	Upflow Packed	1	17	6.2	14	8 x 30	BOD < 5 mg/l COD < 30 mg/l
Windhoek, South Africa	Operating Oct.'68 to Present	National Institute for Water Research Pretoria, So. Africa	1.3	Downflow Pressure	2	30	3.8	15	12 x 40	COD < 10 mg/l

[1] Empty bed (superficial) contact time for average plant flow.

[2] BOD: Biochemical oxygen demand
COD: Chemical oxygen demand

[3] 50 MGD ultimate capacity

TABLE 21

PHYSICAL/CHEMICAL TREATMENT PLANTS

Site	Status 1973	Design Engineer	Average Plant Capacity (MGD)	Contact Time[1] (Min.)	Hydraulic Loading (gpm/ft^2)	Total Carbon Depth (ft)	Carbon Size	Effluent Requirements[2] (oxygen Demand)	
Cortland, New York	Design	Stearns & Wheeler	10	30	4.3	17	8 x 30	TOD	30 mg/l
Cleveland Westerly, Ohio	Construction	Engineering-Science	50	30	3.7	17	8 x 30	BOD	20 mg/l
Fitchburg, Massachusetts	Construction 95% Complete	Camp Dresser & McKee	15	35	3.3	15.5	8 x 30	BOD	10 mg/l
Garland, Texas	Construction	URS Forest & Cotton	30	30	2.5	10	8 x 30	BOD	10 mg/l
LeRoy, New York	Design	Lozier Engineers	1	27	7.3	26.8	12 x 40	BOD	10 mg/l
Niagara Falls, New York	Construction 50% Complete	Camp Dresser & McKee	48	20	3.3	9	8 x 30	COD	112 mg/l
Owosso, Michigan	Design	Ayres, Lewis, Norris & May	6	36	6.2	30	12 x 40	BOD	10 mg/l
Rosemount, Minnesota	Operational	Banister, Short, Elliot, Hendrickson and Associates	0.6	66 (max)	4.2	36 (max)	12 x 40	BOD	10 mg/l
Rocky River, Ohio	Operational	Willard Schade & Assoc.	10	26	4.3	15	8 x 30	BOD	15 mg/l
Vallejo, California	Design	Kaiser Engineers	13	26	4.6	16	12 x 40	BOD	45 mg/l (90% of time)

[1] Empty bed (superficial) contact time for average plant flow.

[2] BOD: Biochemical oxygen demand
COD: Chemical oxygen demand

TABLE 22 "SUMMARY OF PCT PILOT-PLANT AND FULL-SCALE PLANT PERFORMANCES"

	Effluent			Effluent			Effluent		
	Raw COD (mg/l)	COD (mg/l)	% Removal	Raw TOC (mg/l)	TOC (mg/l)	% Removal	Raw BOD (mg/l)	BOD (mg/l)	% Removal
Blue Plains Pilot Plant	320	16	95	100	8	92	150	6	96
Owosso, Michigan	250-350	24-30	-91				140	8	84
Pomona, California	321	19	94				120[1]	7.8	78.5[2]
Rosemount, Minnesota (1st year)				-		-	230	23	90
Rosemount, Minnesota (last 3 to 4 months)									
Battelle Pilot Plant at Westerly	527	42	92	-	-		240	26	89
CRSD Pilot Plant at Westerly	437	56	87	90	21	77	206	32	84

[1] Estimated based on BOD similar to COD removals across clarifier.

[2] Just around carbon columns.

TABLE 23 "CARBON PILOT-PLANT RESULTS FOR PETROCHEMICAL AND REFINING WASTEWATERS"

Type of Wastewater	Design Q (MGD)	Process Application	Influent COD (mg/l)	Effluent COD (mg/l)	Percent Removal
Refinery	28	Physical/Chemical	600	103	83
Refinery	1.9	Physical/Chemical	800	201	75
Refinery	22	Physical/Chemical	670	143	79
Petrochemical	3	Tertiary	150	49	67
Refinery	26	Tertiary	100	41	59
Refinery	28	Tertiary	300	50	83
Refinery	8	Tertiary	100	40	60
Petrochemical	29	Tertiary	150	48	68

TABLE 24 "REFINERY WASTEWATER TREATMENT RESULTS"

Parameter	API Separator Effluent	Carbon Treated Effluent	Biologically Treated Effluent	Biological-Carbon Treated Effluent
BOD (mg/l)	97	48	7	3
COD (mg/l)	234	103	98	26
TOC (mg/l)	56	14	30	7
Oil & Grease (mg/l)	29	10	10	7
Phenols (mg/l)	3.4	0.004	0.01	0.001
Chromium (mg/l)	2.2	0.2	0.9	0.02
Copper (mg/l)	0.5	0.03	0.1	0.05
Iron (mg/l)	2.2	0.3	3	0.9
Lead (mg/l)	0.2	0.2	0.2	0.2
Zinc (mg/l)	0.7	0.08	0.4	0.15
Sulfide (mg/l)	33	39	0.2	0.2
Ammonia (mg/l)	28	28	27	27
Cyanides (mg/l)	0.25	0.2	0.2	0.2
Turbidity, (TTU)	26	11	17	5
Color (Std. Color Units)	30	15	15	1

TABLE 25 "CARBON REGENERATION ACTIVITY ANALYSIS"

	Iodine No.	Molasses No.
Virgin Carbon	1,010	216
API Separator Effluent to Carbon	906	405
Biologically Treated Effluent to Carbon	991	304

TABLE 26 "PILOT-PLANT RESULTS-TERTIARY CARBON APPLICATION"

	Influent Concentration	Effluent Concentration		Average Percentage Removal	
COD (mg/l)	600	280[1]		53[1]	
	500	230		54	
	400	175		56	
	300	120		60	
	200	65		68	
SOC (mg/l)	300	140[2]	250[3]	53[2]	17[3]
	200	95	155	53	23
	100	30	55	70	45
	50	10	25	80	50
BOD (mg/l)	250	88[4]	218[5]	65[4]	13[5]
	200	70	186	65	7
	150	54	135	64	10
	100	36	68	64	32
	50	20	30	60	40
	20	10	12	50	40

[1]Throughput Rate = 0.6 - 1.2 Bed Volumes per hour
[2]Throughput Rate = 0.5 Bed Volumes per hour
[3]Throughput Rate = 2.4 Bed Volumes per hour
[4]Throughput Rate = 0.15 Bed Volumes per hour
[5]Throughput Rate = 1.2 Bed Volumes per hour

TABLE 27 "DESIGN CRITERIA FOR THE ARCO CARBON PLANT"

Number of Rainfall Days Per Year (max.)	30	days
Maximum Rainfall Runoff Rate (per day)	12.6	Million Gallons
Maximum Rainfall Runoff Rate (per year)	378	Million Gallons
Average Influent COD Concentration	250	mg/l
Average Effluent COD Concentration	37	mg/l
Carbon Capacity	1	lb carbon exhausted per 1000 gal. water treated (1.75 lb COD removed/lb carbon)

TABLE 28 "ACTIVATED CARBON ADSORPTION DESIGN DATA AND ACTIVATED CARBON PROPERTIES"

Rated Flow (Each of Three Adsorbers)		667	gpm
Adsorber Diameter		10	ft
Adsorber Bed Depth		45	ft
Contact Time (Empty Bed)		40	min
Hydraulic Loading		8.5	gpm/ft^2
Design Inlet Pressure		60	psi
Pressure Drop Through Carbon		35	psi
Carbon Inventory	Carbon Bed	92,000	lb
	Adsorber Total	100,000	lb
Theoretical Carbon Capacity		0.3	lb TOC/lb carbon
Carbon Dosage		0.86 lb carbon/1,000 gal Throughput	

Activated Carbon Properties Filtrasorb 300
(8 x 30 Bituminous Coal)

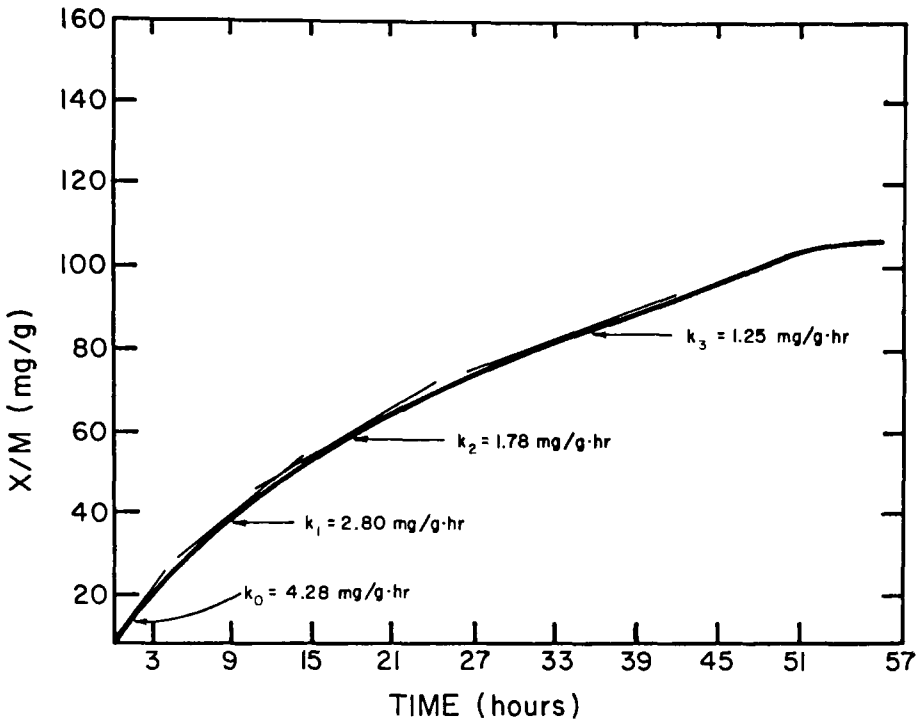
Total Surface Area (N_2 BET Method)	950-1050	m^2/g_3
Bulk Density	26	lb/ft^3
Particle Density Wetted in Water	1.3-1.4	g/cc
Mean Particle Diameter	1.5-1.7	mm
Iodine Number, minimum	950	
Ash	Max 8%	
Moisture	Max 2%	

TABLE 29 "THERMAL REGENERATION DESIGN DATA"

Furnace		60" x 6 Hearth with Integral Afterburner
Regeneration Rate		125 lb/hr
Steam Addition Rate		125 lb/hr
Fuel		Refinery Fuel Gas
Fuel Rate	Hearth 4	188 CFH
	Hearth 6	68 CFH
	Afterburner	310 CFH
Combustion Air Rate	Hearth 4	5,000 CFH
	Hearth 6	1,800 CFH
	Afterburner	8,120 CFH
Design Temperatures	Hearth 4	1,725° F
	Hearth 6	1,750° F
	Afterburner	1,250° F

FIGURE 1

ADSORPTION OF DBS TO EQUILIBRIUM IN CONTINUOUSLY STIRRED FLOW SYSTEMS [2]



ORGANIC CONSTITUENT IS DODECYL-BENZENESULFONATE (DBS)

Figure 2

FREUDLICH ISOTHERM APPLICATION [3]

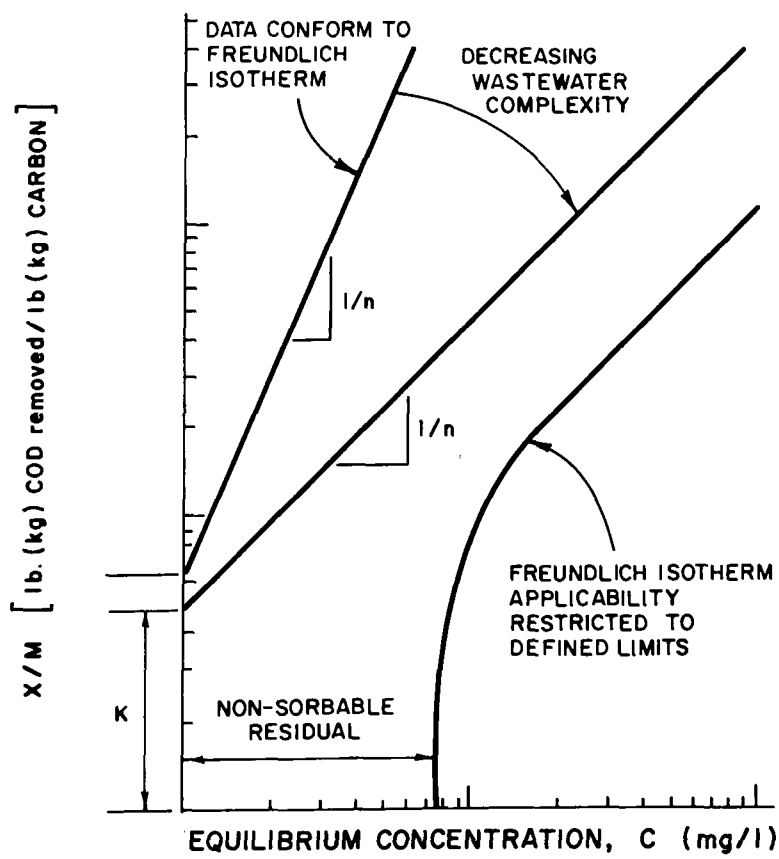


FIGURE 3

CROSS-SECTIONAL VIEW
OF MULTIPLE-HEARTH FURNACE

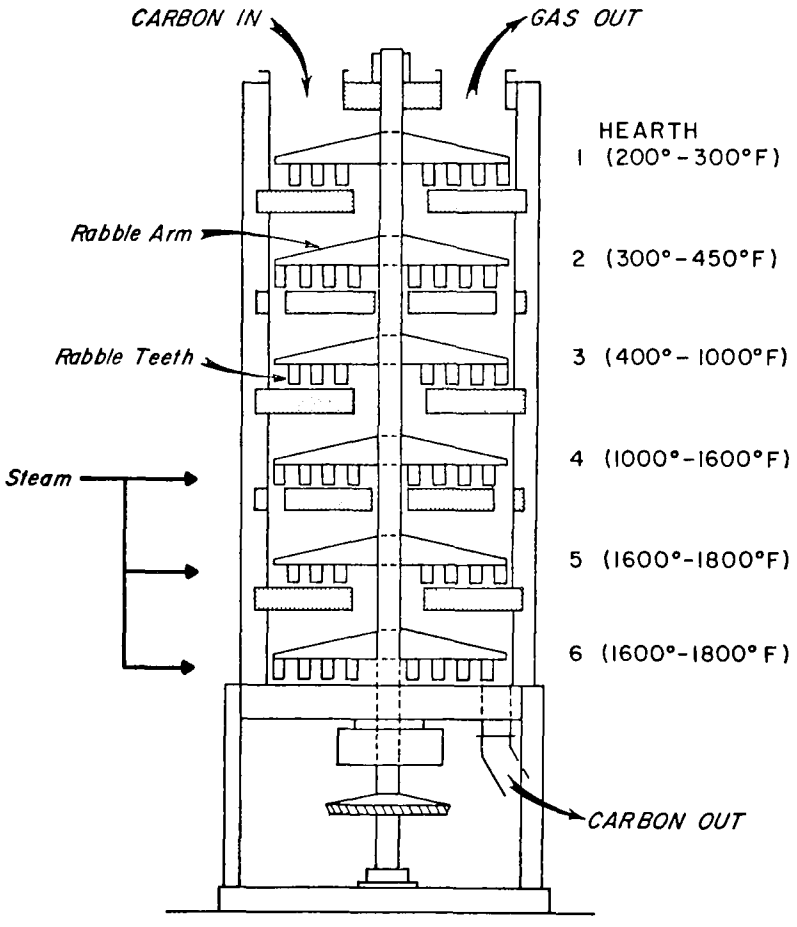


FIGURE 4

SIMPLIFIED FLOW DIAGRAM [15]
SOUTH TAHOE

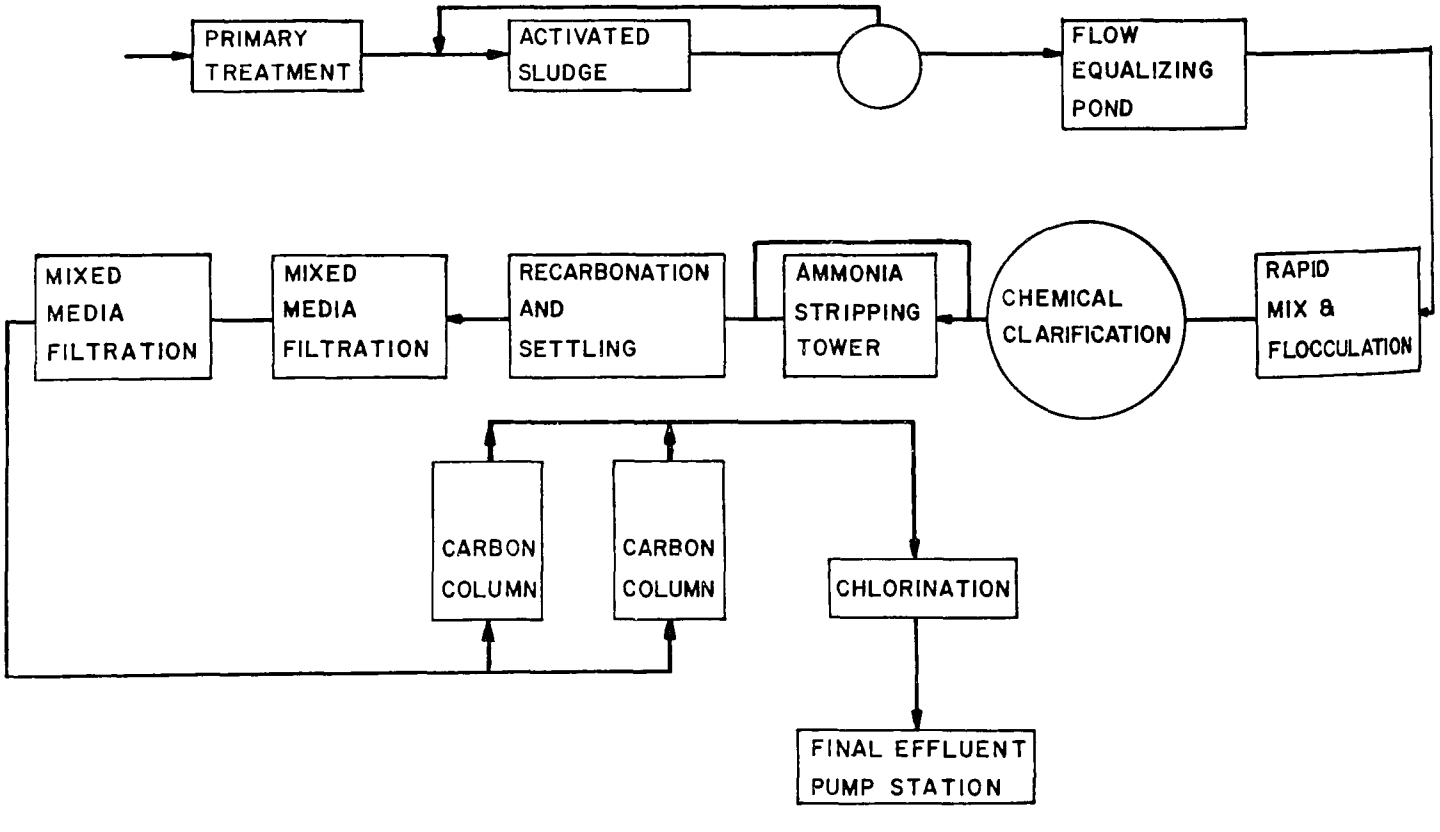
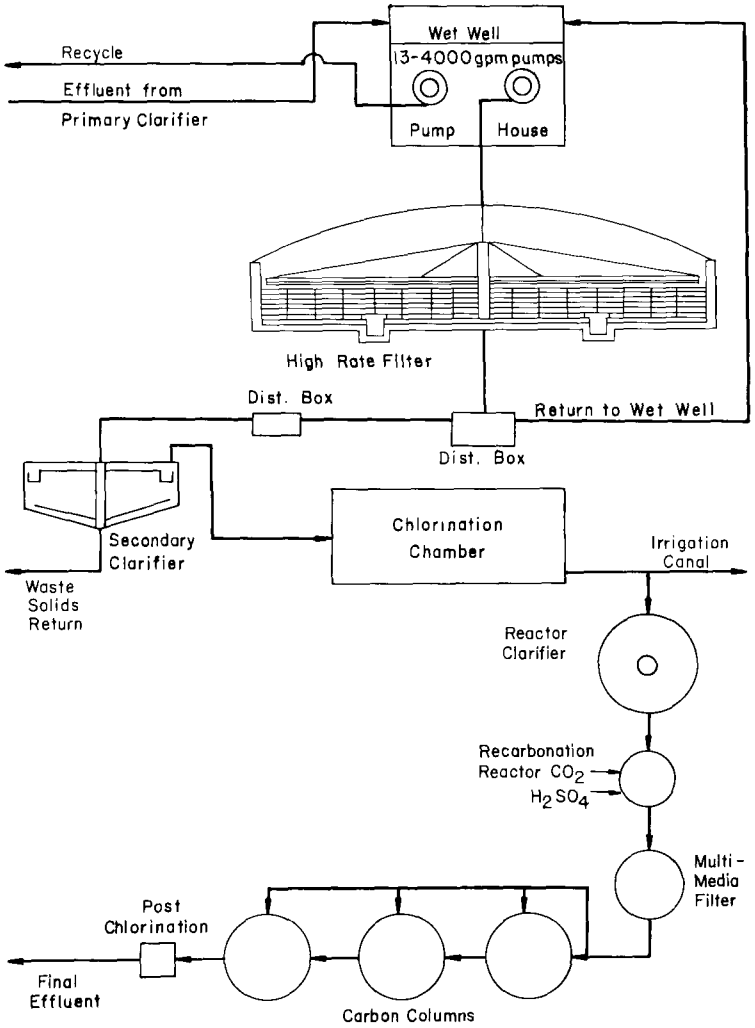


FIGURE 5
SIMPLIFIED FLOW DIAGRAM
COLORADO SPRINGS PLANT



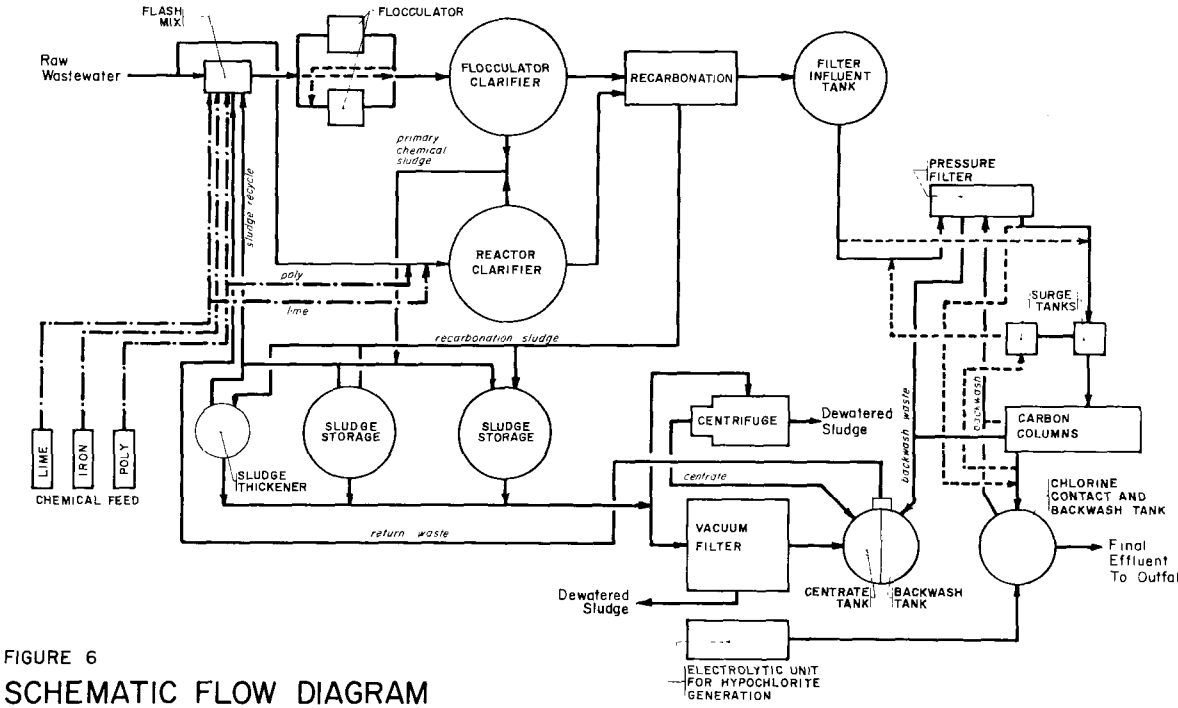
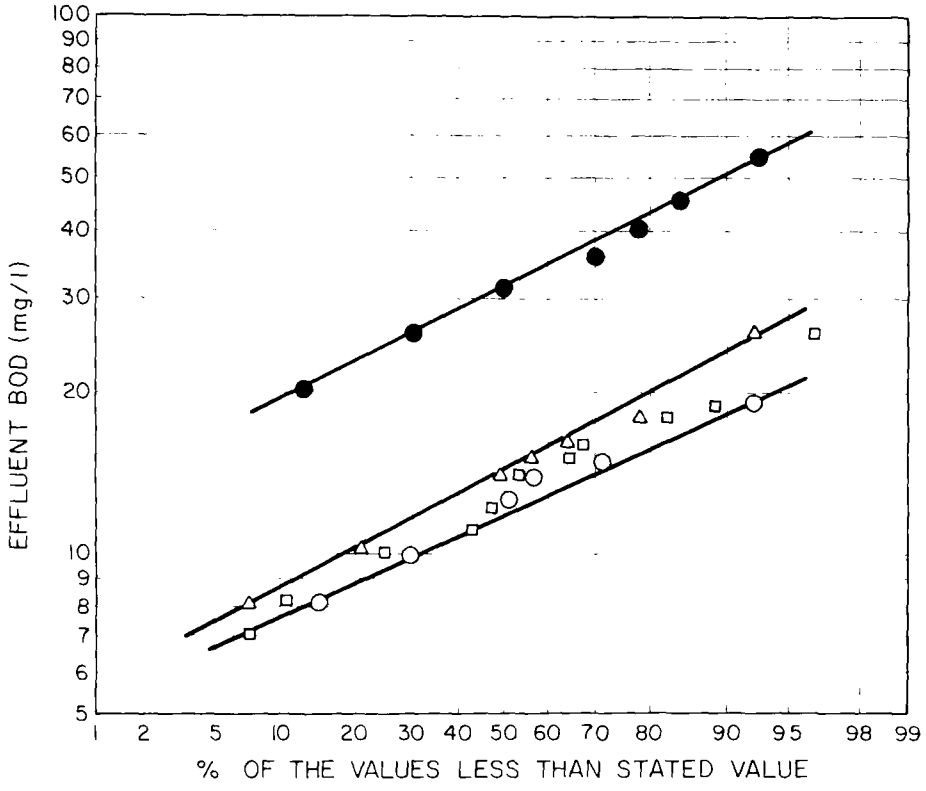


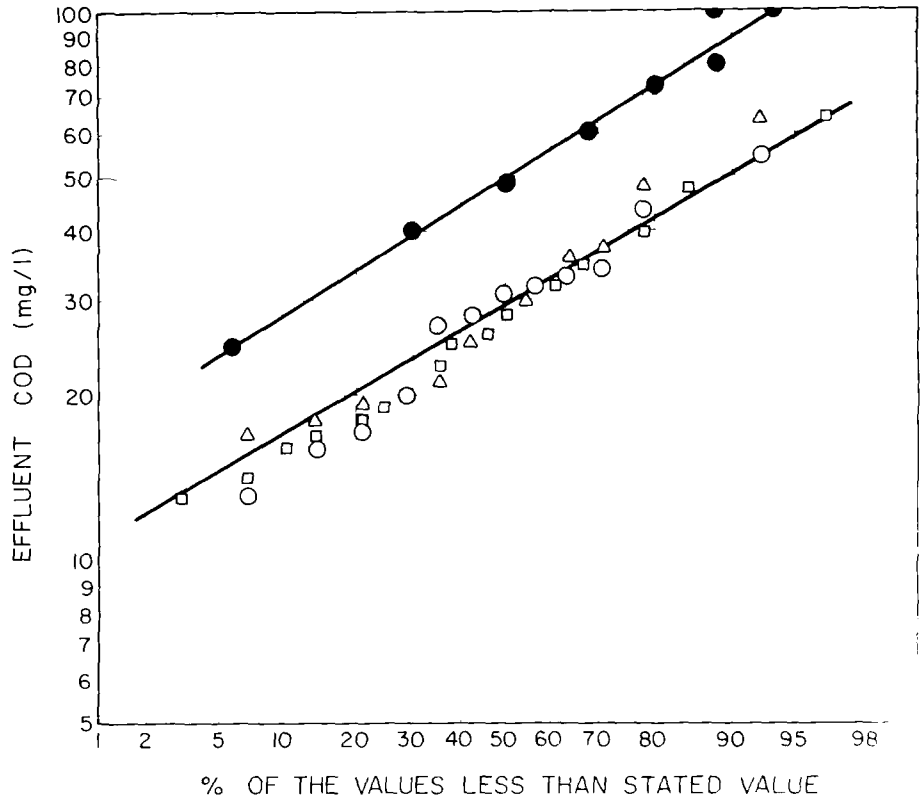
FIGURE 6
SCHEMATIC FLOW DIAGRAM
WESTERLY ADVANCED WASTE TREATMENT PLANT
PILOT PLANT

FIGURE 7
FREQUENCY ANALYSIS FOR EFFLUENT BOD[25]
C R S D PRECARBON OZONATION STUDY
WESTERLY PILOT PLANT



● NO PRECARBON OZONATION
△ OZONE <6.2 mg/l
○ OZONE =6.2 mg/l
□ OZONE =3.2→6.2 mg/l

FIGURE 8
FREQUENCY ANALYSIS FOR EFFLUENT COD[25]
C R S D PRECARBON OZONATION STUDY
WESTERLY PILOT PLANT



● NO PRECARBON OZONATION
△ OZONE <6.2 mg/l
○ OZONE =6.2 mg/l
□ OZONE =3.2→6.2 mg/l

FIGURE 9
FLOW DIAGRAM FOR THE GARLAND PLANT [22]

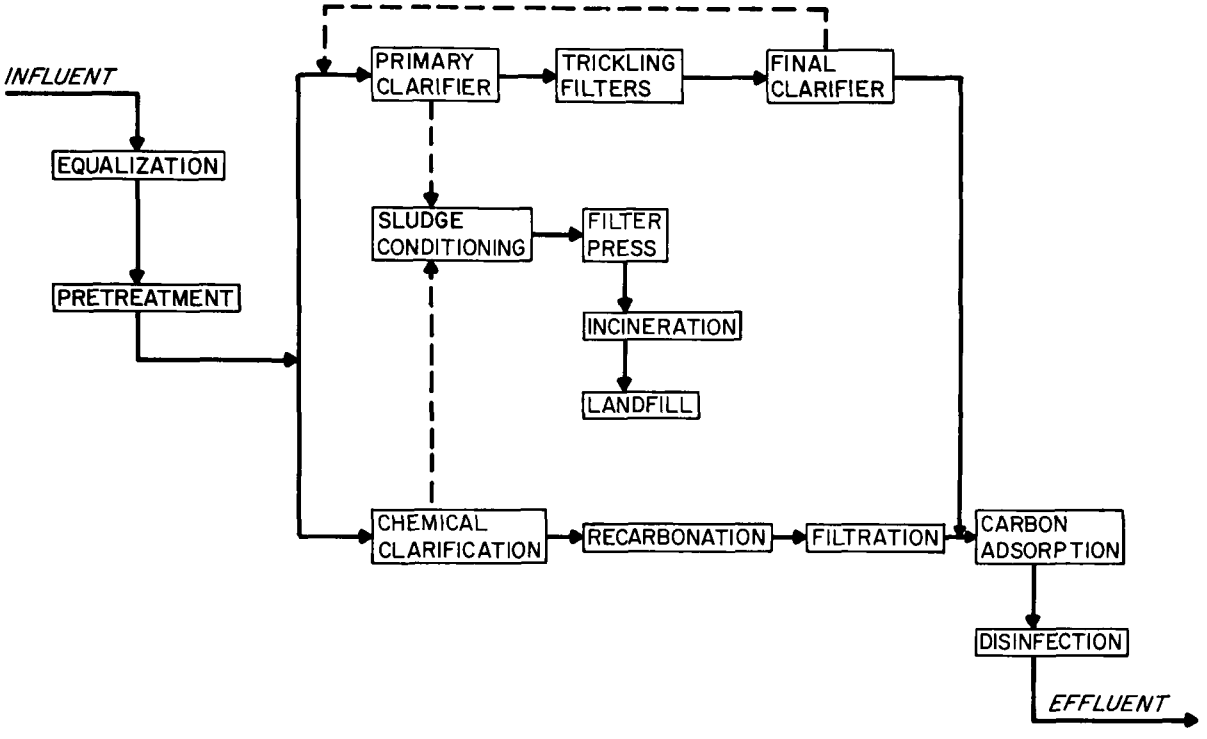


FIGURE 10
PHYSICAL/CHEMICAL PILOT PLANT SCHEMATIC
POMONA, CALIFORNIA

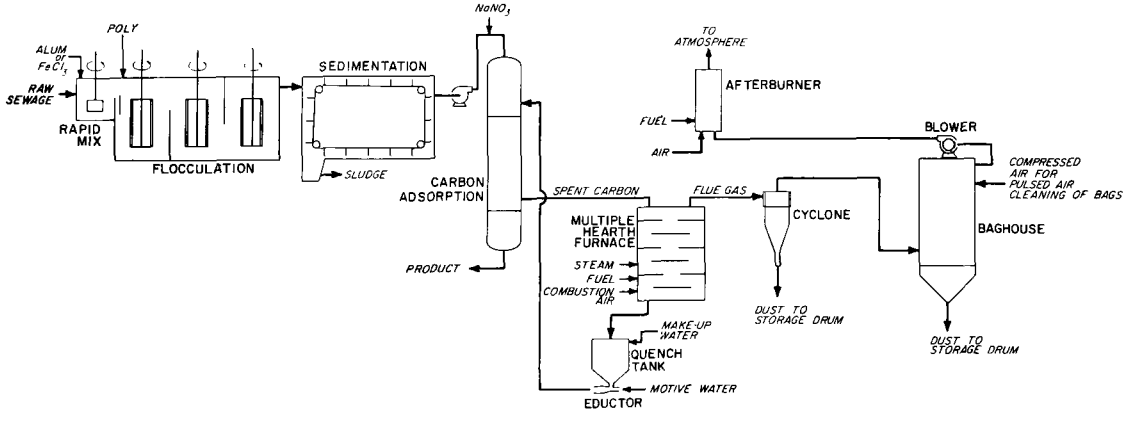


FIGURE 11
SULFIDES AND HEADLOSS vs TIME

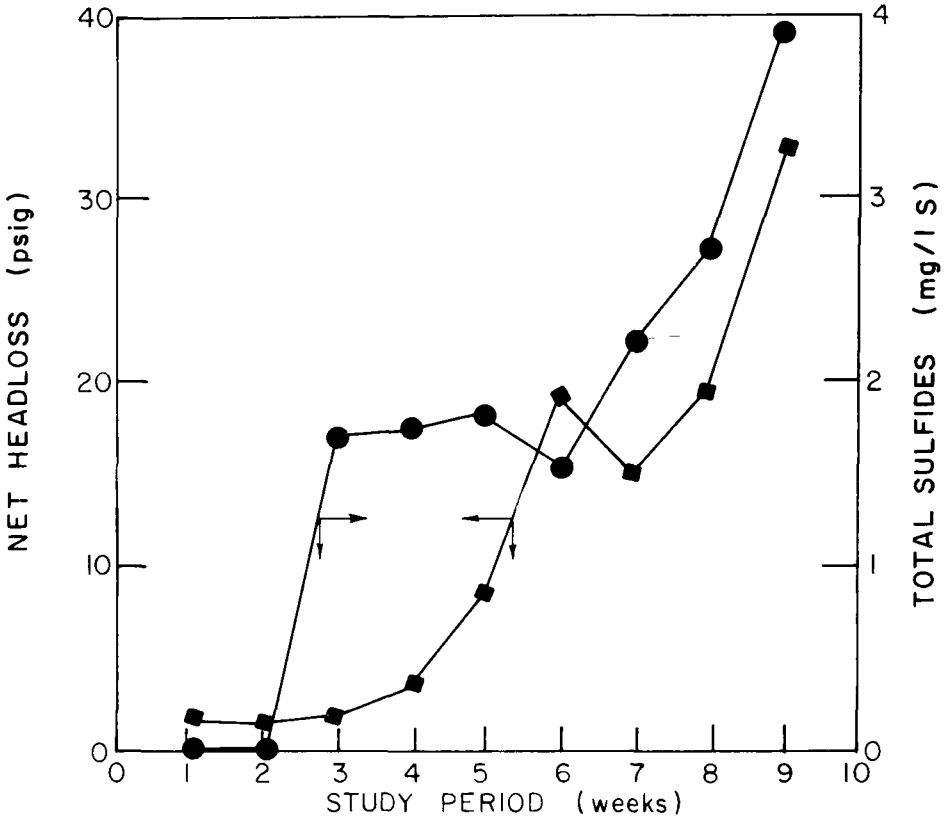


FIGURE 12
BOD REMOVAL TREATMENT RESULTS[27]

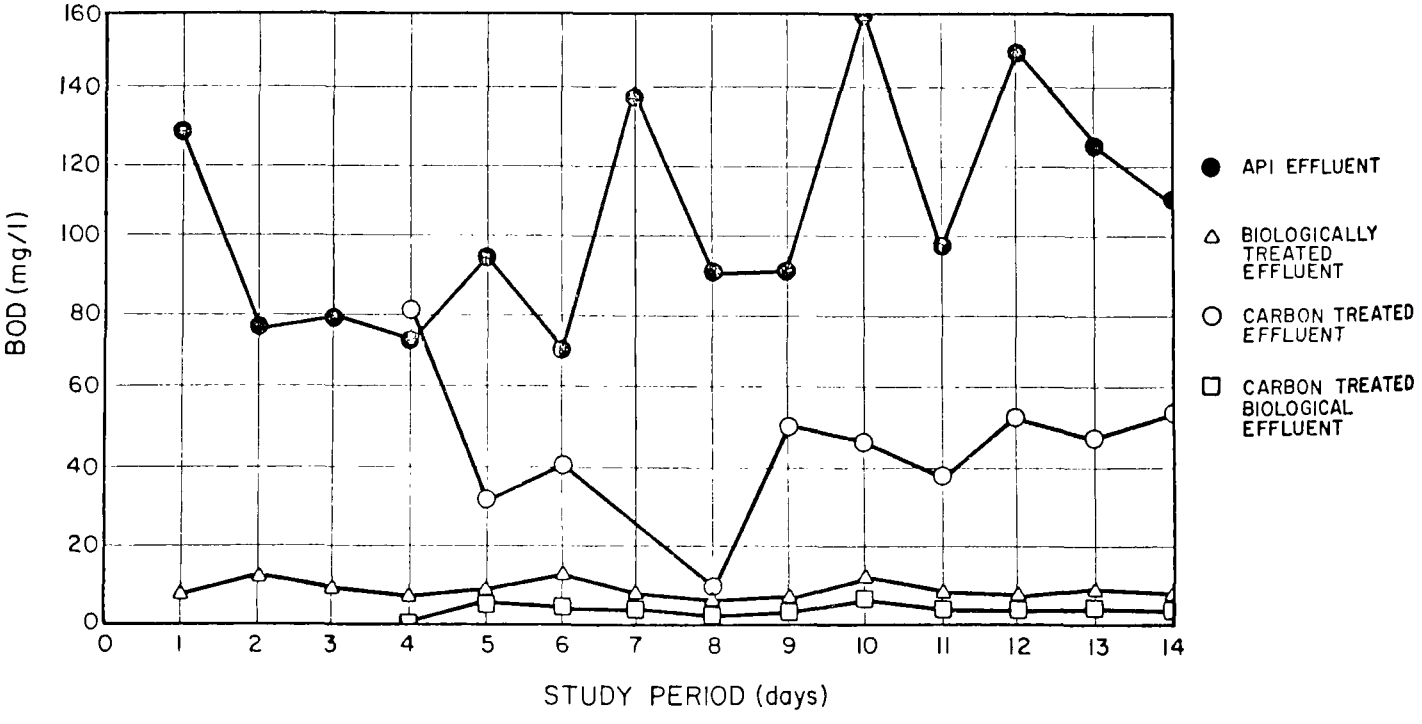


FIGURE 13
COD REMOVAL TREATMENT RESULTS [27]

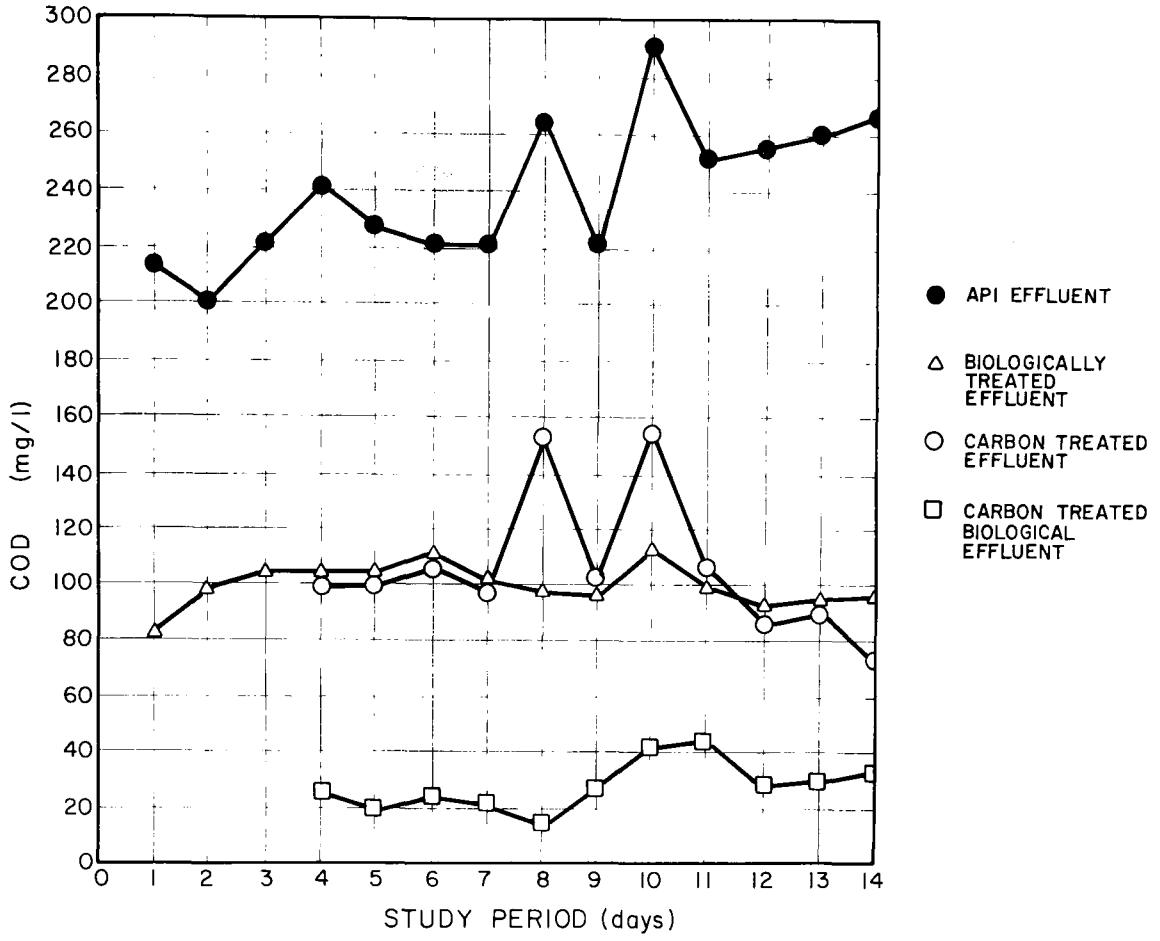


FIGURE 14
ARCO FLOW DIAGRAM
WATSON REFINERY

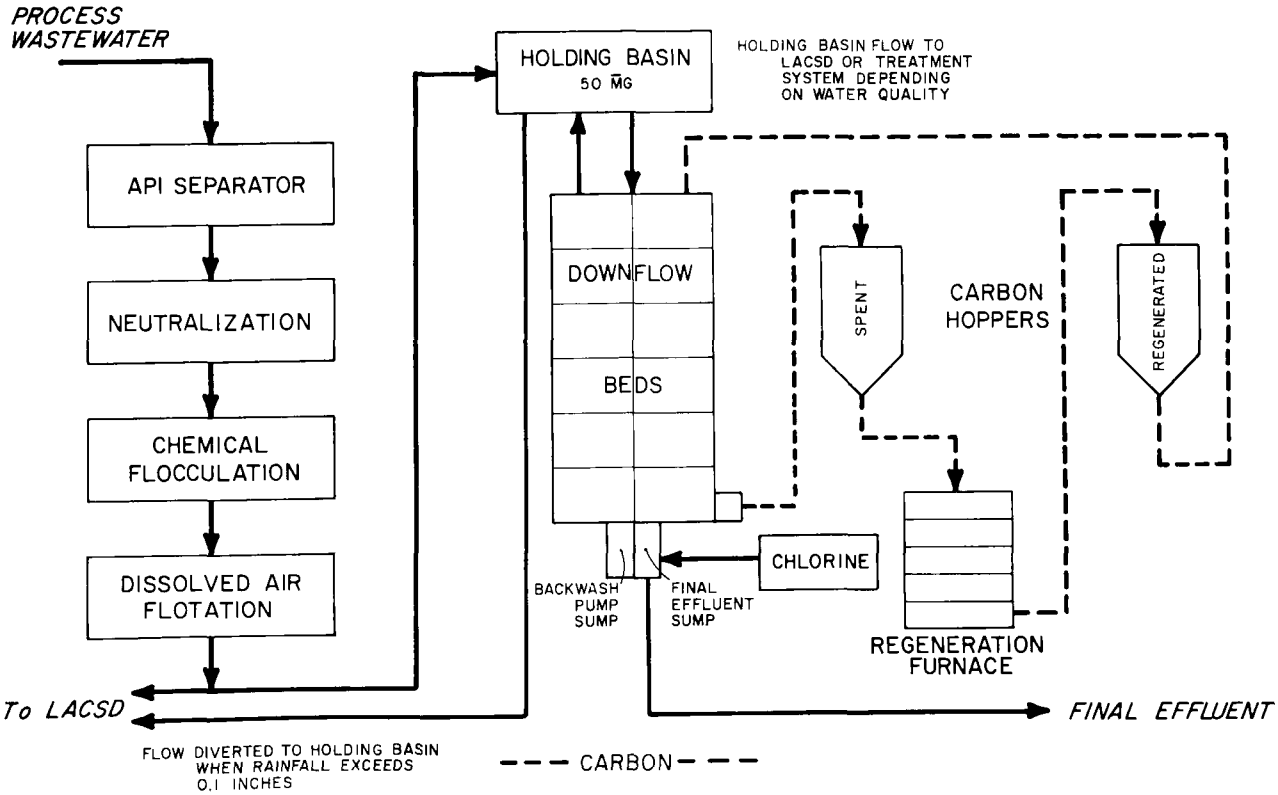


FIGURE 15

PERFORMANCE OF ARCO CARBON PLANT
COD REMOVAL

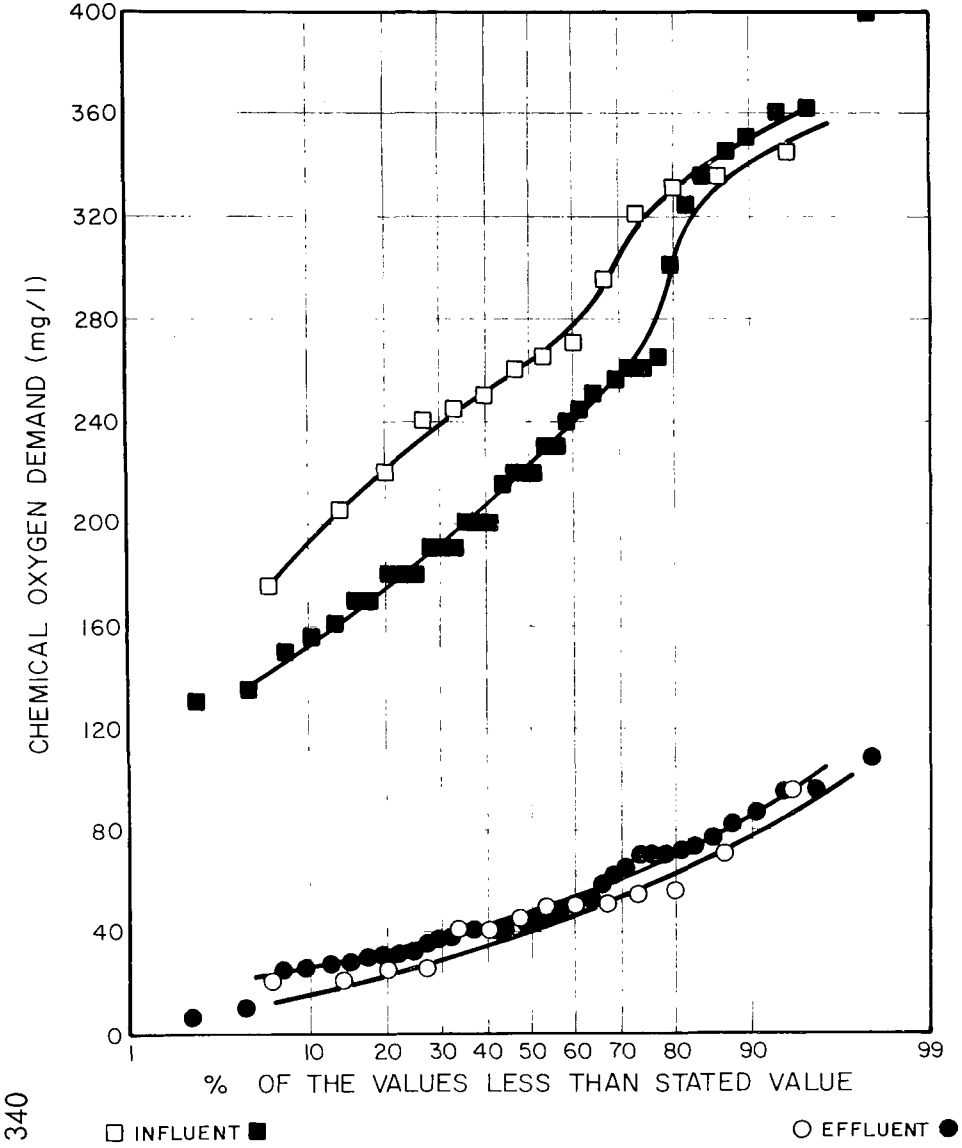


FIGURE 16

PERFORMANCE OF ARCO CARBON PLANT
O&G REMOVAL

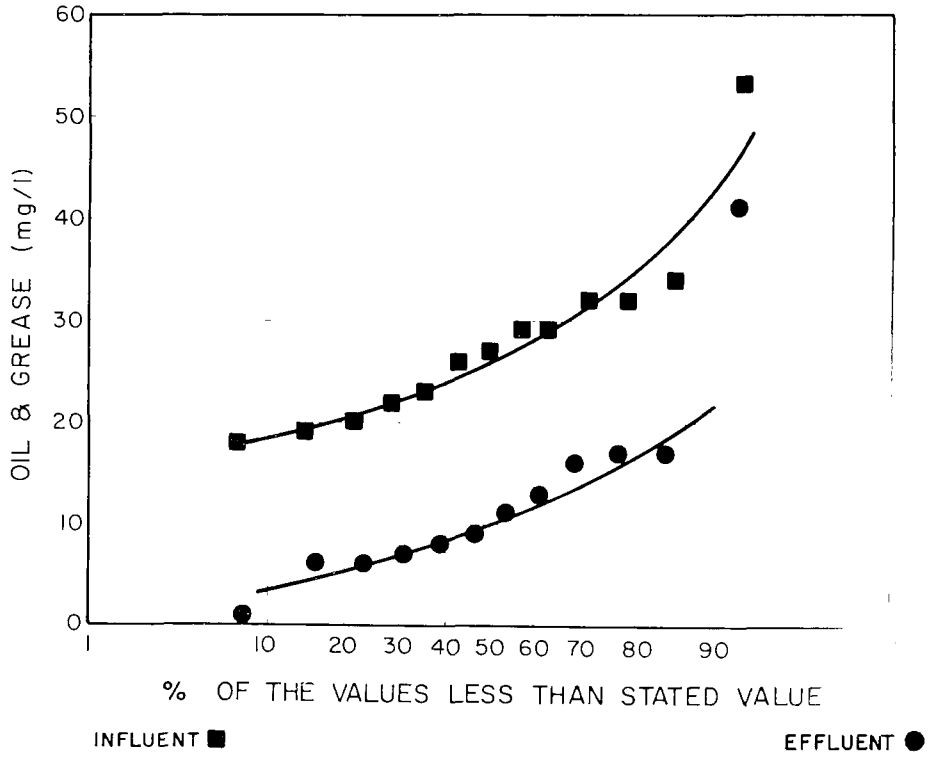


FIGURE 17

CARBON TREATMENT SYSTEM

REICHHOLD CHEMICALS CO.

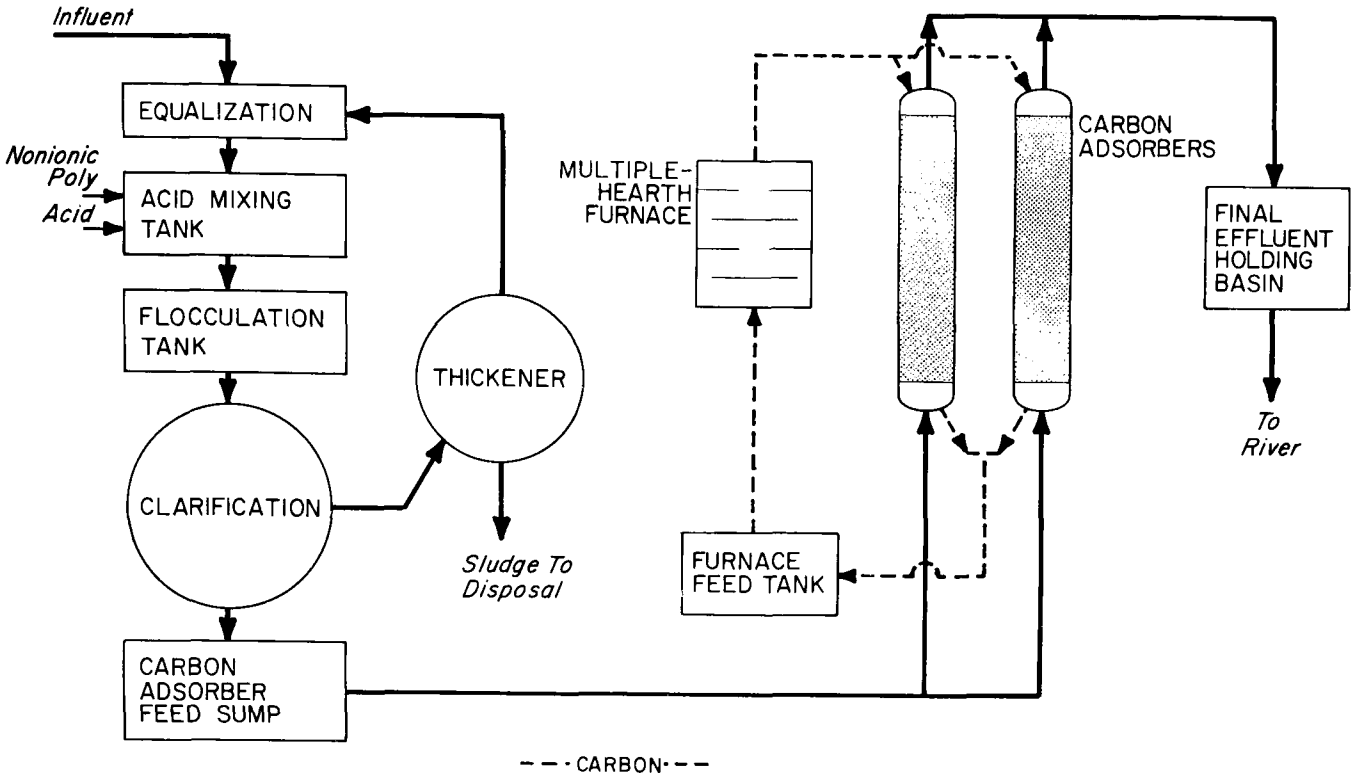


FIGURE 18

BP TREATMENT SYSTEM FLOW DIAGRAM

MARCUS HOOK REFINERY

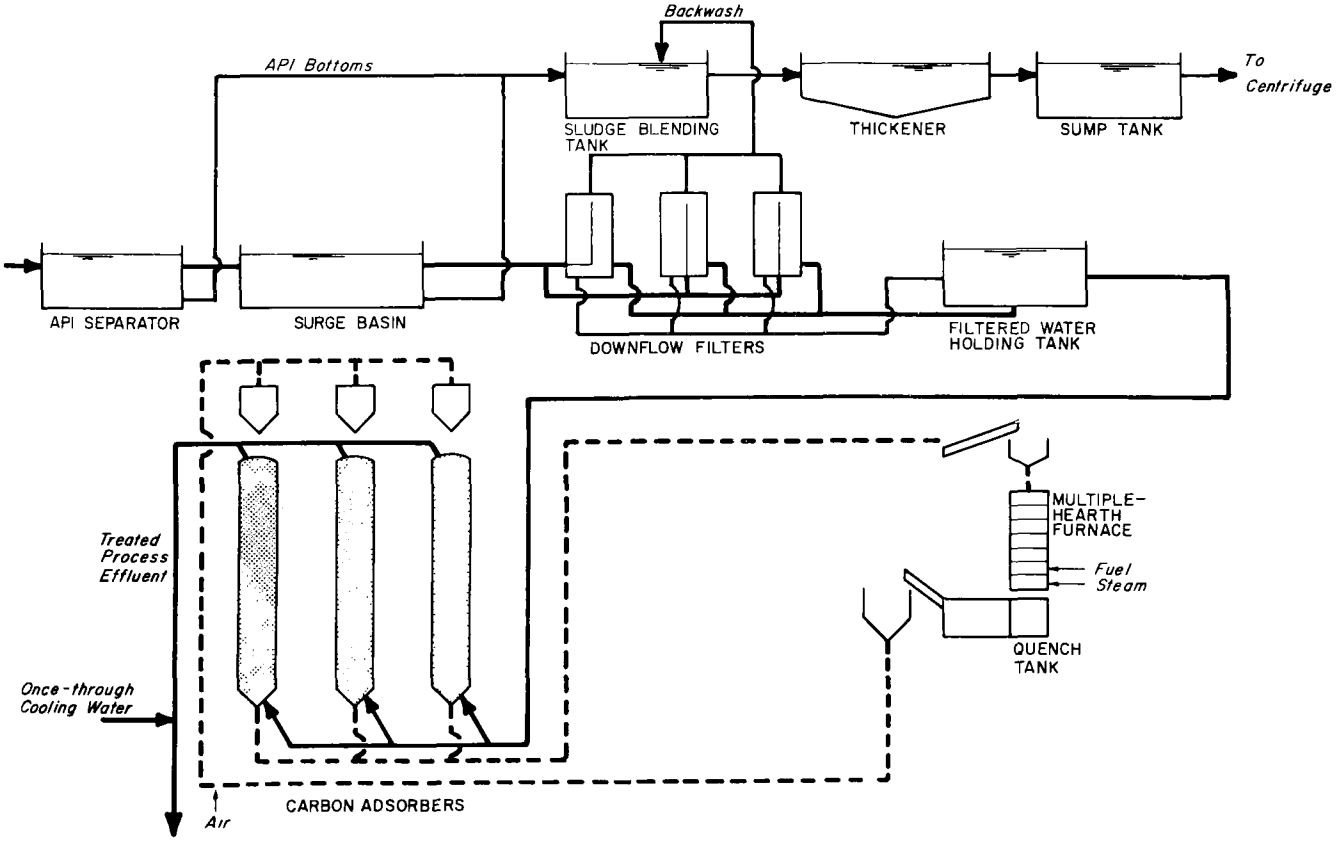


FIGURE 19

COD REMOVAL AS A FUNCTION OF ADSORBER CONTACT TIME [32]

PERIOD I

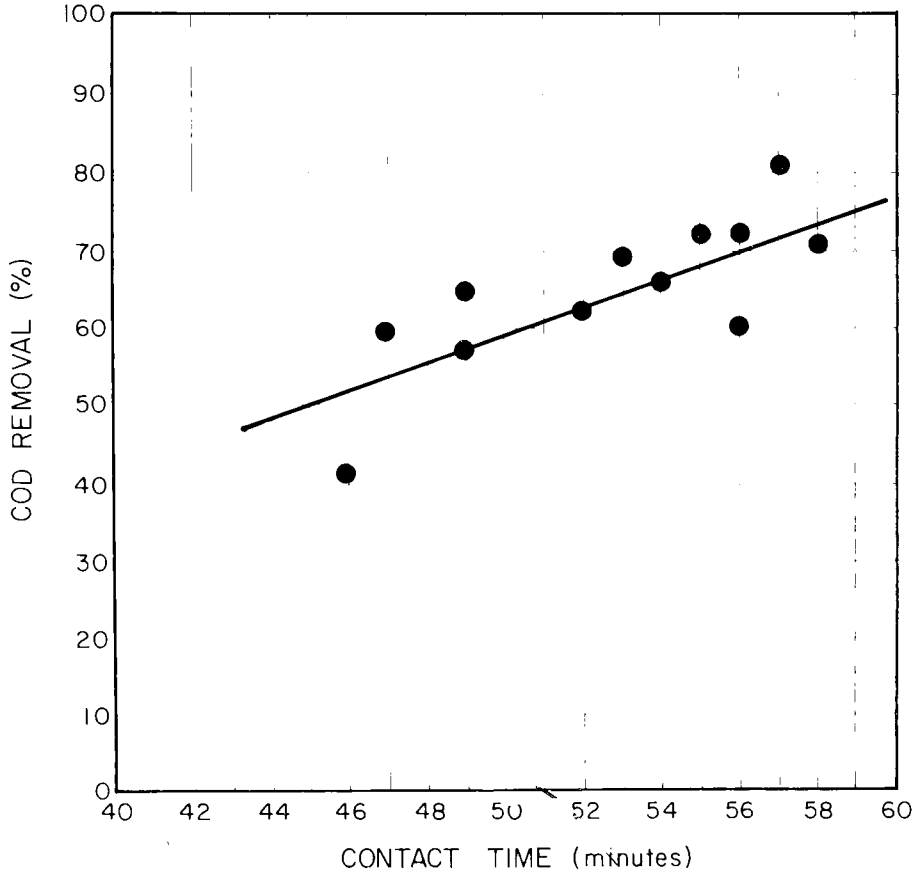
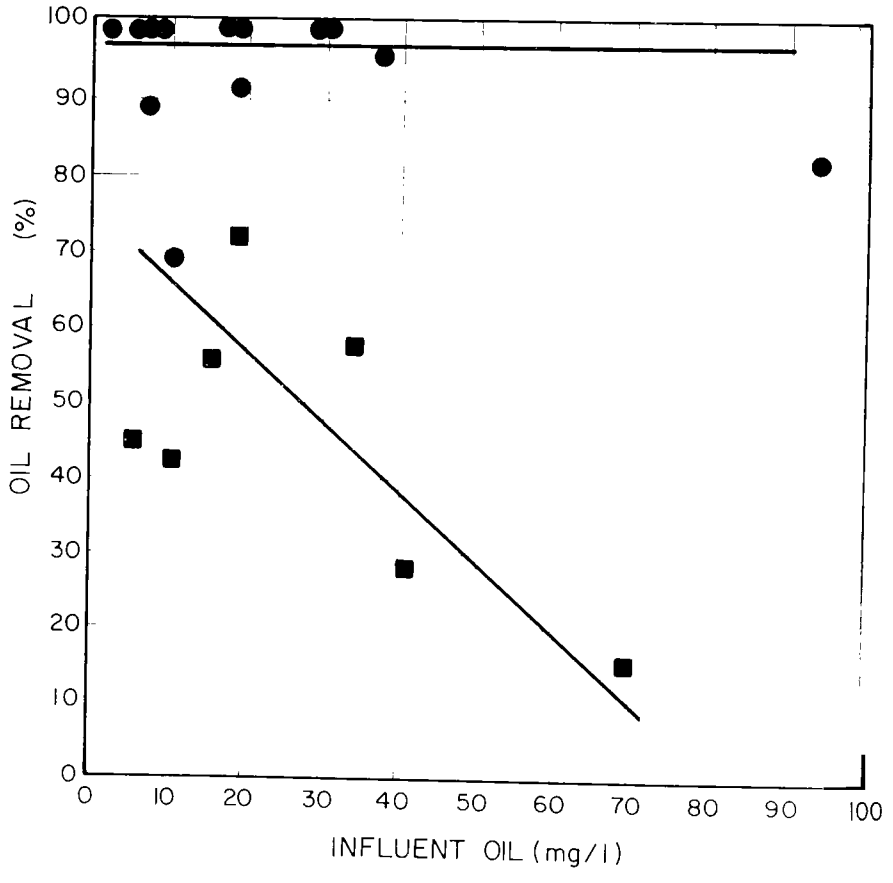


FIGURE 20

ADSORBER OIL REMOVAL AS A FUNCTION OF INFLUENT CONCENTRATION [32]

PERIOD I



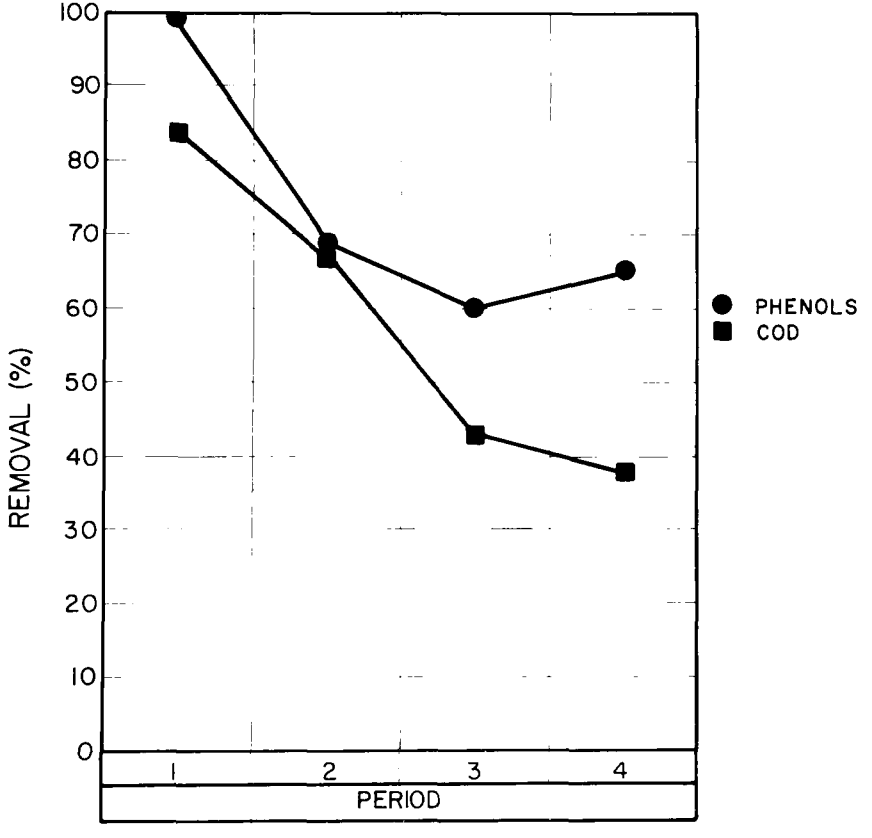
● INITIAL REMOVALS

■ REMOVALS AFTER START OF BED PULSING

FIGURE 21

FULL-SCALE PROCESS PERFORMANCE

BP MARCUS HOOK



PERIOD 1 VIRGIN CARBON, NO FCCU FOUL CONDENSATE

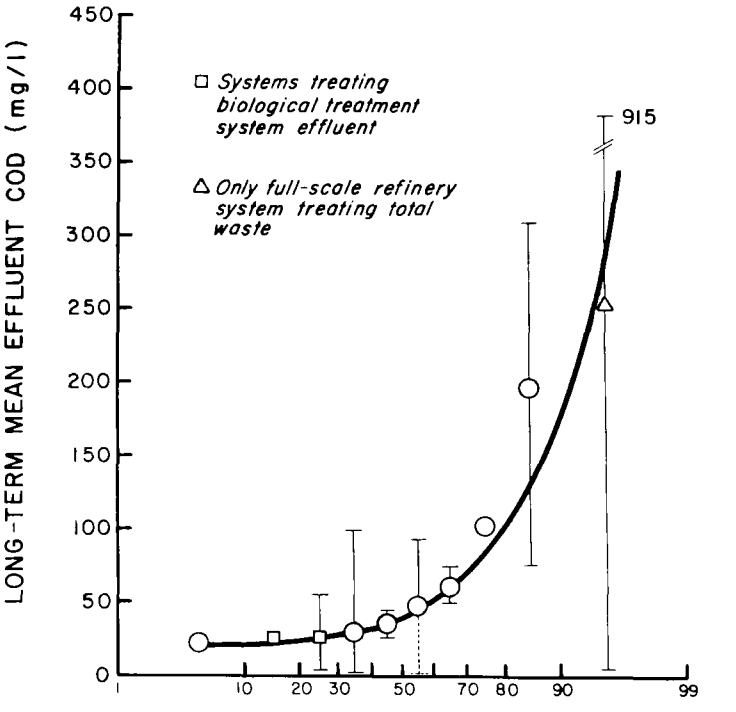
2 CARBON BEDS NOT TURNED OVER, FCCU CONDENSATE INCLUDED

3 CARBON BEDS TURNED OVER, FCCU CONDENSATE INCLUDED

4 EFFLUENT SEPTUMS BENT, NO FCCU CONDENSATE, ONE YEAR OPERATING

FIGURE 22

EFFLUENT COD ATTAINABLE FROM ACTIVATED CARBON SYSTEMS



PERCENT OF PILOT-PLANT OR FULL-SCALE SYSTEMS TREATING REFINERY OR RELATED WASTEWATERS WITH LONG TERM MEAN COD LESS THAN STATED VALUE

FIGURE 23

INFLUENT AND EFFLUENT OIL AND GREASE DISTRIBUTIONS FOR A FULL-SCALE ACTIVATED CARBON SYSTEM

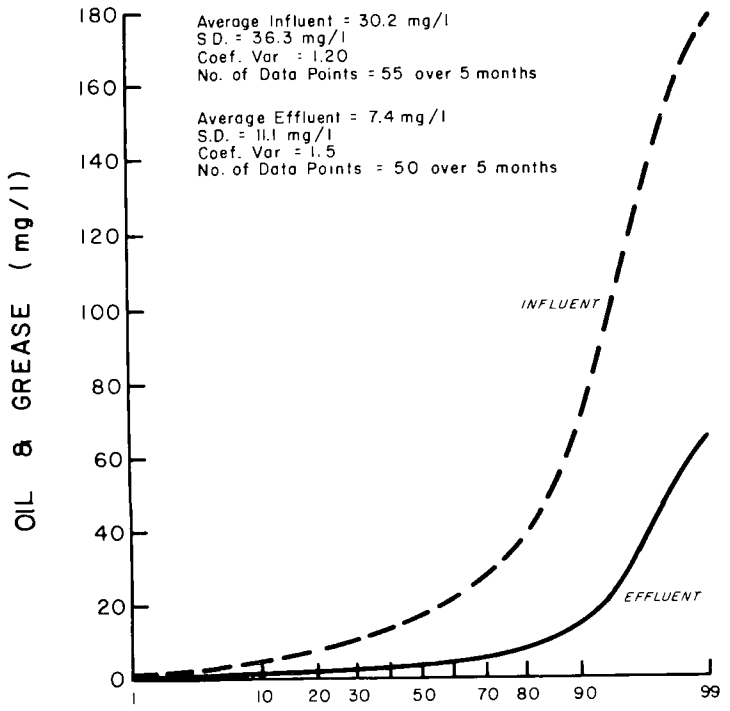
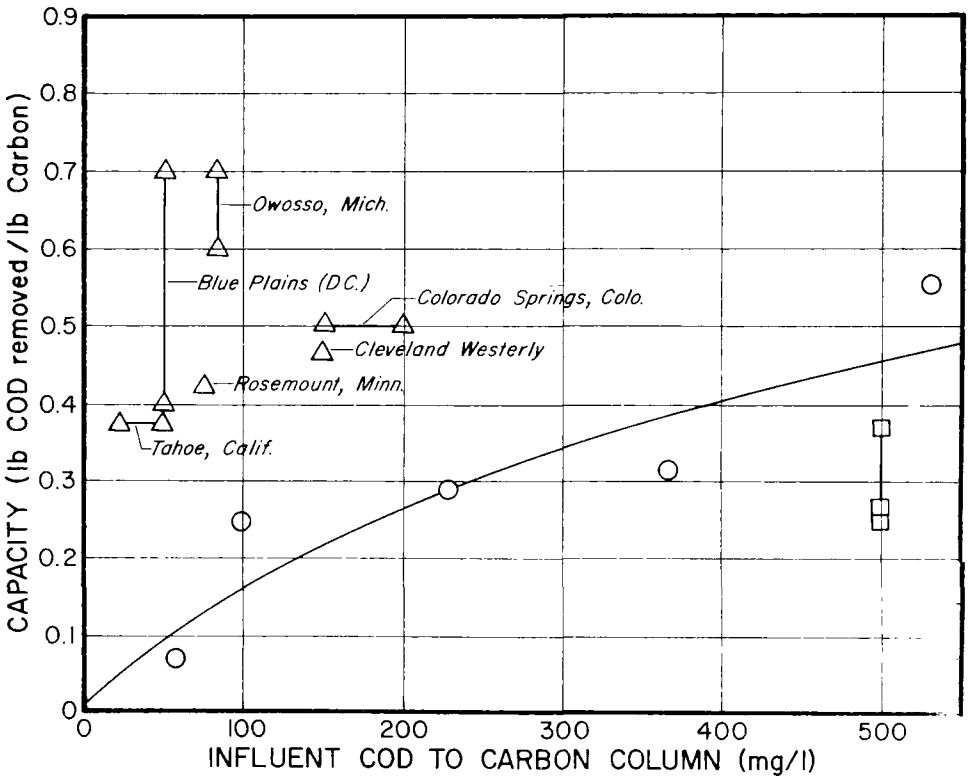


FIGURE 24

CARBON ADSORPTION CAPACITY FOR VARIOUS PLANTS



△ Municipal Wastewater
○ Refinery Wastewater
□ Petrochemicals Wastewater

CAUTIONS AND LIMITATIONS ON THE APPLICATION OF ACTIVATED CARBON ADSORPTION TO ORGANIC CHEMICAL WASTEWATERS

C. T. Lawson
and
J. C. Hovious
Union Carbide Corporation, South Charleston, West Virginia

OBSERVATIONS ON ACTUAL WASTEWATERS

Normal practice in assessing the feasibility of activated carbon adsorption is to first conduct batch adsorption isotherms with powdered activated carbon. These tests provide a relative indication of the amount of organic removal achievable by adsorption and the ultimate adsorptive capacity of the carbon. Unfortunately, these data are useful only in a relative sense - for comparing the relative merits of two different carbons, or for comparing the relative amenability of different wastewaters to adsorption. Isotherm data are not suitable for designing continuous granular carbon adsorption columns, since the dynamic effects and interactions in a continuous bed differ too greatly from the batch equilibrium situation in an isotherm.

Batch adsorption isotherms have been performed on many organic chemical bio-treated effluents and raw wastewaters of widely varying composition and overall organic concentration (COD or TOC basis). Figure 1 shows curves of percent organic removed vs. carbon dosage. It is obvious the amenability of these wastes to adsorption is rather wide - ultimate percentage organic removals vary from 45% to 90%. Even for those cases where 90% organic removal can be achieved by massive carbon dosing in batch tests, the organic removals achievable in continuous adsorbers are lower, often significantly so.

Comparing batch and continuous data for Plant A bio-treated effluent:

Ultimate % removal of TOC in isotherm test	90%
%TOC removal in continuous bed adsorber prior to breakthrough (1 bed vol/hr)	52%
%TOC removal before breakthrough (0.5 bed vol/hr)	64%

Not only was the organic removal predicted by isotherms not achieved, even in early stages of the column run with fresh carbon, but doubling the bed depth (halving the throughput rate) only raised the amount of TOC removal from 52 to 64%.

When batch adsorption data are plotted as log (wt. organic adsorbed/wt. carbon) vs. log (organic concentration remaining in solution), the Freundlich isotherm results - X/M vs. C_e. When the logarithmic plot is extrapolated to $C_e = C_o$ (the initial solution concentration), the resulting $(X/M)_{C_o}$ is called the "adsorptive capacity" of the carbon. These isotherm capacities are usually greater, often very much greater, than the ultimate adsorptive capacity exhibited by a granular adsorption bed at exhaustion. Typical examples from prior publications (1):

Wastewater	Adsorptive Capacity, gm COD/gm carbon	
	Isotherm	Column at Exhaustion
Plant A bio-effluent	1.3	0.26
Plant D bio-effluent	0.65	0.24
Plant G raw wastewater	0.075	0.05

Note that carbon had a very low adsorptive capacity for the constituents in Plant G wastewater.

It was further noted that increasing the carbon bed depth yielded not only the aforementioned limited increase in percentage organic removal, but also a diminished adsorptive capacity. Operating two beds in series until each bed was exhausted at an overall throughput of 0.5 bed vol/hr (1 BV/hr/column) showed:

	gm COD adsorbed/gm carbon	
	Col. 1	Col. 2
Plant A	0.26	0.17
Plant D	0.23	0.13

One may postulate that selective adsorption of the "more adsorbable" organics occurs in the lead bed. Not only that, when the first bed is exhausted, the second bed has little remaining capacity - implying that the "less readily adsorbed" species, which are initially removed in the second bed, block its further usefulness in removing "readily adsorbed" species (available when the first bed breaks through). This phenomenon is shown by the breakthrough curves of Figure 2. Just how "easily adsorbed organics" may be differentiated from "less readily adsorbed" species is a difficult question. The rate of adsorption at the carbon surface, the rate of diffusion within the carbon pores, and the ultimate capacity of the carbon for the adsorbates all play a part in affecting "adsorbability." In isotherm tests these factors are reflected in the measured adsorptive capacity and limiting percentage organic removal. In continuous columns they are reflected in the organic removal achieved and the rapidity with which organic breakthrough and exhaustion occur. The absence, or at least minimization, of diffusion limitations in powdered carbon isotherms can give a markedly different picture of "adsorbability," in terms of both extent and capacity, compared to the complex inter and intra particle diffusion phenomena which occur in a granular carbon bed.

PURE COMPOUND ADSORPTION STUDIES

Because of these observations of low percentage removals of TOC and COD, limited benefits of increasing carbon bed depth, and rather limited adsorptive capacities (in continuous columns), an extensive investigation was conducted (2) to quantify some aspects of "adsorbability" of specific organics. The effects of functionality, molecular weight and structure, aqueous phase pH, solubility, polarity, carbon surface structure, and adsorbate interactions were investigated. Column vs. isotherm comparisons were also made for several pure chemicals and simple mixtures.

In the first phase, 93 organic chemicals from 11 functional group families were subjected to single dosage adsorption tests.

Functional group families:

Alcohols

Aldehydes
Amines and alkanolamines
Aromatics
Pyridines and morpholines
Esters
Glycols and glycol ethers
Ketones
Organic acids
Ethers and oxides
Halogenated aliphatics

Test conditions:
Initial compound concentration = 1000 mg/l (or solubility, if 1000 mg/l)
Carbon: 5 gm/l of powdered Westvaco Nuchar WV-G (surface area = 1100 m^2/gm)
Contact time = 2 hours

Typical graphs of adsorbate loading vs. molecular weight are shown in Figures 3, 4, and 5 for the alcohols, esters, and organic acids tested. The unfavorable effect of branching and the favorable effect of unsaturation can also be seen. Figure 6 is a "map" of percent of compound adsorbed (by 5 gm/l carbon) vs. molecular weight showing the regions which encompass all the experimental data.

Region A	Aromatics (including ring-substituted compounds)
Region B	General trend for aliphatic mono-functional oxygen and nitrogen-containing compounds
Line C	Saturated organic acid line, shown for comparison
Region D	Glycols, glycol ethers

Note that the aromatics, even those containing polar groups (-OH, $-NO_2$, -Cl) are quite amenable to adsorption, while the poly-functional oxygenated compounds (glycols, glycol ethers) are especially difficult to adsorb.

Qualitatively, it was concluded that adsorbability, as reflected in constant dosage tests, is favored by increasing molecular weight, aromaticity, and degree of unsaturation. Increasing polarity, solubility, branching, and degree of dissociation (for amines and organic acids) tended to severely limit the extent of adsorption.

The relative ease of adsorption for simple oxygenated organic compounds may be summarized as follows:

Number of carbon atoms 4
acids aldehydes esters ketones alcohols glycols
Number of carbon atoms 4 (straight-chain compounds)
acids aldehydes alcohols esters ketones glycols

The relatively low adsorption, in general, of compounds containing 4 carbon atoms in these tests is particularly noteworthy. The carbon dosage of 5 gm/l was a rather massive dosage - in a continuous column adsorber it would be equivalent to treating only about 24 gallons of wastewater per pound of carbon. This poor organic removal at high carbon dosage implies that carbon adsorption may have limited application to many organic chemical manufacturing wastewaters, from a cost-effectiveness viewpoint. Low molecular

weight oxygenated organic compounds represent a very large fraction of the production volume in the industry.

In the next phase of the study, Freundlich adsorption isotherms were obtained on 1000 mg/l solutions of five different organic compounds (all containing four carbon atoms) using four different carbons at different aqueous-phase pH levels. Figure 7 shows that pH had a marked effect on the isotherm adsorptive capacity, $(X/M)_{C^\circ}$, for butyraldehyde and ethyl acetate. Data for Carbon A, Witco 517, are shown; similar trends were observed for other carbons. Gas chromatographic analyses indicated that, at acidic or basic pH levels, ethyl acetate was hydrolyzed into its less adsorbable (lower molecular weight) components. At elevated pH, butyraldehyde underwent an aldol condensation into a higher molecular weight (more adsorbable) component. More detailed discussion of differences between the carbons tested and the effects of carbon surface properties are contained in Ref. (2).

A potential problem in successfully applying activated carbon to multi-component wastewaters is indicated. It is not possible to select a pH level that assures maximal adsorption of all wastewater constituents. An acidic pH is required to facilitate adsorption of organic acids (to avoid ionization), near neutral pH favors adsorption of esters, while a highly alkaline pH is necessary to maximize adsorption of aldehydes.

MULTI-COMPONENT ADSORPTION STUDIES

Interactions in multi-component systems were examined in the third phase of the study by adsorption isotherm tests on binary and four-component mixtures. The results are shown in Table 1.

In a test (at pH = 7) of a butanol/ethyl acetate binary mixture (500 mg/l of each compound), the total adsorptive capacity was observed to be 0.237 gm cpds/gm carbon, while the sum of the two adsorptive capacities (at 500 mg/l initial concentration) from pure-component isotherms was 0.27 gm/gm. By gas chromatographic analysis of the residual solutions, the butanol adsorbate loading was 1.05 times the loading in a pure component test while the ethyl acetate loading was 0.76 times the pure component loading. Even though more ethyl acetate was adsorbed from the mixture, on a weight basis, than butanol (as expected from Figure 7), the interaction had a greater deleterious effect on ethyl acetate, in terms of using pure component data to predict mixture adsorbate loadings.

By contrast, in the butyraldehyde/MEK binary test, the total adsorptive capacity from the mixture (0.275 gm cpds/gm) was greater than the sum of the pure component values (0.270 gm/gm), more butyraldehyde (the "more adsorbable component") was adsorbed on a weight basis, and the ratio of mixture loading to pure component loading was greater for butyraldehyde, 1.28 vs. 0.60.

In both four-component mixture isotherms (Table 1), the total adsorptive capacity (0.29 and 0.225 gm/gm for Carbons A and C, respectively) was significantly less than the sum of the pure component capacities (0.575 and 0.312 gm/gm for Carbons A and C, respectively). Also, in the Carbon C test, less butyric acid was adsorbed than butyraldehyde or ethyl acetate, despite the previous pure component conclusion that acids are more adsorbable than

other organic compounds.

Thus, while pure component adsorption data are useful in determining which waste streams are potential candidates for activated carbon treatment, the data cannot be used to quantitatively predict adsorption from multi-component systems.

CONTINUOUS vs. BATCH ADSORPTION STUDIES

In the fourth and final phase of the study, continuous column, granular carbon adsorbers were operated to exhaustion for comparison of ultimate capacities with isotherm capacities. Each column was operated at a throughput rate of 1 bed volume/hour. The feed concentration was 1000 mg/l in the pure component tests, 2000 mg/l (500 mg/l each compound) in the four component test (feed TOC = 1200 mg/l). The four component mixture was butyraldehyde, ethyl acetate, butanol, and butyric acid. In all cases, the ultimate capacity (at exhaustion) was less than that predicted by isotherms (83 to 89%).

	Adsorptive Capacity, gm/gm carbon		
Organic	Isotherm	Column at Exhaustion	Column at Breakthrough
MEK	0.160	0.132	0.103
Butyraldehyde	0.220	0.192	0.141
4-Component Mixture	0.170 (TOC)	0.151 (TOC)	0.124 (TOC)

Note that the usable capacity in a single-column system - the capacity achieved at "breakthrough," where significant organic concentrations appear in the treated effluent - is significantly less than indicated by the isotherms (64 to 72%). Figure 8 shows the experimental breakthrough curve for the four-component mixture.

A second important criterion when applying activated carbon in continuous beds is the amount of wastewater that can be treated before breakthrough (often called the "carbon dosage"). Breakthrough in full-scale practice (where the carbon is removed from service) would be set at the maximum organic concentration allowed by effluent standards. For purposes of discussion, breakthrough was set at the 95% organic removal level in these lab tests. Observed dosages were:

Test	Breakthrough "dosage" gal WW treated/lb carbon
MEK	12.7
Butyraldehyde	19.4
4-Component Mixture	12.4

Treating large volumes of wastewater at these inlet concentrations will, thus, lead to rather short service life (rapid breakthrough), even with the fairly ideal adsorption wavefront shape in Figure 8.

Hydraulic effects (channeling and axial dispersion) are a partial explanation for the failure of column adsorbers to achieve adsorbate loadings predicted by isotherms. The inherent differences between the static equilibrium attained in batch isotherms and the dynamic situation in a continuous column are also limiting factors, particularly when treating complex multi-component (4) wastewaters.

A recent paper (3) by Keinath has shown that competitive adsorption, even in binary

solutions, can lead to chromatographic displacement effects in column adsorbers treating wastewaters of varying composition. In this situation, the weakly-adsorbed solute is retained by the carbon for a time and then is eluted as a rather concentrated "peak" upon prolonged contact with the feed wastewater. Keinath further showed that fluidized bed adsorbers are much less susceptible to this effect than more conventional packed beds - a finding that could have significant impact on adsorber design. Chromatographic displacement and related interaction effects are almost certainly key contributors to the diffused, spread-out adsorption wavefronts and fluctuating organic removals observed when treating multi-component organic chemical wastewaters of high component and concentration variability. The question of dynamic interactions and effects in multi-sorbate systems is an area where further research and development is sorely needed, not only to shed further light on which wastes can be efficiently treated by activated carbon adsorption, but also to ascertain how best to design and operate continuous adsorption systems to minimize the undesirable effects of interactions.

CONCLUSIONS

1. In pure component studies, specific organic chemicals have been shown to differ widely in their amenability to adsorption, depending on molecular weight, structure, polarity and solubility. Low molecular weight oxygenated organics are particularly difficult to adsorb efficiently.
2. The relative ease of adsorption of different functional group compounds can vary strongly with pH, depending on the chemical nature of the adsorbates. An optimum pH cannot be predicted for a multi-component wastewater of unknown or varying composition.
3. While pure component data could be used to predict binary adsorption capacity in isotherms fairly closely, a four-component mixture isotherm showed only about 60% of the adsorptive capacity predicted. Mutual solubility effects competition for adsorption sites, and inability to maintain a pH level optimum for all components contributed to this inability to extend pure component data to more complex mixtures.
4. While isotherm capacities were somewhat extrapolatible to continuous column behavior in pure component adsorption and simple mixture studies, such extrapolations have not proved to be possible with real wastewaters (complex mixtures), particularly with bio-treated effluents.
5. More importantly, the key parameters of interest in real wastewater treatment situations - percentage organic removal achievable and water volume treated per pound of carbon before breakthrough - cannot be predicted from isotherm tests.
6. The physical differences between an equilibrium adsorption situation in a powdered carbon isotherm and the dynamic, multi-component interactions in a continuous granular carbon bed are too great to permit prediction of column performance from isotherms or pure component data. The dynamic interplay of adsorption rates, pore diffusion rates, hydraulic effects, and pure component chemical properties in continuous columns is an area where further research efforts must definitely be applied.

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(2) Giusti, D. M., R. A. Conway, and C. T. Lawson, "Activated Carbon Adsorption of Petrochemicals," JWPCF, 46, No. 5, May (1974)
(3) Keinath, T. M., "Design and Operation of Activated Carbon Adsorbers Used for Industrial Wastewater Decontamination," paper presented at 68th Annual Meeting - AIChE, Los Angeles, Nov. (1974)

DISCUSSION

Frank Manning: Would you care to comment on how you would personally combine activated carbon with biological treatment together, which one is put first?

C. T. Lawson: Our normal thinking is that we would put carbon before biological treatment on specific streams where it has an application. In other words, on a stream say that's noxious for some reason but not biodegradable or perhaps biologically inhibitory, then we consider that a very good application for consideration of carbon. As a post-biological polishing step, it depends on how close we are to meeting a permit. I guess, if a little more treatment would get us to the permit then I would say a tertiary carbon system might be justified. I don't think, and we are convinced of this fact, that you can simply add on a carbon system and make up for deficiencies in your biological system. If you are far away from meeting a permit, the first think to do is make the bio-system work. Then if you need carbon to close the gap and it is effective in doing so, put it on; but I don't think that carbon can ever be considered as a prescription for a poorly operated treatment system.

Sterling Burks: Have you performed any studies on absorption of trace heavy metals? I know this question was asked of Davis Ford.

C. T. Lawson: No, we haven't.

Milton Beychok: As you know, I have congratulated you once before because I think it is long overdue that someone brought some science to this field. If we look at the data you have given us this morning, the isotherms in thermodynamic terms, the isotherms are really equilibrium. Your column data telling us you can't approach that equilibrium the way you think you should and that involves kinetics, and if we look again and make an analogy between that and other refining processes and what has been done in improving kinetics and the approach to equilibrium through catalysis. Do you intend or do you know of any research going on this pretreatment of carbon, trying to do something to improve the kinetics as well as perhaps making kinetic models and seeing what you can learn?

C. T. Lawson: Well the question of pretreating carbon, I really don't know of any work that is going on. It seems to be the kind of thing that the carbon vendors would be interested in and they are pretty competitive and closed-mouth fellows; they don't tell you much about what they are doing. There is some potential here, I would say, for tailoring carbons through pretreatment or through activation processes; but it is not being really studied much to my knowledge. On the question of developing a diffusion model or a kinetic model, there is quite a bit of academic interest I think in doing this. The only papers that I have seen are really for binary systems and that is not of too much interest in a practical application sense. I know Dr. Keinath at Clemson University and Dr. Weber at the University of Michigan have done some work in this modelling area.

Anonymous: It just seems to me from what we all know that the regenerated carbon behaves differently than the fresh carbon and you showed us today percentage wise some remarkable differences between two different carbons, that it would be a fruitful area for research work whether it be on the part of Union Carbide or the carbon manufacturer.

C. T. Lawson: Yes, I don't really want to give a commercial for anybody, but I will say that Witco's carbon in the studies we looked at performed quite well, very good carbon. I think there has been a lot of reluctance over the years to use anything but bituminous coal carbons because its "sturdier, more rugged, easier to regenerate, not as friable as the other carbons." Looking at waste treatment with some of the speciality carbons, coconut-shell carbons, has shown some pretty good results, - a little bit better than bituminous coal carbons. But when you talk about 75-85¢ per pound for carbon, it is really out of the question for large volume waste water treatment.

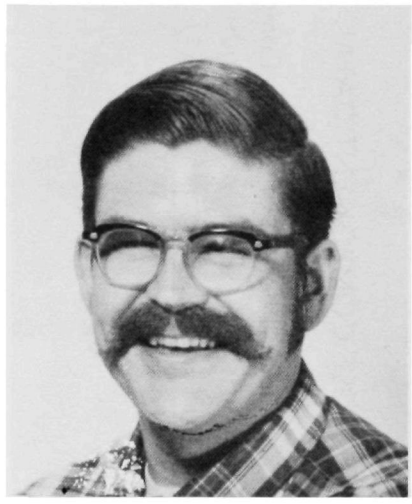
Nick Sylvester: You mentioned at the end of your talk that you have done some more research that you have not reported on and you also mentioned this apparent chromatographic type phenomena in the columns. Have you done more work on that and are you going to report that?

C. T. Lawson: That is what we have tried to do, we have tried to take a column and take samples down through the column at different times and see just where specific compounds end up in the column on a dynamic basis, to see if there is some way that you can predict when something is going to be spit out as a big eluted peak, and I hope that data will be in shape for the Cincinnati paper.

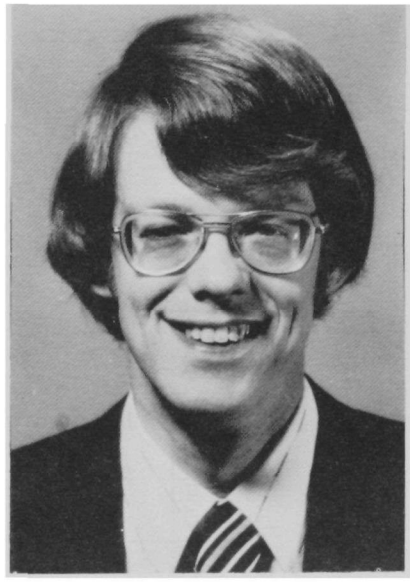
Dave Skamanca: Davis Ford mentioned that if you are going to put in an activated carbon system, you are really better off with biological system in front of it to decrease the loading and apparently improve the performance of the carbon. But as you decrease the loading, the pounds in the concentration to the activated carbon system, you also decrease the isotherm data, you don't get as good a loading on the activated carbon. Are you getting ahead of the game in most of these systems by trying to remove more of these pounds up stream with a carbon, are you gaining on the problem, are you just staying even so to speak?

C. T. Lawson: My own opinion is that the kind of capacities that you see in isotherm tests are really an interesting qualitative observation, but they have no practical significance. Anything you can take out before the carbon column by reasonable treatment means, I think is worthwhile. From what we have seen, running continuous column systems, this 25% or so by weight absorptive capacity (on a COD basis) to petrochemicals seems to be a pretty real number and relatively independent of the feed concentration in continuous systems for the wastes we have examined thus far. The fact remains that isotherm capacities obviously do vary strongly with concentration, you can go up and down. We really see no way to relate that to a continuous system. We use our isotherm data just for relative comparison of one waste water to another and one carbon to another; we don't use it in a quantitative sense at all.

BIOGRAPHY



Cyron T. Lawson is a Project Scientist in the Water Quality Development Group of Union Carbide's Chemicals and Plastics Division, Research and Development Department. He holds the B.Ch.E. and M.S.Ch.E. degrees from Georgia Institute of Technology. He has taught graduate courses in water and wastewater treatment as an Adjunct Instructor at the West Virginia College of Graduate Studies. Cyron is a Registered Professional Engineer (Chemical) in West Virginia and is a member of the AIChE and its Environmental Division.



Joseph C. Hovious is a Group Leader/ Technology Manager in the Research and Development Department of Union Carbide's Chemicals and Plastics Division. Mr. Hovious is an M.S. Environmental Engineer from the University of Illinois. He teaches graduate courses at the West Virginia University College of Graduate Studies. He is a member of the WPCF, AWWA, and a Registered Professional Engineer in West Virginia.

TABLE 1 "COMPARISON OF MULTI-COMPONENT ISOTHERM DATA WITH SINGLE COMPONENT DATA"

	Equilibrium Carbon Loading in Mixture Test g cpd/g carbon (a)	Equilibrium Carbon Loading in Single Component Tests, g cpd/g carbon (b)	Fraction of Single Component Equilibrium Loading from Mixture (c)
Mixture 1 - Carbon A			
Butanol	0.116	0.110	1.05
Ethyl Acetate	0.121	0.160	0.76
	0.237	0.270	
Mixture 2 - Carbon A			
Methyl Ethyl Ketone	0.063	0.105	0.60
Butyraldehyde	0.212	0.165	1.28
	0.275	0.270	
Mixture 3 - Carbon A			
Butyraldehyde	0.072	0.165	0.44
Ethyl Acetate	0.075	0.160	0.47
Butanol	0.031	0.110	0.28
Butyric Acid	0.112	0.140	0.80
	0.290	0.575	
Mixture 3 - Carbon C			
Butyraldehyde	0.072	0.080	0.90
Ethyl Acetate	0.066	0.080	0.83
Butanol	0.023	0.068	0.34
Butyric Acid	0.064	0.084	0.76
	0.225	0.312	

(a) Compounds each initially present at 500 mg/l. Mixtures 1 and 3 dosed at 1 gm carbon/liter and Mixture 2 at 2 gm carbon/ liter. Equilibrium loadings $(X/M)_{C_o}$ are calculated from total TOC loadings and chromatographically determined fractional compositions of removed material.

(b) Equilibrium loadings measured at C_o of 500 mg/l.

(c) Calculated by dividing the equilibrium loading of the individual components in the mixture by the single-component equilibrium loading.

FIGURE 1

ACTIVATED CARBON TREATMENT OF BIOLOGICAL EFFLUENTS
BATCH ADSORPTION ISOTHERM TESTS

C_o = initial COD (or TOC) concentration before carbon treatment

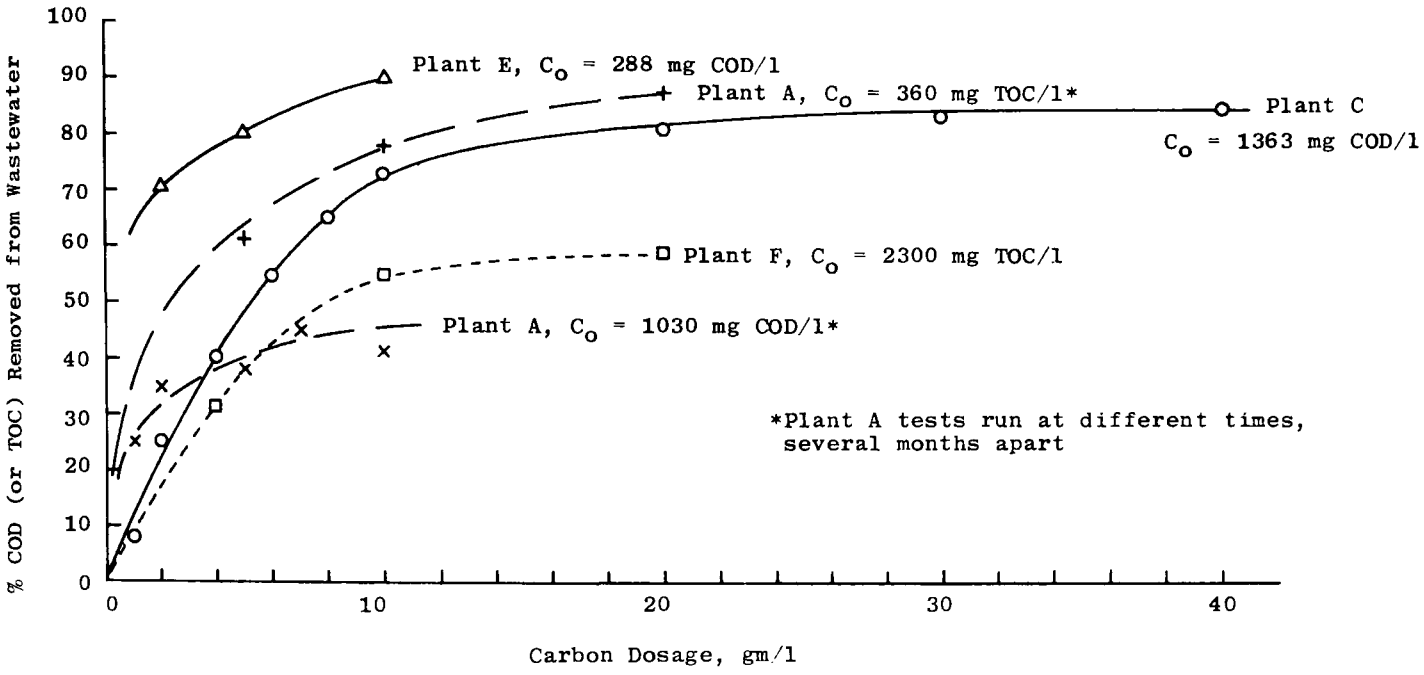


FIGURE 2

BREAKTHROUGH CURVE FOR PLANT A BIO-TREATED WASTEWATER

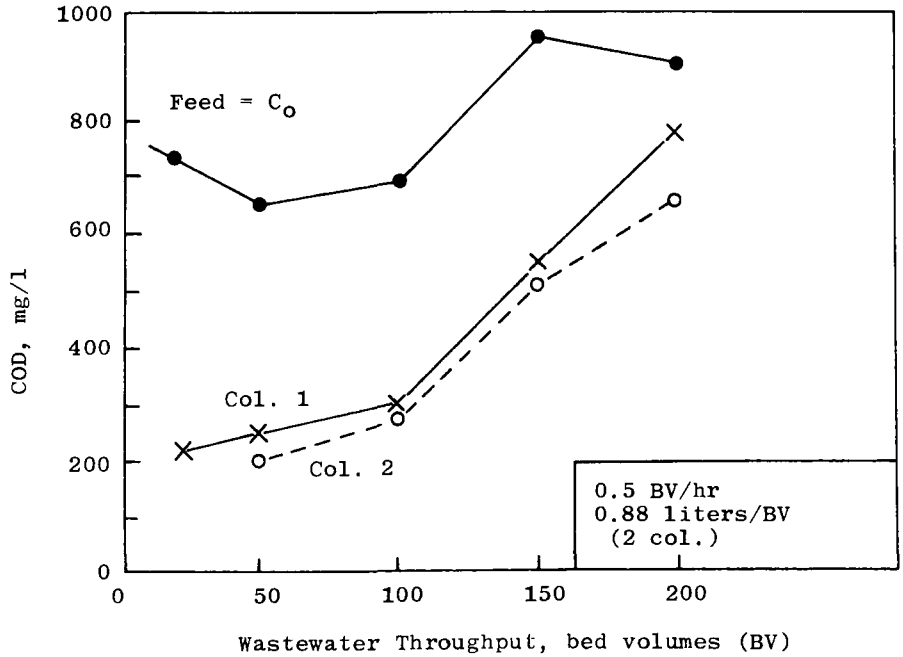


FIGURE 3

EFFECT OF MOLECULAR WEIGHT ON AMENABILITY OF ADSORPTION OF ALCOHOLS

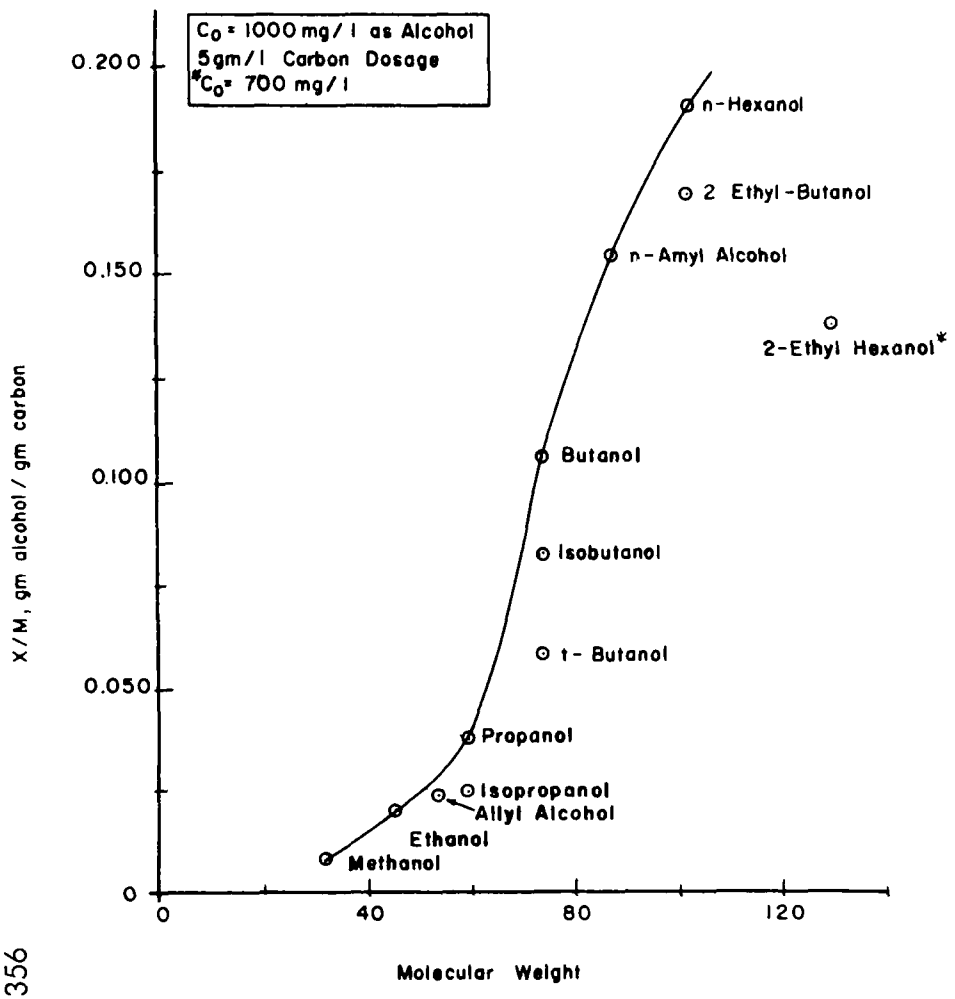


FIGURE 4

EFFECT OF MOLECULAR WEIGHT ON AMENABILITY OF ADSORPTION OF ESTERS

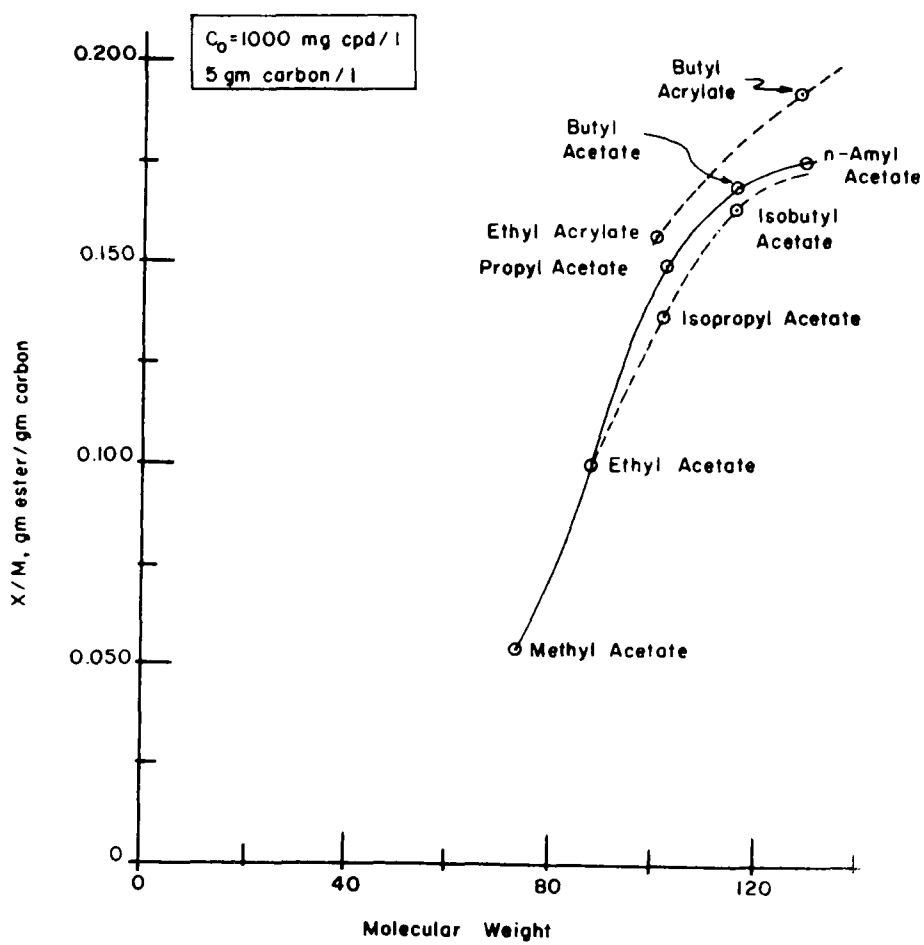


FIGURE 5
EFFECT OF MOLECULAR WEIGHT ON AMENABILITY OF ADSORPTION OF ORGANIC ACIDS

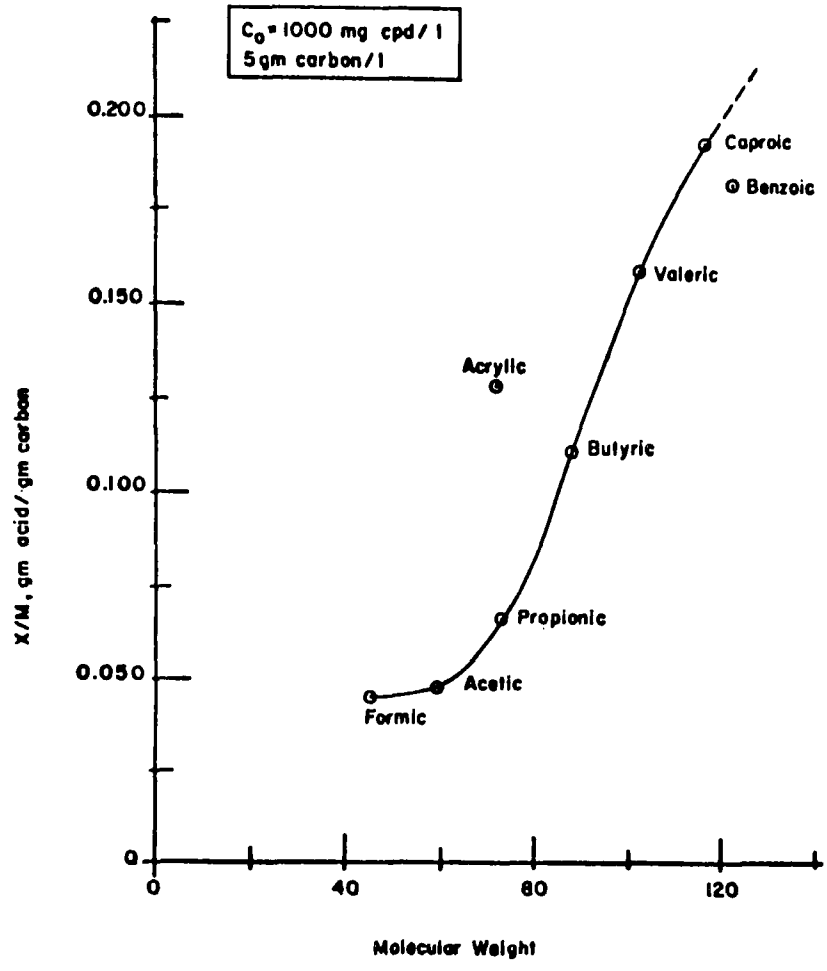


FIGURE 6

PERCENT OF COMPOUND ADSORBED VS. MOLECULAR WEIGHT FUNCTIONALITY EFFECTS

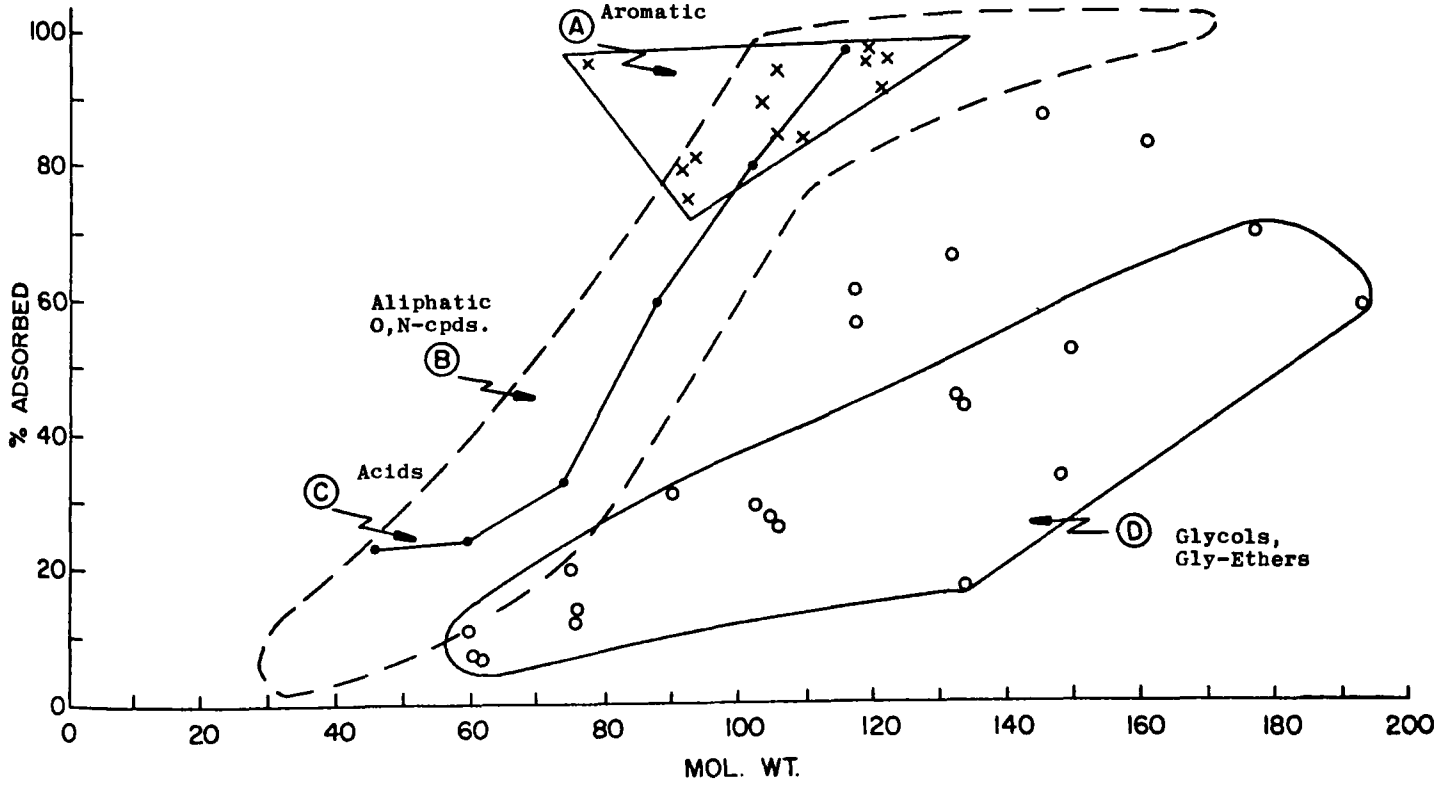


FIGURE 7

pH EFFECTS ON ADSORPTION REMOVALS OF SELECTED ORGANIC COMPOUNDS WITH CARBON A

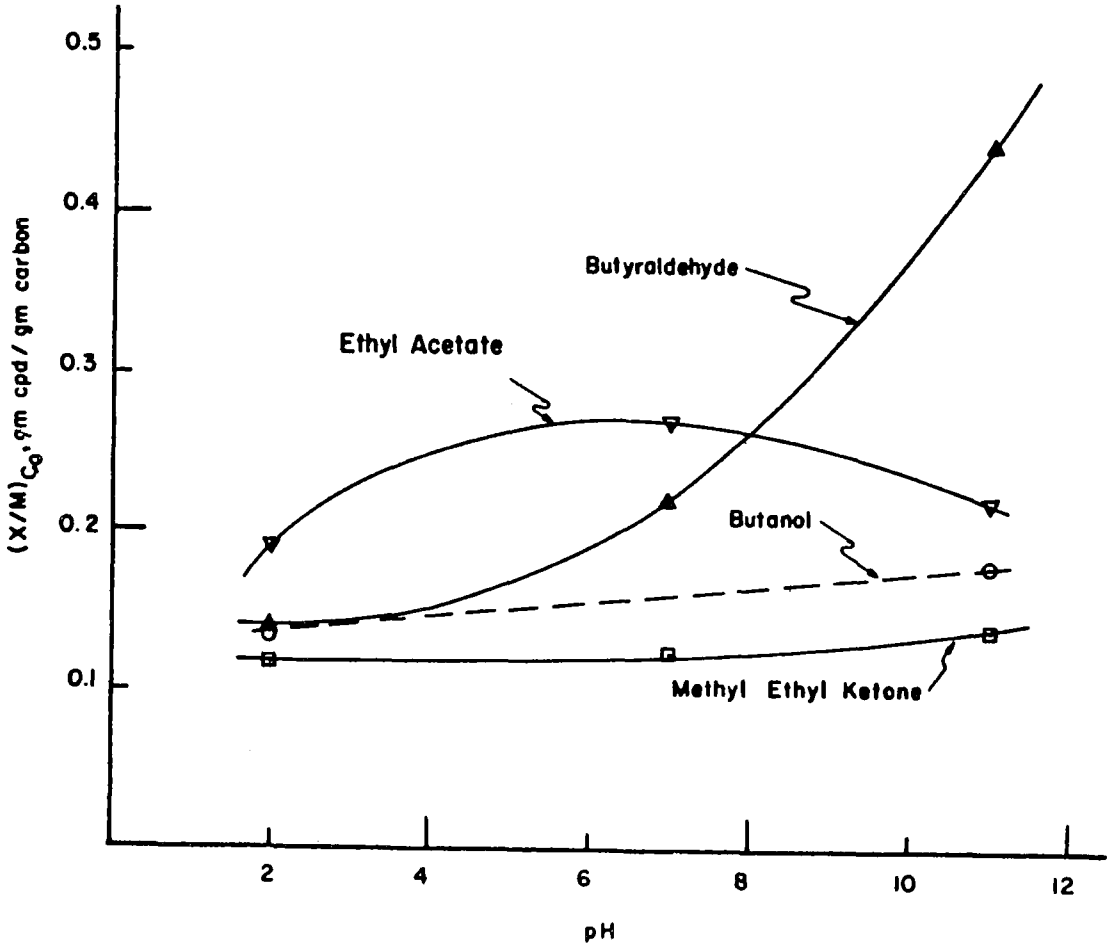
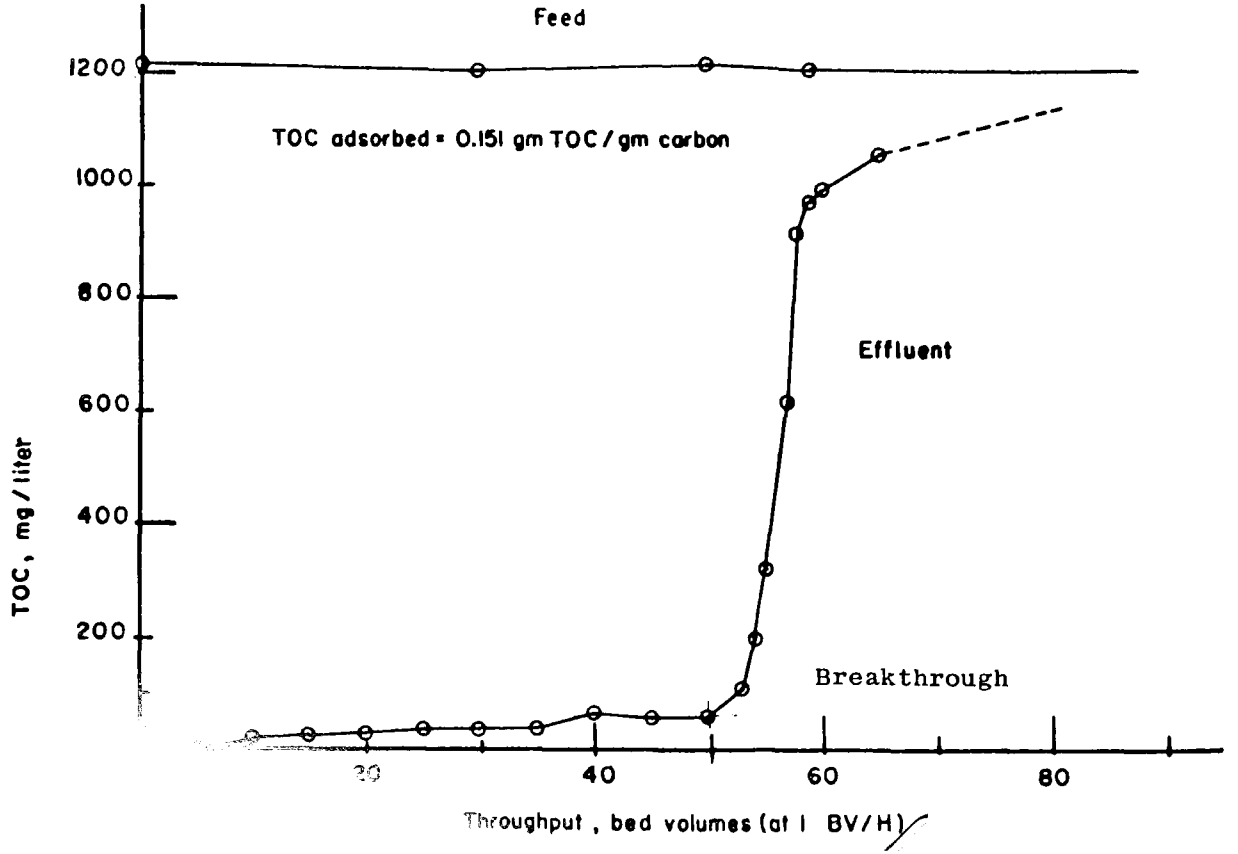


FIGURE 8

BREAKTHROUGH CURVE FOR ACTIVATED CARBON ADSORPTION OF A FOUR-COMPONENT MIXTURE IN A CONTINUOUS SYSTEM



CASE HISTORY: USE OF POWDERED ACTIVATED CARBON IN AN ACTIVATED SLUDGE SYSTEM

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Sun Oil Company, Marcus Hook, Pennsylvania

INTRODUCTION

In an effort to expand the performance of existing biological treatment facilities, full scale trials utilizing powdered activated carbon were conducted at Sun Oil Company's Corpus Christi, Texas Refinery. The main objective of the trials was to reduce the effluent suspended solids loading for compliance with the 1977 NPDES and State permit limitations. Three separate trials were initiated over a one-year period comprising five months of operation with powdered activated carbon addition to the aeration system of the 2.16 MGD biological treatment plant. Although the powdered carbon addition could not guarantee compliance with the 1977 suspended solids' criteria, improvement in the existing system's performance was significant for COD and BOD removal as well as suspended solids. The treatment costs ranged from 1.7 to 4.3¢/10^3 gallons depending on the influent flow and quality. Data have been compiled showing reductions in the refinery's final effluent loadings of up to 56% for suspended solids, 36% for COD and 76% for BOD.

FACILITIES

A simplified flow diagram of the treatment scheme at the Corpus Christi Refinery is shown in Figure 1. The system's operating conditions are outlined on Table 1. The daily average charge to the plant is only half the design capacity; although the peak design rate is often operated during periods of rain and high ballast loading. The refinery wastewater flow (averaging about 600 GPM) is equalized with ballast and contaminated storm water in a 10 MM gallon pond. The combined flow from the pond (averaging about 750 GPM) is pumped through a dissolved air flotation unit for removal of any excess oil and suspended solids. The effluent from the DAF is split between two 760,000 gallon rectangular aeration basins. Air is introduced into each of the basins by two 75 hp floating mechanical aerators. When operating both basins in parallel at average flow conditions, the retention time is about 22 hours; at peak flow, this is reduced to 11 hours. The mixed liquor volatile suspended solids is maintained at about 2200 ppm. With both systems operating, the food to mass ratio averages only about 0.13 lb COD/lb MLVSS or 0.07 lb BOD/lb MLVSS in each basin; this, of course, can be doubled by operating only one aeration system.

Each aeration system is coupled with a 55' diameter x 12' deep clarifier. The overflow from the clarifiers combines for discharge. The settled sludge is collected from each clarifier, combined and returned to the aeration basins. The return rate usually averages about 50% of the charge rate.

OBJECTIVE

Basically, the performance of the biological treatment system is satisfactory and the effluent readily complies with the refinery's NPDES and State permits. With the exception of suspended solids, the limits established for compliance in 1977 are also currently being met. The consistently effective removal of suspended solids in the final clarifier seems to be the only area of concern. Even with substantial organic removal in the biological system, there appear to be two major factors causing the extra suspended solids carryover from the final clarifiers:

- Variability of influent organic and hydraulic loadings. The biological population is thus unstable with erratic growth and variable efficiency.
- Excessive aerator foaming in the aeration basins. This foam, laden with biological solids, tends to carryover into the clarifier and out to the effluent. The problem becomes most severe at high flow periods.

Interim limitations had been set by the State and NPDES permits allowing time to investigate in-plant improvements which could possibly permit compliance with the 1977 TSS criteria without construction of additional facilities. Full scale trials appeared necessary due to the nature of the problems noted -- bench scale studies tended to show excellent settling characteristics which do not reflect the hydraulics of the operating system.

Initial testing was performed with the addition of polymers to the aeration basin effluent. The polymers did improve the solids settling somewhat but their benefit was overshadowed by the problems still being caused by aeration foaming and shock loads. Conversely, defoamers were effective in controlling the foam, nothing more.

In the refinery, every precaution is taken to reduce the possibility of shock loads and spills. However, no matter how efficient, there is no way to completely eliminate the variability: turnarounds, emergency shutdowns and the like. This, coupled with the influx of highly variable loads of ballast, dictated that the treatment plant operation would have to compensate for unstable influent conditions to the plant.

APPLICATION OF POWDERED ACTIVATED CARBON

The addition of powdered activated carbon was initiated in an effort to resolve all the operating problems causing the suspended solids carryover -- the objective being compliance with the 1977 suspended solids' limitations. Although this objective was not achieved, some interesting data resulted. A summary of the three separate carbon trials conducted is shown on Table 2. Unfortunately, it was not possible to operate a "blank" system simultaneously with the carbon system. Therefore, the data obtained 30 days prior to the start of each trial has been utilized as the base period for that trial. As can be noted on Tables 3, 4 and 5, for the most part, the influent loadings of each base period and respective trial are comparable; this is especially true of Trial 3. During each trial, operation was maintined as closely as possible to the conditions observed during the base period. No special problems were encountered that would lead one to believe that any of the trials and base periods' operation were different, especially on the average. Although, the comparison is not ideal, it is relevant, especially in respect to the "real world" effect on the plant's effluent. The

percent reductions shown between the base period and each trial are meant as a guide to point up the improvement in effluent quality; the actual values, of course, cannot be taken as absolute. From an operation's standpoint, there appears to be no question that the addition of the powdered activated carbon to the aeration system realizes a significant improvement in the effluent quality and reduces its variability.

The first trial was considerably longer than the last two -- mainly, because the carbon dose was gradually built up in the system over a four-week period; whereas in the other trials, the carbon was batch loaded in a couple of days up to the operating level. The gradual addition of the carbon allowed the daily observation of its effect in order to determine the appropriate loading to be maintained. In order to minimize the amount of carbon needed to load and maintain the system, only one aeration basin was operated during the trials; the same was true of the respective base period. The carbon was manually batch added daily to the dissolved air flotation effluent as it entered the aeration basin. During the first trial it was found that the optimum operating carbon level needed in the aeration system was 450 ppm with approximately 1000 ppm resulting in the recycle sludge. All three trials were conducted at these levels. This requires about 6100 pounds of carbon to charge one aeration system up to operating levels. An easy indication of the carbon level in the system was found to be the foam level in the basin -- the appropriate amount of carbon would eliminate the foam completely; as the carbon level dropped, the foam would build up. Of course, laboratory analysis utilizing a standardized comparison procedure confirmed the operating level of carbon on a concentration basis.

While gradually adding the carbon daily, it was noted that a distinct improvement in the plant performance did not come about until the 450 ppm level was attained -- however, by letting the level drop off gradually, the peak performance could be maintained down to 300 ppm. It was also noted that more frequent additions of smaller quantities appeared more effective than larger batch additions less frequently.

Referring to Table 2, you will note that the carbon addition rate was much higher during the first two trials; this came about for a couple of reasons:

- More frequent batch additions of larger quantities ($\bar{}$1000 pounds at a time) were necessary to compensate for shock loadings. Although the presence of the carbon in the system greatly reduced the chances of a shock that could inhibit the biological activity, it could not guarantee that a reduction in activity would not occur. However, in general, it was found that if caught in time with the addition of a large batch of carbon, a lapse in system efficiency could be effectively brought back up to normal almost immediately without adverse effects on the effluent quality.
- At the time of the third and most recent trial, the biological system was more stable and it took less carbon to obtain the same results. Better methods of equalization had been put into operation and ballast was being successfully treated at a rateable basis.

The flow rate during the third trial averaged 800 GPM versus 625 - 660 GPM for the first two trials (this was due primarily to increased ballast water treatment). The higher

flow with the reduced carbon addition rate accounts for the lower 1.7¢10^3 gallon treatment cost compared to Trial 1's 4.3¢. It is important to note that these costs only reflect the carbon usage, the manpower utilized in adding the carbon is not included. More efficient means of carbon addition could, of course, be employed with minimal capital investment but was not deemed necessary for a trial basis.

On Table 6, the treatment costs obtained are summarized along with the reduction in effluent loading observed during each trial.

From this data, one is erroneously led to believe that the efficiency seemed to improve because of a lower carbon dose (and subsequently lower cost). As explained, the higher carbon dosages observed during Trials 1 and 2 are directly attributable to a higher frequency of shock loadings to the system. The only valid conclusions to be drawn from the costs versus efficiency data presented is that the carbon treatment costs range from 1.7¢ to 4.3¢/10^3 gallons depending on the variability of the influent and the frequency of batch additions to solve overload problems. Again, it is important to remember that the percent reductions are determined from the trial versus its pre-trial base case and should only be thought of as a guide for comparison purposes.

Total Suspended Solids Reduction. The average effluent suspended solids data obtained are outlined on Table 3. The reduction in the effluent suspended solids' loading was dramatic, between 49.3% and 55.7%. The existing permit limit is easily met; however, the effluent, at the very low level of 405 lbs/day daily average for Trial 3, still would not comply with the 327 lbs/day limit of the 1977 permit. In addition, although the daily maximum values while using carbon were significantly lower and under better control, several peaks still would occur. Referring to Table 7, in the case of Trial 3, four data points out of 20 were above the 561 lb/day 1977 allowable limit, for 80% compliance; 100% compliance is easily obtainable with the existing permit. Of course, the odds of being able to comply with the 1977 limits are better, but still not acceptable.

Referring to the frequency distributions for Trial 3 plotted on Figures 2 and 3, the reduction in effluent suspended solids with carbon addition becomes very obvious. The chance of complying with the 561 lbs/day 1977 maximum was increased from 40% during the base period to 82% with carbon; of course, these percentages are only relative not absolute. Although the permit is written on a mass basis, the effluent concentration of suspended solids is a basis more easily compared between various facilities and is therefore, shown in Figure 3. On each figure, the flat slope of the carbon trial versus the base period also indicates the more consistent effluent obtainable with carbon treatment, the variability having been significantly reduced.

Organic Removal Efficiency - as mentioned, the addition of powdered carbon also improved the organic removal efficiency of the system. A summary of the influent and effluent COD loadings of the system are shown on Table 4. This table also points up the uniformity of influents between the base period and trial period for Trials 1 and 3. As mentioned, the operation was maintained as consistent as possible for each case. During Trial 2 the influent COD loading was about 25% higher than during the base period -- yet, the effluent loading was 30% lower showing a significant reduction on a relative base. The removal efficiency during Trials 1 and 3 was increased significantly up to 70%

from 62.9% and 54.8% respectively for each trial. The ultimate reduction in COD loading to the effluent being 35.7% for Trial 3 as compared to base period 3.

The daily COD removal efficiencies for Trial 3 are plotted in Figure 4. It can be seen that not only was the removal efficiency significantly increased, the variability of the efficiency was reduced. Again, resulting in an effluent of consistently better quality.

Figure 5 is a frequency distribution plot of the effect of the carbon addition on the effluent COD concentration for Trial 3. Not only does the slope again show more consistent results but, for example, the 95% point has been reduced from 280 ppm down to 150 ppm, a 46% reduction assuming a comparable base.

The effect of powdered carbon on BOD is summarized in Table 5. It is obvious from the influent loadings that the data obtained during Trial 3 are most relevant since the base period and trial had the most comparable influent conditions. Again, as in the case of COD, during Trial 2, the influent loading was 38% higher than the base period; yet, the effluent was 51% lower. The reduction in BOD was most sharply noted during Trial 3 when the effluent BOD never exceeded 6 ppm -- the reduction from the base period was 76%.

The frequency distribution comparing the base period and Trial 3 is shown in Figure 6. Again the results are significant. The curve for the effluent BOD during the carbon addition period is virtually flat, showing definite uniformity and consistency of effluent. Figure 7 denotes the distribution of the percent BOD removals obtained -- again, the curve is relatively flat, the variability being virtually eliminated.

Oil Removal. No data were compiled on oil and grease removal since the system is not required to handle any large amounts of oil. The effluent oil and grease usually averages less than 5 ppm with an occasional peak around 10 ppm; the influent is normally 20-25 ppm. Any improvement would be difficult to observe at these low levels. On occasion, however, the influent oil level can be higher, as did happen during the post period of Trial 2 when there was an upset in the Refinery. The carbon still in the system readily adsorbed the excess oil, keeping it in the sludge. Of course, the sludge had to be removed from the system, thus spending the carbon. However, a possible effluent oil and grease violation was avoided at only the expense of a carbon charge.

SPECIAL NOTE

Sludge wasting had always been erratic and unpredictable in this system due to the variable influent and unstable bug growth. When as stable as possible, about 15,000 gallons per day of recycle sludge would be wasted from one operating aeration system. During the carbon trials the wasting was reduced to 10,000 gallons per day under similar circumstances. The basis for this reduction being that the sludge was considerably thicker so less volume needed to be handled to dispose of the same mass.

SUMMARY

As evidenced by the data presented, the addition of powdered activated carbon to the aeration system of the refinery's existing wastewater treatment facilities did not reduce the effluent suspended solids enough to comply with the 1977 permit limitations. However, significant improvements in the system's performance were observed as follows:

- Improved organic and suspended solids removals and reduced effluent loadings

	% REMOVAL		
Trial 3	Without* Carbon	With Carbon	% Reduction in Effluent Loading
COD	54.8	70.5	35.7
BOd	93.5	98.5	75.8
TSS	-	-	49.3

*Pretrial base period

- More uniform effluent quality
- Clearer effluent
- Elimination of foam in the aeration system
- More consistent sludge wasting at 2/3 the volume
- Reduced chances of biological upsets -- the use of powdered carbon does not eliminate biological upsets but it does appear to reduce the opportunity of their occurance; and when they do occur, it appears to maintain the effluent quality under better control. When caught in time, it was found that a reduction in biological activity can effectively be brought back up to normal by massive batch addition of carbon to the existing operating level.

These improvements were obtained by building up the aeration system to a 450 ppm operating level of carbon with about 1000 ppm in the recycle sludge. The system was maintained at this level by the batch addition of about 100 lbs/day of carbon (or 10 ppm) at an average cost of 1.7¢/10^3 gallons of water treated. The amount of carbon necessary to operate the system for peak performance could be readily determined by observing:

- The aeration basin foam level - the proper operating level of carbon eliminates foam in the system.
- Clarity of the effluent - the presence of carbon in the system removes the tint usually characteristic of biological effluent.

It is important to note that the powdered activated carbon utilized in these trials has a high bulk density of 44 lbs/cu. ft. This becomes an important factor when improved settleability is the primary objective of the carbon addition to the system. In addition, the higher bulk density reduces the opportunity for carbon loss to the effluent.

DISCUSSION

James F. Dehnert: We have done considerable work with powdered carbon on a pilot basis and we have done some of the work that you did. A couple of problems we ran into and I wondered if you had solved them, that is the analysis of the mixed liquor solids. Did you determine actual carbon percentage or was this a calculated value?

Joyce Rizzo: We did it by a standard comparison. What we did was make up standard

filters with carbon which we compared. We took samples of our aeration system before we added carbon to it. We added known dosages of carbon and set up a set of standards. So all the numbers we have obtained are 50 ppm, but we could keep track of it pretty easily.

James F. Dehnert: We had not devised a system to determine how much carbon was actually in our system at any one time. The second question: you said you didn't test very many parameters. We have a problem in California with meeting fish toxicity, did you ever run any tests on that?

Joyce Rizzo: Everyone knows that refinery effluent is not toxic. Maybe California is different - they may have a higher breed of fish down there, I don't know. Obviously, we didn't evaluate toxicity.

Les Lash: You mentioned holding about 450 milligrams per liter of activated carbon, Joyce, in your aeration basin, I guess. What is the retention time in that aeration basin?

Joyce Rizzo: About 12 hours at average operating conditions.

Les Lash: When we ran the pilot plant on municipal waste for the EPA on powdered activated carbon in Salt Lake, we used reactive clarifiers and if you didn't allow enough settling, of course the effluent went over black. Now that is a little different than the clear you were talking about.

Joyce Rizzo: The only time we ever had a carryover problem with carbon was during a time when the bug population was upset and they would tend to take the carbon with them. If they were going out, they weren't going to leave the carbon behind. On a normal basis we had no problem with carbon carryover at all. It stayed right with the sludge. In fact, it improved the settleability tremendously. If you look at the clarifier, it has the appearance of being black; of course, the aeration system would turn black versus the dark rich brown color and it appeared like it was all carbon. The carbon color would take over completely, and if you looked at the clarifier surface, it appeared black but the effluent water was virtually clear.

Milton Beychok: I am just a bit curious, I don't know if there is anyone here from duPont or not, but something like four years ago, duPont first used this and called it PACT, powdered activated carbon treatment, and they were licensing it. Does the use of this involve any patent problems or royalty on the part of duPont?

Joyce Rizzo: No, this is quite a different system than what duPont is utilizing in their PACT project, they are also utilizing a regeneration system which I believe is also a part of their patent on that. We used ICI carbon, and the system that we used was outlined to us from ICI as to how to operate. I don't think we did anything really different. I have talked to many people who are also using powdered carbon in their aeration system in a similar manner.

Ed Sebesta: I note you have a centrifuge for your waste activated sludge there. Did

you continue to use a centrifuge both before and after carbon addition and what was the effect?

Joyce Rizzo: We don't use a centrifuge all the time by the way, only when we have to. We have plenty of land out there for land farming and a lot of times put the sludge out wet from the aerobic digester. We did not see any real difference in our sludge handling characteristics on the solid waste handling system - none at all. Actually, the amount of carbon that we used - our aerobic digester is three-quarter million gallons like our aeration system - and the amount of carbon that we used and the amount that was wasted was virtually lost in the system.

Ed Sebesta: I have another question and you indicated that the effluent was very clear. I think the data indicated about an average of 40 parts per million suspended solids. This is pretty high for a very clear effluent, do you have any explanation for the concentration numbers?

Joyce Rizzo: Very fine solids. Color really is what I am talking about. 40 ppm does not represent optimal operation, 10-20 ppm would be more representative of the best effluent obtainable with the carbon. The solids that would settle out by the way would be ones that would settle out after hours. You could take a sample of the effluent and you wouldn't think there were suspended solids in it, but if you let it sit for a while, the solids that would settle would be very, very fine. I would say about half the solids that went out in the effluent were carbon solids. Very, very fine solids.

Pat DeJohn: I'd like to make a couple of comments. One that Mr. Lash made, the carbon that you were using has a density of about 45 pounds per cubic foot, and consequently it settles very rapidly. I believe what they were using out at Salt Lake was a carbon that had a density of about 15 pounds per cubic foot. The higher density is the reason the carbon doesn't go out over the weir. The other thing about the patent situation, duPont just got a patent issued about two months ago on the PACT process and right now there are some negotiations going on with respect to that.

Janis Butler: You mentioned sometime just spreading the wet waste activated sludge. Do you experience any odor problems?

Joyce Rizzo: No - none at all. If we put it out wet, the solids settle rapidly, and there is no odor problem at all. We are using (I have been gone now from Corpus Christi for about six months), but at the time I left we were using the centrifuge all the time for the waste.

Anonymous: Do you add carbon continuously?

Joyce Rizzo: Corpus Christi has just purchased another load of carbon for usage. As I understand it, their main goal is to use it mostly for batch addition for shock loadings and things like that.

Fred Goudy: Does the use of powdered carbon have any long range implications with regard to the operation of the activated sludge plant at Corpus Christi?

Joyce Rizzo: They are using it.

Fred Goudy: Continuously?

Joyce Rizzo: I am not sure, I can't answer that for fact right now. I know they have just purchased some more carbon, and I know they have it in stock and I know that their intentions are to use it. Now whether they will use it all the time, I don't know at this time. I might mention what I think about carbon application in the aeration system. Like I said, although we really were oriented to suspended solids removal, it is obvious that some of the other things that I have mentioned about the system are very true. That is, if you have a plant that is sitting there hydraulically loaded and you need more capacity, it seems to help and gives you that extra capacity that you need. As I mentioned none of the reductions that I presented, of course, should be taken as absolute numbers because it was pretrial versus trial period. But there is no question that the improvement in the plant performance is there and I think the improvement is really dependent on the variability of your influent.

Dave Story: You mentioned adding polymers; could you elaborate a little bit more on that?

Joyce Rizzo: Yes, we didn't do too much work with polymers because it was the very first thing we tried to reduce suspended solids. We were adding about 5 or 6 parts per million of some polyelectrolytes to our aeration basin overflow and we saw a reduction in effluent suspended solids and a little bit better settling characteristics, but nothing very significant. I think this is mostly due to our foaming problem because we still had a lot of foam carrying over to the clarifier which is a significant problem.

Anonymous: How do you account for the reduction in sludge wasting?

Joyce Rizzo: We didn't have to maintain as many bugs in the system and they didn't have to work as hard. But the real reduction was in volume not mass. The recycle sludge was thicker and more uniform with carbon addition.

BIOGRAPHY



Joyce A. Rizzo is a staff engineer in the Advanced Management and Methods Department of Suntech, Inc., a subsidiary of Sun Oil Company. She is based in Marcus Hook, Pennsylvania. Ms. Rizzo joined Sun Oil in 1971 as a process engineer at their Marcus Hook Refinery. Prior to her move into Suntech six months ago, she spent three years in Process Engineering at Sun's Corpus Christi Refinery. She holds a B.S. in Chemical Engineering from Northeastern University in Boston.

TABLE 1

"OPERATING CONDITIONS OF WASTEWATER TREATMENT PLANT"

FLOW

Daily average	1.08 MGD
Daily maximum	2.16 MGD
Design	2.16 MGD

BIOLOGICAL SYSTEM	2 - 760,000 Gal. Rectangular Aeration Basins 2 - 75 HP. Floating Aerators/Basin
Recycle	50% of Charge Rate
MLSS	3000 PPM
MLVSS	2200 PPM
Retention (Per Basin)	11 Hours at Maximum Design Rate 22 Hours at Average Operating Rate
Sludge Age	12 Days
SETTLING	2 - 55 Ft. Diameter Circular Clarifiers 12 Ft. Deep
Average Rise Rate, GPD/FT^2	227
Peak Rise Rate, GPD/Ft^2	455

SOLIDS HANDLING

1 760,000 Gallon Aerobic Digester
1 Solid Bowl Centrifuge
4 Acres of Land Farm
Wasting Rate 30,000 GPD
VSS 7,500 PPM

TABLE 2

"SUMMARY OF POWDERED ACTIVATED CARBON ADDITION TRIALS"

Aeration System: 450 PPM PAC
Recycle System: 1000 PPM PAC

	Period	Duration	Average Carbon Dosage Lbs/D	Average Carbon Dosage $Lbs/10^3$ Gal	PPM	Treatment Cost* ¢/10^3 Gal
Trial 1	Sept.-Nov., 1974	82 Days	179	0.20	24	4.3
Base Case 1	August, 1974	30 Days	-	-	-	-
Trial 2	May, 1975	28 Days	152	0.16	19	3.5
Base Case 2	April, 1975	30 Days		-	-	-
Trial 3	August, 1975	26 Days	87	0.076	9	1.7
Base Case 3	July, 1975	31 Days		-		-

*At 22 ¢/Lb

TABLE 3

"EFFECT OF POWDERED CARBON ON DAILY AVERAGE EFFLUENT SUSPENDED SOLIDS"

1977 Permit: 327 Lbs/Day Daily Average

		Flow GPM	Permit PPM	Effluent PPM	Effluent Lbs/Day	% Reduction
Base Case	1	626	43	115	861	
Trial	1	629	43	50	381	55.7
Base Case	2	645	42	163	1262	
Trial	2	657	41	72	565	55.2
Base Case	3	839	32	79	799	
Trial	3	799	34	42	405	49.3

TABLE 4

"EFFECT OF POWDERED CARBON ON COD"

		Flow GPM	Influent PPM	Influent Lbs/D	Effluent PPM	Effluent Lbs/D	% Removal	% Reduction
Base Case	1	626	459	3445	170	1277	62.9	
Trial	1	629	457	3446	135	1020	70.4	20.1
Base Case	2	645	343	2658	266	2059	22.5	
Trial	2	657	444	3500	183	1445	58.7	29.8
Base Case	3	839	367	3698	166	1670	54.8	
Trial	3	799	379	3632	112	1073	70.5	35.7

TABLE 5

"EFFECT OF POWDERED ACTIVATED CARBON ON BOD"

		Flow GPM	Influent PPM	Influent Lbs/D	Effluent PPM	Effluent Lbs/D	Removal %	Reduction %
Base	1	626	152	1144	15	116	89.9	
Trial	1	629	213	1607	15	114	92.9	1.7
Base	2	645	152	1173	30	232	80.2	
Trial	2	657	227	1898	13.5	113	94.0	51.3
Base	3	839	188	1895	12	124	93.5	
Trial	3	799	207	1981	3	30	98.5	75.8

TABLE 6

"COMPARISON OF CARBON TREATMENT COSTS
AND SYSTEM PERFORMANCE"

	Dose PPM	¢/10^3 Gal.	% Reduction* In Effluent Loading TSS	COD	BOD
Trial 1	24	4.3	55.7	20.1	1.7
Trial 2	19	3.5	55.2	29.8	51.3
Trial 3	9	1.7	49.3	35.7	75.8

*As Compared to Respective Base Case

TABLE 7

"EFFECT OF POWDERED CARBON ON DAILY MAXIMUM EFFLUENT SUSPENDED SOLIDS"

1977 Permit: 561 Lbs/Day Daily Maximum

	Peak Maximum Lbs/Day	Data Points	Number of Times 1977 Maximum Was Exceeded
Base Case 1	1835	22	17
Trial 1	1432	57	12
Base Case 2	2124	22	19
Trial 2	1889	20	7
Base Case 3	2688	22	14
Trial 3	971	20	4

FIGURE 1

TREATMENT PLANT FLOW DIAGRAM

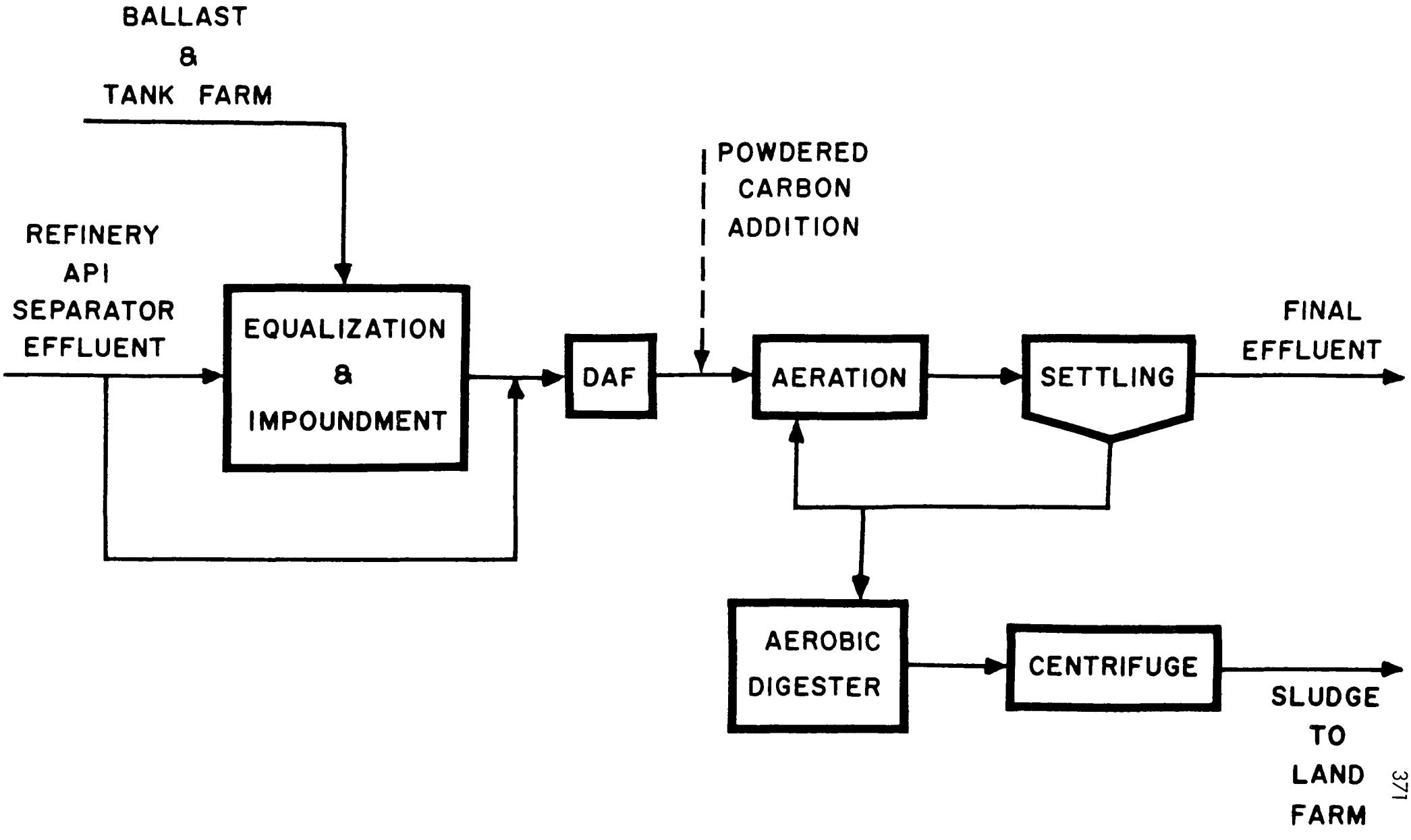


FIGURE 2

EFFECT OF POWDERED CARBON
ON EFFLUENT TSS LOADING

TRIAL 3

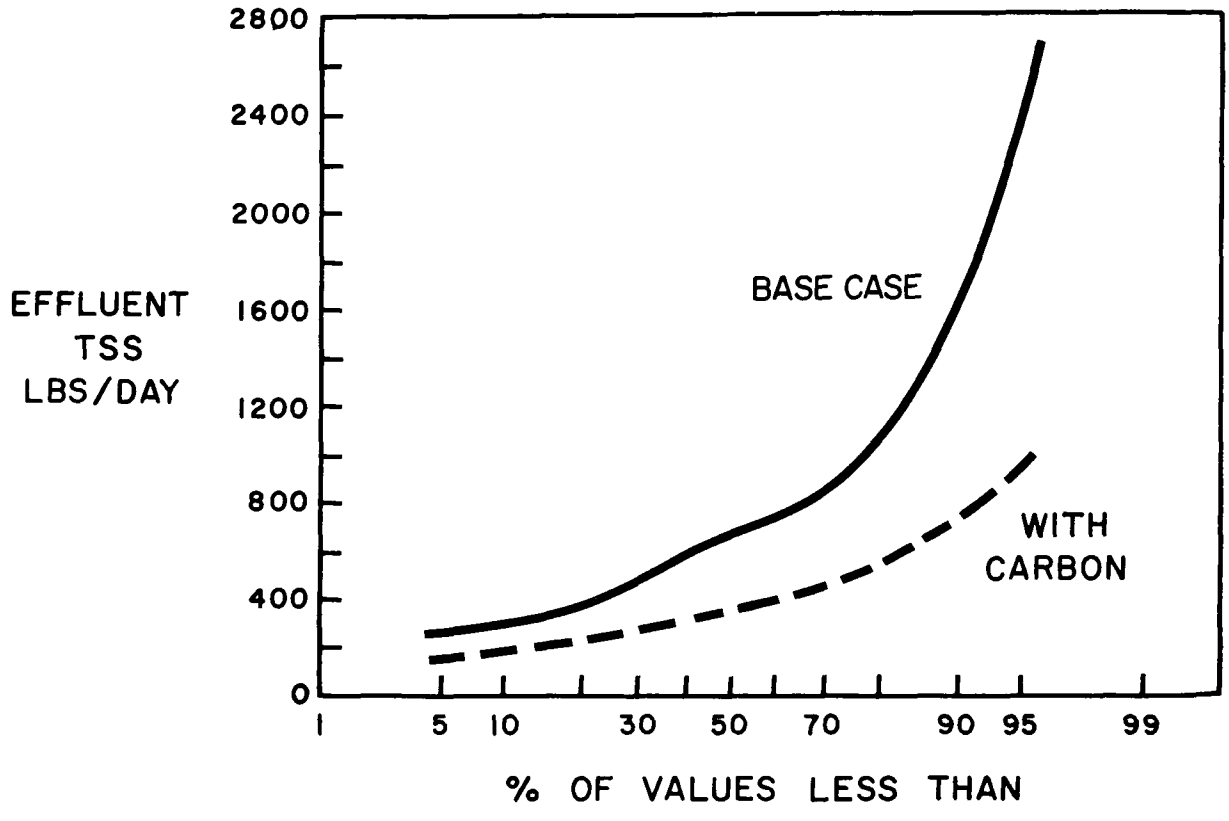


FIGURE 3

EFFECT OF POWDERED CARBON
ON EFFLUENT TSS

TRIAL 3

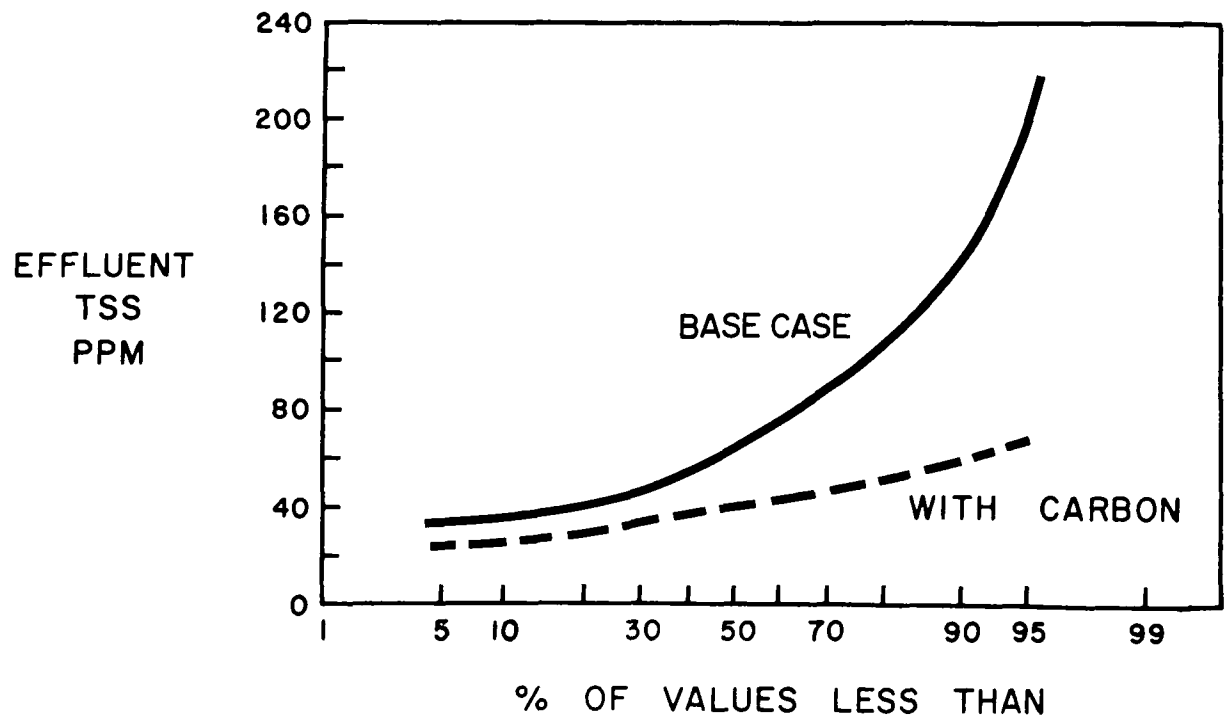


FIGURE 4

COMPARISON OF COD REMOVAL EFFICIENCY

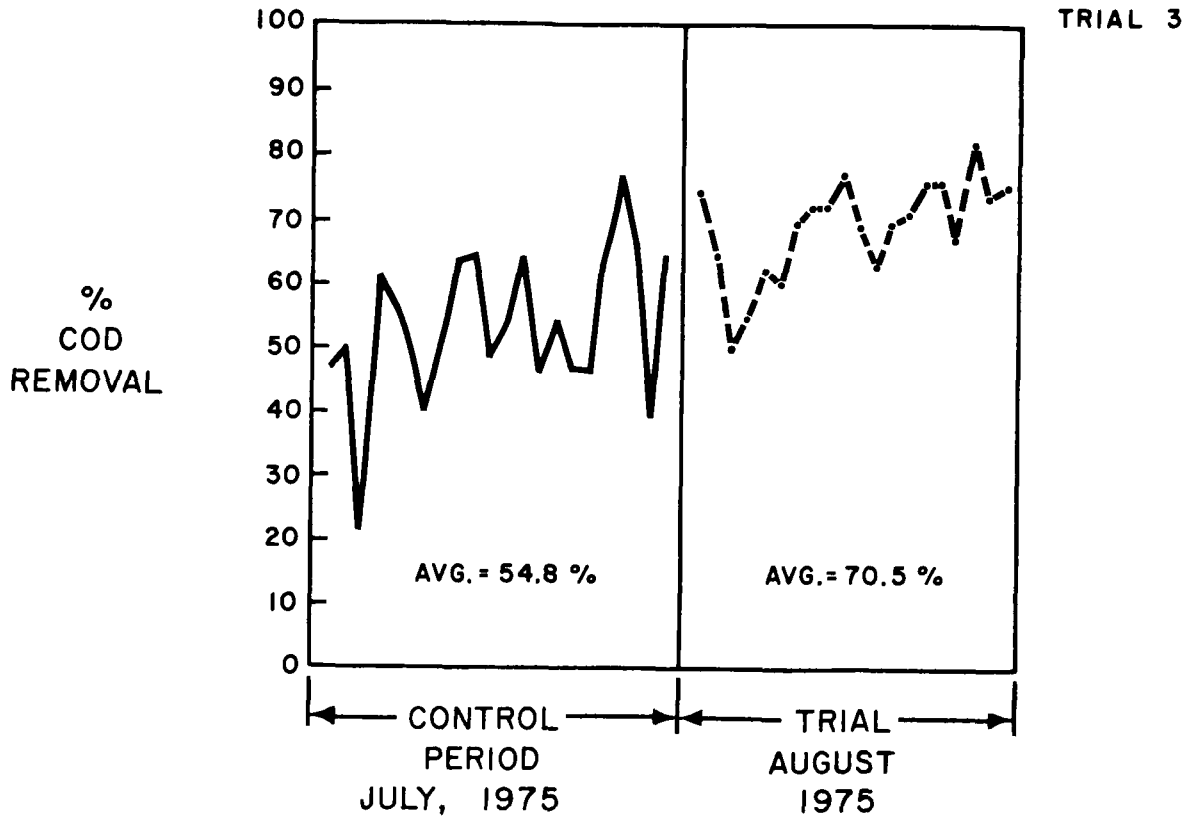


FIGURE 5

EFFECT OF POWDERED CARBON ON EFFLUENT COD

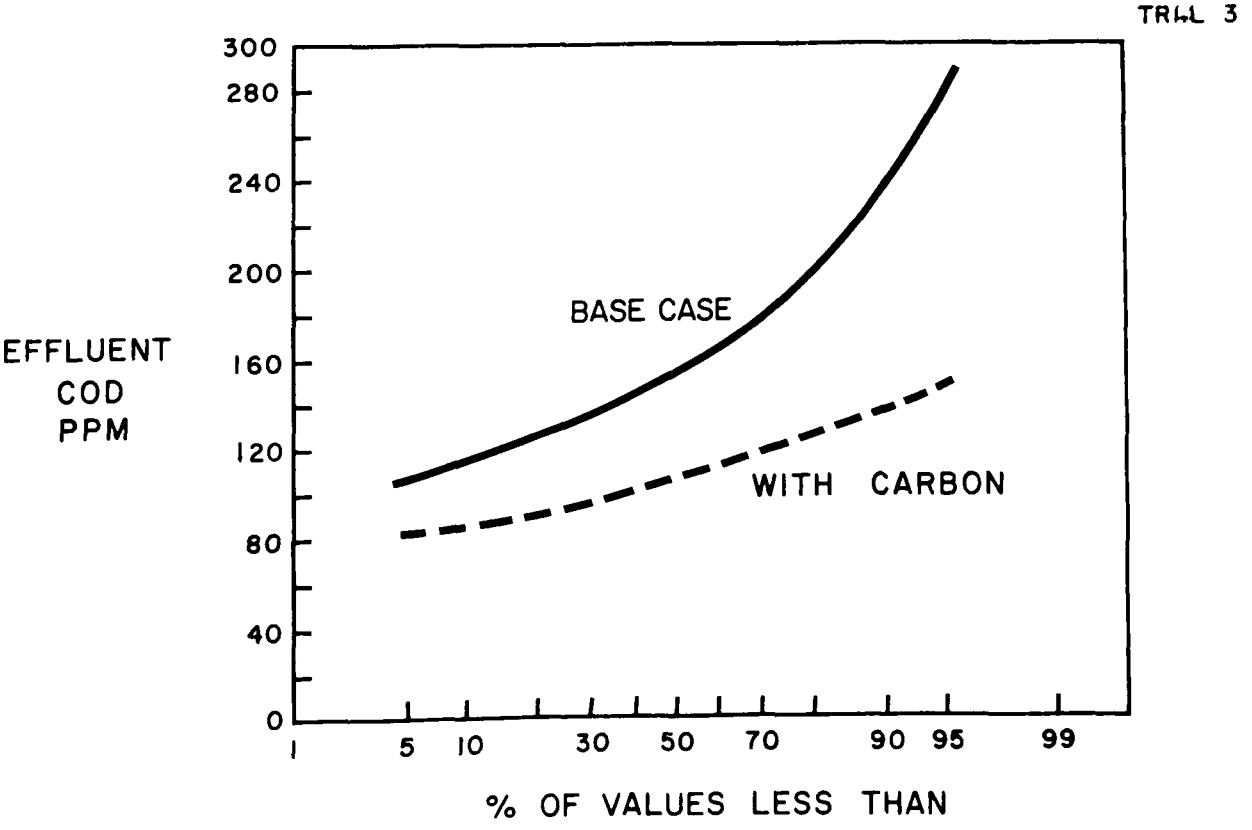


FIGURE 6

EFFECT OF POWDERED CARBON
ON EFFLUENT BOD

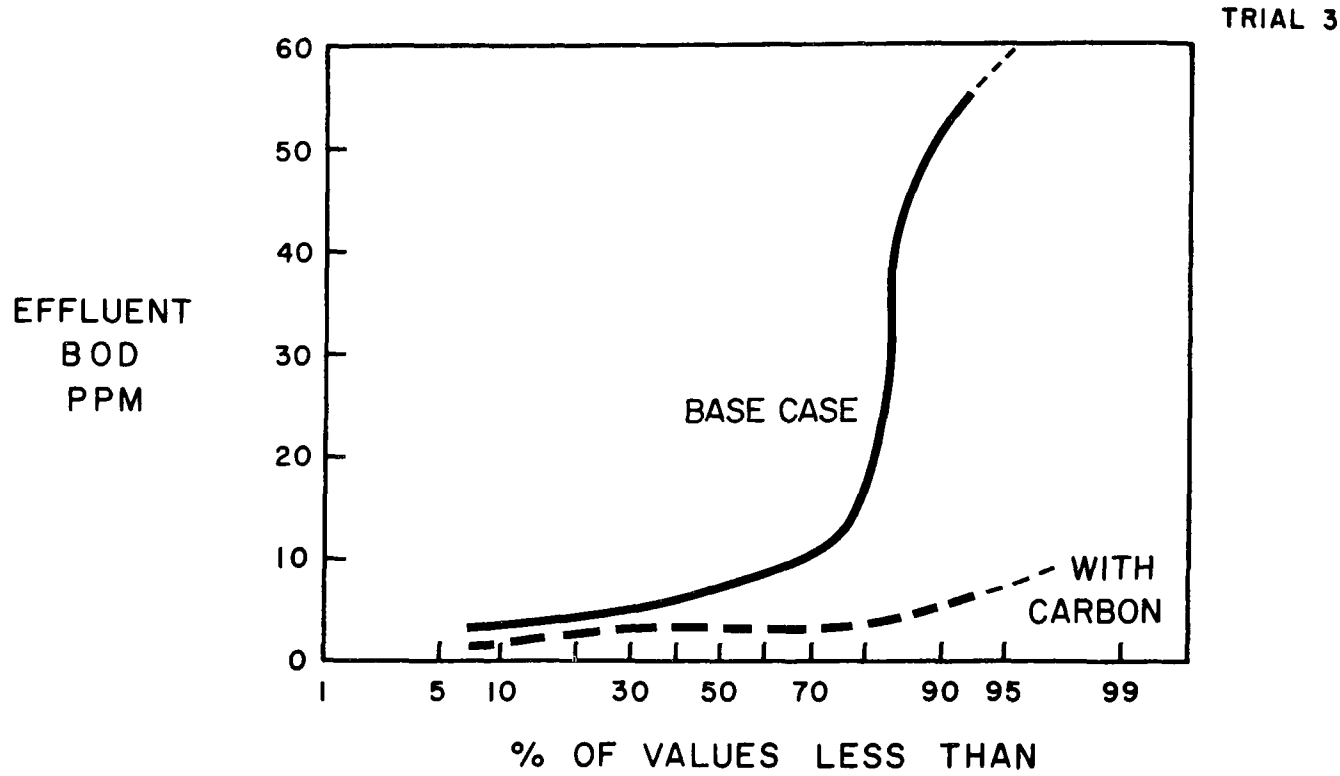
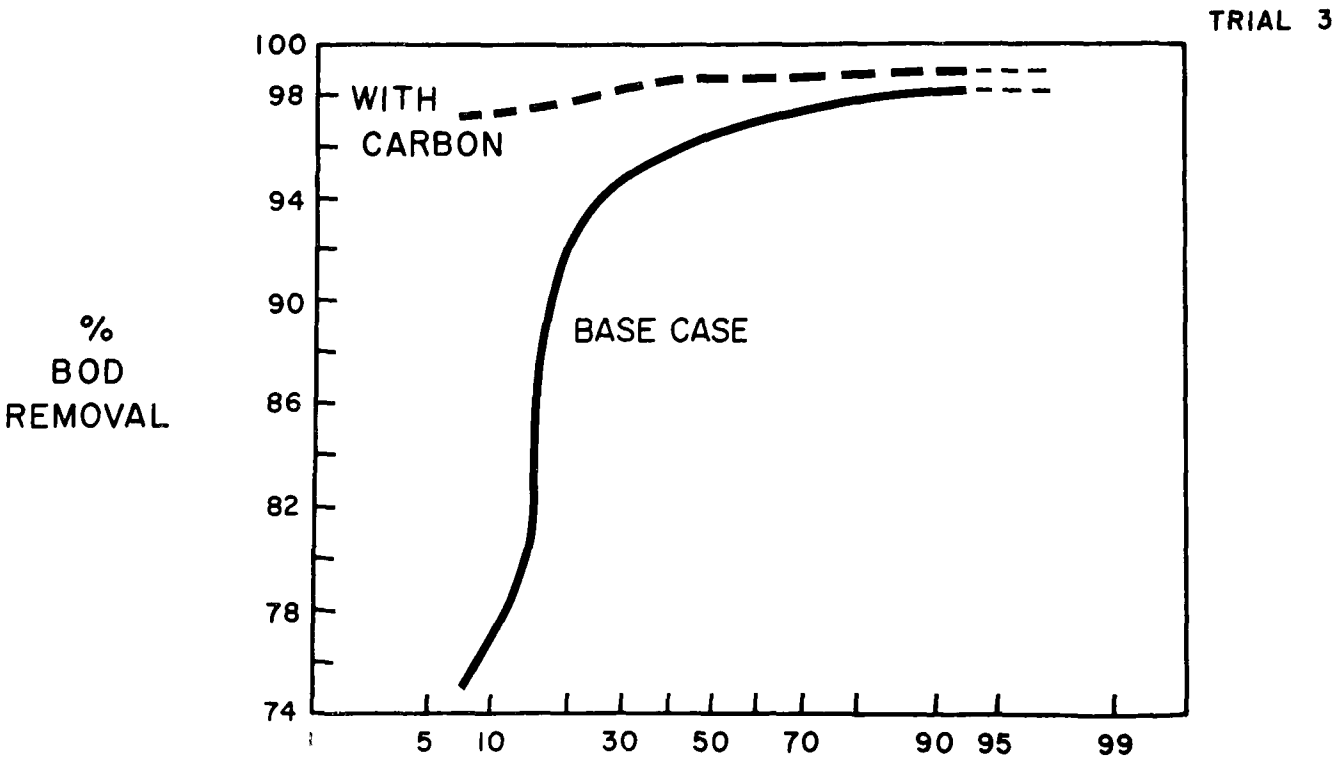


FIGURE 7

EFFECT OF POWDERED CARBON
ON BOD REMOVAL



"PILOT PLANT ACTIVATED CARBON TREATMENT OF PETROLEUM REFINERY WASTEWATER"

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INTRODUCTION

One of the first documented uses of carbon for environmental control was in 1793 when a physician used charcoal to remove the odor associated with gangrene. About sixty years later a scientist by the name of Stenhouse recommended the use of charcoal to remove the odors from sewers. Potable water was "purified" by carbon in 1862.[1] Moonshiners in the hills of Tennessee were using charcoal, not to mellow their product, but to remove "hog track" odors.

Since the mid-1960's, there has been an increasing effort to utilize activated carbon as a secondary or tertiary treatment system to treat wastewater. Two of the most successful uses of activated carbon were demonstrated at Lake Tahoe and in Pomona, California, to treat domestic municipal wastewaters. It is, of course, a natural progression to treat industrial wastewaters with systems that appear successful in treating municipal wastewaters.

The first domestic petroleum refinery to use activated carbon treatment was the Atlantic Richfield Refinery in Carson, California. The system was designed for intermittent use to treat rainfall runoff and process wastewater during storm periods. The second application was designed for the BP Refinery, Marcus Hook, Pennsylvania, to treat process wastewaters. Unlike the Arco system, the BP system was designed to operate in a continuous mode. Neither system relied on biological treatment preceding the activated carbon system.

During the late 1960's, activated carbon treatment of industrial wastewater was gaining momentum as the treatment system of the future. Statements such as "organic removal" or "removal of dissolved organics from wastewater has been demonstrated" and "activated carbon treatment systems will remove dissolved organic contaminants" were prevalent. These innocent gross statements were translated rather rapidly to imply that if you had an organic waste treatment problem, it could be solved with granular activated carbon.

With the complete cooperation of Kerr-McGee Petroleum Refinery, Wynnewood, Oklahoma, a study program was devised to investigate the adsorptive capacity of activated carbon.

ISOTHERM STUDIES

Adsorption isotherms are used to indicate the effectiveness of an activated carbon for a specific wastewater under controlled conditions. When the isotherm is to be used as

a predictive tool, the wastewater should be as representative as possible, pH and temperature adjustments should not be made, and sample collections need to be made in glass containers.

CARBON EVALUATION

Eleven commercially available carbons were evaluated for this petroleum refinery's wastewater. It is necessary to point out that adsorption varies with the carbon being evaluated and the water sample. The data presented is based on specific activated carbon for one petroleum refinery. Comparable results may or may not be achieved using the same carbon at another refinery.

The controlled conditions used for comparison purposes of the eleven carbons are shown in Table 1. Both pulverized and granular modes were evaluated.

The waste sample to be evaluated was collected from the API separator discharge, settled for four hours, and the candidate water was drawn from the middle of the vessel. The adsorption capacity of one gram sample of the candidate carbons, both pulverized and granular, is shown in Table 2.

Graphically expressed, the comparison of pulverized and granular adsorption capacities appears in Figure 1.

CONTACT TIME

A major factor relating to adsorption is the amount of time the water to be treated is in contact with the activated carbon. A sample of wastewater from another refinery was obtained for these studies. Pulverized activated carbon (Filtrasorb 400) was weighed to obtain 0.1, 0.5, 1.0, 2.0, and 5.0 grams of sample, and the isotherm procedure was followed for three hours. Samples were obtained at 20, 40, 60, and 180 minutes, filtered, and analyzed for total organic carbon. Table 3 represents the typical results.

ISOTHERM TESTING

Figure 2 shows the results of an isotherm carried out on wastewater from the refinery used in this study and a candidate activated carbon. Obviously, this curve does not follow the typical "Freundlich" isotherm. Instead of the usual straight line, a curve resulted. At the lower end of the curve the amount of carbon added to the wastewater is increased but the concentration of TOC does not decrease as much as would be expected. In fact, the concentration of TOC changes only very slightly at high carbon dosage. Refinery wastewater is composed of a rather complex mixture of materials. Some of these materials are readily adsorbable while others are not. The initial amount of carbon picks up the easily adsorbed materials and leaves behind the others. Therefore, increasing the carbon dosage does not reduce the concentration of TOC to the same degree. In fact, there is a possibility that this wastewater contains non-adsorbable components that cannot be removed by carbon treatment.

From the "isotherm," the adsorptive capacity of the carbon, tested with this specific wastewater, projects to approximately 0.1 lb of TOC per lb of carbon. This was considered to be a reasonable value and indicated that further investigation of activated carbon treatment was justified.

Results from isotherm tests are considered to be valuable only from an initial screening standpoint. Their results are generally not sufficient for predicting results of full-scale granular activated carbon treatment. For a better evaluation of activated carbon treatment, continuous column pilot plant investigation at the waste stream site yields much more reliable results.

ANTHRAFILT FILTRATION

When treating oily wastes by activated carbon, it appears that a pretreatment system is needed to assist in the removal of insoluble oils and suspended matter. An anthrafilt downflow filter system was evaluated for effectiveness, again using filtrable TOC as the prime parameter. The glass column used for this exercise was five feet in length and 1.5 inches in diameter. A diagram of the system is shown in Figure 3. Total organic carbon results obtained at these time intervals are shown in Table 4.

This particular study lasted 2.5 hours before a pressure drop was noted. The charge water contained an appreciable quantity of oil, and the oil percolated into the anthrafilt layer during the study period. When the column was backwashed with distilled water, the percolated oil was easily removed from the anthrafilt, leaving an apparently clean bed.

MINI-COLUMN STUDY

A downflow mini-column system was designed using stock one inch ID glass tubing that was six feet in length. The system was designed with an electronic sampler to composite hourly samples. A diagram of this system is shown in Figure 4.

The primary study involved dividing the six columns into two sets of three columns each to evaluate comparison of treatment effectiveness. Each column was packed with 1,000 cc of Filtrasorb 400 using potable water was the wetting liquid. The flow rate was set at 400 ml/minute and a column pressure of 6-7 psig was used. Total organic carbon was the primary parameter used for treatment effectiveness. Analytical results of the primary study are recorded in Table 5.

Comparing each column for removal efficiency, using the anthrafilt effluent TOC as the base, the percentages obtained are shown in Table 6. Columns 1 and 2 compare very well for the five-day averages, although they do exhibit considerable daily variances. Columns A-3 and B-3 are not agreeable, and no reason for this deviation is projected.

A second study was conducted by connecting five columns in an upflow mode. Each column contained 1,000 cc of Filtrasorb 400 packed in the same manner as the previous study. TOC results of this study are shown in Table 7.

Percentage reductions of each column based on the anthrafilt effluent are shown in Table 8. The average column trend indicates there is an increase of treatment effectiveness with each succeeding column, as one would expect.

PETROLEUM REFINERY DATA

Listed in Table 9 is the pertinent information needed to characterize the refinery where the study was conducted. This refinery was a 30,000 barrel, Class "B" refinery (using the API classification system); processes included fluid cat cracking, HF alkylation, catalytic reforming, and asphalt production.

The existing refinery eastewater treatment system is shown in Figure 5. Wastewater from the refinery includes cooling tower blowdown, boiler blowdown, oily process water, stripper effluent, and contaminated runoff. These wastes flow to an API separator for oil removal. The effluent from the separator is treated in a "Pasveer Ditch" activated sludge treatment system. The biologically treated effluent then flows through a series of holding ponds and the effluent from the final pond is discharged to a small stream.

Two complete pilot plants were installed and operated simultaneously, one on the refinery's API separator effluent (secondary) and the other on the clarifier effluent from the biological treatment system (tertiary).

ACTIVATED CARBON TREATMENT PILOT PLANT

Figure 6 contains a flow diagram of the pilot activated carbon treatment systems. The wastewater to be treated first flows through a dual-media filter constructed of 4-inch PVC pipe. This filter consisted of an 18-inch layer of sand over pea gravel, topped with a 6-inch layer of anthrafilt.

Dual-media filtration pretreatment was chosen because of its reliability and effectiveness, and because it does not require the use of iron or aluminum salts as coagulants. This latter point is particularly important insofar as regeneration of activated carbon is concerned, since aluminum salts during regeneration can remain on the surface of the carbon at high temperatures. These salts can become permanently attached to the surface. Thus, the effective surface area of the carbon is reduced and its adsorption capacity is seriously reduced. Iron salts present a similar problem. In addition, these salts can catalyze oxidation reactions of the carbon and the gases in the regenerator. Thus, the structure of the carbon becomes permanently damaged.

After pretreatment, the wastewater entered a "Calgon" activated carbon pilot plant. This plant was set up so that the wastewater flowed down three of the 5-inch ID columns. The first column contained an 18-inch layer of granular activated carbon while the remaining columns had a 36-inch layer of carbon.

The flow rate through each pilot plant was adjusted to 1/4 gpm. During the operation of the pilot plant, samples of the API separator effluent, biological treatment effluent, and both pilot plants' effluents were taken every two hours. These samples were

composited and preserved according to recommended EPA methods. Twenty-four hour composite samples were analyzed daily for a spectrum of water pollution control parameters using EPA analytical methodology and analytical quality control techniques.

The dual-media filter and carbon columns were backwashed whenever the pressure in the first column exceeded 20 psi. The pilot plants were operated over a 10-day period, at the end of which time the first columns in both plants were near exhaustion.

Figure 7 shows the BOD_5 daily composite analysis for the API separator effluent before and after treatment by the various schemes studied. Activated carbon treatment was not able to achieve the same level of BOD_5 reduction as bio-treatment. In fact, bio-treatment did a considerably better job. However, carbon treatment following bio-treatment did show further reductions in BOD.

Figure 8 shows the COD daily composite results for the same wastewater streams. Apparently, both bio-treatment and carbon treatment effect about the same COD reductions. Carbon treatment following bio-treatment yielded the best reduction of COD.

The TOC results for the daily composites are shown in Figure 9. Unlike the BOD_5 and COD results, the TOC indicates increased removal can be obtained by the API-carbon combination over the bio-treatment system alone. There is an erratic behavior pattern which indicates unadsorbable organics passing through the carbon columns.

From the BOD_5 and COD plots, it may be concluded that for secondary treatment alone, on the wastewater studied, the biological treatment system is preferable because it gives the greatest BOD_5 reduction and gives COD reduction equivalent to carbon treatment. The best levels of reduction were obtained with biological treatment followed by carbon adsorption.

Table 10 gives the results of other parameters evaluated in this study. As would be expected, both biological and activated carbon treatments are able to produce significant reduction in the organic parameters, such as BOD, COD, TOC, oil and grease, and phenols. It should be noted that carbon has a particular affinity for the removal of phenols. The color and turbidity are also improved. Cyanides and ammonia, for all practical purposes, were not removed by either of these treatments.

Sulfides are a peculiar problem for activated carbon treatment. Apparently, the sulfide content increases as it goes through the carbon system. This is probably due to biological activity occurring at the surface of the carbon. The sulfur containing compounds which are adsorbed upon the carbon are reduced anaerobically to H_2S giving rise to the increase in sulfide content. Bio-treatment, on the other hand, decreases the sulfide content very significantly.

One of the least expected removals by activated carbon was observed for the metals --chromium, copper, iron, and zinc. These metals are significantly reduced by the carbon. Whether these removals are due to adsorption, filtration, or other phenomena has not been evaluated. However, it must be kept in mind that these removals were

accomplished with virgin carbon. The effect of some of these metals upon carbon regeneration has not been determined. Also, whether regenerated carbon can remove equivalent amounts of metals has not been established.

As mentioned previously, the isotherm study indicated that the carbon could adsorb 0.1 lb TOC/lb of carbon. The columns on the API separator effluent indicated a capacity of 0.31 lb TOC/lb of carbon, as shown in Table 11. The most probable explanation for the difference in the capacity as determined in the isotherm test and the pilot plant study is biological activity in the columns.

In the case of the API separator effluent carbon column, this biological activity manifested itself by the anaerobic production of H_2S. While the increased capacity is a desirable situation, the production of sulfides is not. Although anaerobic activity was not apparent in the clarifier effluent columns, it was observed that algae started growing in the carbon beds. In fact, it was necessary to cover the columns to prevent sunlight from making this growth possible.

Because of the considerable cost of granular activated carbon, regeneration of the spent carbon is essential if the cost of treatment is to be kept at a moderate level. Samples of spent carbon were taken from the first column of each pilot plant and sent to Calgon Corporation for regeneration studies. Calgon regenerated these two carbons using their standard evaluation techniques in a muffle furnace at 1750° F and with a normal air, flue gas, and steam atmosphere.

As shown in Table 12, both carbon samples were regenerated to a good activity as indicated by the iodine numbers obtained. The regenerated clarifier carbon appeared to have a little better activity than the API separator carbon. In general, the iodine number can be related to the surface area of pores larger than 10 Å in diameter. The molasses number, likewise, is related to the surface of pores larger than about 30 Å. As can be observed in Table 15, there is an increase in the molasses number with a slight decrease in iodine number. This indicates a shift in pore size distribution. Apparently, the smaller pores are being destroyed while larger pores are being created. Final clarifier carbon appeared to have less destruction of the pore matrix than did the API separator carbon.

GAS CHROMATOGRAPHY STUDIES

Studies by Dr. T. C. Dorris and Dr. S. L. Burks at Oklahoma State University have shown that some organics present in refinery wastewaters are toxic to fish, and some organics are refractory to biological degradation.[2] These organic chemicals persist in lakes and streams for long periods of time. It is also noted that a refractory organic cannot be detected by the TOD test that has been used in the past to evaluate the efficiency of treatment systems. Tests such as TOD, TOC, and COD are much more realistic for the indication of organics in a water sample. Of these tests, TOC is the one that measures only organics.

The laboratory researchers must go further and use sophisticated methods for actually identifying and characterizing the refractory organics so that engineers will know the

type of organics that must be removed, thus designing treatment systems to improve the quality of water discharged to the receiving streams.

Carbon treatment is a relatively efficient method for removing organics from refinery wastewater and may be used as a secondary or tertiary treatment system to reduce the BOD of effluent water to a very low level. In studies to learn more about carbon treatment, carbon columns were installed at a petroleum refinery wastewater treatment plant at a point immediately after the API separator and at a point after the final clarifier for the activated sludge treatment unit. The carbon removed from these columns was extracted with several organic solvents to determine which solvents were most efficient and to provide samples of the organics for silica gel, gas chromatographic (GC), infrared, and GC-mass spectrometric analyses.[3]

About 100 ml of an air dried carbon sample were weighed and placed directly into the soxhlet extraction apparatus with a glass wool plug at the bottom to prevent the carbon from getting into the siphon tube. Three hundred ml of solvent were used in the flask. The rate of solvent reflux was adjusted to give four cycles per hour, and the extraction was continued for 22 hours. After 22 hours, the solvent-oil mixture was cooled to room temperature and filtered through a 10 cm depth of anhydrous sodium sulfate crystals contained in a 20 mm by 25 cm glass tube to dry the mixture and remove any carbon particles that might be present. The dried solvent-oil mixture was then distilled through a 20 mm diameter column containing 12 cm of glass beads until the volume remaining in the flask was slightly less than 50 ml. The concentrated solvent-oil mixture was measured into a sample vial, and the volume adjusted to exactly 50 ml with rinsings from the flask.

A gas chromatograph, with a flame detector and an electronic integrator, was used to determine the amount of oil extracted with each solvent. A 1/8-inch by 20-foot stainless steel column, packed with 70/80 mesh Chromosorb G, AW-DMCS, with 5% OV-101 stationary phase, was programmed to hold at room temperature for four minutes with the oven lid open, then the lid was closed and the program proceeded from 35° to 65° C at 8 degrees per minute and from 65° to 350° C at 6 degrees per minute. The temperature was held at 350° C for up to 20 minutes, if it appeared necessary to elute all of the sample. Injector and detector temperatures were about 370° C.

A solution of 3 gm of diesel fuel diluted to 50 ml with solvent was used as a standard since it was available, although an oil with a higher aromatic content would have been more desirable. The total area of the chromatogram of the standard, excluding the solvent peak and correcting for baseline drift near the end of the chromatogram, was compared with the total areas obtained from the 50 ml samples of extract. Data obtained from the carbon extractions and GC analyses are shown in Table 13.

Chloroform, benzene, and methylene chloride showed about the same efficiency for extracting oil from the carbon, while hexane and methanol were less efficient. Figures 10 through 14 show the chromatograms obtained on the extracts from API carbon using the five different solvents. Comparison of the benzene, methylene chloride, and chloroform extracts (Figures 10, 11, and 14) shows that the oils extracted with these solvents were

almost identical in composition. However, chloroform showed an advantage in the recovery of one low boiling compound which was an appreciable amount of the sample as indicated from the size of the peak. This peak had a retention time of 11.3 minutes which corresponds to the retention time of benzene. This peak could not be seen when benzene was used as the solvent, and shows at a much lower concentration in the methylene chloride extract.

Chloroform was used as the solvent for extracting a sample of carbon that had been used to treat effluent water from the final clarifier of the activated sludge treatment system. This carbon is referred to as FC carbon, and the resultant chromatogram is shown in Figure 15. The FC carbon contained about 1/3 as much oil as the API carbon. A sample of new carbon also was extracted with chloroform to determine whether the new carbon contained any extractable material. This extract contained no measurable oil, as illustrated by Figure 16. This figure also serves as a good illustration of the purity of the chloroform used as the solvent. Figure 17 is a chromatogram of the standard mixture used to quantitate area data in terms of grams of oil extracted.

The API carbon extract and FC carbon extract were each separated into three fractions by selective elution and desorption from silica gel. The columns were pre-wet with hexane and as the last drop of hexane disappeared into the surface of the gel, the sample-gel mixtures in the 10 ml beakers were emptied into their respective columns. The samples were then fractionated by eluting the saturates with 10 ml of hexane, the aromatics with 10 ml of benzene, and finally desorbing the polar fraction with methanol. Each of the fractions was then reduced in volume to 0.5 ml by evaporating the solvents with a gentle stream of air.

Gas chromatography was used to obtain an estimate of the amount of saturates, aromatics, and polar material in each of the samples. The oil extracted from the FC carbon contained such small amounts of saturates and aromatics that it was necessary to increase the sensitivity of the GC by a factor of 10 to obtain measurable areas. These areas were then divided by 10 to get back to the same basis as the area measurements on the polar fraction. The results are tabulated in Table 14.

These data indicate that the activated sludge treatment system has reduced the saturates and aromatics to very low levels in the final clarifier effluent but has been relatively ineffective in removing some of the polar type organic compounds.

Figures 18, 20, and 22 are chromatograms of the saturate, aromatic, and polar fractions obtained by the silica gel separation of the oil from API carbon. Figures 19, 21, and 23 are chromatograms of the saturate, aromatic, and polar fractions obtained by the silica gel separation of the oil from FC carbon.

There was insufficient time for complete GC-MS identifications, but Table 15 lists some of the compounds and types that have been found to date in the saturate, aromatic, and polar fractions. The organic structures shown in the table are those normally found in petroleum and petroleum products, but it is noted that three sulfur compounds were found in the aromatic fraction of the FC carbon extract. It may be that these compounds are not

biologically degraded as much as the aromatics and are a more significant part of the aromatic fraction after biological treatment.

The polar fractions could not be analyzed by GC-MS because of the inability of the gas chromatograph to separate the complex mixture. The complexity of the mixture is illustrated in Figures 22 and 23 by the lack of baseline separation. Differences in the two chromatograms indicate that some of the components have been degraded in the activated sludge treatment system. It is probable that the reduction in phenolic compounds, that is known to occur, would account for some of the differences noted in the chromatograms.

Infrared scans on the polar fractions were almost identical. Functional groups noted were OH and C=O, and CH_2 and CH_3 adsorption bands indicate aliphatic type structures. Further work must be done on the polar fractions to identify a number of the individual compounds in the mixture so that an assessment of their toxicity can be made and treatment methods developed to remove these compounds.

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1. Hansler, John W. Activated Carbon. Chemical Publishing Company, Inc., New York, New York, 1963.

2. Burks, S. L., T. C. Dorris, and G. L. Walker. Identification of Toxic Organic Chemical Compounds in Oil Refinery Wastewaters. Technical Completion Report to U.S.D.I. Office of Water Resources Research, Project BO-17, Oklahoma, 1970. Unpublished.

3. Hale, J. H. and L. H. Myers. The Organics Removed by Carbon Treatment of Refinery Wastewater. Presented at the Oklahoma Industrial Waste and Advanced Water Conference, Stillwater, Oklahoma, April 1973. Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. Unpublished.

BIOGRAPHIES

Jack H. Hale holds a BS in Chemical Engineering from Oklahoma State University. He is currently a research chemist in the Industrial Section of the Source Management Branch at the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

Leon H. Myers holds a BS in chemistry/biology from Southwestern Oklahoma State University and a MS in sanitary science from Oklahoma University. He is currently Chief, Industrial Section of the Source Management Branch at the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

Thomas E. Short holds a BS in Chemical Engineering from Lamar University and a MS and Ph.D. in Chemical Engineering from Oklahoma State University. He is currently a Chemical Engineer at the Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma.

DISCUSSION

Bill McCarthy: When you used solvent extraction for recovering your adsorbent components, could you give us an idea of what efficiency or recovery you got?

Leon H. Myers: No I can't, because we did not attempt a mass balance; however, the quantitative value of three solvents produced similar results. The quantity recovered agrees with the projected isotherm loading.

Bill McCarthy: Do you think solvent regeneration might be a viable process?

Leon H. Myers: Yes, I do believe it is both feasible and viable, and this is determinant on the mixtures of hydrocarbons to be removed. In some cases, particularly with light hydrocarbons, steam regeneration might be the most viable regeneration process. Neither of these alternate regeneration modes have been thoroughly proven.



MYERS



HALE

Table 1. CONTROLLED CONDITIONS FOR ISOTHERM STUDY

1. 325 mesh (pulverized)	5. 100 rpm agitation
2. 200 ml sample	6. 23° C temperature
3. 1 hour contact	7. 75 mg/l TOC
4. 0.05, 0.20, 0.50, 1.0 gm carbon	8. pH 7.4

Table 2. ADSORPTION DATA FOR ELEVEN ACTIVATED CARBONS

Carbon Sample	mg/l TOC Adsorbed on 1 gm Carbon	
	Pulverized	Granular
1	50	38
2	60	37
3	56	37
4	57	48
5	56	29
6	52	31
7	47	41
8	51	47
9	49	38
10	35	13
11	46	34

Table 3. CONTACT TIME ADSORPTION

Gm Carbon (Blank)	Time in Minutes			
	20 (206 mg/l)*	40 (260 mg/l)*	60 (260 mg/l)*	180 (260 mg/l)*
0.1	124	96	82	101
0.5	63	45	51	73
1.0	57	47	106	45
2.0	55	52	77	34
5.0	56	54	50	24

* Results are expressed as mg/l filtrable total organic carbon.

Table 4. ANTHRAFILT FILTRATION ORGANIC CARBON REMOVAL

	TOC	Turbidity
Charge	255 mg/l	11.0
After 5 minutes (0.3 gal.)	220 mg/l	
After 1 hour (3.2 gal.)	210 mg/l	
After 2.5 hours (7.9 gal.)	206 mg/l	2.75

Table 5. MINI-COLUMN TOC RESULTS

Date	Final Clarifier Effluent*	Anthrafilt Effluent*	Columns					
			A-1*	B-1*	A-2*	B-2*	A-3*	B-3*
3/17	35	31	13	9	9	10	7	12
3/18	33	34	11	11	10	12	10	18
3/19	48	40	13	16	14	14	8	12
3/20	37	48	17	23	22	16	11	22
3/21	35	38	18	19	17	25	16	32

* All concentrations are mg/l TOC.

Table 6. COMPARISON OF MINI-COLUMN TOC REMOVAL EFFICIENCY

Date	Percentage Removals					
	A-1	B-1	A-2	B-2	A-3	B-3
3/17	58	71	71	68	77	62
3/18	68	68	71	65	71	47
3/19	68	60	65	65	80	70
3/20	65	52	54	67	77	54
3/21	53	50	55	34	58	16
Average	62	60	63	60	73	50

Table 7. TOC RESULTS OF MINI-COLUMN UPFLOW MODE

Date	Final Clarifier Effluent*	Anthrafilt Effluent*	Columns 1*	2*	3*	4*	5*
3/24	50	38	19	12	11	13	13
3/25	35	33	17	13	10	10	9
3/26	41	33	20	24	18	13	12
3/27	38	35	17	19	17	13	10

* All concentrations are mg/l TOC.

Table 8. PERCENTAGE REMOVAL OF TOC FOR UPFLOW MODE

Date	Columns 1	2	3	4	5
3/24	50	68	71	66	66
3/25	48	61	70	70	73
3/26	39	27	45	61	64
3/27	51	46	51	62	71
Average	47	51	59	65	69

Table 9. REFINERY PROCESS DATA

Capacity	30,000 BPSD
API Class	B
Wastewater Volume	18 gal. per minute
Refinery Processes:	1. Crude Distillation 2. Crude Desalting 3. Vacuum Crude Distillation 4. Fluid Cat Cracking 5. HF Alkylation 6. Hydro Cracking 7. Catalytic Reforming 8. Asphalt Production

Table 10. REFINERY WASTEWATER TREATMENT RESULTS

Parameter	Median Values			
	API Separator (mg/l)	Bio-Treated (mg/l)	Carbon-Treated (mg/l)	Bio-Carbon Treated (mg/l)
BOD_5	97	7	48	3
COD	234	98	103	26
TOC	56	30	14	7
Oil and Grease	29	10	10	7
Phenols	3.4	0.01	0.004	0.001
Chromium	2.2	0.9	0.2	0.2
Copper	0.5	0.1	0.03	0.05
Iron	2.2	3.0	0.3	0.9
Lead	0.2	0.2	0.2	0.2
Zinc	0.7	0.4	0.08	0.15
Sulfide	33	0.2	39	0.2
Ammonia	28	27	28	27
Cyanides	0.25	0.2	0.2	0.2
Turbidity*	26	17	11	5
Color**	30	15	15	1

* Turbidity given in Jackson Turbidity Units.
** Color given in color units.

Table 11. CARBON ADSORPTION CAPACITY

	Capacity Lbs TOC Adsorbed Per Lbs Carbon
Isotherm Study	0.12
API Separator Effluent Carbon Column	0.31

Table 12. CARBON REGENERATION ACTIVITY ANALYSIS

	Iodine No.	Molasses No.
Virgin Carbon	1010	216
API Separator Carbon	906	405
Final Clarifier Carbon	991	304

Table 13. SOLVENT EXTRACTION EFFICIENCY DATA

Carbon Identification	Solvent	Grams Carbon	Grams Oil Extracted	Gram Oil/ Gram Carbon
API	Chloroform	49.3008	5.04	0.102
API	Benzene	50.6917	5.01	0.099
API	Methylene Chloride	54.5660	5.44	0.100
API	Methanol	56.3179	3.71	0.066
API	Hexane	55.3762	4.03	0.073
FC	Chloroform	56.6447	1.95	0.034
NEW	Chloroform	44.6169	0.00	0.000

Table 14. COMPOSITION BY TYPES OF ORGANICS

Organic Type	Oil from API Carbon	Oil from FC Carbon
Saturates	11.1%	0.2%
Aromatics	24.7	1.3
Polar Material	64.2	98.5
	100.0	100.0

Table 15. COMPOUND TYPES INDICATED BY GC-MS

	API Carbon Extract	FC Carbon Extract
Saturate Fraction	C_8H_{16} C_9H_{16} C_9H_{18} $C_{10}H_{20}$ $C_{12}H_{24}$ C_8 through C_{29} n-paraffins	
Aromatic Fraction	Ethylbenzene Xylenes C_9 Benzenes C_{10} Benzenes Naphthalene C_{11} Benzenes C_{11} Naphthalene C_{12} Naphthalene C_{13} Naphthalene	Ethylbenzene Xylenes C_9 Benzenes C_{10} Benzenes C_7H_8 S $C_7H_{10}S$ C_9H_8 S
Polar	Phenol Hydroxytoluene	

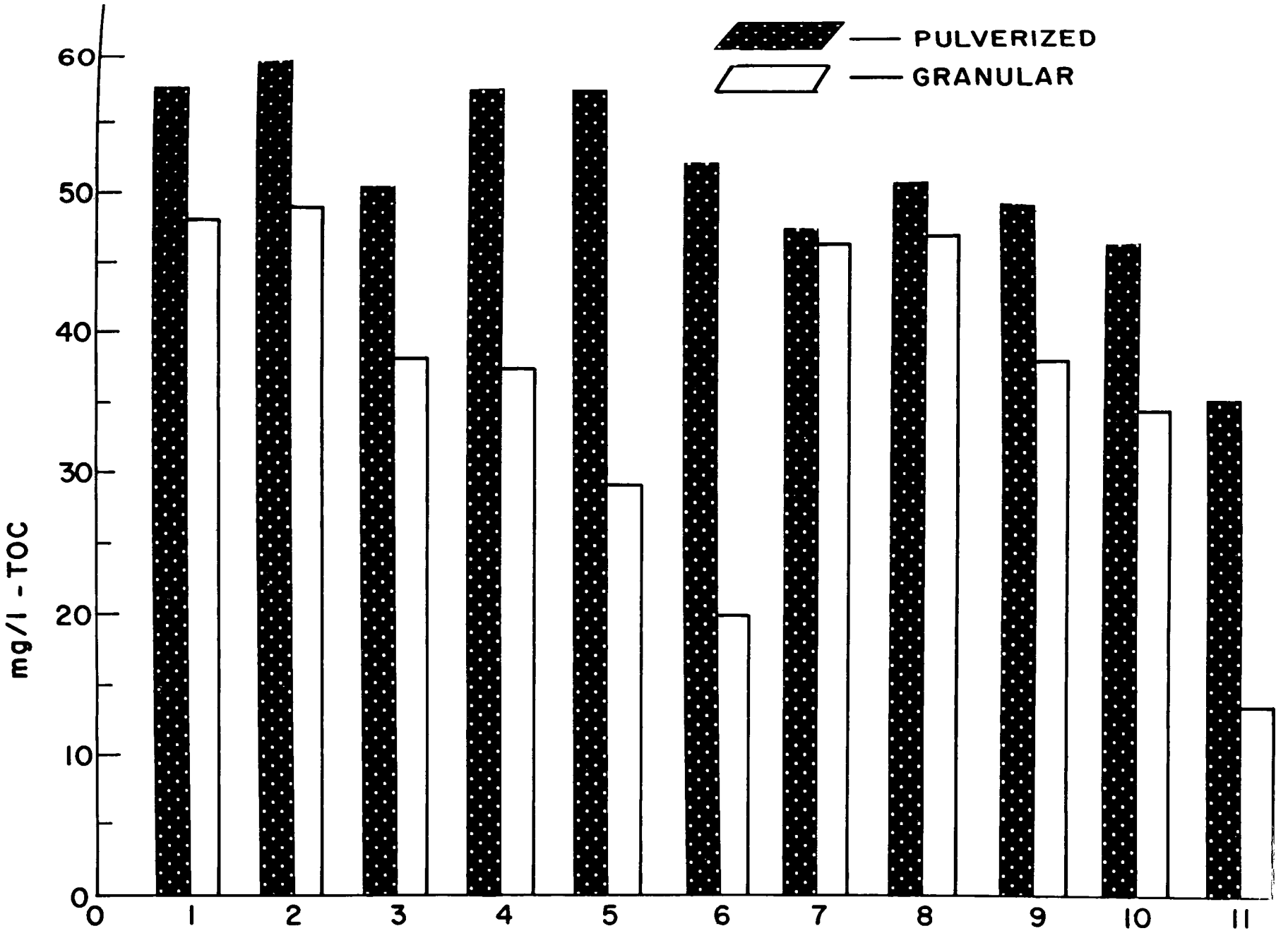

PULVERIZED
GRANULAR
mg/l - TOC
0
10
20
30
40
50
60
0
1
2
3
4
5
6
7
8
9
10
11
CARBON SOURCES

FIGURE - 1

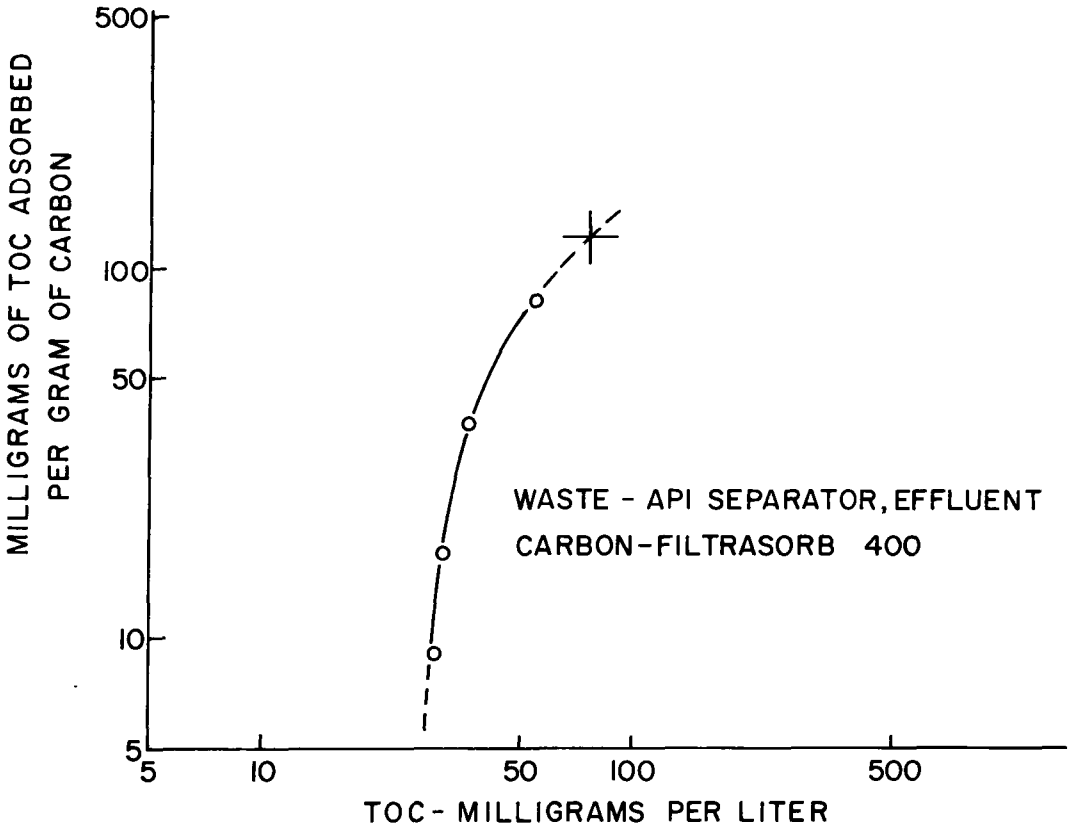


FIGURE 2 – ADSORPTION ISOTHERM

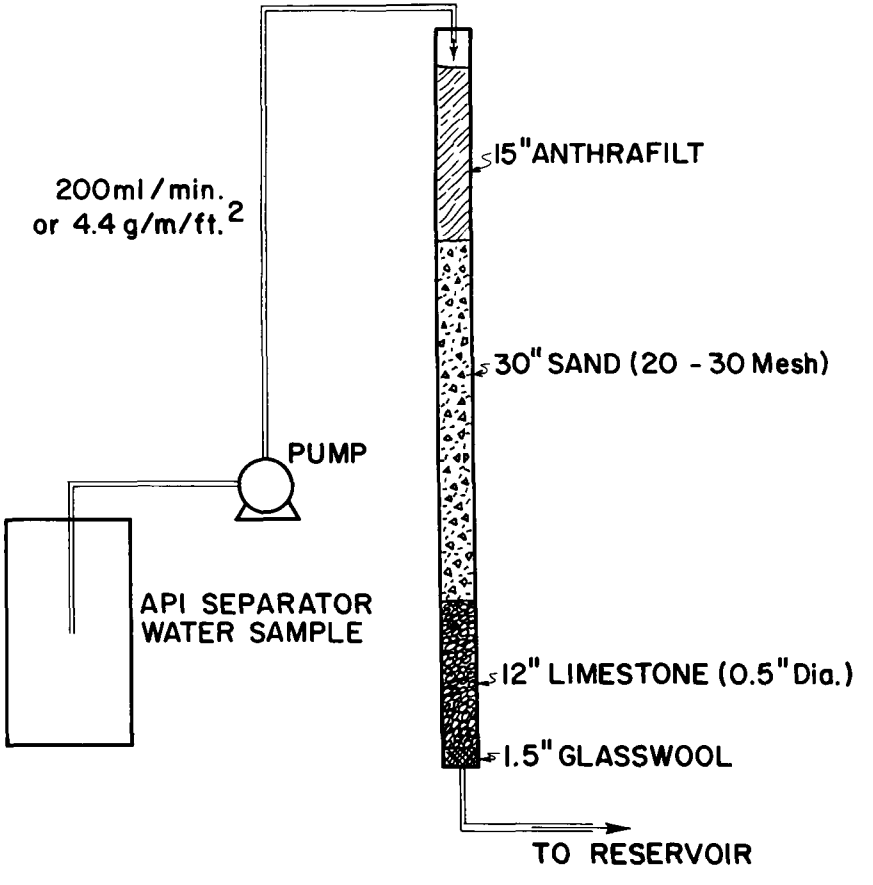


FIG. 3- MULTI – MEDIA FILTER

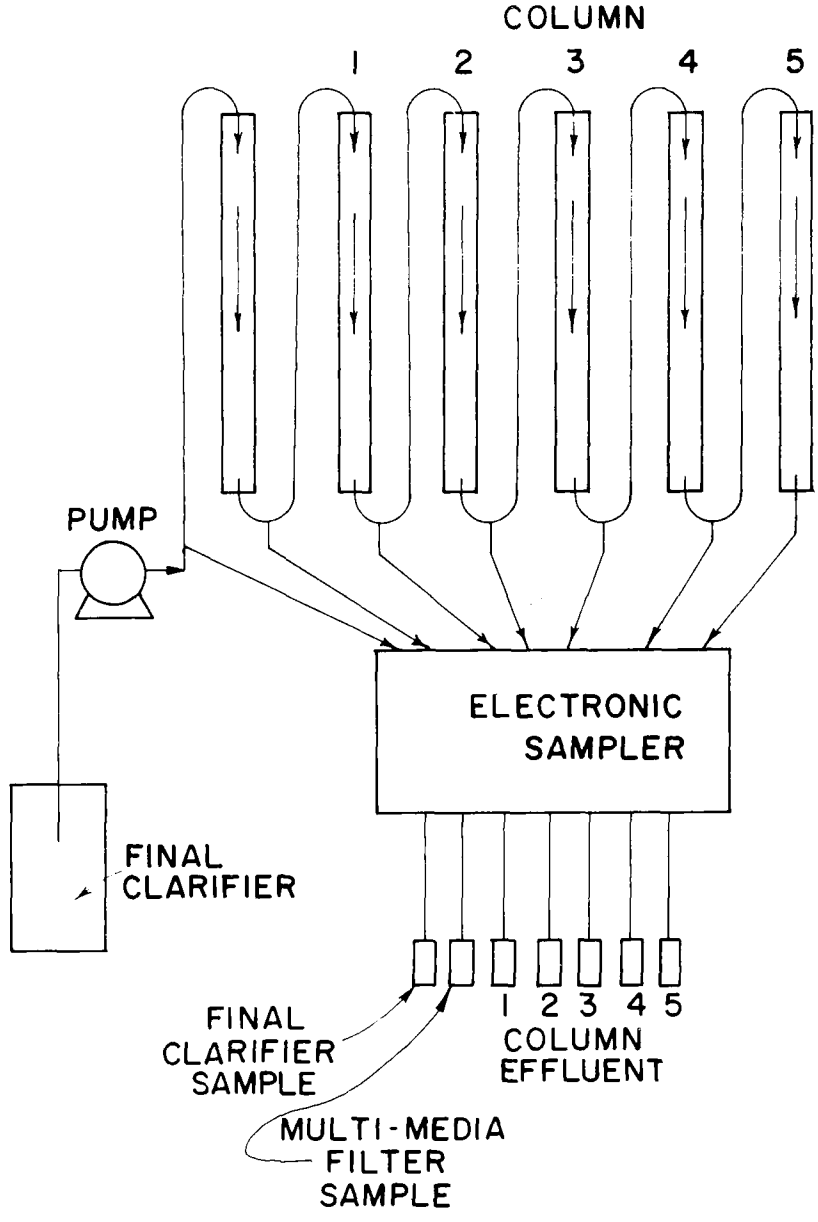


FIG. 4 - MINI COLUMN SYSTEM

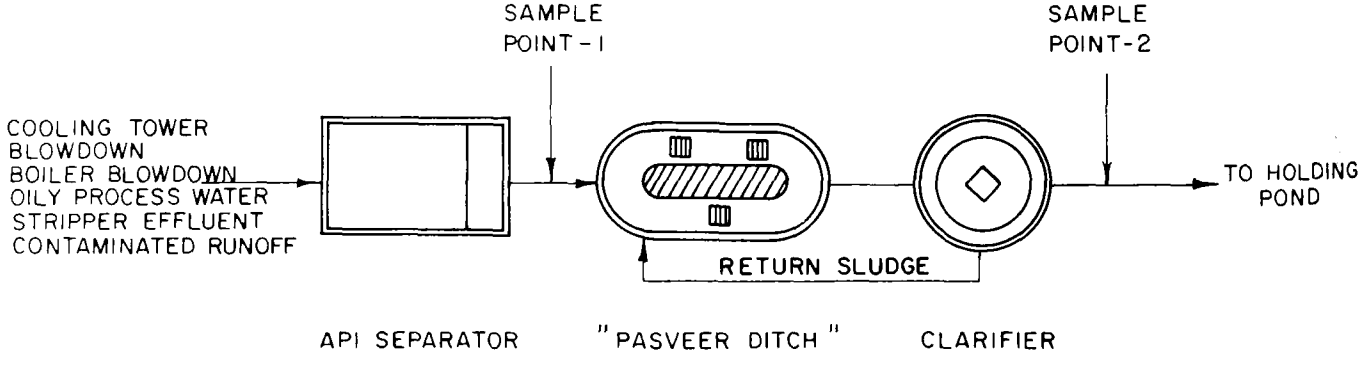


FIGURE 5 - REFINERY WASTE WATER TREATMENT SYSTEM

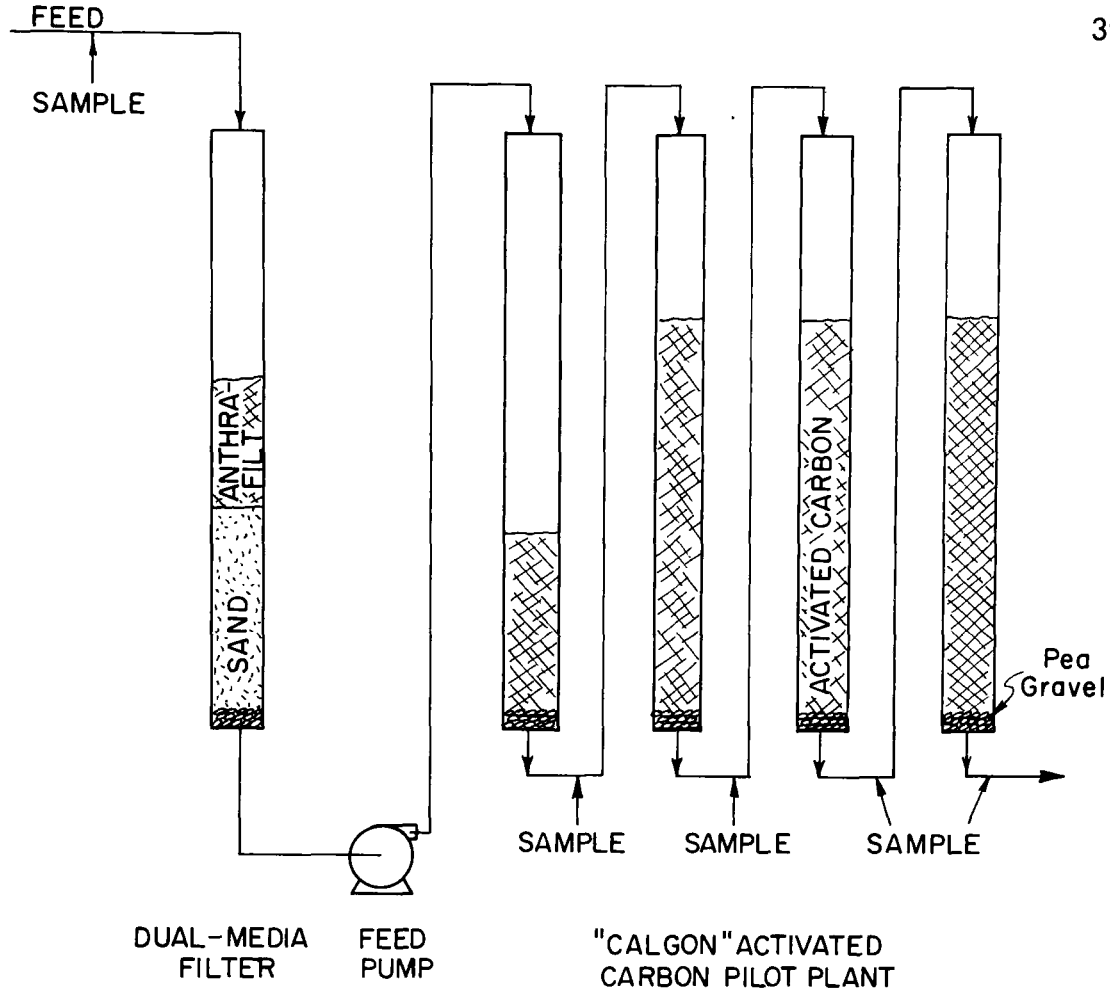


FIGURE 6 - ACTIVATED CARBON PILOT PLANT FLOW DIAGRAM

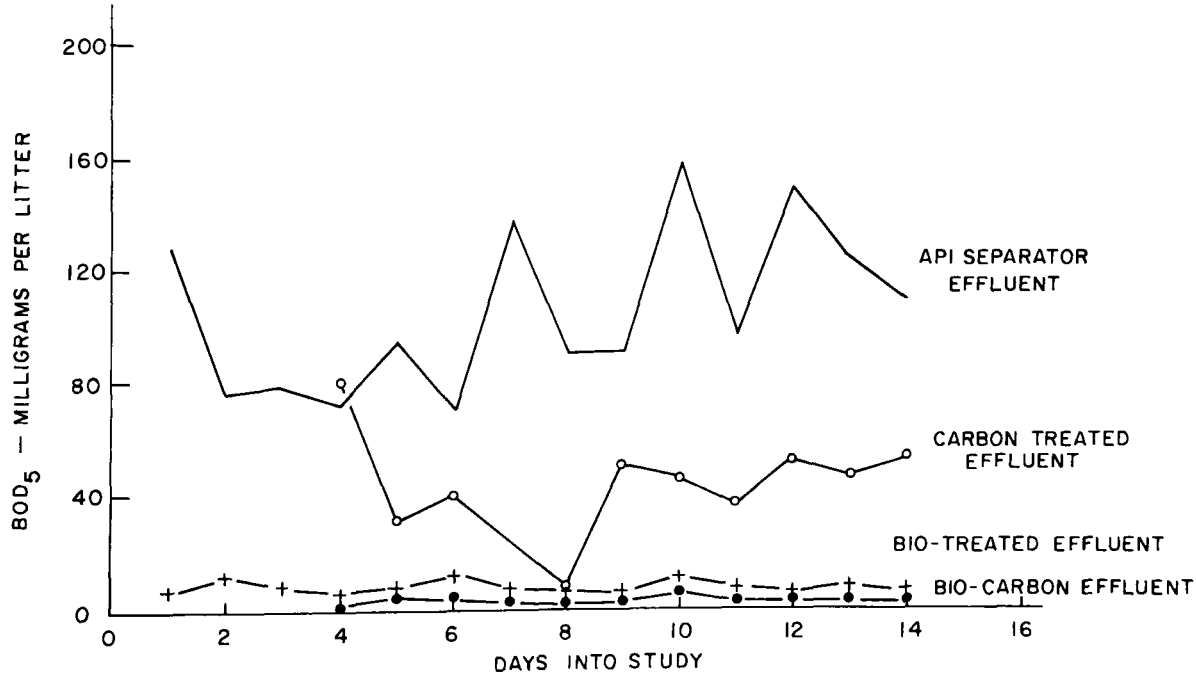


FIGURE 7 TREATMENT RESULTS, BOD

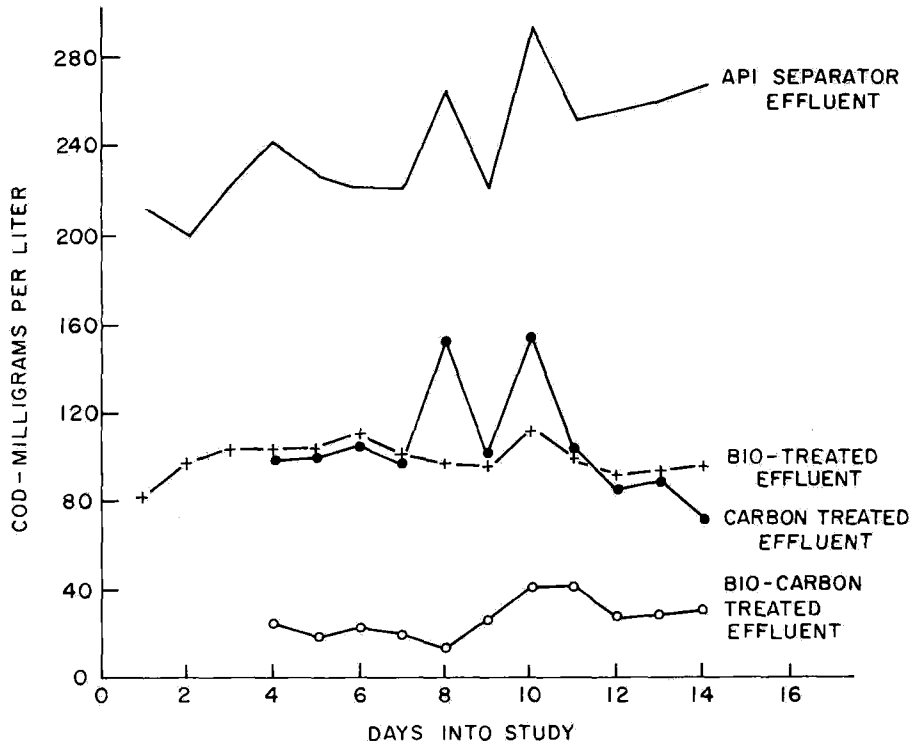


FIGURE 8 – TREATMENT RESULTS, COD

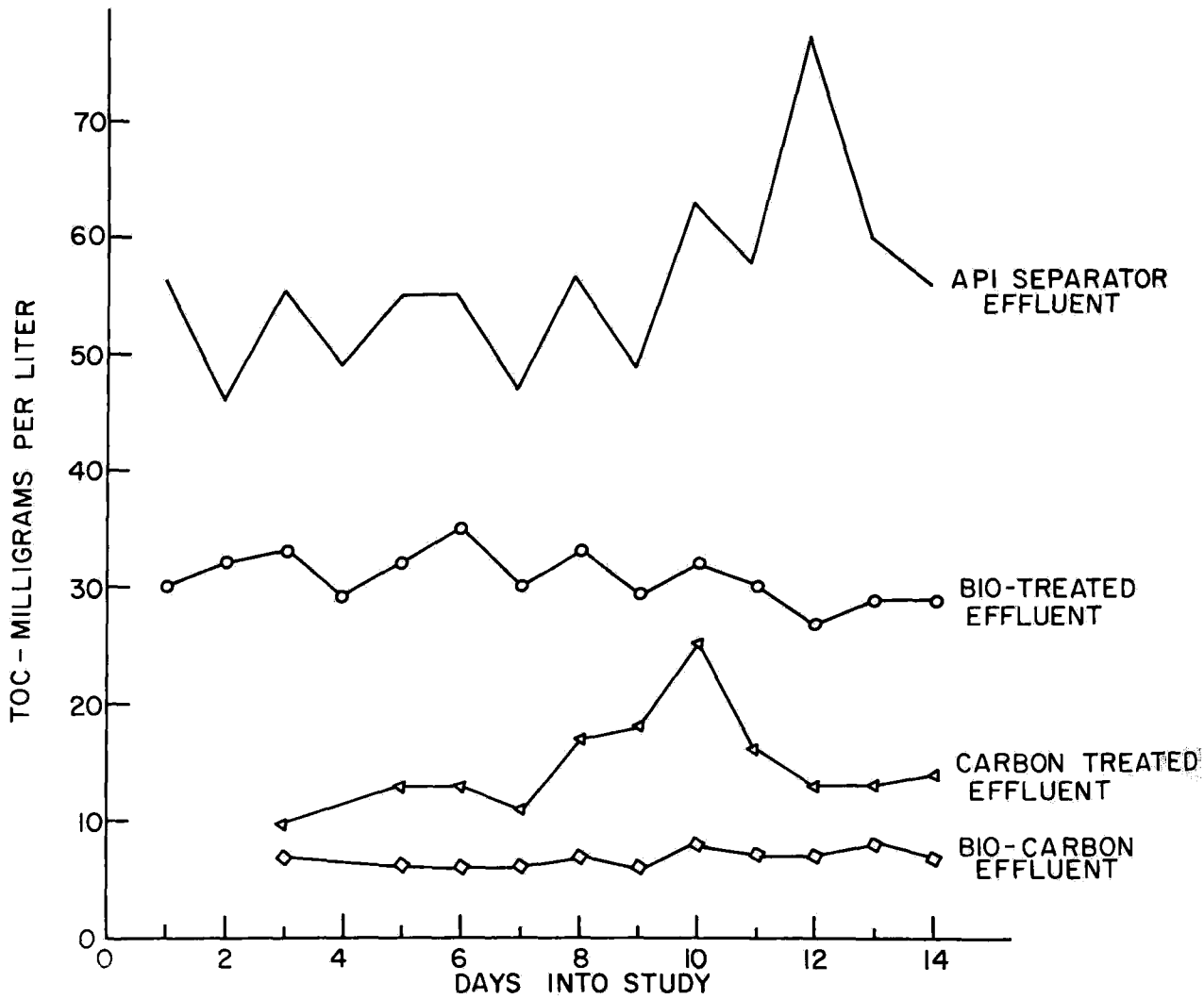


FIGURE 9 - TREATMENT RESULTS, TOC

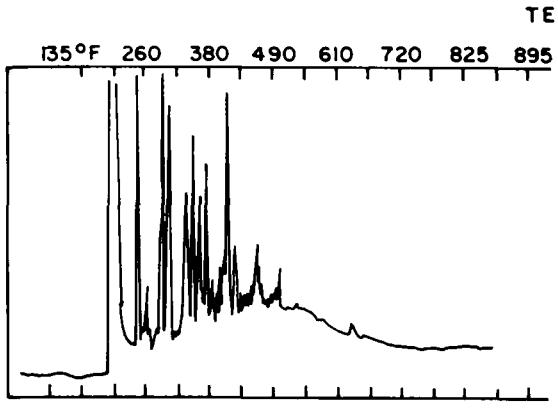


FIGURE 10 – BENZENE EXTRACT OF API CARBON

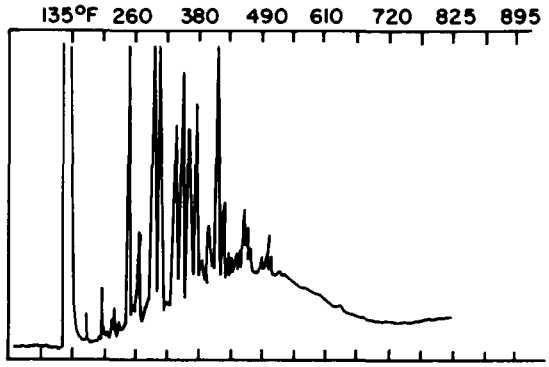


FIGURE 11 – METHYLENE CHLORIDE EXTRACT OF API CARBON

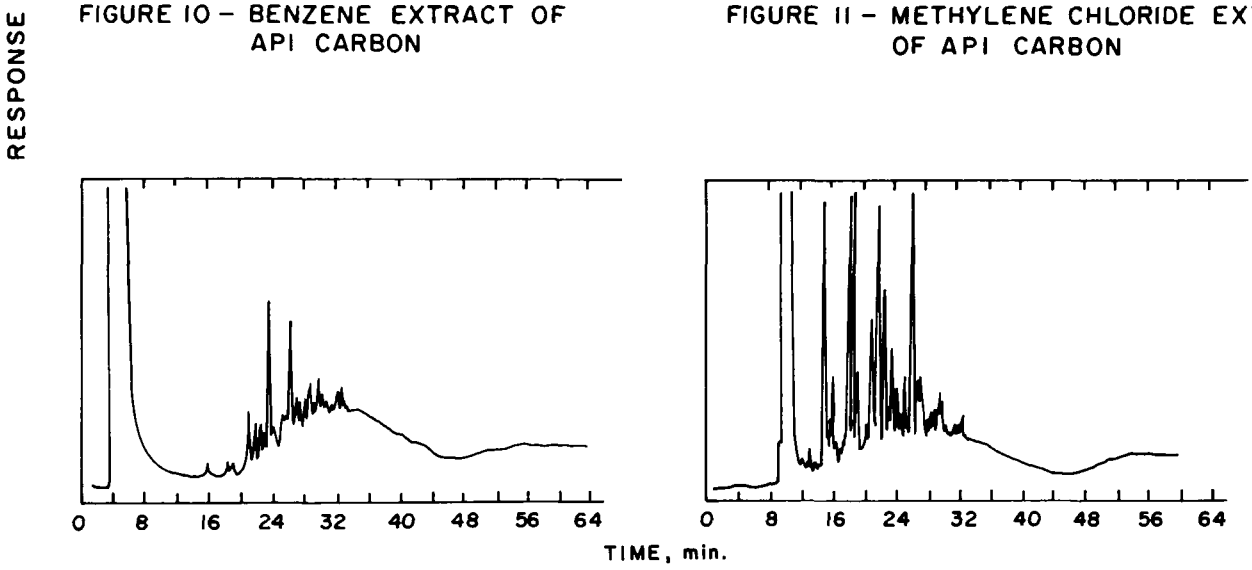


FIGURE 12 – METHANOL EXTRACT OF API CARBON

FIGURE 13 – HEXANE EXTRACT OF API CARBON

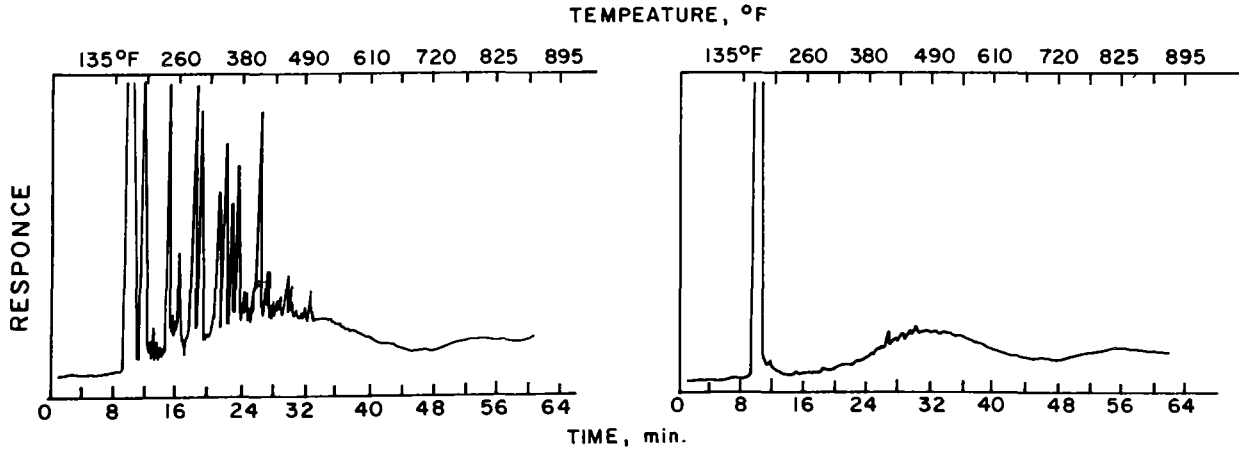


FIGURE 14 – CHLOROFORM EXTRACT OF API CARBON

FIGURE 15 – CHLOROFORM EXTRACT OF FC CARBON

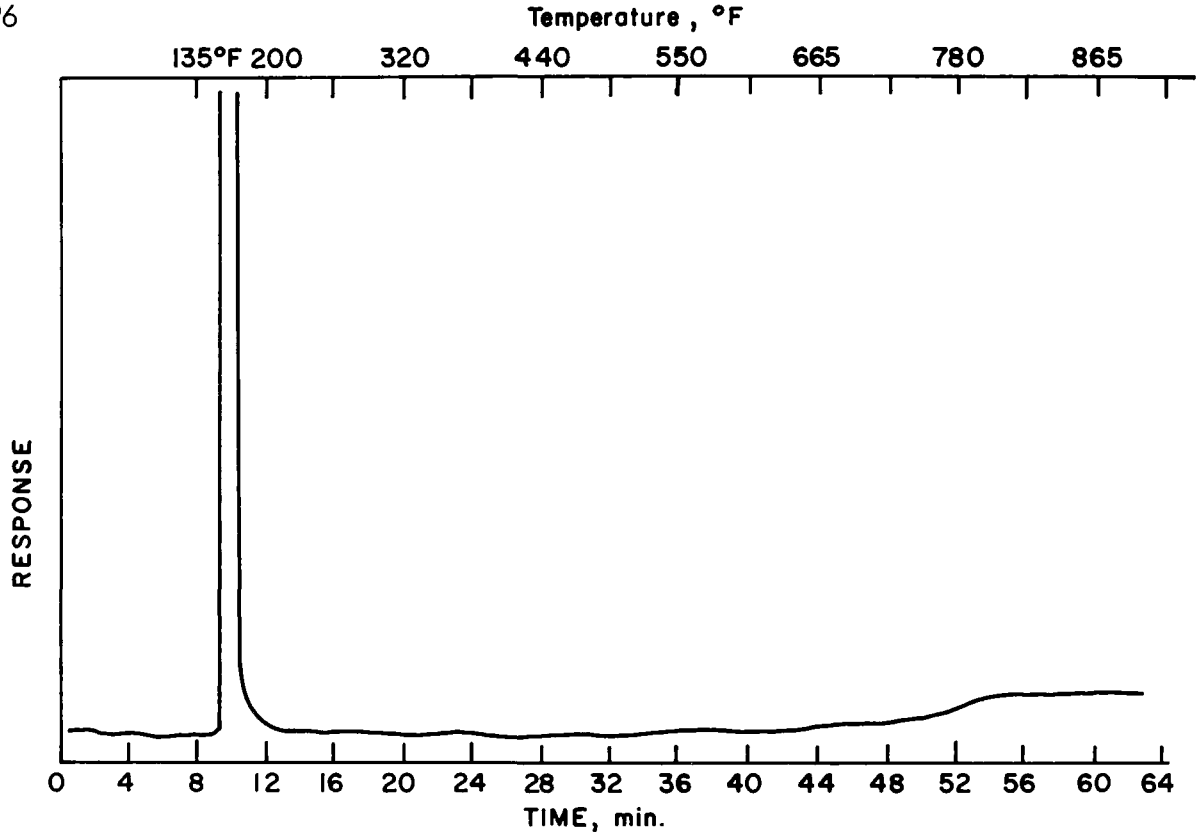


FIGURE 16 - CHLOROFORM EXTRACT OF NEW ACTIVATED CARBON

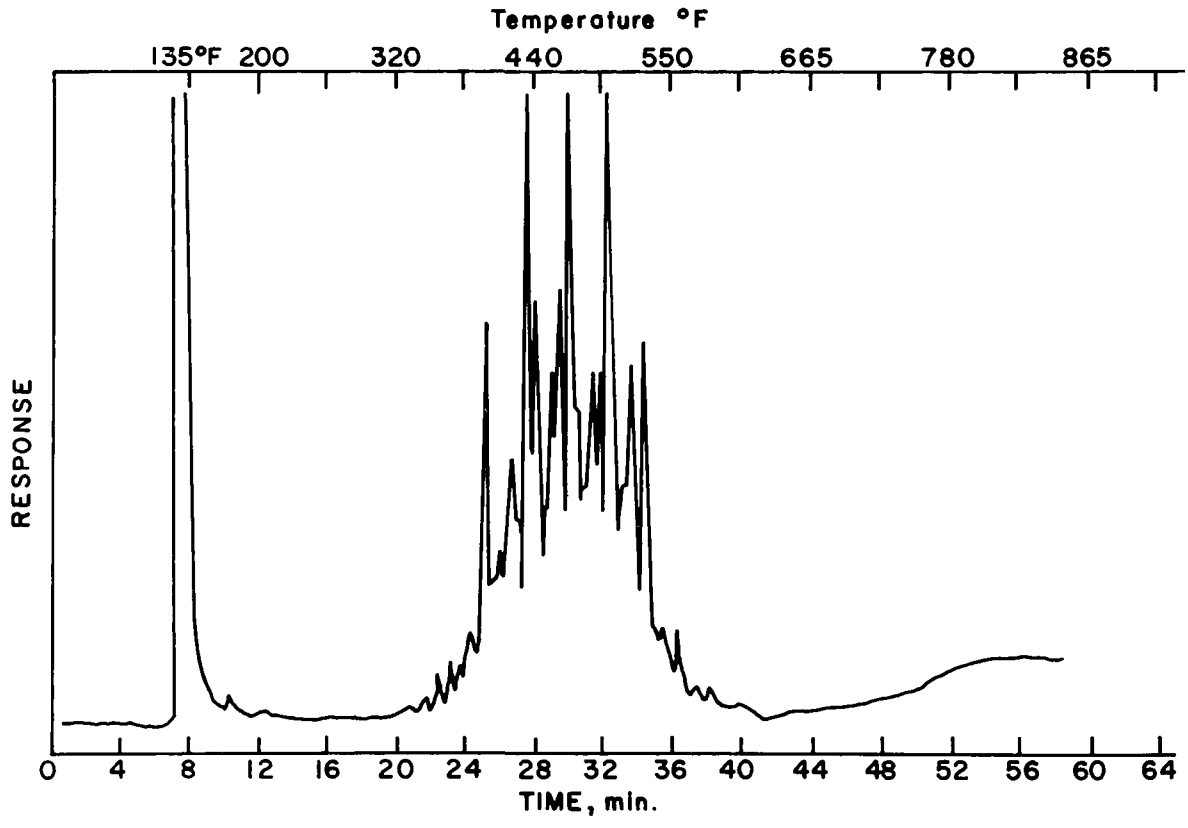


FIGURE 17 - STANDARD OIL MIXTURE

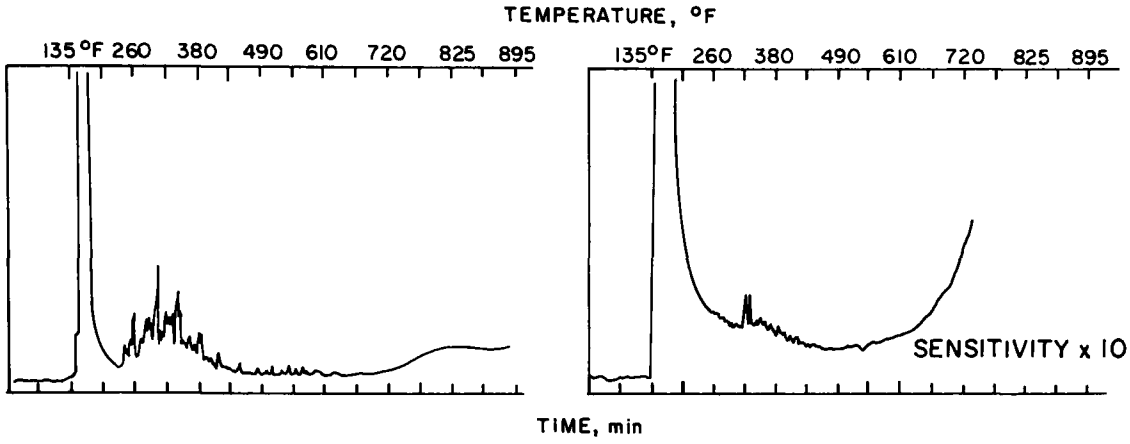


FIGURE 18 – APIC EXTRACT SATURATE FRACTION

FIGURE 19 – FCC EXTRACT SATURATE FRACTION

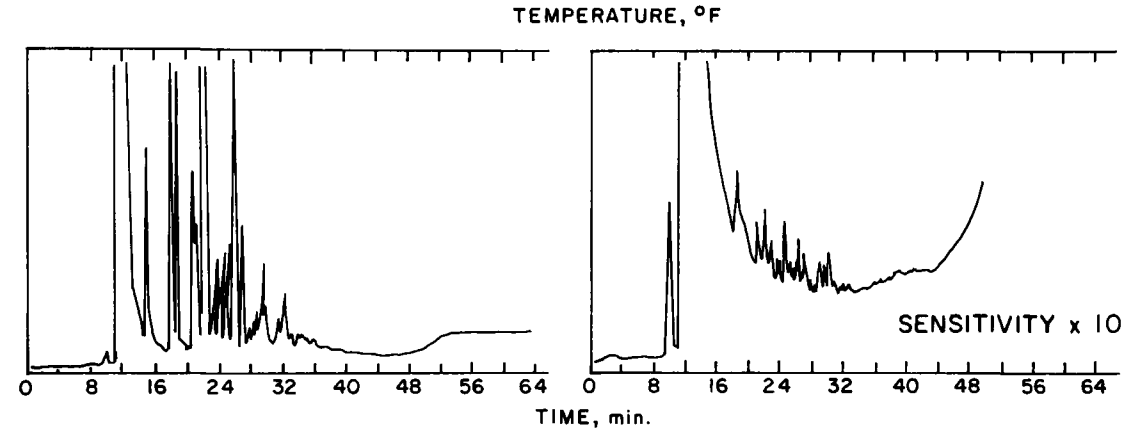


FIGURE 20 – APIC EXTRACT AROMATIC FRACTION

FIGURE 21 – FCC EXTRACT AROMATIC FRACTION

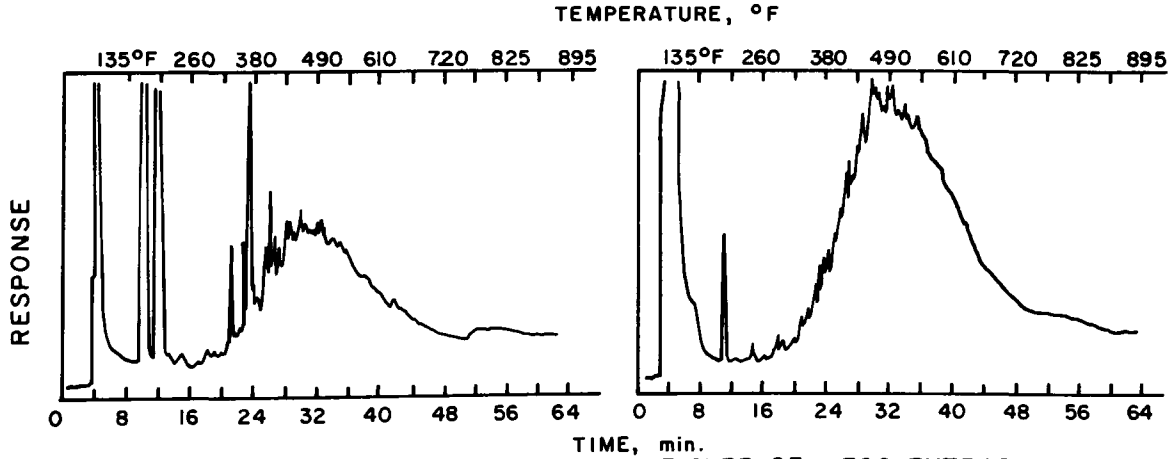


FIGURE 22 – APIC EXTRACT POLAR FRACTION

FIGURE 23 – FCC EXTRACT POLAR FRACTION

ACTIVATED CARBON TREATMENT OF COMBINED STORM AND PROCESS WATERS

M. A. Prosche
Atlantic Richfield Company, Watson Refinery, Carson, California

The Watson Refinery of the Atlantic Richfield Oil Company is located adjacent to the Dominguez Channel in Los Angeles County. This Channel is a non-navigable dredged tidal estuary which is lined with rip-rap and used specifically for the discharge of refinery and chemical plant waste waters and for rain water runoff.

In 1968, the Los Angeles Regional Water Quality Control Board made a study of the Dominguez Channel and determined that petroleum and chemical plant discharges were causing a problem due to the oxygen demand of their waste waters entering the Channel. The Control Board, in accordance with these findings, issued a resolution in February, 1968, which limited the total chemical oxygen demand (COD) from all industrial discharges into the Channel. These discharges also included any contaminated rain water runoff. The resolution was to be complied with by February, 1971.

As defined by the resolution, the Watson Refinery was limited to 1330 pounds per day of COD in its discharge water to the Channel. Meeting this requirement meant reducing the COD in its discharge waters by 95 per cent.

Fortunately, the Watson Refinery as a taxpayer of Los Angeles County was able to make arrangements with the Los Angeles County Sewer District to have its process waste water handled in the County's primary treatment unit. However, due to limitations in the County unit, the County was unable to handle rain water runoff. This presented a problem for the Watson Refinery due to the fact that the rain water collection facilities were interconnected with the process waste water collection system. Therefore, during periods of rainfall, the process waste water and rain water mixture could not be sent to the sewer district facilities, nor could it be sent to the Dominguez Channel due to high COD content of the process waste water.

To solve this problem a system was needed which would treat all the process water plus rain water during the rainy season for the removal of COD and allow its discharge to the Channel. A system was needed which could be started up easily when rain fell and then shut down when no longer required. The system selected was impounding of rain plus process water during the storm followed by activated carbon treatment to adsorb the COD material.

ADSORPTION SECTION DESIGN AND DESCRIPTION

Since it was planned to operate the plant only during the rainy season, it was felt there was no need to design for continuous carbon regeneration and changeout of the beds. Therefore, the design was based on use of only the carbon beds during the rainy season, and then regeneration of all the beds during the dry summer months in preparation for the next rainy season. The significant design criteria for the plant and impounding basin were as follows:

Design Criteria	
Flow Rate	100,000 BPD 3,000 GPM
Inlet COD	250 ppm
Outlet COD	37 ppm
Impounding Basin	1.2 million barrels capacity

Following the accumulation of 0.1 inches of rainfall, regulations call for diverting process water from the sewer system. This is accomplished automatically by means of a solenoid operated valve actuated by a rain gauge. Process water plus commingled rain water is then switched to the 1.2 million barrel impounding basin. Depending upon the specific situation, the carbon plant can be started up immediately for discharge to the Channel or it can be started up later following the rain. A flow diagram of the adsorption section of the plant is shown in Figure 1.

Impounded water is delivered to the plant through a 14" line from the basin. The water is then delivered to a distribution trough where it is distributed to 12 adsorber cells by adjustable slide gates. Each of the twelve cells is 12' by 12' square and 26' feet deep. Each cell originally contained 13' of carbon having a dry weight of about 50,000 pounds.

The water passes down through the carbon bed where it collects in the underdrain system. Supporting the carbon is a one-foot layer of gravel on top of a Leopold tile underdrain system. The treated water then flows through 6" lines from each cell to a 24" collection header leading to the effluent retention sump. Each 6" discharge line has a sample point and an air-operated pinch valve which can be shut during backwashing.

If necessary to further control COD, a chlorine-water solution may be injected into the incoming treated water stream. Approximately 15 minutes retention time is allowed for chlorine contact in this sump. From the sump the water flows by gravity to the Channel.

Each carbon bed must be backwashed whenever it will not pass its share of water flow due to buildup of solids on top of the carbon. This is indicated by the rise in the level of the water in each carbon cell. When the level rises to the height of the backwash troughs, the flow to and from the bed is stopped, and treated water from the backwash sump is pumped up through the bed to expand it and flush out accumulated solids. The turbid water overflows into the backwash troughs to the backwash effluent sump where it is pumped back to the reservoir for settling and retreating.

EPA DEMONSTRATION GRANT

Following completion of the plant, a demonstration grant was received sponsored by the Water Quality Research Division of Applied Science and Technology of the Environmental Protection Agency. The specific objectives of the demonstration project were as follows:

1. Determine feasibility of activated carbon as a treatment system for storm runoff and refinery process waters.
2. Evaluate performance of the system.
3. Determine operating costs.
4. Assess reliability of the system.

The report relative to this project has now been published by the EPA.

ADSORPTION SECTION OPERATION AND PERFORMANCE

The carbon plant was first placed in operation in May, 1971 for some preliminary test work prior to the rainy season. At that time the test water was synthesized using process water diluted with service water. Operation with rain water and process water was not required until later that year in December. At that time sufficient rain fell to require placing the unit in full operation at the design rate of 3,000 gpm total to all twelve cells. Subsequent to that a total of 6 runs were made processing impounded water from the intermittent rain storms that followed. The performance data for all of these runs are shown in Table 1.

Typical Performance Data First Rainy Season

Table 1

Run Number	Length of Run, Hours	Feed Rate, GPM	Average COD	
			Feed	Effluent
1	44	3000	326	43
2	48	3000-2000	360	48
3	38	2000	374	86
4	18	2000	310	67
5	95	1000	237	100
6	22	2000	147	93

During the initial runs the COD of the feed was higher than design and the plant was unable to produce the desired removal. Therefore, the feed rate was reduced to 2,000 gpm. Even at this lower rate the effluent COD content was greater than the regulations allowed and feed rate was again reduced to 1,000 gpm. By the end of the season the reservoir COD had dropped to 147 ppm due to rain dilution and the rate was increased to 2000 GPM. However, performance continued poor even at this low concentration.

A good evaluation of the performance of the plant during this first season of operation is difficult due to the significant variations in feed COD and the necessity of having to reduce the feed rate from 3000 to 1000 gpm. However, COD data for each cell was recorded during the course of the run and some generalizations are possible. At the end of the season the COD loading in each cell varied from 0.2 pounds of COD per pound of carbon to a high of 0.3 pounds of COD per pound of carbon. During the season a total of 52,000,000 gallons of water were processed. The average feed COD concentration was 377 ppm while the effluent averaged 67 ppm. The carbon loading averaged 0.23 pounds COD per pound of carbon. It also appeared that the potential maximum carbon loading at a constant effluent COD concentration was quite sensitive to the COD of the feed.

Other data collected during the first season's operation included measurement of the carbon's adsorptive ability at various depths in the bed after a period of operation. One of the cells was taken out of service after 208 hours of operation and the carbon was sampled at various depths to test its relative adsorptive efficiency as compared to virgin carbon. The data are shown in Figure 2. The data show that the top two feet of carbon were completely exhausted while the last five feet were still 65 per cent of virgin adsorptive

ability.

Prior to the second rainy season, we made several significant changes in operation. In order to increase the adsorptive capacity of the unit, 15,000 pounds of carbon were added to the existing 50,000 pounds in each of the cells. This increased the bed depth from 13 feet to 17 feet. It was also decided to recycle effluent water back to the feed in order to control the feed COD to a concentration of not greater than about 250 ppm. This change in operation was made after noting during the first rainy season of operation that the effluent COD level varied directly with the feed COD concentration and the specification COD quantity to the channel would be exceeded during periods of high feed COD. It was also felt that controlled feed COD would allow a higher ultimate COD loading of the carbon. One other modification made was the aeration of the effluent recycled back to the feed to prevent growth of anaerobic bacteria in the beds.

For the second rainy season of operation, we elected to operate part of the plant on a continuous basis, regenerating each bed as it became spent, and returning the regenerated carbon for use again. To accomplish this five of the cells were placed in continuous staggered operation along with the regeneration furnace. This was the largest number of cells operating in a progression mode that could be accommodated by the capacity of the regeneration furnace. The remaining seven cells were used for once-through processing as was done during the first rainy season. In all cases the flow to each cell was held constant at 250 gpm which included the waste water feed from the reservoir plus the recycle dilution.

Typical performance data for one of the five cells operated in staggered mode are shown in Figure 3. This figure shows the relationship between feed and effluent COD and the COD loading on the carbon. During initial operation of this cell, it was elected to discontinue service and regenerate after the effluent from the cell reached a COD concentration of about 50 ppm. This corresponded to a carbon loading of 0.20 pounds of COD per pound of carbon and a run length of 22 days.

The carbon was regenerated and returned to the same cell. In the second run the cell was allowed to operate until the effluent reached a COD concentration of about 100 ppm. This corresponded to a carbon loading of 0.40 pounds COD per pound of carbon and a run length of 38 days.

The performance of the seven cells that were operated on a once through basis with no regeneration is shown in Figure 4. Effluent COD concentration was allowed to reach 50 ppm before all the cells were shut down for later regeneration. As shown in the figure, the corresponding carbon loading attained in all of these cells was 0.30 pounds COD per pound of carbon and the run length was approximately 30 days.

The evaluation of performance of the carbon plant for this second rainy season was again based on the combined operation of all the cells. During the season a total of 102,000,000 gallons of water were processed. The average diluted feed COD concentration was 233 ppm while the effluent averaged 48 ppm. The carbon loading averaged 0.26 pounds COD per pound of carbon.

A summary of the performance of the plant during the two rainy seasons of operation is shown in Table 2.

Adsorption Data
Table 2

Commercial Operation	Feed COD, PPM Average	Effluent COD, PPM Average	Carbon Loading Lb. COD/ Lb. Carbon Average
First Rains	377	67	0.23
Second Rains	233	48	0.26

As noted previously, problems with varying feed COD and algae growth were experienced during some of the runs. These problems undoubtedly limited the performance to poorer levels than could have been attained under ideal steady state conditions. However, these are the real problems that exist when treating refinery waste waters and we therefore feel the carbon loadings attained are indicative of the true performance of the commercial plant.

CARBON HANDLING AND REGENERATION

This system is shown in Figure 5. The spent carbon is removed as a water slurry through a carbon removal trough and nozzle even with the top of the gravel layer. The slurry flows by gravity and with the aid of water jets in the carbon removal trough to the spent carbon transfer pump sump. From here a rubber lined pump transports the carbon slurry into the spent carbon tank. The tank has capacity to contain the contents of one cell. From this tank the carbon is educted with high pressure water to the dewatering screw above the regeneration furnace. A timer valve on the spent carbon line feeding the eductor opens and closes at timed intervals to allow close control of the carbon flow to the regeneration furnace. The dewatering screw separates most of the water from the spent carbon slurry and the drained water is returned to the reservoir. The carbon discharging into the furnace contains approximately 50 per cent by weight of water.

The regeneration furnace is a 56" I.D. multiple hearth type with a total of six hearths. It is gas fired and internal temperatures are controlled to about 1600°F. A center shaft with rabble arms moves the carbon across each hearth and downward through the furnace. An elaborate flue gas quench and scrubber system is installed to meet local Air Pollution Control District requirements. The furnace is designed to regenerate 8,000 pounds of carbon per day or one bed in about 6 to 7 days.

The regenerated carbon drops into a quench tank just below the furnace from where it is educted into the regenerated carbon tank. From this tank the carbon is then educted and transported through a hose back to the same cell where it originated.

The carbon handling system has worked very well. The original 1" cast iron eductors were too small and soon lost capacity due to erosion. Larger stainless steel eductors and a reduction of motive water pressure from 110 psig to 50 psig have remedied this. Also originally we had some problem with displaced support gravel from the bottom of the cells plugging up the eductors. This was remedied by constructing a gravel screen in the top of the spent carbon tank to remove the gravel. The time required to transfer the carbon out of the cell to the spent carbon tank is about 14 hours while transfer back to the cell from the regenerated carbon tank takes about 7 hours.

Operation of the regeneration furnace has been excellent. The major effort relative to this operation has been to develop a reliable method for determination of the quality of the regenerated carbon. After operational guidelines were developed, the furnace consistently regenerated the spent carbon to near virgin activity.

Our experience indicates that about a 5 per cent loss is incurred during carbon handling and the regeneration. We feel the majority of this is due to attrition of the carbon and resulting production of fines. These fines are backwashed out of the cells prior to being placed in operation and end up back in the reservoir where they settle out.

OPERATING COSTS

Actual operating costs for the second year of operation are shown in Table 3.

Cost Data
December, 1972 - March, 1973
Table 3

Cost Areas	Cents Per Thousand Gallons of Water Treated	Cents Per Pound of COD Removed
Utilities	9	4
Repair Labor	3	1
Operating Labor	15	7
Carbon	11	5
Miscellaneous	2	1
Total	40	18

Updating these costs to 1976 levels would give about 56 cents per thousand gallons of water treated, or about 25 cents per pound of COD removed.

CONCLUSIONS

The plant has proved to be easy to maintain, easy and quick to start up, simple to shut down and leave in a standby stage, and very reliable in its performance.

For the unique intermittent type operation required at the Watson Refinery, we feel the Carbon Adsorption Process has been successful. However, we do not feel that this conclusion would necessarily be the same for a continuous operation requirement or some other unique situation.

DISCUSSION

Gantz: Did you experience any solids handling problems?

M. A. Prosche: We had no solid handling problems. We had some concern about the silt, sand, and carbon fines building up in the bottom of the reservoir. But during the summer months we just moved in a front-end loader and removed all solids.

Ben Buchanan: I was wondering what control methods you used on your reactivation furnace to control the reactivation.

M. A. Prosche: What we finally did was measure the ABD, apparent bulk density, of the carbon being fed to the furnace and the regenerated carbon from the furnace. We found that a reduction of gm/cc in ABD was sufficient to bring the carbon back up to 100% adsorption efficiency. In actual practice the operators had a pre-weighed cube and a balance at the unit. The cube was then used to weigh a fixed volume of feed and product carbon and the difference used as the guide to furnace operation. As a generality, spent carbon had an ABD of 0.56 gm/cc and the regenerated 0.50 gm/cc.

Ben Buchanan: How did you determine how much of your carbon was lost by attrition, and how much was lost through burning in your regeneration furnace?

M. A. Prosche: The only insight we had was to roughly know how much carbon we put back into the cells after regeneration, and the amount of carbon that had accumulated in the bottom of the reservoir after a season of operation. It appeared to us that the accumulated fines in the reservoir about equaled the loss in volume in the beds.

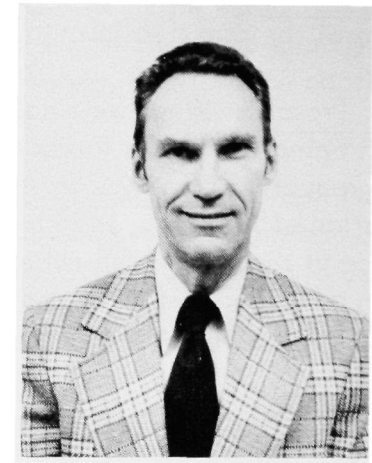
Ben Buchanan: There is a little problem with measuring volumes because I think the losses that you have from burning the carbon do not necessarily reduce the size but many of those losses are inside the particle and do not show up. You will get a weight loss but you do not necessarily get the same volume loss.

M. A. Prosche: That could very well be. This was not a research project but strictly a demonstration project to determine feasibility and costs.

Larry Echelberger: Has there been any attempt to reuse this water in your refinery after you clean it up? Is it high in TDS? Do you attempt to reuse the water at all?

M. A. Prosche: The discharge is primarily refinery waste water diluted with rain water. The waste water consists of untreated service water, desalter waters, and water from tank bottoms. So this water would require extensive pretreatment prior to any reuse. Our primary thrust now is to reuse stripped sour water which is essentially contaminated consensate. Following the successful utilization of all of this water, we can then turn our attention to the more difficult problems of reusing the waste water.

BIOGRAPHY



Marvin A. Prosche is Manager of Refinery Technology at Atlantic Richfield's Watson Refinery. He holds a B.S. in ChE from the University of Notre Dame and an M.S. in ChE from the University of Illinois. His experience includes 25 years of petroleum refinery process design and process engineering.

FIGURE 1

WASTE WATER ACTIVATED CARBON TREATMENT PLANT

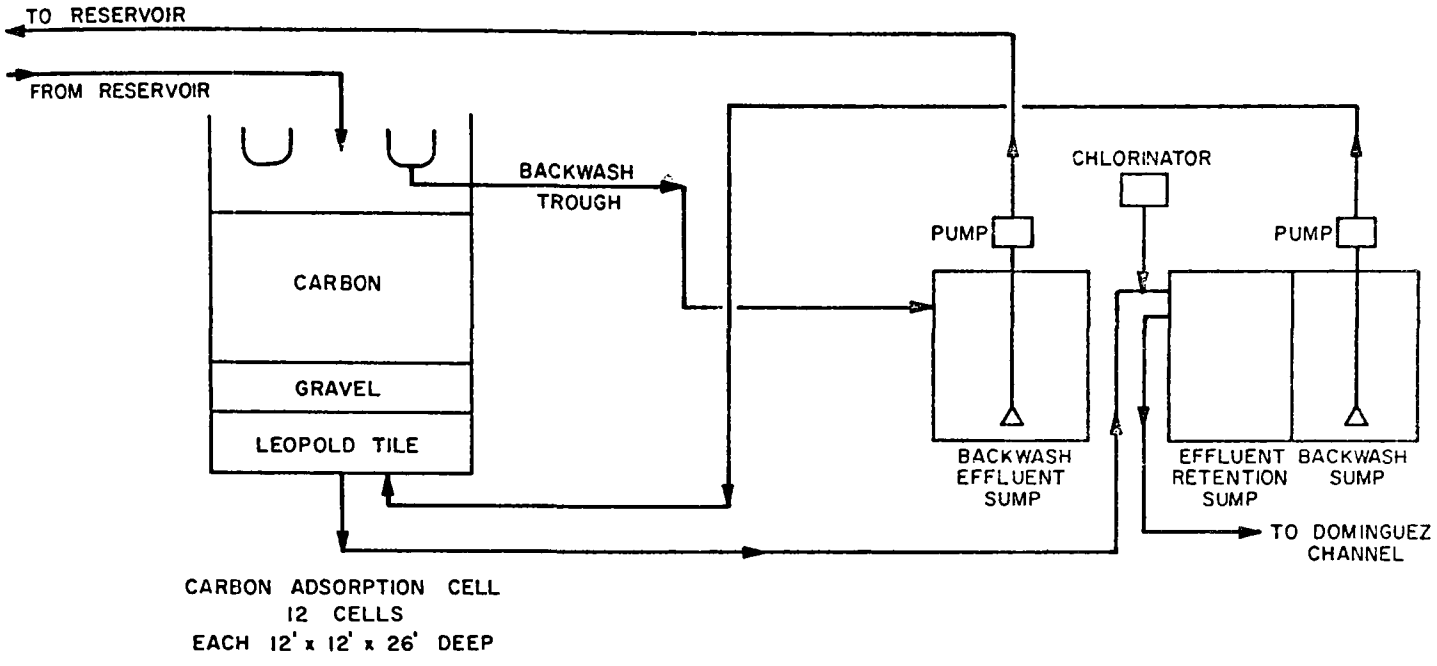
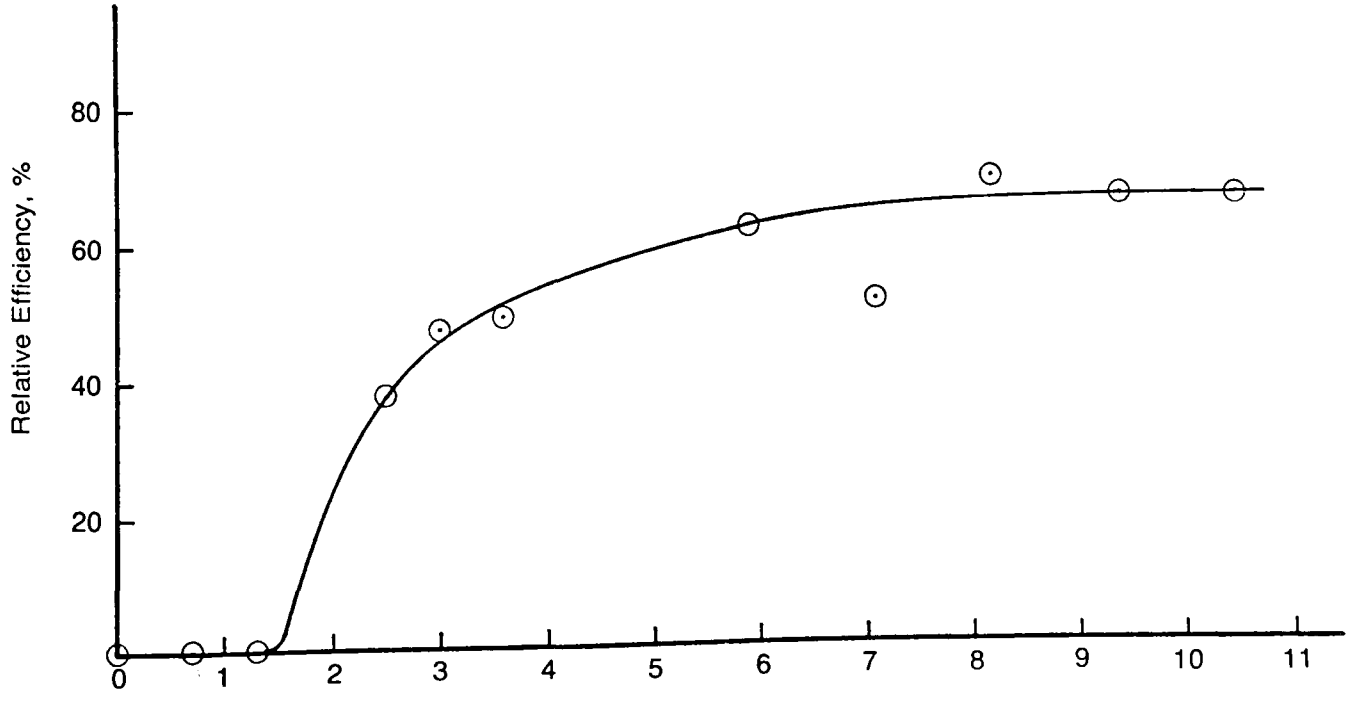


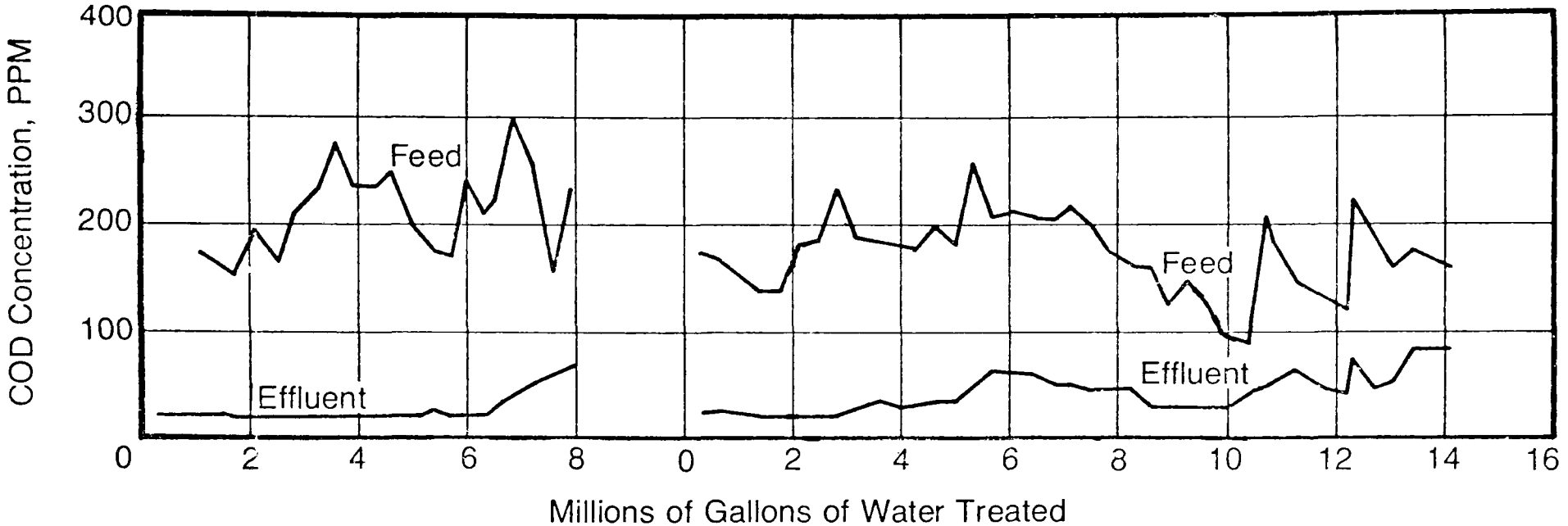
Figure 2

Relative Efficiency Profile of Cell
After 208 Hours of Operation @ 250 GPM and
650 to 600 PPM COD in Feed



Typical Performance Data—Staggered Operation
Second Rainy Season

Figure 3



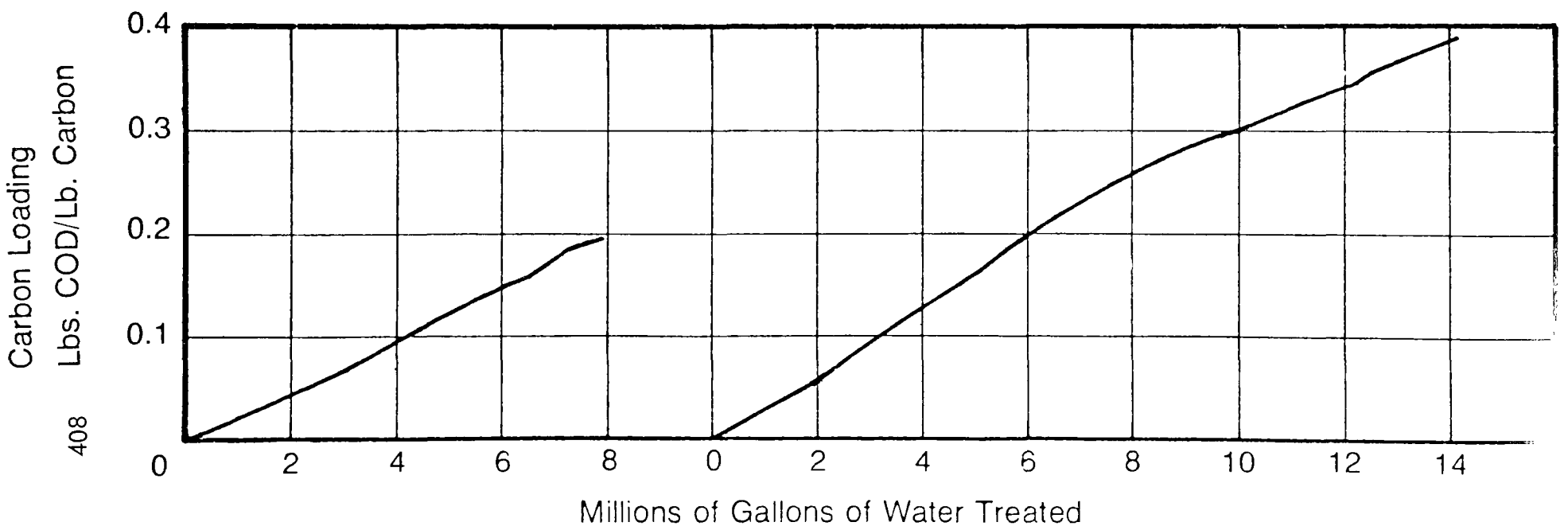
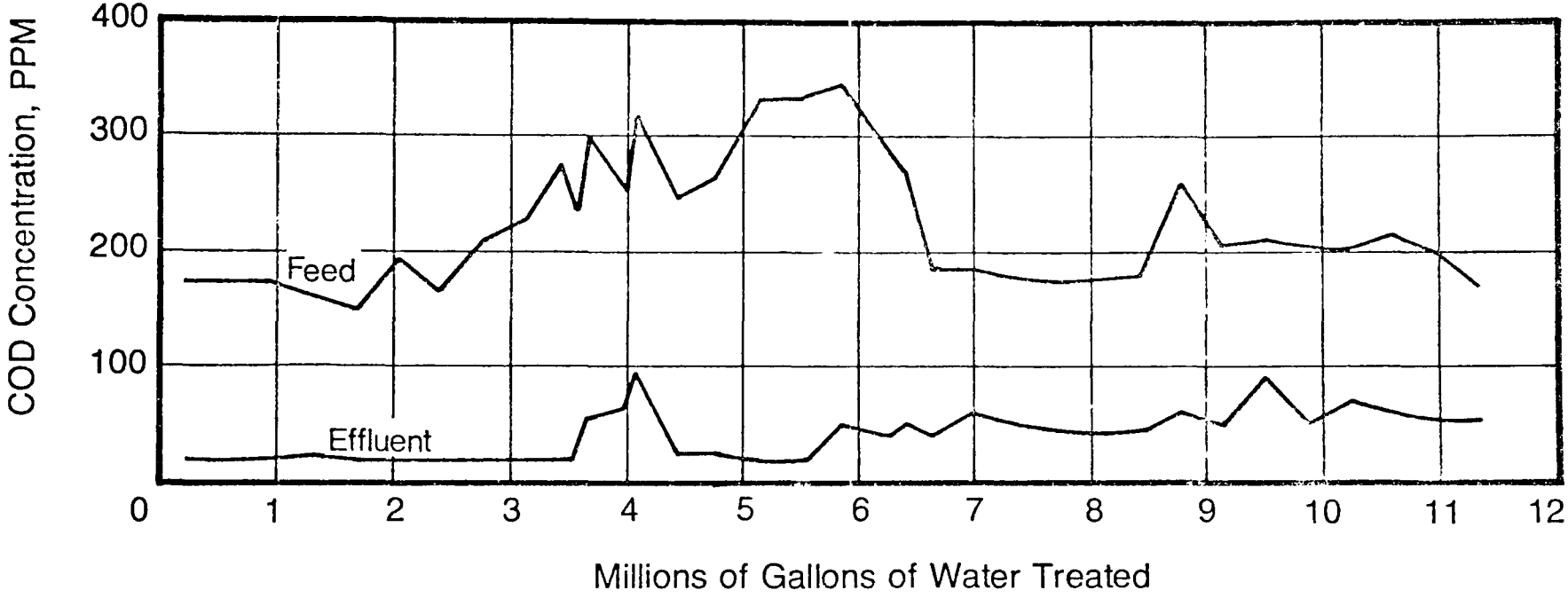
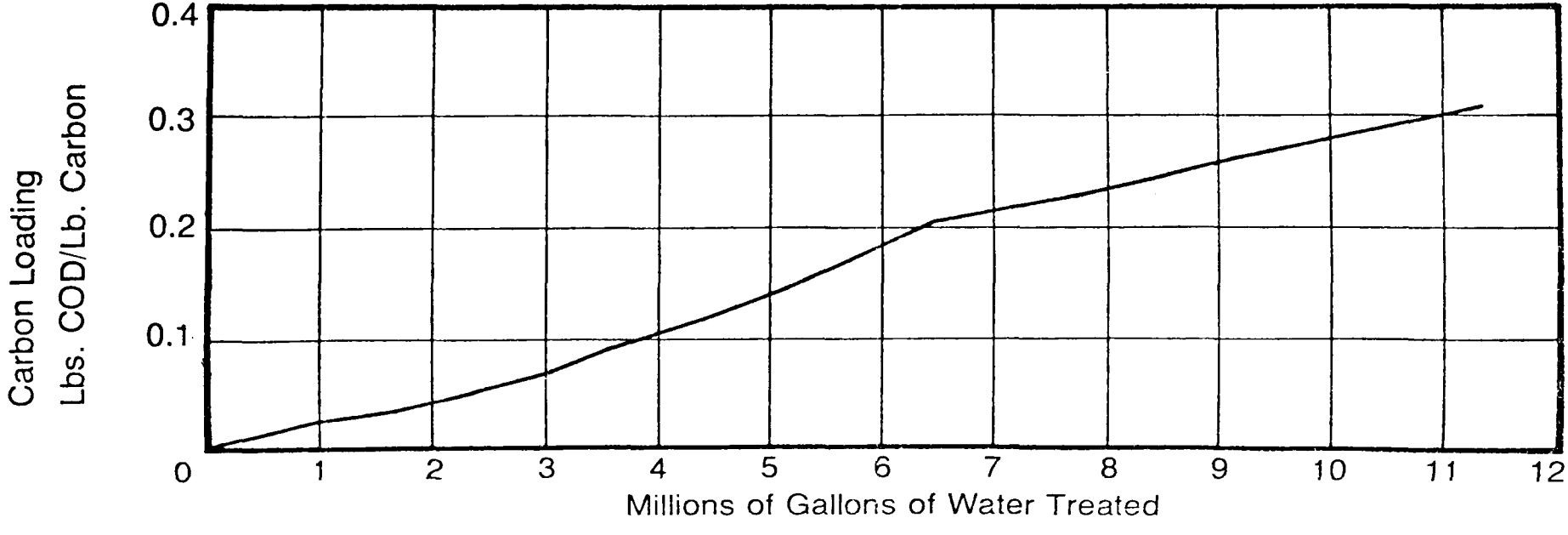


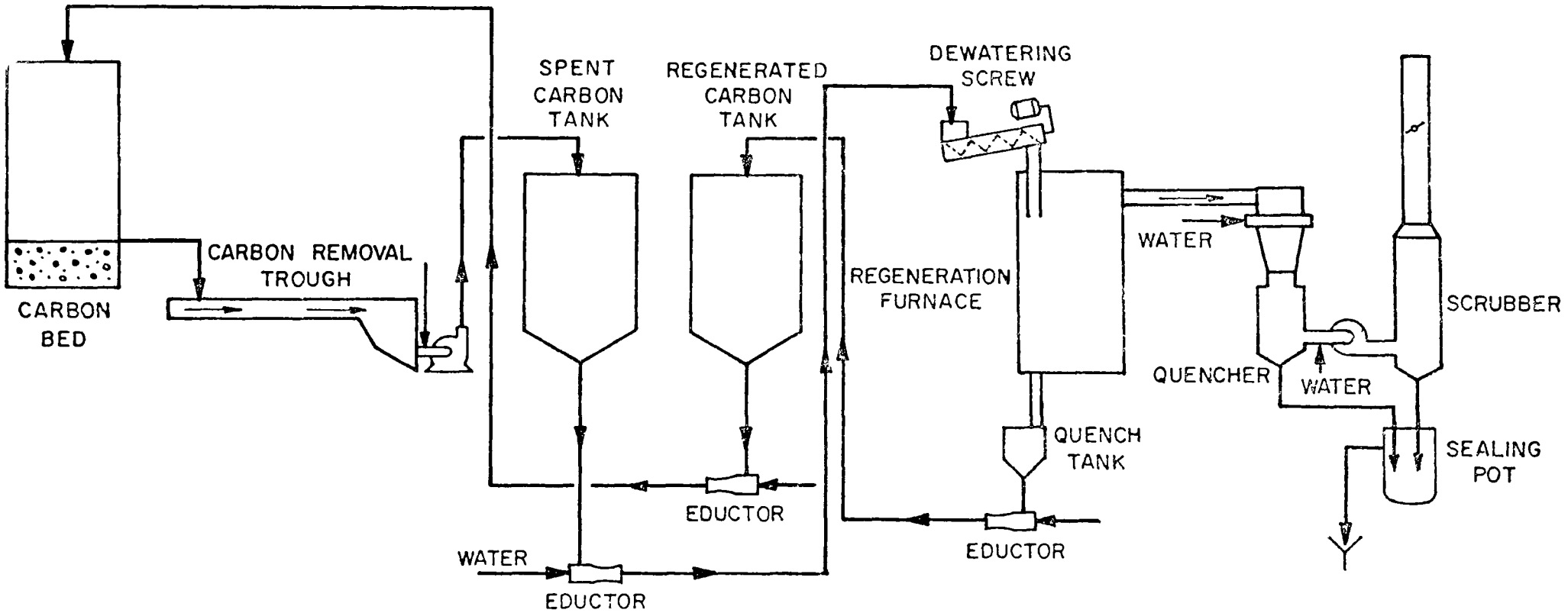
Figure 4

Performance Data—Bulk Processing Cells
Second Rainy Season





CARBON TRANSFER AND REGENERATION SYSTEM



SESSION VI

"MISCELLANEOUS TOPICS"

Chairman

M.K. "Don" Hutton

Manager, Mechanical and Environmental Engineering
Kerr-McGee Refining Corporation
Oklahoma City, Oklahoma

Speakers

Lial F. Tischler

"Inherent Variability in Wastewater Treatment"

R.T. Milligan

"Reuse of Refinery Wastewater"

Sterling L. Burks

"Biological Monitoring of Petroleum Refinery Effluents"

Ronald G. Gantz

"API - Sour Water Stripper Studies"

BIOGRAPHY M. K. "Don" Hutton

Graduate of Oklahoma State University. B.S. in Mechanical Engineering, 1956. Upon graduation employed as Engineer at Shell Oil Company, Deer Park Refinery until March of 1964 at which time he was transferred to Shell Oil Company's Odessa Refinery as Plant Engineer until July 31, 1966. August 1, 1966 employed as Engineering Assistant to the General Manager of Petroleum Refining, Kerr-McGee Corporation, Oklahoma City, Oklahoma. Present position is Manager, Mechanical & Environmental Engineering, Kerr-McGee Refining Corporation, Oklahoma City, Oklahoma.

INHERENT VARIABILITY IN WASTEWATER TREATMENT

Lial F. Tischler
Engineering Science, Inc., Austin, Texas

INTRODUCTION

The term "inherent variability" as applied herein can be defined as that variability in effluent quality from a properly designed and operated waste treatment system which is attributable to the basic nature of the treatment processes, the characteristics of the wastewaters, and climatological conditions - none of which can be significantly altered by externally applied changes. Simply stated, it is the minimum variability which can be practically obtained assuming proper system design, management, and operational control (including in-plant changes, equalization, and effluent holding capacity).

Variability in effluent quality has assumed more importance in recent years since the effluent limitations guidelines promulgated by the U.S. Environmental Protection Agency (EPA) for the petroleum refining industry and for other industrial point source categories are based on selected long-term attainable effluent qualities and allowable daily and monthly variability for each controlled constituent. The published EPA effluent limitations are based on maximum allowable daily and monthly average discharges; since traditionally treatment system design has been on more of an "average" or steady-state basis, it becomes mandatory to consider the potential variability in a treatment system's effluent quality if it is to comply with the limits in a cost-effective manner.

To accomplish this it is necessary to consider the effect of each unit process in a complete system on the overall effluent variability. Each unit process can either attenuate or increase variability, depending on process characteristics, wastewater quality, and external stimuli. This paper examines the inherent effluent variability of the major unit processes which are found or will probably be found in petroleum refinery treatment systems designed to comply with the 1977 (BPCTCA) or 1983 (BATEA) EPA effluent limitations. This is done by analyzing data collected from a number of full-scale refinery treatment units. Bench-scale and pilot-scale data are inadequate for an analysis of effluent variability since the phenomena which are responsible for variability are not amenable to scaling down. After this evaluation of effluent variability for various treatment systems, a basis for using the results of this analysis to estimate potential effluent variability in petroleum refinery treatment units is presented.

DEFINITION OF VARIABILITY PARAMETERS

Before proceeding it is desirable to define variability in a probabilistic sense in order to be consistent in all analyses so that data can be compared directly. The easiest way to define variability is in the form of a ratio of the value of a constituent at a specified maximum probability to the mean value of that constituent (or

median for log-normal distributions). One way of doing this is to use a multiple number of standard deviations from the mean. This is convenient for a normal (Gaussian) population but is not as useful for log-normal distributions. In this investigation, variability is defined as the ratio of the 99 percent probability of occurrence value to the 50 percent value. Although the 50 percentile value for a log-normal distribution is the median, the arithmetic mean was used to conform to the basis used by EPA in the guidelines (Ref. 1). It is important to note when the variability is for monthly average data as opposed to daily data. Monthly average and daily variability ratios cannot be compared since the averaging technique masks variability to a considerable extent. The same fact holds true, of course, for grab samples versus daily composites, however, in most cases this paper has considered the latter two sample types as interchangeable.

The ideal approach in formulating variation allowances is to measure inherent variability in exemplary treatment units which reflect a wide spectrum of raw waste load, temperature, and dissolved solids. These data can be resolved statistically and the long-term (one year or more) distribution can be determined. The shorter-term limits can be calculated statistically from this distribution. The EPA has used this concept in developing variability factors for 24-hour maximum and maximum 30-day average variations based on annual observations. (It should be recognized that states have the prerogative under the law (Ref. 2) to add grab sample provisions to the NPDES permit, and the proper establishment of these limits requires a comprehensive review of performance data and a detailed statistical analysis (Ref. 3, 4).) A significant difference in the variability of effluent quality between flow-weighted samples and grab samples during the same period was recently demonstrated and it emphasized the potential inaccuracy of using an insufficient number of grab samples as a basis for determination of compliance or as an input for operational decision (Ref. 5).

Almost all of the data distributions analyzed in the investigation were found to approximate log-normal distributions; most other distributions, being of a higher order, could be approximated by assuming a log-normal distribution. The variability factors were calculated in the following manner for each constituent of the refinery wastewater data base used in this study:

(1) the effluent loading data were grouped, rank-ordered, and plotted on log-normal probability paper;
(2) the line of best fit was determined;
(3) a daily variability factor was defined as the ratio of that effluent loading encompassing 99 percent of the expected daily variation to the long-term arithmetic average effluent loading; and
(4) a monthly variability was defined as the ratio of that effluent loading encompassing 99 percent of the expected monthly variation to the long-term arithmetic average effluent loading.

The 99 percentile values were taken directly from the best fit curves. The

99:50 variability ratio can be interpreted as a multiplier which, when multiplied by the long-term average concentration or mass discharge rate, will give a value which will only be exceeded once in every 100 samples collected. If it is assumed that the effluent data follow a log-normal probability distribution, the 99:50 ratio can be used to define the median value of the distribution, the geometric standard deviation, and thus the concentration at any other desired probability of occurrence.

CAUSES OF EFFLUENT VARIABILITY

There are many factors which cause "inherent variability." The most significant "cause and effect" aspects are discussed below.

Variations in Raw Waste Load (RWL)

Although the impact of raw waste load variation can be minimized by in-plant changes and by installing equalization, surge, and off-specification storage basins prior to treatment, transitory loads from most refinery processes cannot be completely sequestered. Changes in feedstock, such as crude oils of varying specific gravities, sulfur, nitrogen, and trace metal content, result in raw waste loads which vary both in quantity and quality, with subsequent effects on treatability. Changes in product mix and product specifications have a similar effect. The reduction of wastewater flow from production units through water reuse and good housekeeping practices normally results in higher influent concentrations of organic constituents to the treatment plant. This, according to most biochemical kinetic models, will correspondingly result in an effluent of higher concentration. Thus, cyclic changes in raw waste loads not fully sequestered will result in effluent quality variation in each type of treatment used. Other events, such as maintenance turnarounds, production of specialty items, changes in calendar production patterns, and contrasts in dry weather and wet weather operations simply increase the variability range. It should be emphasized that the effluent variation due to RWL as discussed here includes only those changes necessary for manufacturing the product and excludes effects due to accidental dumps or spills and poor housekeeping.

The inclusion of storm water in waste treament facilities can also increase variability, depending on the handling procedures used. If separate storm sewers, impoundment facilities, and controlled discharge to treatment are used, the effect on variability will be low. Conversely, if a combined storm/process sewer system is used and impoundment facilities are not available, variability in treatment performance will be high.

Table 1 presents variability ratios for the raw waste loads at four "case history" refineries. It can be seen that the ratios between the mean and peak values are not too extreme for these refineries. This illustrates an important concept in comparing variability ratios for various unit processes and treatment systems: variability expressed as a ratio to the mean value for a given parameter is often a function of the magnitude of the mean value. For example, when the mean is a relatively large number as in the raw waste load figures, the variability expressed as a ratio will tend to be low. Conversely, at extremely low effluent concentration values for some

constituents, the chance of getting one sample out of 100 which is three or four times the mean value is much greater. This concept will be illustrated graphically later in this paper. Note that the raw waste loads given in Table 1 are not truly untreated wastes; these samples are taken after primary oil/solids separation. These ratios can be considered to be representative of the variability attainable for each parameter shown if storm water is carefully controlled and the separators are adequately designed.

Variations in Temperature

The effect of temperature on biodegradation rates has been extensively investigated and is generally well documented (Ref. 6, 7). This component of inherent variability is therefore accepted, although the significance of the temperature effect on variability is open to debate. Although this influence is primarily evident on a long-term or seasonal basis, short-term variations are also possible in some geographical areas. The degree of variation is not only attributable to water temperature, but also to the nature and complexity of the wastewater. When most of the organic constituents are in the colloidal or suspended form, for example, the performance of an activated sludge system is less subject to temperature fluctuations than when treating soluble organic materials. This is attributed to the fact that biochemical reactions removing soluble organics are more temperature-sensitive than are physical or "biosorption" mechanisms which remove colloidal or suspended organic matter. Observed temperature effects on biological systems treating complex soluble wastewaters (such as petrochemical discharges) are more pronounced than when more readily degradable soluble wastewaters are treated (such as food processing effluents).

Physical and chemical treatment processes can also be affected by temperature particularly rapid temperature changes. Density currents can form in units which rely on gravitational process for solids/liquid or liquid/liquid separation. These density currents can cause short circuting and loss of treatment efficiency. An example of this would be the sudden discharge of cold storm water into a gravity separator filled with warmer water. Thus, careful attention must be given to the design of treatment units to minimize these effects. Most chemical reactions are also affected by temperature, including chromium reduction/precipitation and similar processes. In general, reactions proceed more slowly at lower temperatures and a chemical treatment unit process designed for optimum operation at high temperatures may perform poorly if the wastewater cools substantially.

Data showing the effect of temperature on treatment processes have been presented in the literature. However, the effect of temperature variation on a full-scale refinery waste treatment plant has not been rigorously treated. Figure 1 shows the effect of temperature on effluent variability of BOD for a refinery using an aerated lagoon system (Ref. 8). An aerated lagoon, because of its large surface area and long hydraulic retention time, can be expected to show more temperature impact on efficiency than any other type of biological treatment unit with the exception of facultative waste stabilization ponds. As an illustration, if all of the 13 monthly averages are averaged to determine the annual average mass discharge of BOD, and this average is compared to the maximum of the monthly averages (February), a ratio of 2.56 is obtained. However, if the data are arbitrarily divided

into two groups, warm weather (May through November) and cold weather (December through April) the corresponding seasonal variabilities are 1.15 and 1.48, respectively. This example illustrates the potential effect of temperature on effluent variability from a biological treatment system and this effect must be considered in the design of these units.

Variations in Dissolved Solids

Fluctuations of inorganic dissolved solids concentrations are inherent in refinery wastewater discharges. This can be attributed to changing volumes of cooling tower or boiler blowdown (high TDS), cyclic treatment of contaminated ballast waters (high TDS), or varying discharges of process wastewater (high or low TDS). Biological treatment systems normally function more efficiently when treating low TDS waters, although effective activated sludge treatment of wastewaters with a TDS approaching that of sea water has been demonstrated (Ref. 9, 10). Abrupt changes in dissolved solids, however, have a pronounced effect on biological system efficiency. The change of osmotic pressure, for example, disrupts biochemical mechanisms and reduces the organic removal capacity of the biological population until the system can readjust. This reduction in efficiency is often magnified by a noticeable increase in effluent suspended solids discharged from the final clarifier when the wastewater TDS level increases. This can be attributed to several factors; namely, a biological shift from flocculation to nonflocculation microorganisms, a partial biological die-off, and an increase in water density which adversely affects gravity sedimentation of biological particles. Although sea water has a specific gravity of only 1.025, the effect is significant when attempting to settle most biological flocs.

Analytical Accuracy

An important factor in defining effluent variability is the precision and accuracy associated with the analytical tests used to measure the concentration of each of the controlled contaminants. Chemical analysis of wastewaters is a difficult task; these wastes contain a great array of potentially interfering materials which can drastically alter the results of an analysis with respect to the true value. Precision is a measure of the repeatability of a certain analysis; accuracy is a measure of how close the analytical results are to the "true" value. Precision data are usually easy to obtain, but the accuracy is often difficult or impossible to ascertain for an actual sample. Thus, accuracy measures for a given analysis are usually based on a "spiked" sample and may have no relation to the actual recovery obtained in a wastewater sample.

In order to provide a basis for estimating the potential impact of analytical variability on effluent variability, Table 2 is presented. The data presented in this Table are taken from the recently published EPA manual on wastewater analyses (Ref. 11). It should be noted that many of these analyses were conducted on synthetic samples and thus represent the best attainable analytical performance, which probably cannot be duplicated on a refinery wastewater. The analytical variability of the BOD, COD, TSS, and oil and grease methods are particularly important to the refinery guidelines. This will be particularly true for the 1983 limitations as they are currently promulgated. The case-history effluent data given in this paper reflect this analytical variability and thus the results obtained from the analyses presented herein

should be tempered by this variability. Another detailed study of variability conducted for API using data from the 1972 Raw Waste Load Survey (Ref. 12) showed that a substantial variation in calculated mass loadings could be attributed to analytical accuracy (Ref. 13). Neither of these evaluations include potential sampling errors, which also increase the variability of the effluent quality data.

Miscellaneous Factors

There are miscellaneous factors which cause effluent variability from biological processes, such as changed in pH, nutrient deficiency, loss of dissolved oxygen, or the presence of substances in the aeration basin at toxic or inhibitory concentrations. These can be controlled, however, in the design and operation of a biological treatment plant and are therefore excluded as determinants responsible for inherent variability. Various factors which can be included in this category and not previously discussed are: abrupt changes in wet weather/dry weather flow patterns or climatological disturbances; extended changes in organic loading attributable to emergency situations in production units; and diurnal effects on photosynthetic activity in polishing lagoons and facultative waste stabilization ponds.

INHERENT VARIABILITY IN TREATMENT UNITS

Primary and Intermediate Treatment

In petroleum refineries, primary treatment is invariably oil/solids separation, often in a separator of conventional API design. The raw waste load data shown in Table 1 reflect the effluent variability from typical, well-operated and well-designed, gravity oil separators (without chemical aids).

Secondary oil/solids separation is used extensively in the petroleum refining industry to reduce the levels of these contaminants prior to subsequent treatment for organics removal. Chemically assisted air flotation is the most frequently used unit process, although granular-media filtration has been successfully used in this application at some refineries. Table 3 presents case-history data on effluent variability for four air flotation units and one granular-media filter. Oil is the primary constituent of interest for these unit processes. Figure 2 presents the data from one of these case histories. Note that the variability ratio for the unit effluent is increased relative to that for the influent; this is due to the extremely low average effluent concentration from this unit and the magnitude of the variation between the average and 99 percentile values is much less than the corresponding influent values. Another air flotation unit shown in Table 3 showed a decrease in variability of the effluent relative to the influent; this is probably due to highly effective unit operation and chemical dosing plus the fact that the effective unit operation and chemical dosing plus the fact that the influent had an extraordinarily high variability considering the magnitude of the mean. The one granular-media filter for which data were available for this application showed considerably more afluent variability than the flotation units.

Biological Treatment Processes

Case-history information from 17 different petroleum refinery wastewater treatment systems was analyzed. The data base consisted of:

(1) 11 sets of effluent data, each of which covered greater than 12 consecutive months of system operation;
(2) three sets of effluent data, each consisting of 12 consecutive months of system operation;
(3) two sets of data, each covering 11 months of operation; and
(4) one set of data covering four months of operation.

The important characteristics of the refinery treatment systems are summarized in Table 4.

As noted in the Table, some of the refineries used in this analysis were taken from the EPA variability analysis presented in Supplement B to the Development Document (Ref. 14).

All available effluent quality data for the case-history refinery treatment plants were analyzed and the long-term average concentrations for the contaminants controlled by the effluent guidelines are presented in Table 5. These concentrations can be considered as annual averages although, in most cases, the data base used was greater than 12 months in length. These data illustrate that the refineries used in this analysis represent the "state of the art" in terms of biological treatment effectiveness and water use and the variability of the effluent from these plants should be indicative of the minimum attainable effluent variability to be expected in a well-designed and well-operated facility.

The daily and monthly variability factors calculated for the case-history refineries are shown in Tables 6 and 7, respectively; including both the range and the average factors for each pollutant parameter. Comparison of the variability factors for the two major types of end-of-pipe treatment systems shown reveals that the effluent from an activated sludge system is more variable than that from an aerated lagoon and polishing pond system.

The lower variability of the aerated lagoon and polishing pond effluent is probably attributable to the long hydraulic detention time required in this type of system to obtain the long-term effluent qualities consistent with those attainable with activated sludge systems. For example, the aerated lagoon/polishing pond system used in this study with the lowest short-term effluent quality variability has better than six days of hydraulic detention time. Moreover, this refinery is in the southwestern United States and temperature effects on effluent variability should be negligible. In general, the aerated lagoon/polishing pond system provides low effluent variability although the control of suspended solids in these effluents may be a problem. An activated sludge plant followed by a large holding pond also produces low effluent variability. An activated sludge plant with large holding pond (six days hydraulic

detention time or greater) could be expected to have variabilities similar to the aerated lagoon/polishing pond system

For some wastewater constituents, an aerated lagoon followed by a dissolved air flotation unit with chemical addition decreased the effluent variability. However, this system did not produce minimum effluent concentrations for most wastewater constituents (see Table 5).

No full-scale data are available for rotating biological surface (RBS) systems. However, for comparison, variability data from an RBS pilot-plant operated at a large refinery is included. The effluent variability from this unit is quite similar to that of the activated sludge units.

Effluent Filtration

Long-term operating data on the use of granular-media filtration for polishing of biological effluents were available from two refineries. The variability ratios for these two plants are shown in Tables 6 and 7, while the long-term average effluent quality is shown in Table 5. For comparison, data from the pilot study of polishing filtration on a pilot RBS effluent is also presented in Table 6. The addition of the filtration unit reduced both the monthly and daily variability for the activated sludge plant, however, the aerated lagoon with polishing filtration showed higher variability than the aerated lagoons followed by large polishing ponds. This does not necessarily indicate that the latter had better effluent quality, as is evidenced by the operating data in Table 5.

Carbon Adsorption

There are two existing full-scale carbon plants in the industry: one which treats refinery process wastewaters after secondary deoiling and another which intermittently treats contaminated storm waters. Neither has the biological treatment plant preceding the activated carbon which EPA has used as its 1983 BATEA model. Thus, all performance estimates must be made using data from these two full-scale systems and pilot studies operated on biologically treated refinery wastewaters.

Case History 1 data are from a refinery process wastewater treatment system consisting of gravity oil/solids separation, sand filtration, and activated carbon adsorption. There have been operational and process problems both within the refinery and in the treatment plant since start-up, so the variation is higher than may be expected in an "exemplary" system. Daily effluent concentration data were analyzed by the method outlined previously and daily variability factors are presented in Table 8. The data did not cover a sufficient period of time to calculate monthly variability data. Figures 3, 4, and 5 show the effluent quality probability plots for this plant.

Case History 2 is a refinery treatment system consisting of an equalization/settling basin followed by activated carbon adsorption. A mixture of retaind contaminated storm water runoff and process wastewater is routed through this system at a constant rate. This wastewater is considerably more dilute than normal refinery

process wastewater. Again, monthly variability factors could not be calculated because of the short duration of the data base. The calculated daily variability factor for COD for this case is also listed in Table 8. An important consideration in the evaluation of the variability for this plant is that the wastewater is fed to the system at a constant volumetric rate because it is retained storm water. Thus, these data are not influenced by the flow variations normally encountered in refinery process wastewater systems.

Case History 3 is an activated carbon pilot plant following a pilot RBS system. The variabilities are low, probably for two reasons. The first is that the loading on the biological system was relatively closely controlled. In addition, the preceding biological treatment process probably reduces the carbon effluent variabiality due to lowered feed variability compared to the Case History 1 system.

The variability data shown above for activated carbon treatment are consistent with that shown in Table 6 for the biological systems. There seems to be little improvement in effluent variability from a carbon system compared with a well-designed and well-operated biological system. This is not to indicate, however, that carbon adsorption following biological treatment does not improve the overall effluent quality.

DESIGN CONSIDERATIONS

Variability data for major refinery wastewater treatment processes have been presented. The inherent variability in refinery wastewater treatment processes should be carefully considered in designing a treatment plant to comply with effluent limitations. Based on a rather limited data base, some variability ratios for the maximum 24-hour and 30-day average concentrations can be postulated using the data in Tables 3, 6, 7, and 8 in this paper. If adequate control of storm water is practiced, spills are minimized, and sufficient equalization capacity is available in the system, the average values shown in these Tables can be used as a design basis for variability. If there is a large amount of equalization provided ahead of a biological unit and/or carbon system, or a large polishing pond following complete treatement, the lowest variabilities presented herein should provide a conservative estimate of effluent variability. Conversely, if equalization is nonexistent, the units are underdesigned, and/or storm surges can be expected, variabilities greater than the higher recorded values for the exemplary plants used in this investigation can be expected.

In general, as the effluent concentration or loading from a treatment system is decreased, the effluent variability expresses as a ratio increases. This phenomenon is primarily due to the fact that the distribution of effluent concentrations or 1 adings is bounded at the lower end by the nonremovable portion of a particular constituent and by the sensitivity of the analytical tests involved. There is no similar boundary on the upper end of effluent concentrations. For example, a 15 mg/1 variation in BOD when the long-term effluent concentration is 15 mg/1 represents a variability factor of 2.0 whereas the same 15 mg/1 variation represents a variability factor of 3.0 if the long-term average is 5.0 mg/1.

Another important consideration is the fact that some of the variability factors are derived from concentrations rather than mass discharges. To illustrate the effects of deriving variability factors from concentration data rather than from mass loading data, monthly variability factors for several constitutents have been calculated by both methods. From the results in Table 9 it can be seen that mass-basis factors may exceed concentration-basis factors by as much as 42 percent due to wastewater flow variations.

Examination of the variability factors for each individual system studied revealed that the variability may be high for one waste constituent and low for another in any given system. This fact is undoubtedly related to the differences in constituents in different refinery wastewaters which can be related to product mix and refiner complexity and the inherent variability in biological systems. These are often manifested in the form of different effluent qualities from two similar treatment systems receiving the same type of wastewater. It should be noted that the results presented herein are in general agreement with an earlier study of variability of refinery wastewater effluents conducted for API (Ref. 8).

One final observation concerning the variability factors developed as a result of this study is the fact that the choice of a variability factor encompassing 99 percent of the expected variation implies that the maximum daily effluent loading predicted on this basis may be expected to be exceeded four days of the year (one percent of 365 days). Likewise, the maximum monthly average may be exceeded one month out of every 50 months of operation if the 98 percentile is used. Such occurrences are inherent in a probabilistic approach to effluent variability and present no major problems with respect to design, provided they are properly considered.

It is informative to establish the effect that low variability ratios would have on noncompliance of a refinery effluent. Basically, the question must be asked: if we choose a ratio of the 99 percent concentration to the annual mean and we are in error by 25 percent in the low direction, how many days can be expected to be noncompliant with the effluent limitations in a year? This could be answered by a rigorous statistical analysis; however, a graphical analysis can be used to serve the same purpose. Referring to Figure 6, let us choose an arbitrary log-normal distribution with a median of 10 units and a 99 percent value of 35 units. The log standard deviation for this distribution is 0.536 and the mean is 11.6. The variability ratio is thus 3.0 for this distribution. Now, assume that the variability ratio should have actually been 4.4 and the distribution median remains at 10 units. This implies that the previous 99 percent concentration of 35 now occurs five percent of the time. This results in the effluent being noncompliant 18 days of the year, or 14 days over and above the four days per year inherent in the selection of the 99 percent probability value. The reasoning can be extended to the variability ratios show in this paper and illustrates the impact of selecting variability ratios when the resulting effluent limits can result in large economic and criminal penalties.

CONCLUSIONS

Several important conclusions may be drawn from this analysis:

(1) Inherent variability, which is defined as the effluent quality variability attributable to the basic nature of the unit process and the pattern of the raw waste loads, is an unalterable characteristic of any industrial wastewater system. The raw waste load variability, the effects of water temperature and dissolved solids, and other treatment process idiosyncracies which cannot be altered to enhance overall stability are the primary factors responsible for inherent vraiability. The use of flow equalization will lessen this variability, but will not eliminate it.

(2) The most accurate approach in developing variability baseline information from which effluent quality ranges can be predicted and effluent limitations formulated is to analyze case-history information from selected operating plants. The plants should be selected on the basis of good design and operation so that the demonstrated variation is essentially that which is inherent to the treatment process and wastewater being considered. Observation of pilot-plant data is much less realistic, as inherent variability of full-scale plants is considerably more pronounced than that observed in pilot plants in most cases. Plants selected for this study were deemed to satisfy the aforementioned criteria.

(3) The trend toward higher variability at lower effluent concentrations is supported by the fact that aerated lagoon systems produce a less variable effluent than the more efficient activated sludge systems.

(4) Failure to consider effluent variability in the design and operation of refinery wastewater treatment plants will probably result in frequent noncompliance with effluent limitations.

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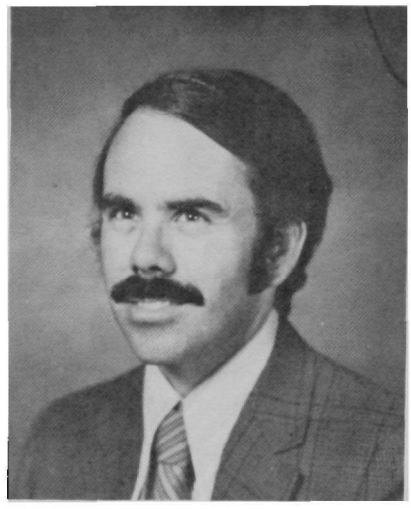
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DISCUSSION

Frank Manning, "Would you please compare your variability ratios with those implied by the petroleum refining effluent guidelines?"

Lial Tischler, At BPCTCA level technology (1977), the average daily and monthly variability factors for all constituents controlled by the petroleum refining industry guidelines exeed the respective variability ratios used by EPA. In a few cases, those systems with very long hydraulic detention times, the EPA variability ratios or better are obtained for some, but never for all, constituents. Although realistic long-term data for BATEA technology are not available to adequately define variability ratios, it seems likely that the problem is exacerbated since EPA lowered the 1983 ratios with respect to the 1977 values.

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TABLE 1: VARIABILITY IN RAW WASTE LOAD
RATIO OF 90%: 50%

PARAMETER	MONTHLY AVERAGE		DAILY DATA	
	Case 1	Case 2	Case 3	Case 4
Flow	1.4	1.3	--	--
BOD	1.7	2.9	--	--
COD	1.5	--	--	--
Oil & Grease	--	3.9	3.33	1.54

Note: Case 1 includes stormwater
Case 2 median oil and grease = 220 mg/l
Case 3 median oil and grease = 68 mg/l
Case 4 median oil and grease = 580 mg/l

TABLE 2 VARIABILITY ASSOCIATED WITH ANALYTICAL TESTS FOR TYPICAL REFINERY WASTE CONSTITUENTS

Constituent	Method	Test Concentration (mg/l)	Standard Deviation (mg/l)	99% Probabilty (mg/l)	Variability 99/50
BOD	Bottle @ 20°C	175	± 26	± 67	1.38
		2.1	± 0.7	± 1.8	1.86
COD	Regular	270	± 17.8	± 45.9	1.17
	Low Level	12.3	± 4.15	± 10.7	1.87
	Chloride > 1000 mg/l		NOT AVAILABLE		
TOC	Infrared, Combustion		NOT AVAILABLE		
Phenolics	Extraction	0.0096	0.00099	0.0025	1.26
		0.0483	0.0031	0.008	1.16
		0.0935	0.0042	0.011	1.12
	Direct Photometric	4.7	0.18	0.46	1.1
		48.2	0.48	1.24	1.02
		97.0	1.58	4.08	1.04
Oil and Grease	Infrared - Freon	13.86[1] (17.5)[2]	1.4	3.6	1.26
	Separatory - Freon	13.0 (12.6)	0.9	2.3	1.18
	Soxhlet - Freon	12.3 (14.8)	1.1	2.8	1.23
Sulfides	Titrameteric Iodine		NOT AVAILABLE		
TSS	Gravimetric		STATED PRACTICAL RANGE 10-1000 mg/l		
Ammonia	Distillation	0.21	0.122	0.315	2.5
		0.26	0.07	0.18	1.69
		1.71	0.24	0.62	1.36
		1.92	0.28	0.72	1.37
	Selective Ion Electrode	1.00	0.04	0.10	1.1
		0.77	0.17	0.044	1.06
		0.19	0.007	0.018	1.09
		0.13	0.003	0.008	1.06
	Automated	0.43-1.41	0.005	0.013	1.03
Chromium, Total	Atomic Absorption	0.353 (0.370)[4]	0.105	0.27	1.76
		0.380 (0.407)	0.128	0.33	1.87
		0.072 (0.074)	0.029	0.075	2.04
		0.084 (0.093)	0.035	0.09	2.07
		0.0102(0.0074)	0.0078	0.02	2.96
		0.016 (0.015)	0.009	0.023	2.44
Cyanide, Total	Distillation	0.06	0.005	0.013	1.22
		0.13	0.007	0.018	1.14
		0.28	0.031	0.08	1.28
		0.62	0.094	0.22	1.35

[1] Represents recovery of 14 mg/l of a known oil mixture from sewage

[2] Represents recovery by each method from a sewage sample

[3] Using two-tailed normal distribution

[4] True concentration in "spiked" synthetic sample

TABLE 3: SECONDARY OIL/SOLIDS SEPARATION

UNIT TYPE	INFLUENT OIL Median Concentration mg/l	INFLUENT OIL Variability 90/50	EFFLUENT OIL Median Concentration mg/l	EFFLUENT OIL Variability 90/50
Induced Air Flotation	55	1.75	9	2.4
Dissolved Air Flotation	580	3.33	68	1.9
Dissolved Air Flotation	--	--	12	2.3
Dissolved Air Flotation	68	1.54	15	1.7
Granular Media Filtration	--	--	19	3.8
Average Variability 90/50 - Flotation Units Only				2.1
Adjusted Variability 99/50 - Assuming log normal probability - Flotation Units				3.8
- Assuming Gaussian probability - Flotation Units				3.0

TABLE 4: REFINERY CASE HISTORIES - BIOLOGICAL TREATMENT

Case History Number	Refinery Subcategory	End-of-pipe Treatment System	Average Wastewater Flow (gal/bl)	EPA Guide-line Flow (gal/bl)	Sampling Frequency	Data Base (months)	Location Within U. S.
1	C	Activated Sludge	17.8	22.7	Daily Composite	22	South Central
2	C	Activated Sludge	17.9	19.9	Daily Composite	26	South Central
3	B	Activated Sludge	9.6	25.0	Daily Composite 3 days/week	31	South Central
4	B	Activated Sludge	19.6	22.8	Daily Composite 3 days/week	36	South Central
5	B	Activated Sludge	14.8	31.0	Three-day Composite	22	Midwest
6	D	Roughing Filter Activated Sludge	12.7[1]	53.5	Daily Composite	35	South Central
7	B	Activated Sludge Polishing Pond	31.2	31.0	Daily Composite	12	Midwest
8	D	Aerated Lagoon Polishing Pond	28.6	41.6	Daily Composite 2 days/week	11	Midwest
9	D	Aerated Lagoon	82	58.4	Daily Composite	19	Midwest
10	B	Aerated Lagoon Polishing Pond	8.4	16.4	Daily Composite 2 3 days/week	11	South Central
11	C	Aerated Lagoon Polishing Pond	33.4	21.8	Daily Composite	35	West Central
12	D	Aerated Lagoon Dissolved Air Flotation with Chemical Addition	82	58.4	Daily Composite	19	Midwest
13	B	Activated Sludge Sand Filtration	14.8	31.0	Three-day Composite	17	Midwest
14	C	Aerated Lagoon with Alum Addition Mixed-media Filtration	31	29.1	Daily Compositie	12	East Coast
15	C	Activated Sludge Polishing Pond	21.5	29.4	Daily Composite	34	West Central
16	E	Aerated Lagoon Polishing Pond	44.2	50.0	Daily Composite	12	South Central
17	D	Activated Sludge	33.3	36.4	Daily Composite	4	South Central

[1] This does not constitute the total process effluent discharge at this refinery.

TABLE 5: CASE-HISTORY LONG-TERM EFFLUENT CONCENTRATIONS BIOLOGICAL TREATMENT

Annual Average Concentrations in mg/l

Case Number	Subcategory	Throughout Capacity (1,000 b/sd)	Treatment System	BOD	COD	TOC	TSS	Oil and Grease	Phenol	NH_3H	Sulfide	Cr^T	Cr^{+6}
1	C	60	AS	13	174		78	9.4	0.053	1.10	0.27	0.41	--
2	C	63	AS	16	130		30	9.0	0.15	6.7	0	1.35	--
3	B	135	AS	18	132		23	--	--	--	--	--	--
4	B	63	AS	28	183		41	--	--	--	--	--	--
5	B	205	AS	12	112		15	9.9	0.04	8.2	0	--	--
6	D	293	TF+AS	18	121		19	--	--	--	--	--	--
7	B	160	AS+PP	--	87		7	--	--	13.7	--	--	--
8	D	175	AL+PP	--	68		28	5.1	0.04	28	--	--	--
9	D	331.6	AL	36	--		47	35	0.43	3.9	--	--	--
10	B	63	AL+PP	21	187		24	--	--	--	--	--	--
11	C	85	AL+PP	10	148		20	--	--	--	--	--	--
12	D	331.6	AL+DAF	15	--		15	5	0.35	3.8	--	--	--
13	C	53	AL	25	--		58	13	0.80	54	1.3	--	--
14	C	95	AS+PP	24	142		41	--	--	--	--	--	--
15	E	420	AL+PP	7	98		21	--	--	--	--	--	--
16	D	90	AS+PP	8	174		30	7.0	0.08	--	--	--	--
17	B	205	AS+GMF	11	104		13	8.6	0.05	3.4	0	--	0.12
18	C	53	AL+GMF	16	--		27	7.8	0.47	53	0.9	--	--

AS - Activated Sludge AL - Aerated Lagoon GMF - Granular Media Filtation DAF - Dissolved Air Flotation
PP = Polishing Pond

TABLE 6: DAILY CASE-HISTORY VARIABILITY FACTORS

	Parameter									
	BOD	COD	TOC	TSS	O&G	Phenols	Ammonia Nitrogen	Sulfide	Total Chrom.	Hexavalent Chrom.
BIOLOGICAL TREATMENT										
Activated Sludge (8 plants)										
Range	3.7-7.6	1.8-5.0	-1	2.2-5.2	3.9-5.4	4.5-7.5	9.5-10.9	--[1]	--	NA[2]
Average	5.2	3.4	3.5	3.6	4.7	5.2	10.2	5.6	4.6	NA
Aerated Lagoon and Polishing Pond (7 plants)										
Range	1.6-3.6	1.4-2.4	NA	1.8-2.7	2.9-6.1	2.4-6.7	2.8-3.4	NA	NA	NA
Average	2.5	2.0	NA	2.5	4.5	4.5	3.1	NA	NA	NA
Aerated Lagoon & Dissolved Air Flotation with Chemical Addition (1 plant)										
Average	5.8	NA	NA	2.3	3.6	2.2	3.2	NA	NA	NA
Rotating Biological Surface (Pilot Plant)										
Average	6.7	2.6	NA	NA	NA	9.0	NA	NA	NA	NA
EFFLUENT FILTRATION										
Activated Sludge, Sand Filtration (1 Plant)										
Average	4.7	4.3	NA	4.2	3.5	8.6	7.2	NA	NA	11.4
Aerated Lagoon, Mixed-Media Filtration with Alum Addition (1 plant)										
Average	4.9	NA	NA	2.5	3.1	2.1	6.0	NA	NA	NA
Rotating Biological Surface, Sand filtration (Pilot)										
Average	6.1	3.7	NA	NA	NA	NA	NA	NA	NA	NA

[1] Dash indicates one set of values [2] NA indicates information not available [3] Three-day composite used to determine daily variability factor.

TABLE 7: MONTHLY CASE-HISTORY VARIABILITY FACTORS

	BOD	COD	TOC	TSC	O&G	Phenols	Ammonia Nitrogem	Sulf-ide	Total Chrom.	Hex-avalent Chrom.
BIOLOGICAL TREATMENT										
Activated Sludge (7 plants										
Range	2.2-4.6	1.5-1.9	-1	1.5-3.3	1.8-2.9	1.4-3.4	2.1-4.1	--	1.8-2.3	NA[2]
Average	2.7	1.8	2.9	2.5	2.2	2.5	3.4	1.6	2.0	NA
Aerated Lagoon and Polishing Pond (6 plants)										
Range	1.7-2.2	1.4-2.1	NA	1.4-2.3	1.9-5.7	2.2-4.1	1.7-2.6	NA	NA	NA
Average	2.0	1.8	NA	1.9	3.8	3.1	2.2	NA	NA	NA
Aerated Lagoon and Dissolved Flotation with Chemical Addition (1 plant										
Average	3.2	NA	NA	1.6	1.9	1.7	--	NA	NA	NA
EFFLUENT FILTRATION										
Activated Sludge, Sand Filtration (1 plant)										
Average	4.1	2.2	NA	3.2	1.9	3.2	6.2	NA	NA	2.9
Aerated Lagoon, Mixed Media Filtration with Alum Addition (1 plant)										
Average	2.6	NA	NA	2.0	5.0	NA	NA	NA	NA	NA

[1]Dash indicates one set of values [2]NA indicates information not available.

TABLE 8: ACTIVATED CARBON EFFLUENT VARIABILITY

Case History	Parameter	Daily Variability*	Remarks
1	Oil & Grease	7.8	After Secondary Oil Removal
1	Phenols	8.6	After Secondary Oil Removal
1	COD	4.0	After Secondary Oil Removal
2	COD	2.6	Stormwater
3	COD	2.9	After Biological Treatment (Pilot Scale)
3	Phenols	5.7	After Biological Treatment (Pilot Scale)

*Ratio of 99% concentration to long-term average.

TABLE 9: COMPARISON OF CALCULATED VARIABILITY FACTORS FOR MASS-BASIS AND CONCENTRATION-BASIS

Parameter	Case No.	Monthly Factor Mass Basis	Monthly Factor Concentration Basis	Ratio
BOD	5	2.8	2.6	1.07
	9	2.2	2.2	1.00
	12	3.9	3.2	1.21
COD	1	1.8	1.6	1.12
	5	2.7	1.9	1.42
TSS	1	1.8	1.5	1.20
	5	3.2	2.9	1.10
	9	1.4	1.4	1.00
	12	1.6	1.5	1.06
Oil and Grease	1	2.9	2.4	1.20
	5	1.8	1.7	1.05
	9	2.0	1.8	1.11
	12	2.1	1.9	1.10
Phenols	5	3.6	3.4	1.05
Cr^T	1	2.6	2.3	1.13

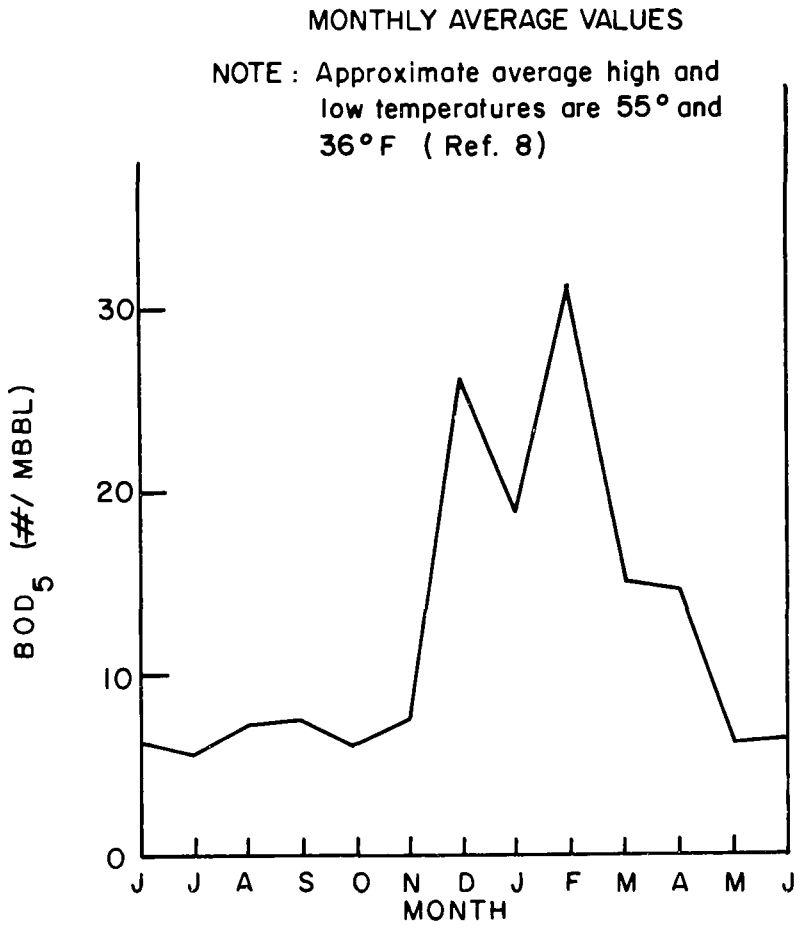


Figure 1. EFFECT OF TEMPERATURE ON EFFLUENT VARIABILITY OF BOD

Figure 2. INDUCED AIR FLOTATION PERFORMANCE OIL REMOVAL

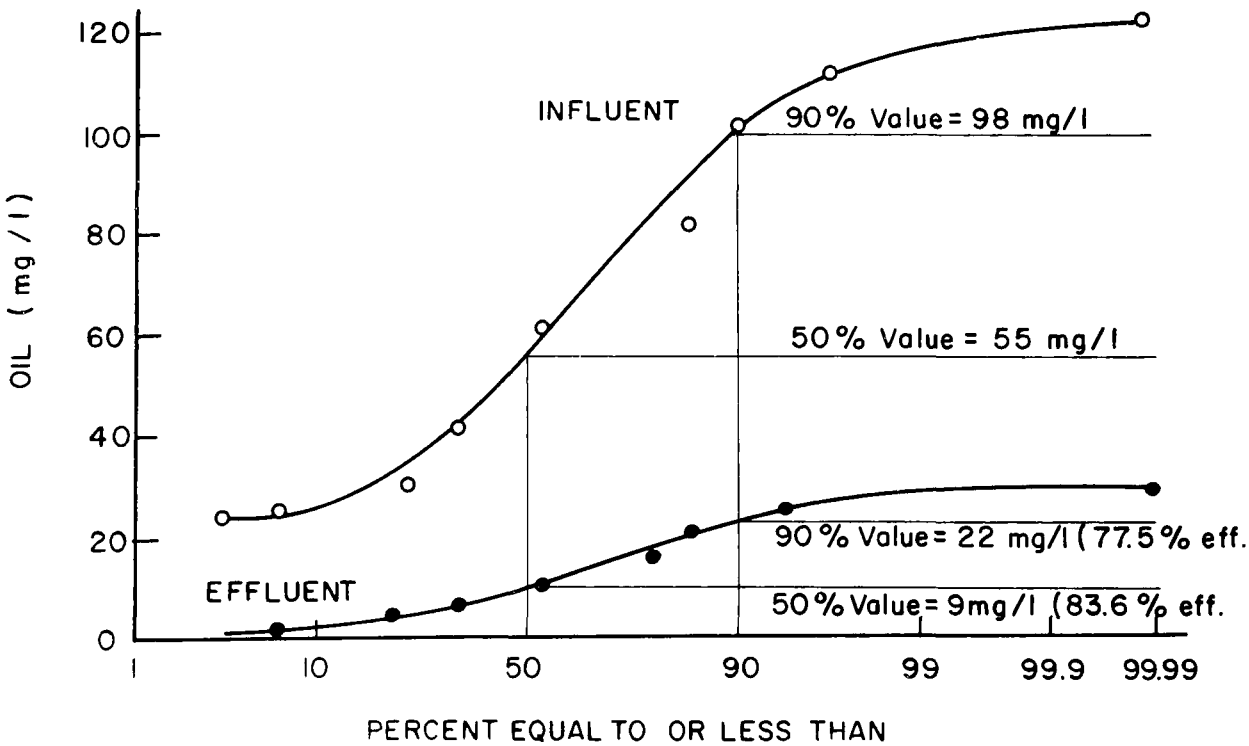


Figure 3. INFLUENT AND EFFLUENT OIL AND GREASE DISTRIBUTIONS FOR FULL-SCALE ACTIVATED CARBON SYSTEM

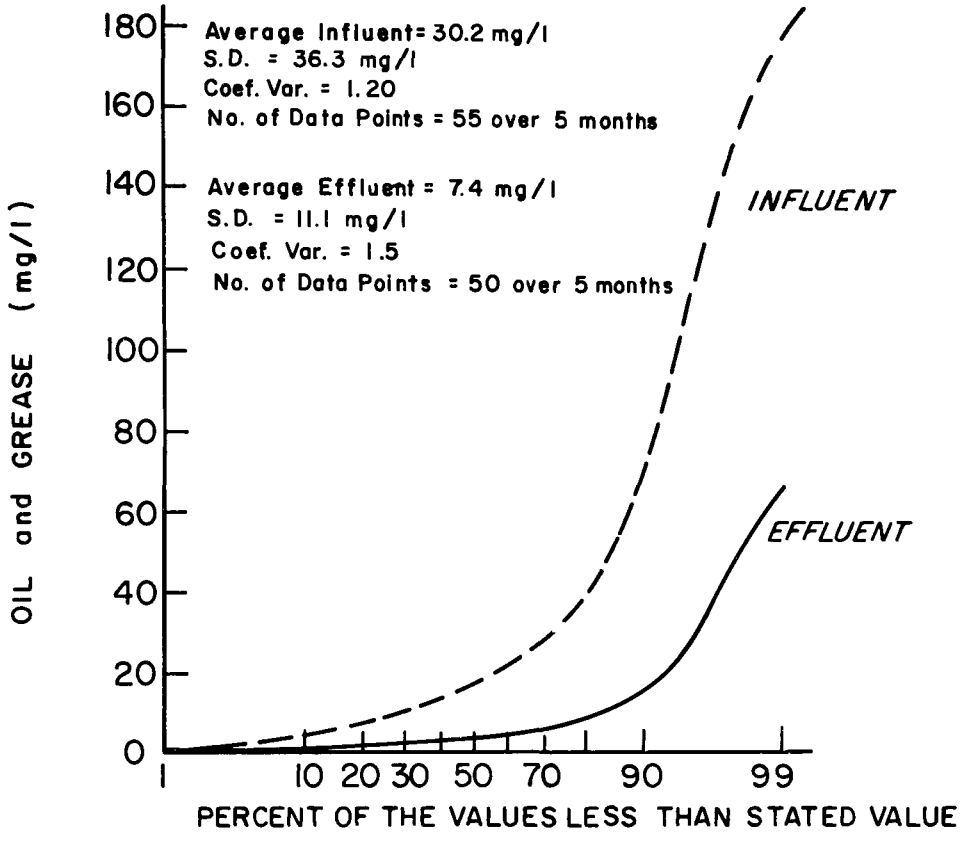


Figure 4. INFLUENT AND EFFLUENT PHENOLS DISTRIBUTIONS FOR FULL-SCALE ACTIVATED CARBON SYSTEM

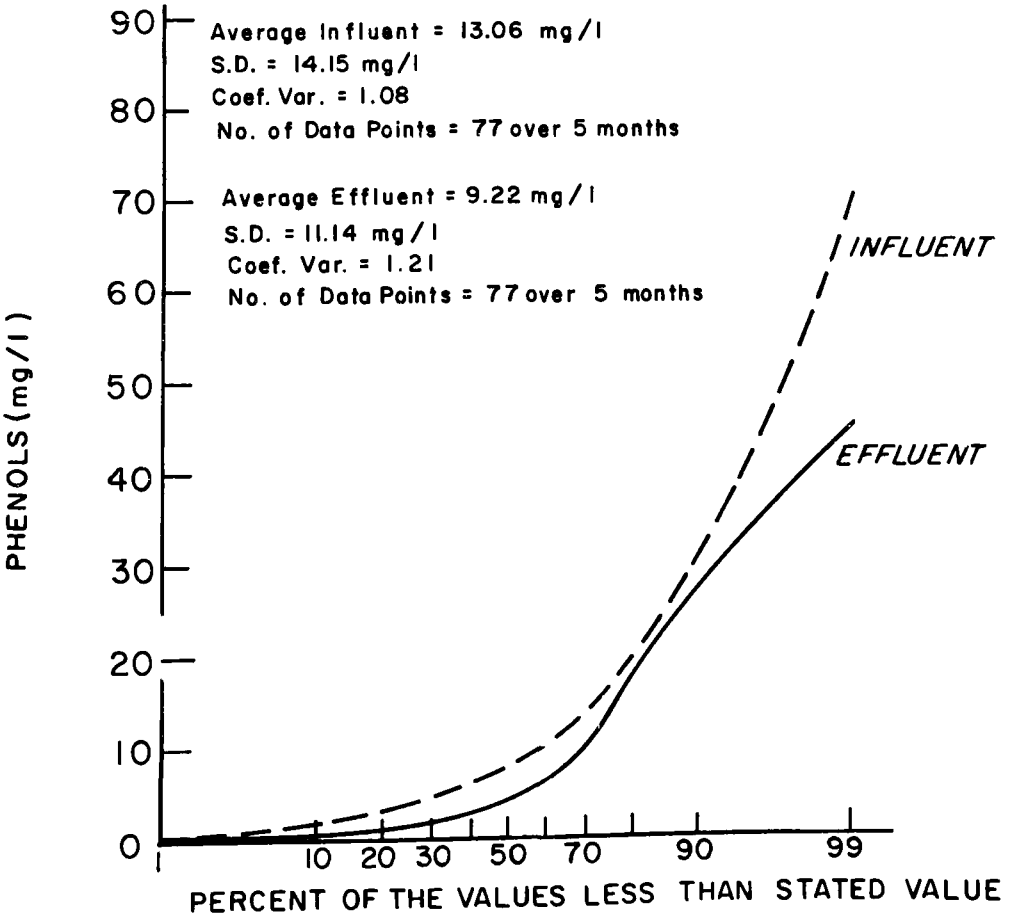


Figure 5. INFLUENT AND EFFLUENT COD DISTRIBUTIONS FOR FULL SCALE ACTIVATED CARBON SYSTEM

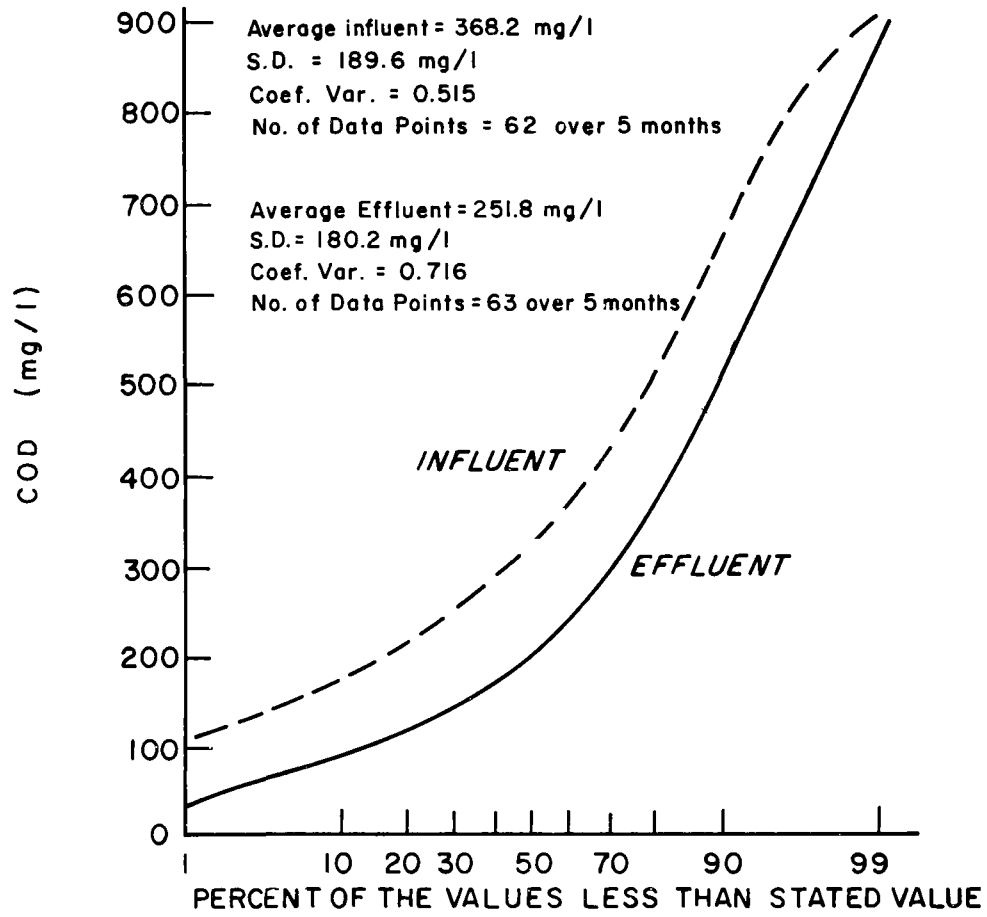
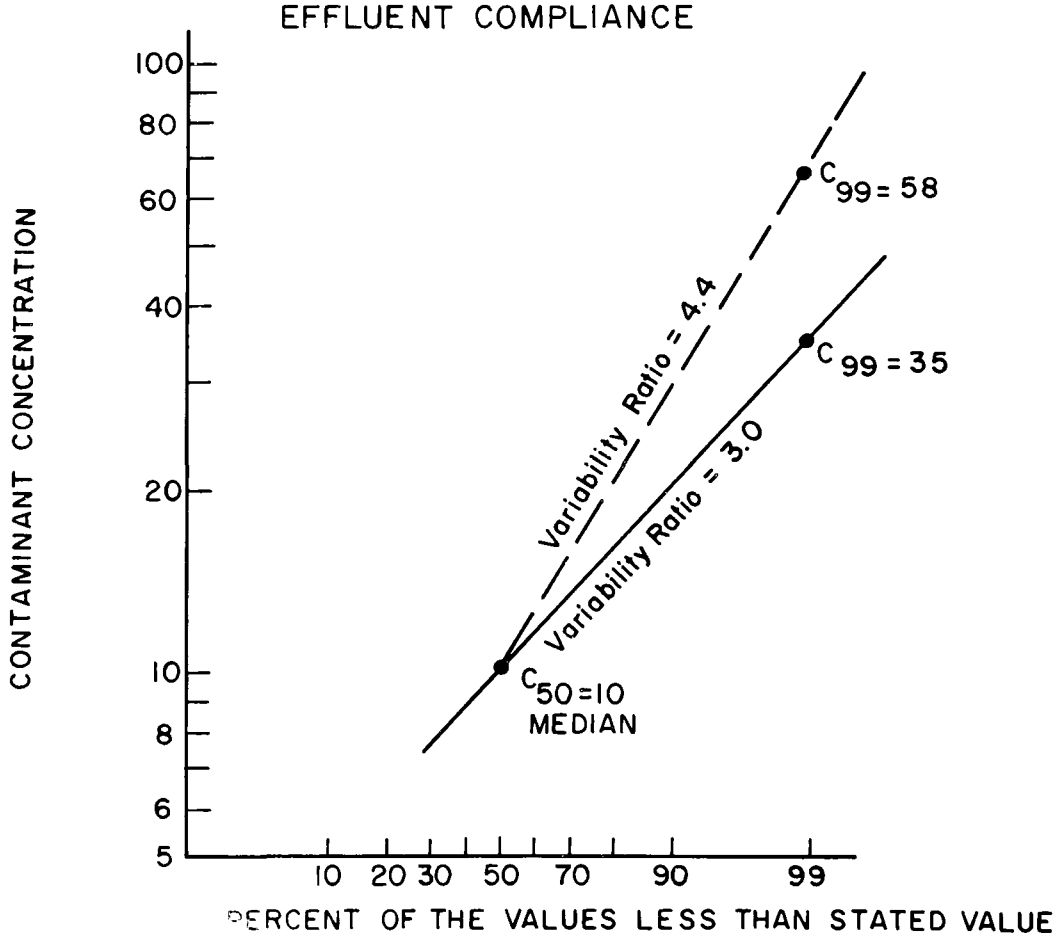


Figure 6. IMPACT OF VARIABILITY RATIO SELECTION ON EFFLUENT COMPLIANCE



REUSE OF REFINERY WASTEWATER

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The enactment of Public Law 92-500, the Federal Water Pollution Control Act Amendments of 1972, established goals for the clean-up and elimination of pollutants discharged into navigable waters. These goals are to achieve Best Practicable Control Technology Currently Available (BPT) by July 1977, Best Available Treatment Economically Achievable (BAT) by July 1983, and Zero Discharge of Pollutants by July 1985. Maximum reuse of wastewater must become a normal operating practice if we are to achieve these goals at any practical cost.

Numerous papers [1,2,3] directed toward water reuse have been written in the past few years. The purpose of this paper is to summarize ideas for the reduction of water use and for reuse of wastewaters in the petroleum refining industry, and to suggest a step-by-step progression from BPT to BAT and to Zero Discharge for existing refineries. A "broad brush" approach has necessarily been used in this paper and some of the concepts proposed may not be applicable in specific cases.

EXISTING REFINERY PRACTICES

Most petroleum refiners are now far along with their plans to achieve the 1977 goal of Best Practicable Treatment (BPT). Allowable limits on the quantities of pollutants permitted within this goal have been set in the individual NPDES (National Pollutant Discharge Elimination System) permits issued to each refinery. Many refineries will achieve these discharge limits by the addition of secondary treatment such as biological oxidation to such existing refinery treatment as sour water stripping, API separators, air flotation units and water retention basins. Conservation measures which have been used in refineries to reduce both flows and contamination of wastewaters include:

- Elimination of once through cooling water
- Use of air cooling instead of water cooling
- Better sewer segregation to exclude uncontaminated runoff and to permit separate treatment of highly contaminated streams
- Hydrotreating instead of caustic washing for sulfur removal
- Eliminating direct contact of water with oil such as in barometric condensers, jet ejectors, open steam stripping, etc.
- Eliminating bleeds of clean condensate to waste
- Use of sour water stripper bottoms as feed water to the desalter unit. (This practice not only reduces demand for treated make-up water and the discharge of wastewater but also helps to recover some of the phenols present in the sour water by their adsorption in the crude oil.)

- o Cascading blowdowns from boilers and cooling towers - i.e., using blowdown from one system as make-up to a lower pressure or more concentrated system
- o Use of treated wastewater for fire water
- o Better refinery housekeeping and maintenance practices

To better visualize the wastewater treatment steps for a representative refinery after implementation of BPT, a simplified flow sketch, Figure I gives approximate flows for a modern 100,000 bbl/day integrated refinery in which most of the cooling is provided by air coolers. With this schematic representation of treatment steps for BPT, some prorposed alterations required to meet BAT and Zero Discharge are discussed in the following paragraphs.

COOLING TOWER OPERATION AND TREATMENT OF MAKE-UP WATER

The cooling towers are key factors in the pollution control strategy for refineries. They contribute a large part of the wastewater by blowdown and bleed losses and their make-up water is a large part of a refinery's water requirement. However, they can tolerate a certain amount of organic pollutants and dissolved salts in their make-up water and they serve to oxidize and concentrate these pollutants. Thus cooling tower make-up offers the greatest potential for wastewater reuse in a refinery.

The bleed losses referred to above include the cooling water used on a once through basis in bearing cooling, pump gland seals, and flare seals. It is important to minimize these bleeds and to control them so as to operate the tower near the maximum level of dissolved solids that can be tolerated without excessive fouling and corrosion. Minimizing the cooling tower bleed of course means lowering demand for feedwater and for chemicals for controlling corrosion and scaling.

The quality of cooling tower make-up water is a prime factor in setting the permissible cycles of concentration which is usually dictated by a calcium sulfate or silica scaling problem. Methods for cooling tower and boiler make-up water treatment to prevent such scaling problems include:

- o Filtration with polymer addition
- o Cold lime softening
- o Weak acid zeolite
- o Sodium zeolite
- o Hot lime soda
- o Hot lime zeolite
- o Demineralization
- o Reverse osmosis

Each of these treatment methods has a different function and/or ion removal efficiency and a combination of methods is usually required. Selecting the optimum overall economic treatment scheme (i.e., softening plus organic removal) is most important in the water management planning. It is indicated that with the increasingly stringent discharge limits dictated by pollution control regulations, the optimum economic balance will involve a much greater make-up water treatment than is now being applied.

Sun Oil's Toledo Refinery has demonstrated,[3] that a cooling tower can operate satisfactorily with make-up water containing significant amounts or organics. In fact the cooling tower can actually serve as a biological treatment stage in wastewater reuse as long as the level of organics is low enough to avoid excessive fouling or corrosion. Thus stormwater runoff and other low salt containing refinery wastewaters, except heavily contaminated foul waters, could be used as make-up water to the cooling towers with less pretreatment than is needed for discharge from the refinery. Oil removal and/or filtration would most probably be required of these streams before reuse but a high degree of biological treatment would not be necessary. However, wastewaters which are highly contaminated with organics would certainly require further treatment before reuse because of the possibility of biological fouling problems. Stripped sour water high in phenol would normal y be used for desalter make-up and would, therefore, not be a candidate for make-up to the cooling tower.

BOILER FEEDWATER TREATMENT AND REUSE OF CONTAMINATED CONDENSATE

As is cooling tower make-up, boiler feedwater is a big water use. Furthermore, boiler feed normally receives a high degree of treatment, and it would seem that treating wastewater to make boiler feed would combine two necessary treatments and save on both cost of treatment and cost of fresh water. This strategy has considerable potential but not enough is known about the kinds and concentrations of organic contaminants which boilers can tolerate. Oily materials which would foam or carbonize on hot surfaces certainly require almost total removal, whereas low molecular weight water-soluble organics which activated carbon will not remove, may be far less damaging. Surface waters now treated for use as boiler feed water often contain significant amounts of organic matter but uniformly recognized specifications on permissible kinds and concentrations are lacking.

Stripped sour condensates, because they are low in dissolved salts, are also potential sources of boiler feed water, but besides the organics, residual sulfides would have to be removed as well.

A CONCEPTUAL DESIGN FOR BAT

In planning ahead for the 1983 goal of BAT, consideration must be given to stepwise or evolutionary changes in the BPT design which can achieve the new goal at minimum cost. In general, large steps rather than piecemeal measures will be required. A proposed scheme and water balance is presented in Figure 2 for the BAT case using the same refinery basis as was used in Figure 1. The principal difference is that this case segregates the high salt content wastewaters and reuses the low salt wastewaters as cooling

tower make-up. Since some of the low salt wastewaters will have high oil and organics contents, an oil separation step and a biological oxidation step are included ahead of the reuse of this water as cooling tower make-up. However, since the cooling tower can tolerate some organics in the make-up water, a high degree of organics removal in the biological oxidation step is not necessary.

Reuse of the stripped low phenol condensate as low pressure boiler feed water was not considered for this design, as the cooling tower can use all the low salt wastewater. The wastewater streams passing to the low salt treatment system and on to the cooling tower include:

- o Contaminated stormwater
- o Sanitary wastewater (if not sent to a municipal system)
- o Oily wastewaters from the process and process area washdowns
- o Sour water stripper bottoms in excess of those fed to the desalter (low phenol condensate)

Reuse of these streams in the case studied reduces the raw water make-up by 750 gpm. By improved treatment of the raw water used as make-up to the cooling towers to permit operation with more cycles of concentration, it is estimated that the blowdown from the cooling tower could be controlled at 100 gpm (9 cycles of concentration with the drift loss) with essentially no additional fouling or corrosion problems.

The wastewaters passing to the high salt treatment system would include:

- o Desalter water
- o Cooling tower blowdown
- o Ballast water (if any, and if saltwater)
- o Any neutralized spent caustic and acid streams not specially handled

After oil removal, these waters would be equalized, treated by biological oxidation and filtration before finally passing to an activated carbon unit.

Regeneration waters from the ion exchange treatment of feed waters and boiler blowdown could flow directly to a retention basin for mixing with the other treated wastewater before discharge from the plant.

A CONCEPTUAL DESIGN FOR ZERO DISCHARGE

The stepwise changes required to convert the wastewater treatment system from BAT to Zero Discharge primarily involve removal of salt from the final effluent of the BAT scheme and reuse of the clean, salt-free water either as boiler feed (if it is as clean as condensate) or as cooling tower make-up water.

Since brine concentration and salt removal are quite expensive, part of the Zero Discharge strategy should involve minimizing the amount of salt brought into the refinery water. Several techniques for this are:

- o Minimize the input of raw water by reusing as much as possible and reducing evaporative losses by use of air cooling and control of steam losses
- o Use of reverse osmosis rather than ion exchange for demineralizing boiler feed water
- o Hydrotreat to sweeten and desulfurize instead of caustic treat
- o If possible, reduce the amount of salt ballast water received

There are numerous possible alternatives for brine concentration and salt removal and further study and plant demonstrations are required to achieve the optimum design. A proposed conceptual design shown in Figure 3 includes reverse osmosis followed by an evaporation system and a flash dryer. A wet coil concentrating cooling tower is a good alternative to the reverse osmosis unit but may prove to be more expensive than reverse osmosis when one considers modification of an existing refinery which already has sufficient cooling capacity.

This study is based on concentrating the waste salts to dryness and transporting these solids to an arid disposal site. Although the waste solids are concentrated to dryness, their disposal will not be easy and an alternative using direct disposal of the evaporator blowdown slurry should be considered.

CAPITAL COSTS

Order-of-magnitude capital costs of $6 million and $10 million respectively, have been estimated in 1975 dollars for the modifications and additions required in changing the 100,000 bbl/day refinery treatment system from BPT to BAT and to Zero Discharge treatment technology. These costs indicate the large capital investment required to meet the 1983 and 1985 goals.

CONCLUSIONS

Some of the principal conclusions from this study regarding the reuse of refinery wastewater and achievement of the Public Law 92-500 goals are:

- o The large water requirements of refinery cooling towers and their ability to oxidize organic impurities and concentrate salts, make them logical candidates for water reuse.
- o The correct degree of treatment for make-up water to refinery cooling towers and boilers is important in obtaining an economic overall water and wastewater treatment system.

- o More information is needed about acceptable levels of organic impurities in boiler feed water if refinery wastewaters are to be reused in this service.
- o Petroleum refineries can probably reach the goals set in PL 92-500 using existing technology but further verification of this technology needs to be made by demonstration tests.
- o Because BAT and Zero Discharge treatment will be complex, adequate surge storage and equalization will be needed to get the necessary degree of reliability.
- o Large capital investments will be required by petroleum refiners to meet the 1983 and 1985 goals.

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(2) Willenbrink, R. "Waste Water Reuse and Inplant Treatment" presented at AIChE Meeting, Houston March 1973.
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DISCUSSION

Milt Beychok: Before I make this comment, Bob, I would like everyone to know that you and I have been good friends for quite some while. I know that you weren't here the first day when I discussed the impracticality of zero discharge. I submit that the process designs you have shown us are not zero discharge, but rather the transformation of a saline water problem into a solid waste problem. Obviously, we engineers can evaporate water to remove dissolved inorganic salts (such as chlorides, carbonates and bicarbonates). But unless we store the salts indefinitely in closed silos or lined ponds, they will return to Mother Nature during the next rainfall whether by surface runoff or by leaching into underground aquifers. I therefore repeat what I said in my keynote address, that we cannot justify the large expenditure of capital and energy required simply to remove water-solluble inorganic salts from our industrial and municipal effluents. To think otherwise is to delude ourselves.

Bob Milligan: I agree with what you say Milton regarding the lack of justification for removing non-toxic salts and I am sorry to have missed your talk the first day. However, I believe that what I have presented is what at least the law, Public Law 92-500 implies as zero discharges or elimination of discharge and it is zero discharge of pollutants to navigable waters if the solid salts are transported far enough away from navigable waters such as to a desert area.

Bill Ruggles: I would like to echo Mr. Beychok's comments. One of the difficulties that those of us in industry have had over the years with this environmental situation is that

vendors of equipment and chemicals often get over-enthused with the efficiency of their products. They make public utterances about them from time to time. They "sell" the enforcement people on them. Then, those of us who are in industry are stuck with trying to explain why we often can't use them.

This has been a real serious problem. It is therefore urged that your written paper indicate these methods you are advocating are methods that may be possible under some circumstances and that the situation not be oversimplified. As an example, you mentioned the use of cooling towers for handling organic-bearing waste. It is well known that in some cases this works very nicely. We very blithely started out trying it ourselves. Talk about clogged heat exchangers -- you never saw the like of that biogrowth. One might say "why don't you use a biocide?" Well, there seems to be a reason or two these days why we can't use biocides as we might like, including the fact they themselves can sometimes be objectional in plant effluents.

There is also, as Mr. Beychok said, the question about disposal of solid materials that result from some of these processes you (Milligan) describe. This is also true in using an organic-bearing water for such things as better make-up. All you will probably do in most cases, is just concentrate the organic in the blowdown. Then what do you do with it? You are back to about the same situation as where you started. So, you really have to think these things out carefully. People such as yourself in the consulting business, in making positive statements on these methods instead of putting them in true perspective as procedures that possibly may work in certain instances, may be selling us in industry (your clients) down the river.

Bob Milligan: You will note that in the design presented that a treatment system to remove the bulk of the organics was incorporated ahead of reuse of the wastewater as feed to the cooling tower. The small amount of organics that are remaining after this pretreatment does not have to be removed in most cases before feeding to the cooling tower if we believe Sun Oil's experience and the experience of a number of other companies. I am not suggesting that refineries incorporate this water reuse scheme blindly but I am saying that this is a good possibility and that it should be considered not only from the standpoint of further removal of organics but also from the standpoint of conserving the amount of raw water taken into the refinery.

BIOGRAPHY



Robert T. Milligan is Manager of Pollution Control Technology for the Bechtel Corporation in San Francisco, California. He has the responsibility for the operation of three sections which provide consulting services on air, water and solids and noise pollution control.

Dr. Milligan holds the following degrees in Chemical Engineering: B.S. from University of Illinois and Ph.D. from Ohio State University. He is a registered Professional Engineer in the State of California. Dr. Milligan has had 28 years of experience in process engineering and technical management with Shell Development and Shell Chemical Companies before joining Bechtel.

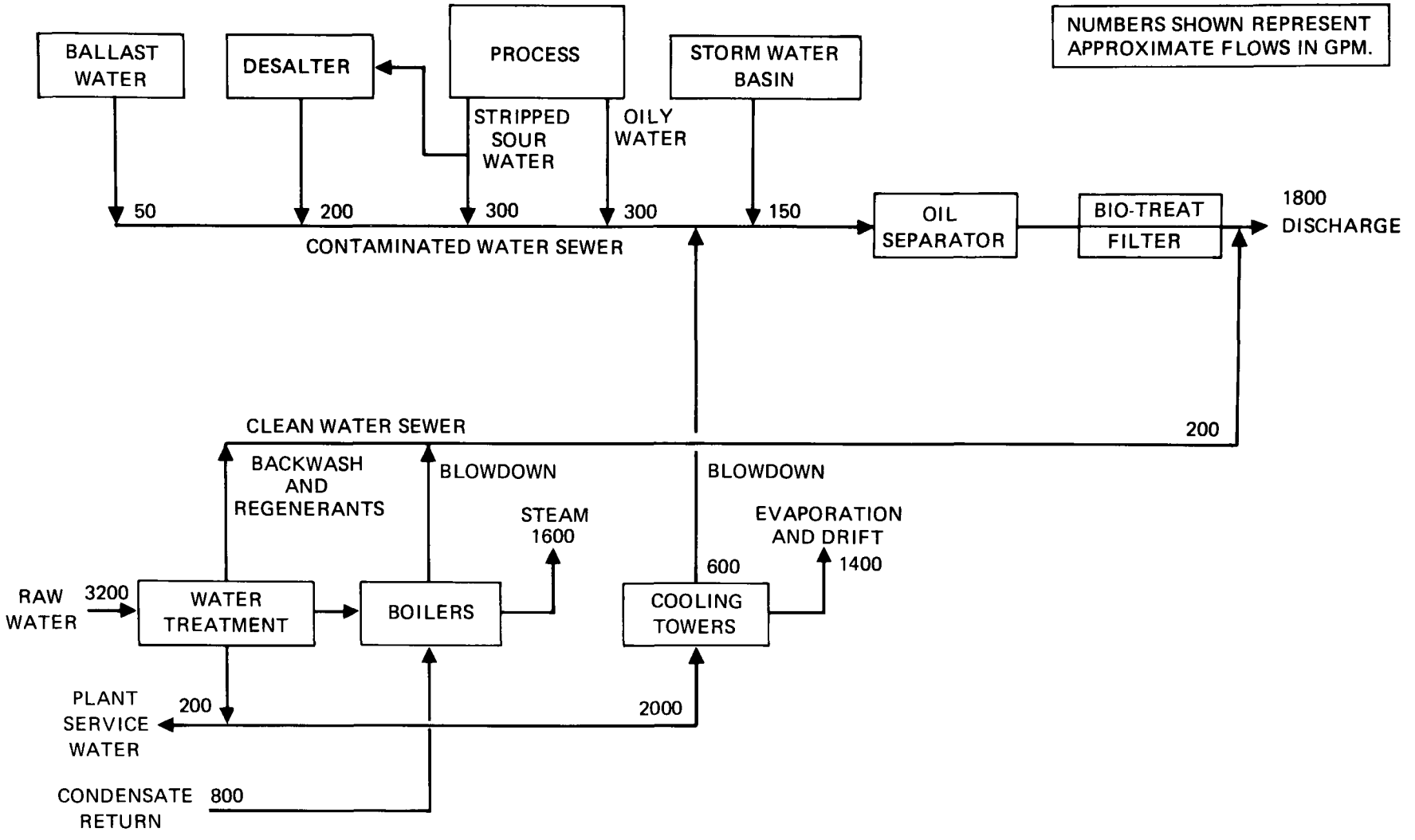


Figure 1. BEST PRACTICABLE TREATMENT (BPT) CASE

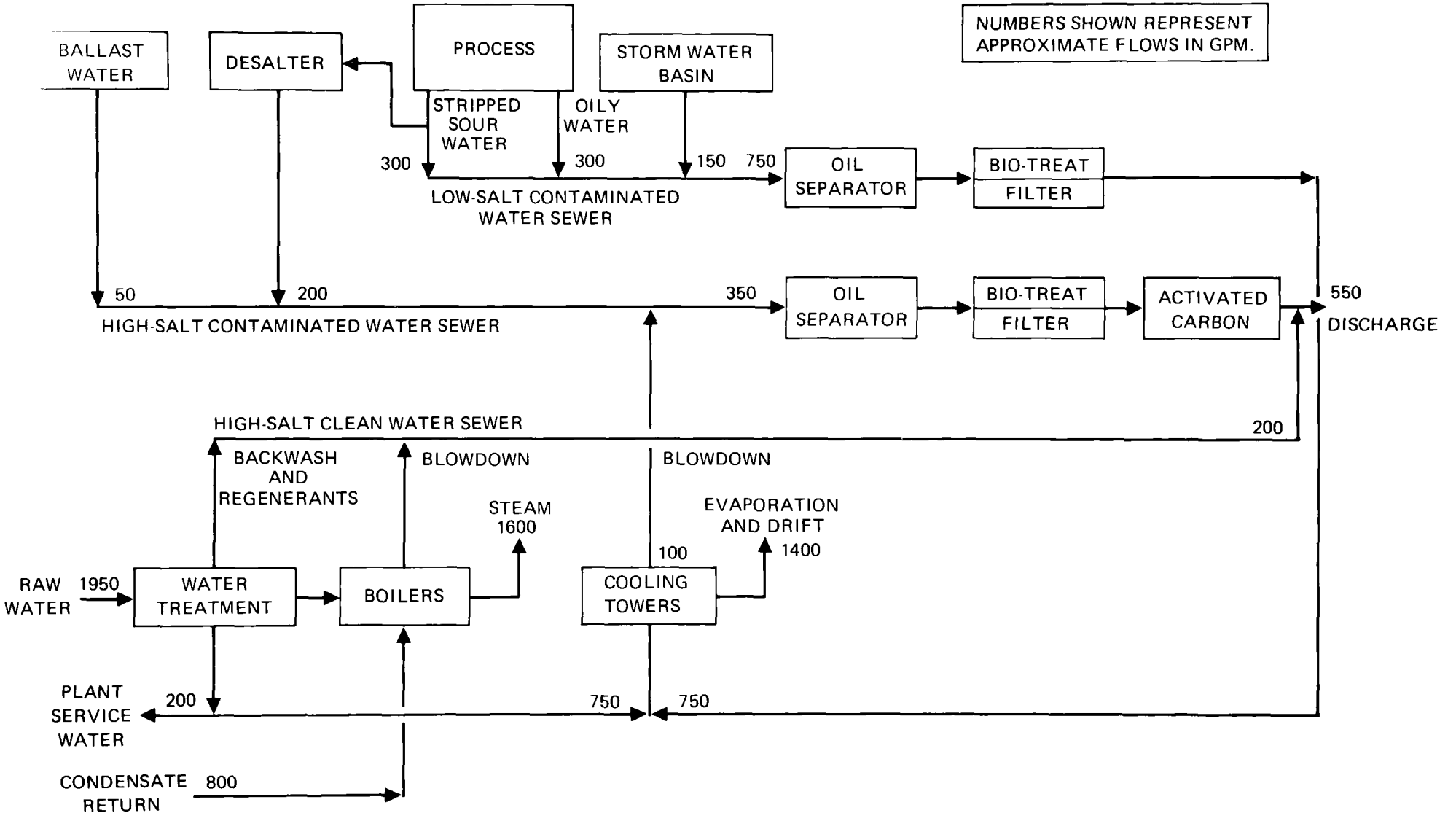


Figure 2. BEST AVAILABLE TREATMENT (BAT) CASE

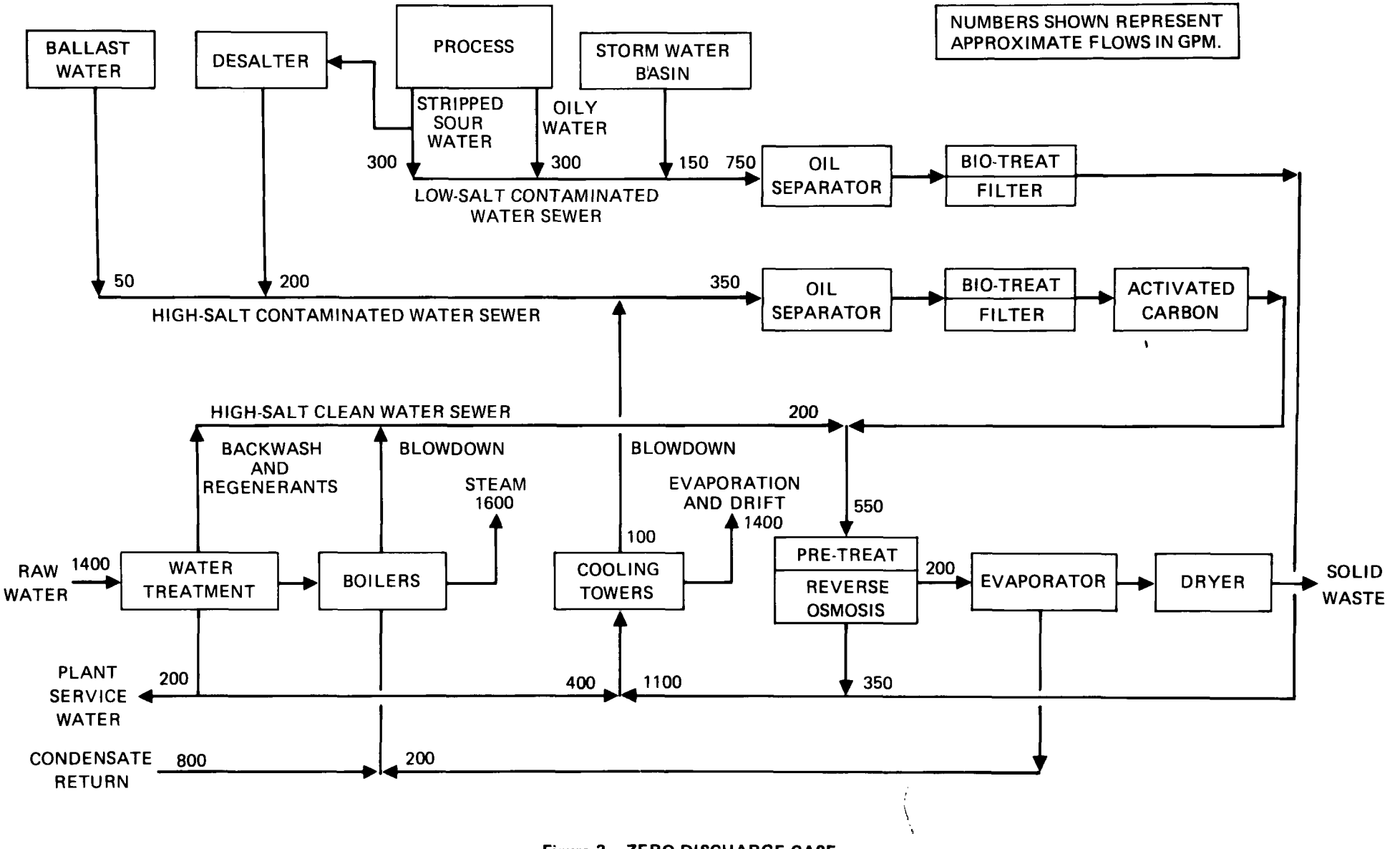


Figure 3. ***ZERO DISCHARGE CASE***

BIOLOGICAL MONITORING OF PETROLEUM REFINERY EFFLUENTS

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Increasing awareness of the problem in predicting the environmental effects of waste water discharges based upon chemical parameters has caused a renewed interest in biological toxicity tests. The 1972 amendments to the Federal Water Pollution Control Act were enacted by Congress to give some support to states efforts to control pollution and to insure uniformity in regulation of water quality. The goal of the act was to achieve "zero pollutant" discharge by 1985. Where a pollutant was defined as any substance which, directly or indirectly through the food chain, causes a deleterious effect upon any organism within the aquatic environment. Thus, the problem facing water pollution scientists and engineers is the definition of a "zero pollutant" discharge. Effluent criteria attempt to achieve this goal by regulating the maximum amount of chemical substances which may be discharged to the receiving stream. This approach has achieved a beneficial effect in preventing the discharge of gross quantities of known toxic chemical compounds, however, this approach to establishing effluent criteris has some limiting features which may cause inequities by restricting maximum allowable concentrations at an unnecessarily low level or the criteria may not adequately protect the organisms when the combined action of the chemical pollutants is more than additive. In addition, many chemical toxins have not been identified yet and therefore can not be regulated based upon chemical criteria. As a consequence, effluent guidelines based upon biological toxicity tests alone, or in combination with chemical criteria, may be more equitable to both the regulated point source dischargers and the organisms in the receiving body of water. The results of several different projects using both biological toxicity tests and chemical analyses to evaluate the quality of petroleum refinery effluents are presented in this paper. The objective is to illustrate how biological toxicity tests can be utilized, either alone or in conjunction with chemical analyses, to more effectively manage petroleum refinery waste waters.

The most commonly used biological test for determining water quality is the fish bioassay. Basically, the fish bioassay is performed by exposing a number of fish, usually six to twenty, to several different concentrations of a prepared chemical pollutant solution or an effluent and the effect is determined by recording the percent mortality (quantal response) at preselected time intervals. The percent response is then plotted versus the log of the concentration to graphically interpolate (may be calculated by statistical methods) the concentration which causes 50% mortality, usually expressed as the median tolerance limit (TL_M) or median lethal concentration LC50 (APHA Standard Methods, 1971).

The mechanisms of performing fish bioassay tests generally fall into two categories as far as the method of exposing the fish to the test solution; i.e., a static method and a continuous-flow method. In static tests, the test solution is prepared and the fish exposed to the original test solution without any replacement or renewal of the test solution for the duration of the test interval. In continuous-flow tests, the test solution is continually passed through the test containers so that renewal or replacement occurs many times during the test interval.

The static test requires much less effort by trained personnel, less complicated mechanical equipment and may be performed at laboratories some distance from the source of sample. Continuous-flow tests require more complicated mechanical equipment to pump the test sample through the bioassay containers. It is difficult to maintain a uniform constant rate of flow and thus must frequently be checked by trained personnel. The volumes of water required to perform continuous-flow bioassays make it very expensive and inconvenient to perform the test at locations other than the source of the sample.

The Oklahoma State University Reservoir Research Center, in cooperation with the Oil Refiners Waste Control Council, has been performing static acute fish bioassay tests on effluent samples since 1959. The oil refiners collected samples of final effluent and shipped them to OSU for analyses. The samples were testes for acute toxicity by a static 96 hour Fathead minnow bioassay in accordance with APHA Standard Methods (1971). The chemical parameters ammonia, pH, sulfide, phenol, chemical oxygen demand, and alkalinity were analyzed by personnel of the oil refineries.

The combined chemical and fish bioassay data have been used as indicators of water quality to detect upsets in water waste treatment systems and to determine the relative efficiency of the systems for producing good quality final effluents. A comparison of the mean annual LC50, expressed as percent effluent, of the influent and the effluent of a lagoon waste water treatment system illustrates the value of fish bioassays (Fig. 1). The long range trend from 1960 to 1964 was a definite improvement in the influent to the treatment system. Since the influent had received only oil separation through an API separator, the improved quality must have been due to changes either in crude oil or processes within the refinery. From 1964 to 1975, the long range trend shows the influent has become more toxic. The increase in toxicity of the influent to the lagoon system places a greater load on the biodegradation capacity of the system until eventually the capacity is exceeded. This is reflected by the LC50 of the effluent from the lagoon. Prior to 1970, the mean annual LC50 was always 95% or greater. Since 1970, the mean annual LC50 of the effluent has decreased to below 95%. This indicates that the load of chemical poisons is exceeding the capacity of the lagoon system to degrade them. Examination of the mean annual COD data for this system shows that the COD in the influent was increasing up to a maximum in 1971 but has decreased since 1971 (Fig. 2). The mean annual COD of the effluent, although showing a slight increase, has not changed much since 1961. Thus the capacity of the system to degrade COD has not been exceeded and the use of COD data alone would not permit the problem to be identified.

A significant change in water quality occurred when a refinery installed an activated sludge waste water treatment system (Fig. 3). The mean annual LC50 had gradually improved from 1960 to 1964 as the refinery had made improvements in their treatment system, however, installation of new processes and increase in crude capacity caused a decline in effluent water quality from 1965 to 1968. The company decided to install an activated sludge system and a dramatic improvement in water quality occurred from 1970 to 1972.

These two examples illustrate the value of fish toxicity tests as indicators of water quality. Fish bioassay data have often indicated problems were occurring in a treatment system where chemical parameters did not detect a problem. Used in conjunction with

chemical analyses, fish bioassay tests can help identify problem process effluent streams which can be segregated and subjected to more intensive treatment than possible with the total combined waste water flow from a refinery. This approach has been successfully used by several members of the Oil Refiners Waste Control Council.

The trend today in fish acute toxicity testing is towards a continuous-flow method of exposure. It has been suggested that static acute toxicity tests might not be obtaining a reliable measure of the toxicity of an effluent because the effluent may contain biodegradable poisons, volatile toxins and was not homogeneous. A project was initiated to compare the LC50's measured by static and continuous-flow methods of exposing fish to effluents. The large volumes of water required to perform continuous-flow tests necessitated that the tests be performed on-site at a refinery. A mobile trailer (96 ft^2 of floor space) equipped with heating and air conditioning was modified for performing fish bioassay tests. The trailer was equipped with aquaria racks, plumbing, air compressor, and serial dilution devices for delivering selected percentages of test effluent. In order to perform toxicity tests with different percentages of effluent, it was necessary to obtain dilution water. For purposes of simulating the conditions which occur in the receiving stream, the most logical source of dilution water would be the stream just above the outfall of the test sample. However, the depths of the stream banks and its inaccessability prevented the use of the stream. The dilution water was obtained from a reservoir approximately 15 miles upstream from the outfall. The dilution water was transported to the refinery test site with a 5,000 gallon tank truck. The test refinery effluent, treated with activated sludge, was taken from the final clarifier prior to the final discharge to the receiving stream.

The test fish, Fathead minnows (Pimephales promelas), were raised in the laboratory from a breed stock which has been maintained since 1970. The fish were exposed to duplicate concentrations of 0, 18, 42, 55, 74, and 100 percent effluent. The percent dilutions for the continuous-flow tanks were prepared by continuously passing the effluent through a glass serial diluter (modified from Brungs and Mount, 1971) where it was diluted with water from the reservoir on the stream. The percent mortality was recorded at 0, 2, 4, 8, 16, 24, 48, 72, and 96 hours when possible. The exact time sequence could not be maintained for all samples. The data were interpreted by the methods of Lichtfield and Wilcoxon (1949) when possible. Most of the mortality occurred between 55 and 74 percent effluent and could not be analyzed by Lichtfield and Wilcoxon's method, so the LC50's were determined by graphical interpolation. An LT50, median lethal time, was also calculated by graphical interpolation (Sprague, 1969).

A comparison of the LT50 values from eight tests (Table 1, Fig. 4) indicates that the median lethal time was of shorter duration in the static tests than in the continuous-flow tests. Thus, the fish in the static test were under more stress and succumbed to the toxic effects earlier than fish in the continuous-flow tests. However, in only two of the tests does the difference appear to be significantly different. A comparison of the LC50's shows no significant differences between the static and continuous-flow bioassay tests (Table 2, Fig. 5). Based upon these results, it would appear that there is no significant difference in estimating an LC50 by the static 96 hour acute toxicity bioassay as contrasted with a continuous-flow 96 hour acute toxicity bioassay.

The most significant difference between the two tests was the difficulty in maintaining uniform flow of the test sample in the continuous-flow tests. The flow of the effluent was dependent upon a pump. If the pump failed, then the flow was stopped. If the flow of effluent stopped, the proportional diluter became inoperative and there was no flow of water to the test containers.

In my opinion, the added expense of obtaining dilution water, building diluters and of maintaining pumps does not justify the slight improvements in LT50's or LC50's. The major advantages of continuous-flow tests accrue when the sample of analyses contains volatile toxins which might escape in a static test or biodegradable toxins which could be degraded in a static test. Apparently, these conditions did not cause a significant effect in the oil refinery effluent tested during this study.

By mid-1977, all industries must attain a level of waste water treatment equivalent to Best Practicable Treatment Control Technology (BPTCT) and Best Available Treatment Control Technology (BATCT) by mid-1983. For the petroleum refining industry, BPTCT has been defined as equivalent to sequential treatment with activated sludge followed by dual media filtration. The BATCT level of treatment was defined as equivalent to sequential treatment with activated sludge, dual media filtration, followed by adsorption on activated carbon.

Based upon reduction of specific chemical contaminants, these levels of treatment will meet effluent criteria recommended by the regulatory agencies responsible for attaining goals established by the 1972 amendments to the Federal Water Pollution Control Act. However, effluent criteria based upon maximum allowable concentrations of chemical contaminants were developed by attempting to relate acute toxicity concentrations measured in the laboratory with anticipated responses of organisms within the aquatic environment. The ultimate test of the acceptibility of a treatment method must be the effect of the waste water discharge upon the biological organisms within the receiving environment.

The fiscal year 1976 and 1977 project of the Oil Refiners Waste Control Council-USDI, Office of Water Resources Technology-OSU Reservoir Research Center was designed to use biological monitoring to evaluate the effectiveness of BPTCT and BATCT for producing a non-deleterious effluent. This concept of using biological organisms to determine the effectiveness of a treatment method is in accord with the intent of the 1972 amendments, since "zero pollution" was defined by biological criteria.

Although this research project has only begun, the approach used for evaluation of the advanced waste water treatment methods is unique and will be presented as an example of the potential of biological monitoring.

Effluents from a control stream, an activated sludge unit, a combined activated sludge-dual media filter unit (BPTCT), and sequential activated sludge-dualmedia filter-activated carbon (BATCT) units will be continuously pumped through fish bioassay tanks to determine fish toxicity, through artificial streams to determine effects upon diversity of benthic organisms and periphyton.

The purposes of the fish bioassay tests are to relate the research results to commonly

accepted short-term bioassay procedures and to explore the effects of long term exposure of the fish to the test effluents. The fish will be considered to have completed the life cycle if they produce viable eggs.

In addition to the fish bioassays, effects of the test effluents on benthic organisms will be tested in simulated streams. Changes in diversity of the benthic aquatic invertebrates have been shown to be useful parameters for determining the quality of an aquatic environment (Wilhm and Dorris, 1968). The benthic invertebrate assemblage is composed on many species of organisms, some of which are sensitive to changes in environmental quality and others which are relatively tolerant to changes. Adverse changes in environmental quality cause reduction in the numbers of individuals and species of sensitive organisms and may cause an increase in numbers of individuals among species of tolerant organisms. The changes can be quantified by a diversity index (Shannon and Weaver, 1963):

$$\bar{d} = - \frac{n_i}{n} \log_2 \frac{n_i}{n}$$

Where $\bar{d}$ = species diversity
n_i = numbers of individuals in the ith species group
n = total number of individuals

Nondisturbed benthic communities usually exhibit a diversity index of 3 or greater, whereas the diversity index of benthic communities in polluted environments is less than 1.

Benthic organisms for the artificial streams were obtained by installing artificial substrate samplers in a nearby unpolluted stream and allowing the natural organisms to colonize the samplers for a period of six to eight weeks. The colonized samplers were then transported to the refinery test site and installed in the effluent streams from the test treatment units. Mean diversity of the colonized samplers was determined by analysis of four samplers before exposure to the test effluents. Two artificial substrate samplers were removed from each duplicate stream at 2, 8, 16, and 30 days after start of exposures to the test effluents.

The diatom community was also used as a biological test monitor. New microscope glass slides were placed in each artificial stream in specially constructed racks. The slides were supported vertically and oriented parallel to the current of the stream. Slides were removed at 8, 16, and 30 days after start of exposure. Two kinds of information were obtained from the diatom exposures. The composition and diversity ($\bar{d}$) of the assemblages were determined after full colonization and compared among control and test streams to yield the same kind of information as in the benthic communities. In addition, a physiological measure of growth was obtained by using ash free biomass and numbers of individuals (Kevern, Wilhm, and Van Dyne, 1966).

A thirty day test has just been completed at a refinery, from Nov. 4 to Dec. 4, 1975, and the data which have been analyzed will be presented as an example of the potential biological monitoring has for determining waste water quality. The results of the continuous-flow fish bioassay tests show that no mortality occurred in the first six days of the exposure (Fig. 6). These results indicate that in the normal 96 hour bioassay test, the response of

the fish would not be sensitive enough to perform an evaluation of the "zero pollutant" level of the treatment methods. After thirty days exposure to the test effluents, there was 70% mortality in the activated sludge effluent, 20% in the combination activated sludge-dual media filter (BPTCT) effluent, and 15% in the combined activated sludge-dual media-activated carbon (BATCT) effluent. Thus, on the basis of fish mortality, the additional treatment by dual media filters or activated carbon improved the quality of the effluent. However, the activated carbon did not improve the quality as much as would be expected, since it is advocated as the Best Available Treatment Control Technology.

Analyses of species diversity values have been completed on 26 samples (40% of the total exposed) of benthic invertebrate organisms. After 9 days of exposure, no significant changes in species diversity of the benthics had occurred (Table 3). Thus the benthic organisms, like the fish, showed almost no response the test effluents for short-term exposure.

The data presented in this report are too preliminary to permit any conclusive evaluations of Best Practicable or Best Available Treatment Control Technologies, but the approach illustrates how biological monitoring may be used to evaluate advanced waste water treatment technologies. Such an approach could be very valuable to personnel in the petroleum industry who must make a decision on the type of treatment facility to install to meet the "zero pollutant" discharge by 1985.

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DISCUSSION

Neale Fugate: In the next to the last slide, I believe you showed the mortality at the end of the 30-day period, so there is a 15% mortality, is that a crack of doom?

Sterling Burks: No, I don't think so. I think we really don't understand going beyond acute toxicity, we are out there in a brand new world. We don't know other than the laboratory studies that have been conducted on chemical poisons by the Duluth National Toxicology Laboratory, we know very little about the long term effects upon aquatic organisms. When we get past 30 days, what is a significant effect? Let's use the organisms in the receiving stream, let them tell us what is a significant effect and that is why we proposed the species

diversity index ($\bar{d}$). Now I am hoping that within a year we will have a lot more data and will be able to tell you what the biological evaluation of BPT and BAT is. I think they will give us an answer.

Frank Martin: I would like for you to comment on the Gambasia test that the Texas Water Quality Board is talking about as a quick test to determine toxicity?

Sterling Burks: Well, I think this is a good test that will give you some reliable indices of toxicity. I think any time we talk about an acute test, really what we are looking at is an index of toxicity. We find that there is a lot of variability in biological organisms. As you all know when you run a BOD test. You can't always predict what those critters are going to do - the environment effects them tremendously. The dilution water, temperature, pH, everything, so use a biological test as an index. I hate to see hard and fast numbers put on them, but I think they are a good index of toxicity.

Lial Tischler: I want to speak to that particular point and get your comment on the use of a number three or better for species diversity as being polluted or unstressed if you like. I think in certain types of natural water, stressed eco-systems, I am thinking particularly of some of the tidal estuaries in the Texas Gulf Coast, you do see species diversities in "natural or unpolluted waters" which are quite a bit lower. I just think that you ought to emphasize that species diversity to 1.5 may be caused by natural conditions; also, I think that is the case.

Sterling Burks: Maybe I didn't make that point clear and I appreciate your bringing that point up. The species diversity value of three or greater is generally found in an unpolluted, unstressed situation. The sampler trays that I showed you were installed in a natural stream. In Oklahoma we are subject to variabilities of the weather. We installed these samplers in a stream that had a nice flow of about one foot and a half deep, six or eight feet wide and a nice clear looking stream. Six weeks later we went back and the stream had stopped flow, was down in stagnant pools, lot of leaves, decomposing in the water, etc., so we had a natural stress on that system. But the $\bar{d}$ on the organisms that we took out of this stream was 2.75, so I think that natural communities have an ability to respond to stress. Some organisms may disappear, but other organisms take their place. What I am trying to say is let's strive for diversified aquatic communities. I am not saying that we should protect every rare very sensitive species out there, I am saying let's strive for a balanced community in the receiving stream. If we have a stream that should support a large mouth bass, then I think we should have large mouth bass there; but if he is not very sensitive, not as sensitive as some of the invertebrate organisms that might disappear.

Bob Huddleston: How big a job is it to carry out the assay on the benthic organisms?

Sterling Burks: I can tell you more before too long. We have people who have to take these rocks and wash off the debris, sort the organisms, and then classify the organisms. It is not an easy job and it is a fairly time consuming operation. I would guess about three hours to wash and sort, and somewhere between five and six hours to identify the organisms, depending upon the taxomony of the invertebrates present. It is not an easy task.

Ben Buchanan: Do you control the dissolved oxygen in the flow systems that you run the bioassays?

Sterling Burks: We had to, because we found the water coming out of the final clarifier was coming out of the final clarifier was running about two parts per million so we had to aerate in order to get the water up to adequate desired oxygen level so we would not stress the fish due to low dissolved oxygen. The reason I did this is because we feel like we want to measure dissolved poisons or pollutants that might be toxic in the effluent not low dissolved oxygen. I don't want to measure that effect. I want to measure the effect of the dissolved pollutants.

Anonymous: Of course, the high dissolved oxygen, the higher it is well that usually provides a better environment for the fish and so they will survive. Better if you had ten parts per million than you had five or six.

Sterling Burks: True. In this particular refinery they have a good lagoon system following their activated sludge system and their dissolved oxygen going to the stream is very good. Out of this clarifier, it just was not very high at this time.

Anonymous: What has been your experience with dissolved salts on the osmotic effect on your minnows?

Sterling Burks: We have not set up any tests, to test for this specifically, but I would think that fish can tolerate quite a range in dissolved solids as long as they are not instantly changed from maybe a 100 parts per million total dissolved solids to 5,000. Sudden changes really affect aquatic organisms, gradual changes they can acclimate to, quite a range in chemical environment.

BIOGRAPHY

Sterling L. Burks is an Assistant Professor of Zoology at Oklahoma State University, Stillwater, Oklahoma. He is the Assistant Director of the Reservoir Research Center. Sterling received his B.S. degree from Southwestern State College, Weatherford, Oklahoma, in Biology and Chemistry. M.S. and Ph.D. degrees in Zoology (Aquatic Biology) were earned at Oklahoma State University. Sterling spent two years on a Federal Water Pollution Control Administration Post Doctoral Fellowship before joining the faculty at Oklahoma State University in 1972. Research interests are the analyses and determination of the effects of chemical contaminants upon aquatic organisms.

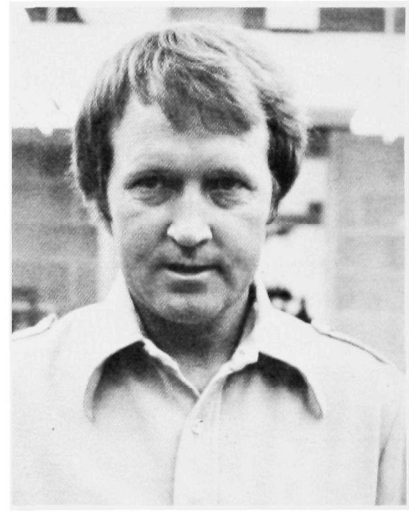


TABLE 1 "COMPARISON OF MEDIAN LETHAL TIMES OF FATHEAD MINNOWS EXPOSED TO OIL REFINERY EFFLUENTS IN CONTINUOUS-FLOW AND STATIC TESTS"

Date	LT 50 (min.) Continuous-Flow	LT 50 (min.) static
5/5-5/10	690	360
5/12-5/17	380	380
5/21-5/25	550	90
5/28-6/3	1,600	500
6/4-6/9	2,100	2,100
6/9-6/15	1,460	1,075
6/16-6/20	800	800
6/23-6/27	1,150	890

TABLE 2 "COMPARISON OF MEDIAN LETHAL CONCENTRATIONS OF OIL REFINERY EFFLUENTS TO FATHEAD MINNOWS IN CONTINUOUS-FLOW AND STATIC TESTS"

Date	LC 50 Continuous-Flow	LC 50 static
5/5-5/10	60%	60%
5/12-5/17	55%	53%
5/21-5/25	42%	32%
5/28-6/3	77%	75%
6/4-6/9	81%	81%
6/9-6/15	78%	79%
6/16-6/20	74%	64%
6/23-6/27	70%	61%

TABLE 3 "SPECIES DIVERSITY OF BENTHIC MACROINVERTEBRATES EXPOSED TO OIL REFINERY EFFLUENTS TREATED BY ADVANCED WASTE WATER TREATMENT"

Effluent Stream	Date 1975	Stream #	Rep. #	Species Diversity $\bar{d}$	Mean of Reps. $\bar{x}$ $\bar{d}$
Peavine Crk.	10/27		1	1.84	
Peavine Crk.	10/27		2	2.76	2.75
Peavine Crk.	10/27		3	3.69	
Peavine Crk.	10/27		4	2.71	
Control	11/6	1	1	2.59	
Control	11/6	1	2	2.62	2.53
Control	11/6	2	1	2.59	
Control	11/6	2	2	2.34	
Act. Sludge	11.6	1	1		
Act. Sludge	11/6	1	2	2.32	
Act. Sludge	11/6	2	1	2.29	
Act. Sludge	11/6	2	2		
Dual Media	11/6	1	1	2.41	
Dual Media	11/6	1	2		
Dual Media	11/6	2	1	2.86	
Dual Media	11/6	2	2	2.82	
Act. Carbon	11/6	1	1	2.46	
Act. Carbon	11/6	1	2	2.50	
Act. Carbon	11/6	2	1	3.32	
Act. Carbon	11/6	2	2	3.37	
Control	11/13	1	1		
Control	11/13	1	2	1.54	
Control	11/13	2	1		
Control	11/13	2	2	2.52	
Act. Sludge	11/13	1	1		
Act. Sludge	11/13	1	2	2.91	
Act. Sludge	11/13	2	1	2.61	
Act. Sludge	11/13	2	2	2.83	
Dual Media	11/13	1	1		
Dual Media	11/13	1	2	2.69	
Dual Media	11/13	2	1		
Dual Media	11/13	2	2		
Act. Carbon	11/13	1	1	2.16	
Act. Carbon	11/13	1	2		
Act. Carbon	11/13	2	1	2.31	
Act. Carbon	11/13	2	2	2.43	

Blanks in species diversity column represent samples which have not been analyzed at this time (12/30/75)

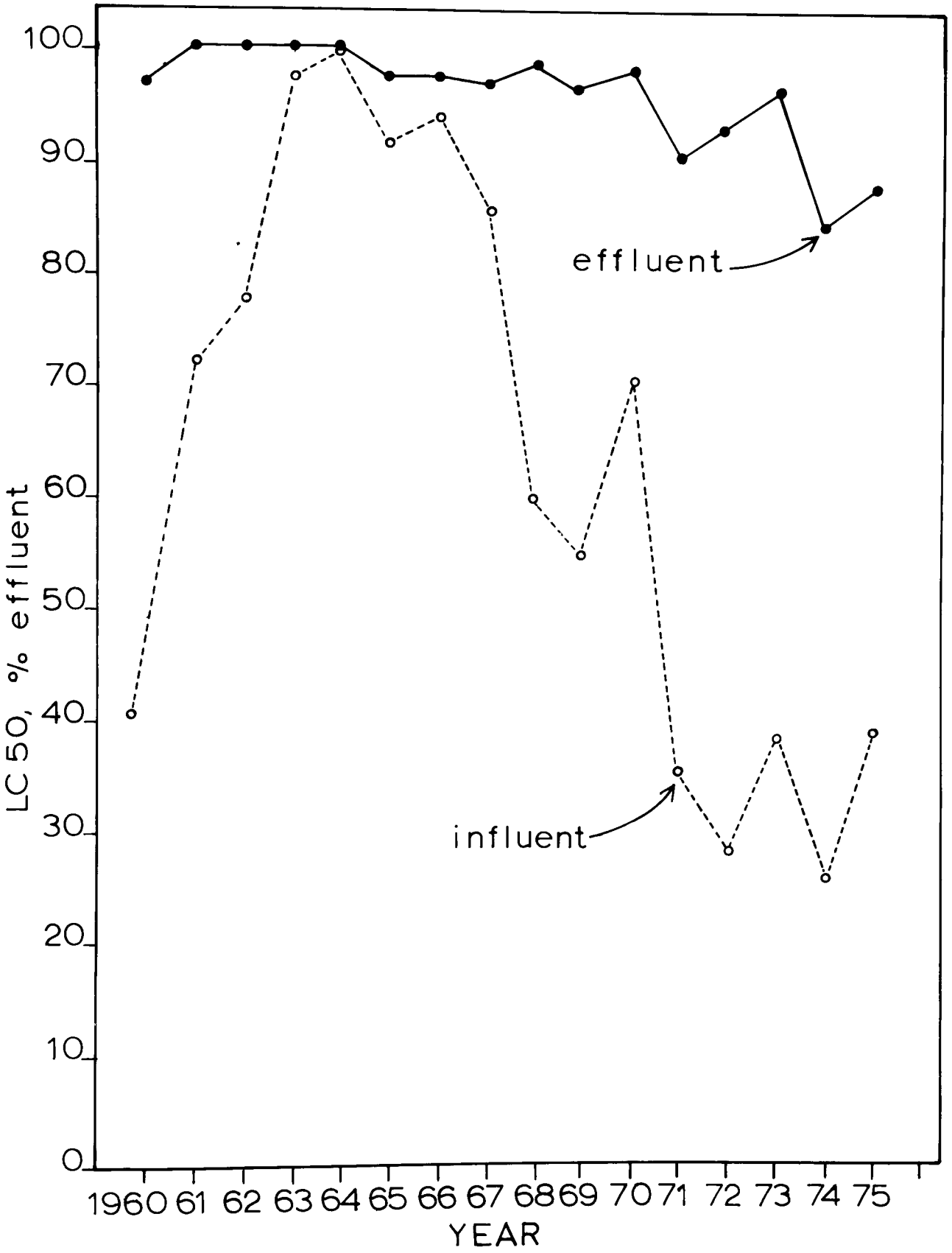


Fig. 1. Comparison of mean annual Fathead minnow LC50's of the influent and effluent streams to an oil refinery lagoon waste water treatment system.

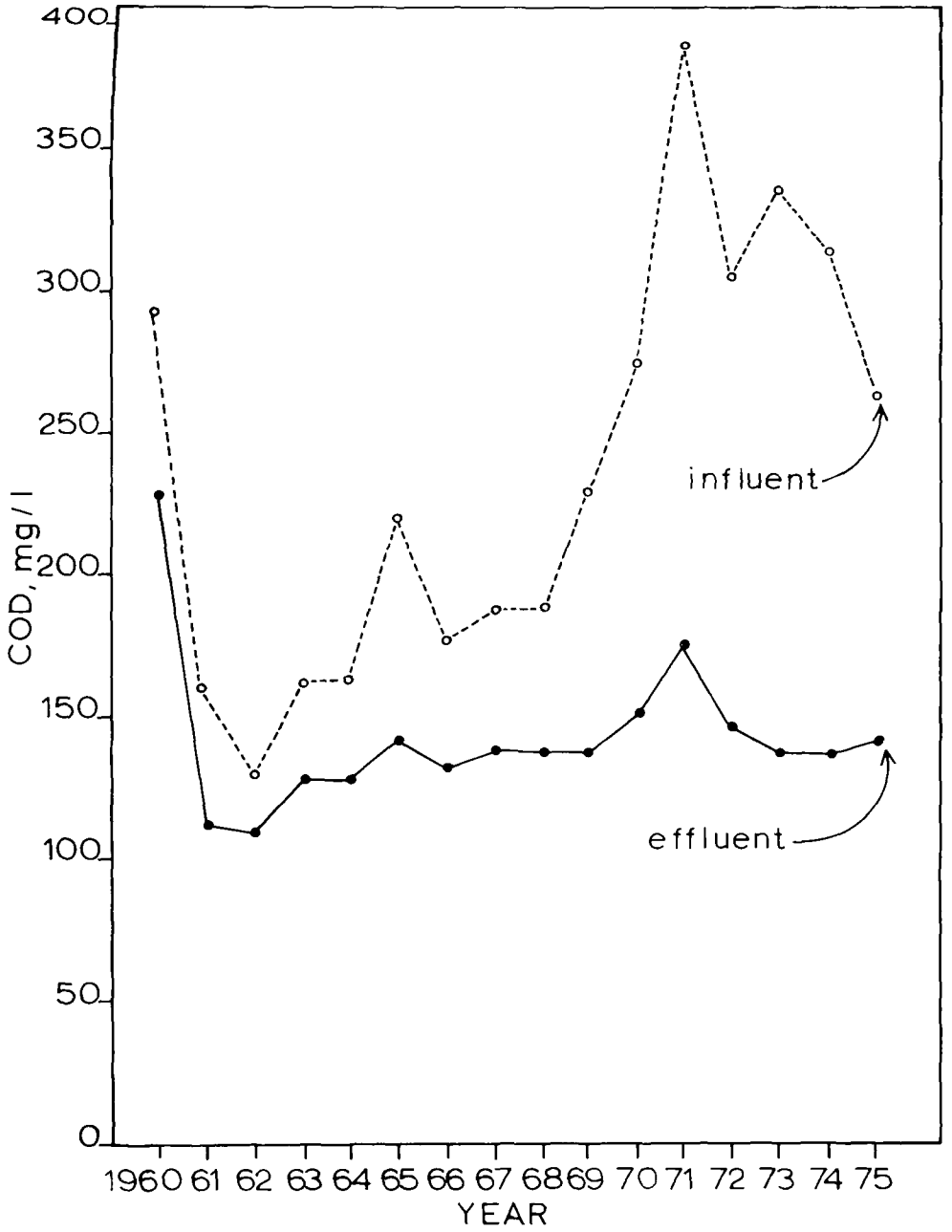


Fig. 2. Comparison of mean annual COD concentrations of the influent and effluent streams to an oil refinery lagoon waste water treatment system.

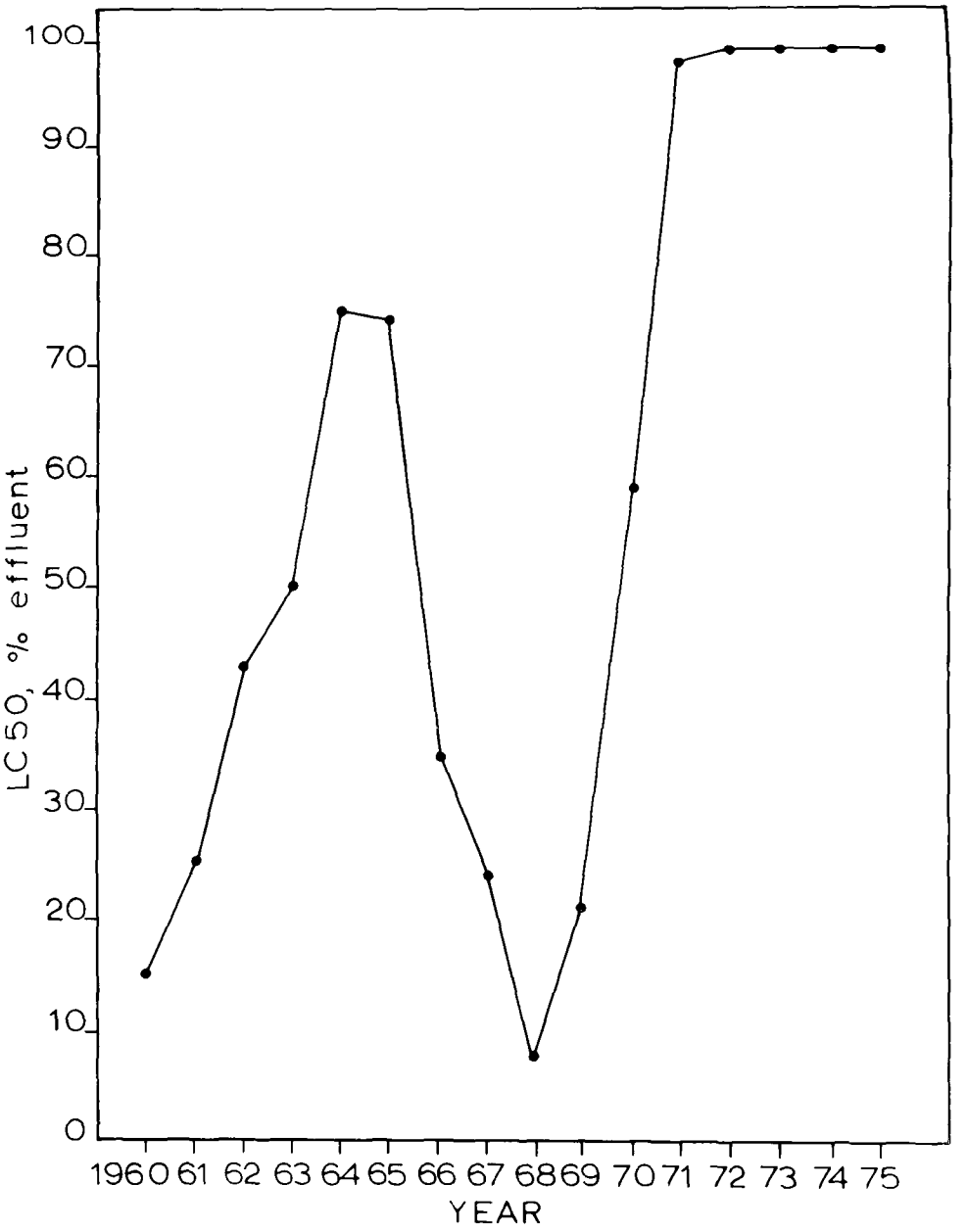


Fig. 3. Long range trends of the mean annual Fathead minnow LC50 illustrating improvement after installation of an activated sludge treatment system.

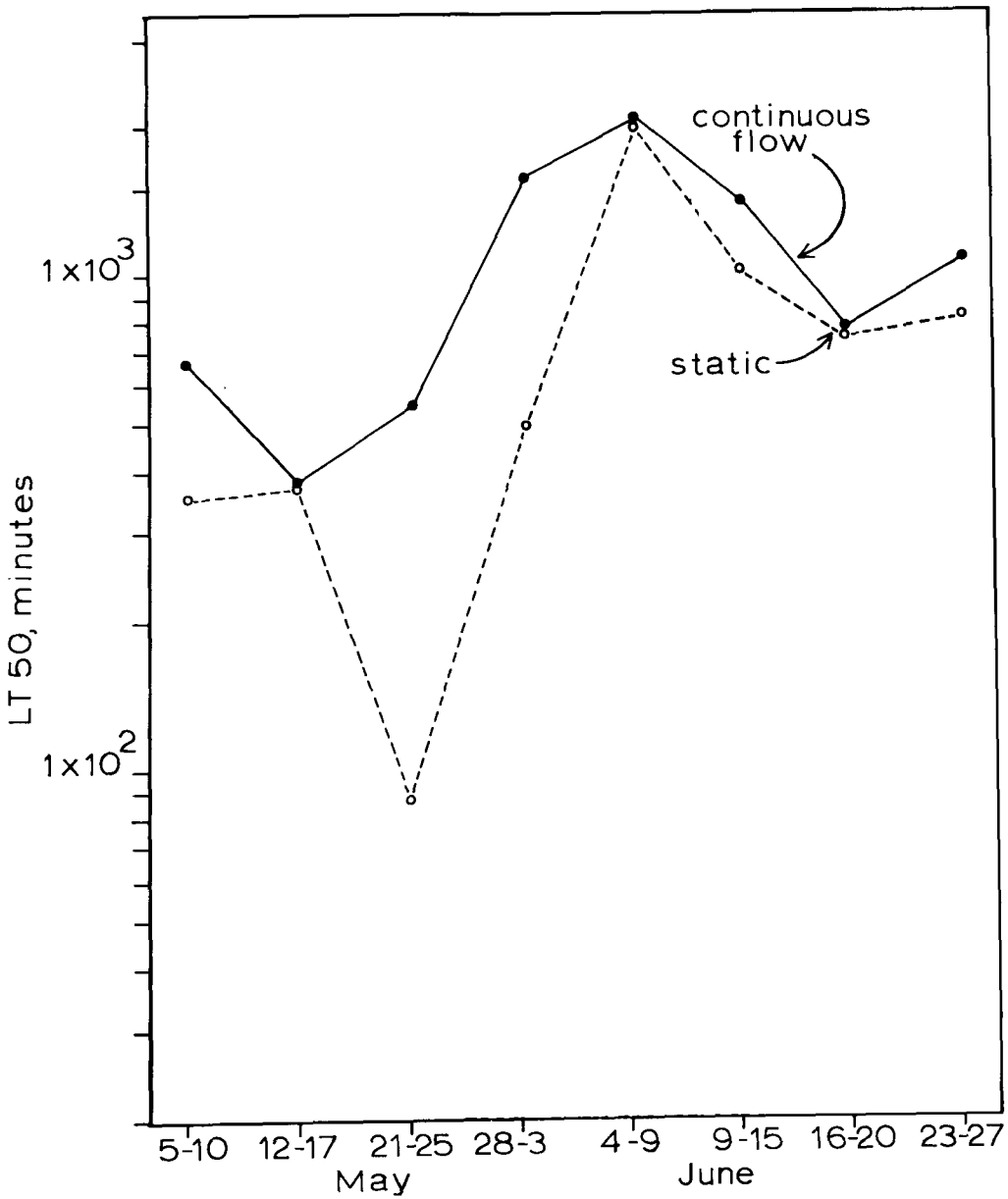


Fig. 4. Comparison of median lethal time of Fathead minnows exposed to an oil refinery effluent by static and continuous-flow methods.

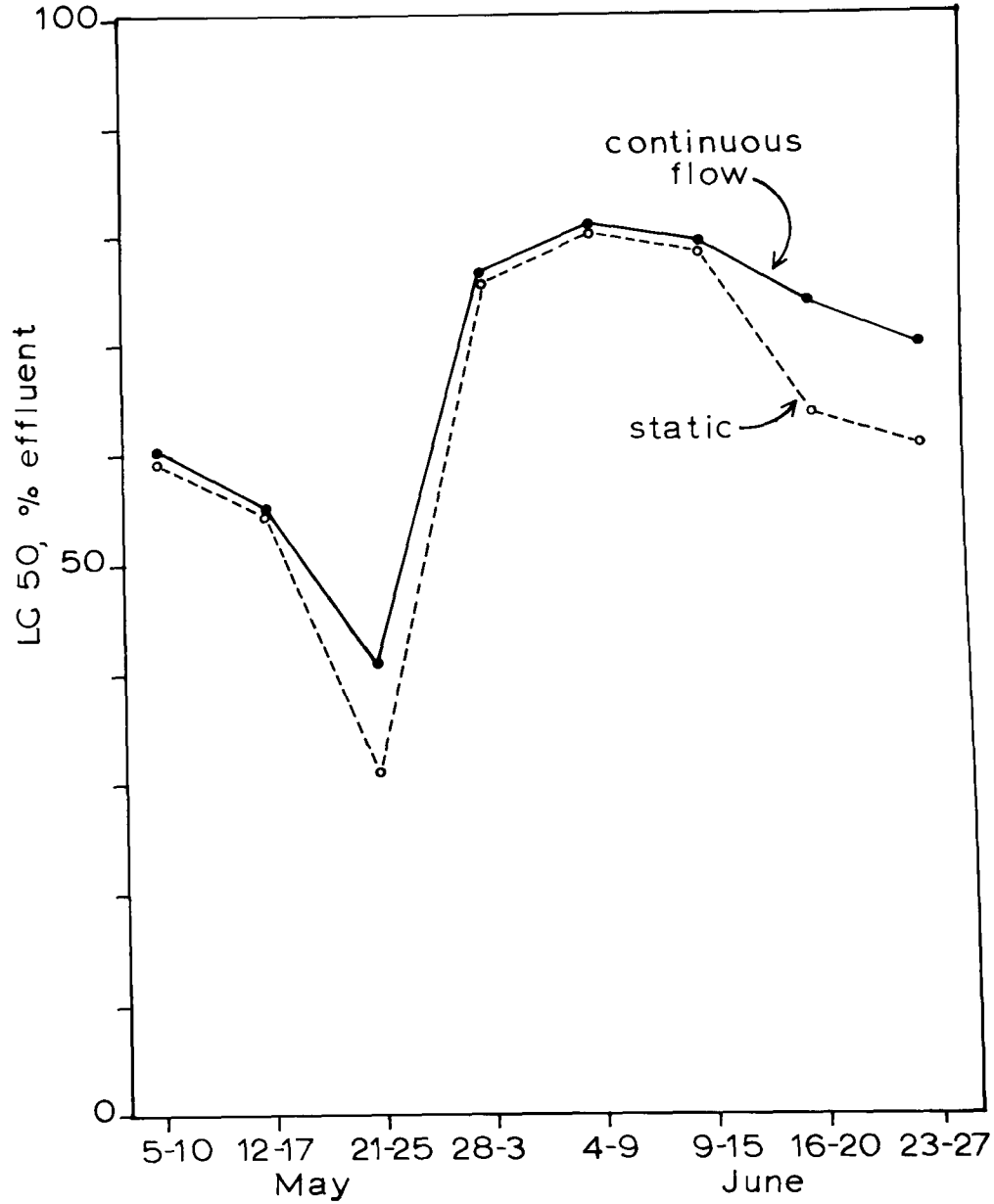


Fig. 5. Comparison of the 96 hour median lethal concentration of Fathead minnows exposed to an oil refinery effluent by static and continuous-flow methods.

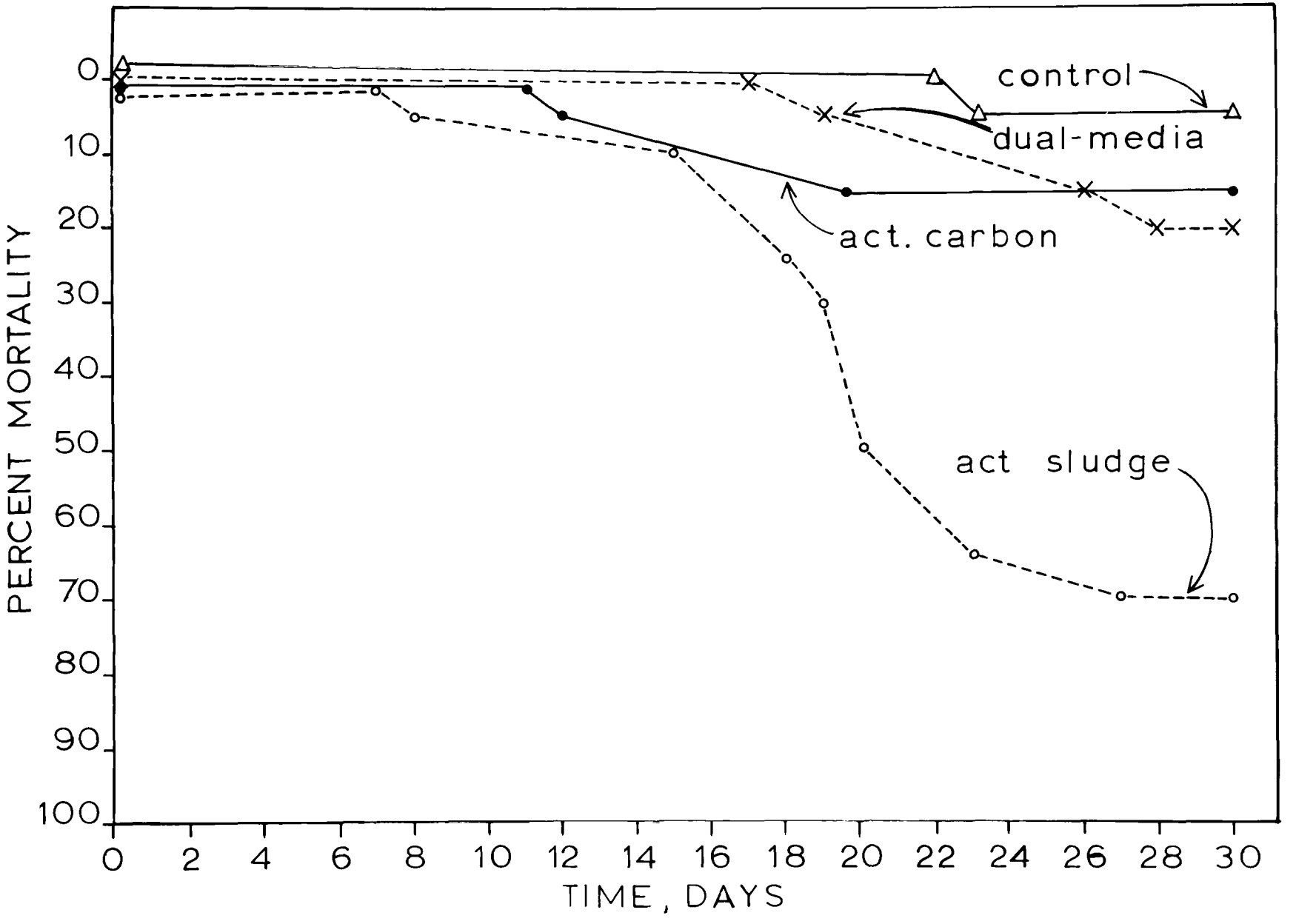


Fig. 6. Response of Fathead minnows in continuous-flow exposure to control, activated sludge, acitvated sludge-dual media, and acitvated sludge-dual media-acitvated carbon test effluents.

API - SOUR WATER STRIPPER STUDIES

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ABSTRACT

Promulgation of national effluent guidelines and stringent new air pollution regulations make the sour water stripper a critical unit in most refineries. Yet, many plants report difficulty in achieving low ammonia levels. Others experience severe corrosion and fouling in the overhead reflux system. In response to these problems, the API - Division of Refining initiated in 1972 a program to improve stripping technology. First step in the study was to circulate two comprehensive questionnaires throughout the industry.

Bench-scale studies conducted in 1974 by the Committee on Refinery Environmental Control showed widely different stripping characteristics for sour waters from three refineries. Despite excessive steam usage and a large number of theoretical trays, ammonia concentrations could not be reduced below 520, 100, and 38 mg/l, respectively. Analyses of the acidic bottoms revealed the presence of organic acids and amides. Adjustment of the pH to 9.0 allowed further ammonia reduction, without fixing H_2S in solution. Similar stripping tests on synthetically prepared sour waters achieved 10-20 ppm NH_3 with even modest steam rates.

Tray-by-tray calculations using Van Krevelen NH_3-H_2S-H_2O equilibrium data showed good correlation with actual performance on a full-scale stripper down to the point that only fixed ammonia remained in solution.

Also during 1974, the Technical Data Subcommittee conducted fundamental vapor-liquid equilibrium studies to check and expand the range of the Van Krevelen data. In addition, vapor pressure data were obtained for synthetic sour water containing HCN, ethyl mercaptan, and cresol.

The Subcommittee on Refinery Corrosion conducted research using a dynamic corrosion loop system to study metallurgy problems related to refluxed strippers.

INTRODUCTION AND PURPOSE

In 1972, the API Division of Refining initiated an extensive program to develop sour water stripping technology. This effort was in response to concern expressed by member companies regarding tough new environmental regulations. Initially, the study was conducted by the Committee on Refinery Environmental Control (CREC) and the Subcommittee on Corrosion of the Committee on Refinery Equipment (CRE). In 1974, the program was expanded to include fundamental vapor-liquid equilibrium studies by the Committee on Research Data, and Information Services (RDS). During the course of the studies, CREC served as overall coordinator to ensure that the technology developed was sufficient to meet environmental requirements.

The purpose of this paper is primarily to discuss results of the CREC program to-date. Simultaneously, the roles of CRE and RDS will be described and their programs briefly mentioned. A detailed discussion of the CRE and RDS studies is impossible in this write-up, since each easily constitutes an individual paper. All three committees are preparing detailed reports concerning their work.

The CREC program first included a detailed survey of the industry to define the state of the art. Then in 1974, numerous bench-scale tests and analytical studies were performed to compare the stripping characteristics of actual and synthetically prepared sour waters. Available vapor-liquid equilibrium data are based on such synthetic solutions.[1] Results of tests on a full-scale tower were then used for comparison with the bench-scale data and tray-by-tray calculations using the procedure outlined by Beychok.[2]

BACKGROUND

Until recent years, sour water strippers were built to remove mainly H_2S. Many units were installed with a minimum of engineering attention. The sour off-gases were usually burned in a flare or furnace.

New air and water pollution regulations have now made the stripper a critical unit in most refineries. Careful attention must be given both to design and operation. Best Practicable Control Technology Currently Available (BPCTCA) and Best Available Technology Economically Achievable (BATEA) wastewater effluent guidelines[3] promulgated by the Federal Environmental Protection Agency (EPA) severely limit NH_3 and H_2S discharges. Some states and localities have requirements that are even more stringent.

When expressed on a concentration basis, most refineries will have to meet an effluent NH_3 value by 1977 ranging between 2 and 20 mg/l. In 1981, this range must be reduced to about 1-8 mg/l, if the BATEA guidelines are implemented and water usage is not significantly reduced per barrel of crude processed.

To compound these problems, EPA is now considering cyanide for possible inclusion on the list of toxic pollutants that must be controlled. The principal source of cyanides in refinery waste waters is sour water from cracking operations. Very little is known about the types of cyanides that occur nor to what degree they are removed during stripping. Efforts in this regard have been hampered by lack of a reliable analytical method due to sulfide interferences.

Today, air pollution regulations prohibit the direct burning and release of stripper off-gases to the atmosphere in some localities. Recovery in a sulfur plant is usually necessary in these cases. This requires refluxing of the stripping tower to minimize overhead water and complicates control of the Claus unit due to the NH_3 present. In addition, contaminants in the sour water concentrate in the overhead system and cause numerous corrosion problems.

Ammonia is much more difficult to strip than H_2S due to its strong affinity for water. In years past, a 90 percent removal efficiency for H_2S was satisfactory to meet most state and federal effluent requirements. Consequently, only three or four equilibrium stages were necessary in the stripper. However, current limitations sometimes require a bottoms ammonia value below 50 mg/l. This usually corresponds to 98 percent removal of NH_3. Consequently, the number of theoretical stages required is drastically increased.

It should be emphasized that the calculation procedure outlined by Beychok, using Van Krevelen data, will take the bottoms ammonia concentration down to essentially zero, if enough stripping stages and steam are supplied. To the contrary, field experience indicates that low ammonia values are difficult to achieve in many cases.

PROJECT CONCEPTION

Verbal reports at the semiannual meetings of the CREC in the early 1970's indicated that some refineries, particularly those on the West Coast, have difficulty in achieving bottoms NH_3 values below 100-200 mg/l. The bottoms pH simultaneously drops to the acidic side, although it should be alkaline if the system contains only NH_3-H_2S-H_2O. Other individuals reported that their plants could achieve 50 ppm NH_3 under similar stripping conditions. This suggested the possibility that acidic components may be present in some sour waters.

Stripping is dependent on the hydrolysis reaction(2):

$$NH_4SH \qquad NH_3 + H_2S$$

Small amounts of strong acid would shift the equilibrium to the left and prevent complete stripping of NH_3 from solution.

There were conflicting reports in both CREC and CRE regarding corrosion problems with refluxed towers. These problems ranged from complete loss of the overhead exchanger tube bundle in a few months to no noticeable corrosion after several years.

In order to clarify the conflicting stories and establish a better overall understanding concerning stripper problems, both the CREC and CRE circulated detailed questionnaires throughout the industry in mid-1972.

RESULTS OF QUESTIONNAIRES

A. CREC Questionnaire

The questionnaire circulated by CREC was intended to obtain information concerning all aspects of sour water stripping. Sixty-three (63) plants participated and supplied information on 73 units. Williams Brothers Waste Control Inc. collated and evaluated the voluminous amount of data received. The information is available as API Publication 927.

2.5-3.5 feet. It was of interest to note that about 75 percent of the plants use trayed columns. All columns in the survey built since 1970 indicated use of trays. Greater turndown capability is the most logical explanation, especially where valve trays are utilized.

Data reported on phenol stripping showed that, for towers with 90 percent NH_3 removal, refluxing reduced the average phenol removal from 55 percent to 39 percent. Fourteen companies reported information on cyanide removal. The data were very erratic but suggested an average removal of 37 percent. This information should be viewed with caution since the available analytical procedures are subject to sulfide interference. Also, there was no breakdown in regard to cyanide type (i.e., simple, complexed, etc.).

Questionnaire No. 34 supplied data for a more in-depth review of stripping performance. The data are plotted in Figure 1 along with tray-by-tray calculations using the procedure outlined by Beychok. It appears that slightly less than five theoretical trays (i.e., 4.6-4.8) give a good fit with measured data down to about 50 mg/l. Below this point the measured NH_3 concentration drops almost straight down and appears to bend a little back to the left. It is very unlikely this could happen in a system with constant feed conditions. It is suspected the feed characteristics changed or an analytical error occurred. Additional data are needed for confirmation; however, it is speculated that the curve normally bends to the right in a manner illustrated by the dashed line. If 15 feet of 3-inch Raschig rings in the tower equals 4.7 theoretical stages, the Height Equivalent to a Theoretical Plate (HETP) equals 3.2 feet. Calculations using Fractionation Research Procedures [4] gave a predicted HETP of 4.5 feet. A more detailed discussion of tray-by-tray calculations will be given later in this paper.

2. Corrosion

Accumulative data in the questionnaires indicated only minor corrosion problems with the tower, trays, and feed-to-bottoms exchangers. Most of the towers are fabricated out of carbon steel. Some cases of localized corrosion were indicated due to lack of proper insulation around nozzles and manhole covers. This encourages condensation at the metal surface and promotes corrosion. It appears tower internal linings and metals other than carbon steel are seldom necessary. Corrosion on trays was also minor regardless of whether carbon steel or stainless steel was utilized. Perhaps stainless steel is warranted in the tope of the tower if the reflux is fed directly back to the stripper. Very little corrosion was reported in the shell or tubes of the bottoms exchanger although both are almost always made of carbon steel.

As suspected, the major area of corrosion was the overhead system on refluxed columns. However, the 18 replies to this questionnaire were

The questionnaires were first classified by stripper type as follows:

Refluxed Strippers	31
Nonrefluxed Strippers	24
Flue Gas Strippers	5
Fuel Gas Strippers	2
Oxidizing Strippers	4
Reject Questionnaires (insufficient information)	7
	73

Only the 55 replies concerning refluxed and nonrefluxed steam strippers need be discussed. The others are limited in regard to meeting BPCTCA and BATEA guidelines.

1. Stripping Efficiency

As expected, ammonia stripping efficiency varied widely between plants. It was difficult to find common grounds for comparison due to the various types and sizes of towers and contacting media utilized. Also, many towers were operating at nonoptimum vapor and liquid loadings.

Perhaps the most important point observed was that seven refiners indicated bottoms NH_3 values averaging 50 mg/l and twenty plants reported 100 mg/l. As shown in Table 1, an even larger number of plants indicated achievement of these levels periodically. A review of the data indicated that perhaps a few more plants could average below 50 and 100 mg/l, respectively, if higher steam rates were used. Several questionnaires reported only average bottoms data and did not indicate the minimum attainable NH_3 concentration. One should not conclude from the data that refluxed units strip better than nonrefluxed units. The refluxed units look better in the table simply because they are generally newer and probably better designed. A detailed listing of the individual plants is given in Table 2.

One surprising result was that none of the reported bottoms pH values dropped below 7.0. However, as shown in Table 3, there were a few cases where bottoms ammonia fixation could possibly have been a problem. However, it must be emphasized that the data reported are insufficient to reach a firm conclusion. The observation is merely made that from the author's experience and a few calculations using Van Krevelen data, the bottoms NH_3 data reported appear high considering the stripping ratios and tower internals reported.

The report concluded that the tray efficiency ranged between 30 and 50 percent in most cases and the HETP for 3-inch Raschig rings averaged

inconclusive regarding the best metallurgy. Experience with aluminum was particularly erratic. In some cases poor performance appeared to be caused by errosion due to excessive velocities.

3. Miscellaneous

Table 4 gives the final disposition of the reported stripper overheads and bottoms. As shown, the majority of plants still burn the sour off-gas and release it to the atmosphere as SO_2, N_2, and H_2O. This is usually done in a flare, CO boiler, or furnace. However, the trend throughout the industry is toward recovery in Claus sulfur units.

There were reports of hydrocarbon carry-over to the stripper causing problems in the combustion furnace and sulfur units. This was particularly true for hydrocarbon slugs entering the system. Very little information was obtained about sulfur plant operations. Air cooling is reportedly utilized in about 50 percent of the overhead reflux systems.

Over one-half of the plants practice water conservation by using the stripper bottoms for desalter make-up. Most towers have a feed-to-bottoms exchanger. A typical heat transfer coefficient appears to be 100-150 Btu/Hr/Sq Ft/^{o}F.

Only three plants reported problems with excessive foaming; however, some form of solids deposition was indicated in about one-half of the questionnaires. Carbonate scale was experienced in several plants due to hard water inadvertently entering the tower. Others reported phenolic and amine based polymeric sludges. One plant reported a ferrocyanide deposit.

B. CRE Questionnaire

In May 1972, the CRE sent its questionnaire throughout the refining industry. Eighty-seven (87) replies were received from 67 plants. This questionnaire concentrated solely on corrosion and is consequently much more detailed on this subject than the CREC questionnaire. Results of the survey are available in API Publication No. 944 prepared by Exxon Research. In addition to conventional single-stage refluxed and nonrefluxed strippers, information is also tabulated on two-stage units with pH adjustment before each stage.

Similar to the CREC study, the report concluded that the only area of severe corrosion in refluxed and nonrefluxed columns is the overhead on refluxed systems. In general, carbon steel and stainless steel tubes in the reflux condenser were unsatisfactory. Experience with aluminum was mixed, primarily due to erosion from excessive velocity.

CREC 1974 STUDIES

A. Background and Objectives

During 1974, CREC conducted an extensive bench-scale testing program using actual and synthetically prepared sour water solutions. This study was initiated to help answer some of the questions unresolved from the CREC questionnaire. The program had the following general objectives:

1. Determine if stripping characteristics of actual refinery sour waters are the same as synthetically prepared solutions for which Van Krevelen vapor-liquid equilibrium data are available.

2. Compare theoretical tray-by-tray stripping calculations to actual field performance.

3. Outline methods of handling stripper off-gases to effectively achieve sulfur recovery and ammonia destruction.

4. Prepare a written discussion of sour water stripper operating problems and special design considerations.

A detailed report was completed by the contractor, Bechtel Corporation, in April 1975.

B. Laboratory Experimental Procedures

Laboratory stripping studies were made using the Oldershaw column apparatus shown in Figure 2. The column is insulated by a vacuum jacket and the number of plates (sieve trays) can be varied by combining sections with various numbers of plates. One section each of 5, 10, and 30 plates was available for this work.

To start a run, the equipment was brought up to temperature and a level attained in the reflux receiver before initiating feed to the column. After the column had been operating a few minutes, the NH_3 content of the bottoms was measured periodically to determine when it attained a constant value, indicating that the column had reached equilibrium.

All of the condensed overhead was returned to the column feed as reflux ahead of the preheater. The reflux rate was controlled by holding a constant level in the reflux receiver with a variable speed condensate return pump. This pump, like those for the fresh feed and bottoms, was a positive displacement peristaltic pump, the speed of which could be manually set.

The feed preheater was closely coupled to the top of the column and the short connection insulated with aluminum foil and heated with a radiant lamp to minimize temperature changes. Likewise, the vapor connection between

the column and the condenser was similarly insulated and heated.

The overhead condenser was changed from time to time during the laboratory investigation. Cooling water was used for the first seven runs. This overly cooled the overhead and had to be discontinued. For runs 8-18, the reflux receiver was kept warm and held at a constant temperature with a heating tape. To be sure that the reflux was in equilibrium with vapor at the measured condenser temperature, the heated, water jacketed, condenser shown in Figure 2 was utilized for the remainder of the program.

Part of the steam generated in the reboiler of the stripper passed overhead into the condenser as stripping steam, and part condensed in the column (mostly on the top tray) to heat the downflowing liquid. The latter is heating steam and its quantity depends on the temperature of the feed and reflux. Since most of the heating steam travels up through nearly all of the column, it also does considerable stripping. Flow of total steam was measured, and the flow of stripping steam was calculated by subtracting the quantity of heating steam required.

C. Laboratory Test Program

For the bench-scale tests, actual sour water samples were collected from two West Coast and one Gulf Coast refineries. These waters were labeled A, B, and C, respectively, and stripping tests performed as quickly as possible in the contractor's laboratory. Synthetic samples of NH_3-H_2S-H_2O were then prepared to simulate the actual sour waters. The synthetic samples were stripped in a similar manner using the same bench-scale equipment and operating conditions.

1. Sample Aging

Initial synthetic samples were prepared by dissolving a commercially available solution of $(NH_4)_2S$ in distilled water (designated as Synthetic I). It was soon discovered that the synthetic samples prepared in this manner could not be stripped below 125 mg/l NH_3. It was suspected that partial oxidation of the stock solutions produced acid impurities which fixed NH_3 in solution since the bottoms pH dropped below 7.0.

Further experiments using commercial $(NH_4)_2S$ solutions were abandoned, and throughout the rest of the program synthetic sour waters were prepared by dissolving H_2S gas in dilute NH_4OH (Synthetic II samples) immediately before stripping. This is similar to Van Krevelen's experiments.

Additional tests were run to determine if aging affected Synthetic II and actual sour waters. A series of samples were taken from a large flask containing Refinery B sour water. An air space was allowed above the liquid level in the container during the tests. Each individual sample was batch boiled and then checked for residual ammonia. Distilled water was periodically added to

replace any water lost during boiling. A similar series of tests were run on Synthetic II sour water.

Figure 3 shows a plot of the residual NH_3 values after batch boiling. These data show that sample aging is detrimental to high ammonia removal efficiencies for both Synthetic II and actual sour waters if oxygen is allowed into the system.

2. Stripping of Synthetic II Sour Waters

Synthetic II solutions stripped very easily in all tests. As shown in Figure 4, residual ammonia levels of 10-15 ppm were attained using very low steam rates. As further illustrated, the addition of several hundred ppm phenols and 30-93 mg/l cyanide failed to fix significant ammonia in solution.

3. Stripping of Actual Sour Waters

Bench-scale stripping of actual sour waters gave results considerably different than when using Synthetic II sour waters. Figure 5 shows stripping data for Refineries A and B. Figure 6 shows Refinery C. As illustrated, the bottom of each curve appears to have flattened and very little additional NH_3 removal is possible despite a large steam usage. The fixed ammonia in the bottoms appears to average about 520, 100, and 38 mg/l, for A, B, and C, respectively. A comparison of these curves with Figure 4 indicates considerably poorer stripping.

4. Characterization of Stripped Sour Waters

Since Refineries A and B had considerable fixed NH_3, a brief analytical program was conducted in an attempt to identify contaminants present in the stripped bottoms. A similar characterization was conducted on another Mid-Continent sour water (Refinery D) which had a fixed bottoms NH_3 of approximately 40 mg/l. The original samples were first analyzed for total organic carbon (TOC) and metals content. Next they were boiled to dryness and the residues subjected to infrared analyses.

As seen in Table 5, Refinery A had a TOC of 3,800 mg/l but very little inorganic carbon. The sample contained 1,580 mg/l nonvolatile residue, most of which would burn as evidenced by an ash content of only 80 mg/l. Refineries B and D were considerably different than Refinery A. Each had TOC values of only 360 and 330 mg/l, respectively. Although Refinery B had a high nonvolatile content similar to Refinery A, the residue was largely inorganic as evidenced by the high ash content. This is verified by high Na, Ca, Mg, and Si concentrations in the residue. Refinery D had only 460 mg/l nonvolatiles, which was much lower than either of the other plants. An ash content was not run on the residue.

Concentrates of samples from Refineries A and D were analyzed by both infrared and mass spectroscopy. The organic content of Refinery A was identified as a complex mixture of low molecular weight amides and inorganic salts. High concentrations of thiocyanate were identified in the infrared spectra. Analysis of Refinery D disclosed no discernible organic functional groups. Thiocyanates were evident. Attempts to identify specific compound types were unsuccessful. The amides in the sample from Refinery A were probably formed during evaporation, from ammonium salts of carboxylic acids. Infrared spectra did not show the presence of sulfonic or naphthenic acids.

5. Effects of Caustic Addition

Brief pH adjustment studies were conducted using continuous and batch boiling apparatus. The continuous study results were erratic due to poor pH control. However, the batch boiling results given in Table 6 clearly show that addition of caustic allowed ammonia to be further stripped from solution. Since pH adjustment studies were not in the original project scope and limited funds remained, this program could not be pursued. Future studies are needed to determine the optimum operating conditions and caustic injection point(s).

D. Full-Scale Stripping Test Program

Initially, full-scale studies were to follow the bench-scale program for Refineries A, B, and C. Since Refinery A had such high fixed ammonia, it was decided to abandon field studies in lieu of the sample characterization program previously discussed. Due to similar reasons and limited funds, plans were abandoned for Refinery B as well. Therefore, full-scale tests were conducted only on Mid-Continent Refinery C. The objective was to provide a comparison of field and bench-scale data plus theoretical tray-by-tray calculations.

1. Experimental Results

Figure 7 shows how NH_3 in the bottoms varied for:

- o the full-scale stripper at Refinery C.
- o the bench-scale stripper using Refinery C sour water.
- o the bench-scale stripper using Synthetic II sour water.

As shown, the full scale stripper using ten valve trays performed slightly better than the small-scale unit using five sieve trays. However, the stripping curve for Synthetic II sour water is quite different. A lower limit of residual NH_3 (i.e., 15 mg/l versus 38 mg/l) is reached at high steam rates. The synthetic sour water also obviously strips easier at low steam rates.

2. Tray-by-Tray Calculations

To provide a further comparison, the Van Krevelen equilibrium data were used to perform stage-to-stage calculations to determine bottoms NH_3 as a function of stripping steam rate. It was found that six theoretical stages (i.e., five trays plus bottoms reboiler) gave results corresponding most nearly to the large scale test data. Both the actual and calculated data are for refluxed systems. The actual system contained ten valve trays, but was not reboiled. Results are shown in Figure 8.

As might be expected, the calculated NH_3 concentration in the bottoms continues to fall as the steam flow increases. When these results are compared with the actual sour water, it is obvious that the calculations do not predict the residual level of NH_3 actually measured once the calculated value drops below 50 mg/l. The correlation seems to be good above this point.

A quick review of Refineries A and B bench-scale tests indicated that calculated bottoms ammonia values for these cases would also be inaccurate below the fixed ammonia levels measured. Questionnaire No. 34 previously discussed is a little harder to predict.

The data given indicate a fixed ammonia level probably exists much of the time. If this is true, the same calculational error is predictable.

3. Tray Efficiency

To provide a further comparison, overall stage efficiencies were estimated for large-scale Refinery C, small-scale Refinery C, and small-scale Synthetic II. The efficiencies were obtained by running tray-by-tray calculations for each column using a computer program based on the Beychok procedure. Various numbers of theoretical trays were assumed for each case until the assumed value gave a good curve fit with the measured data. The efficiency was then obtained by dividing the number of theoretical trays by the number of actual stages.

All three columns had an overhead reflux system. It was assumed that equilibrium existed in each reflux receiver. Therefore, the term "tray efficiency" applies only to the column internals and bottoms reboiler. The full-scale unit contained ten actual stages and the bench-scale system six (i.e., five trays plus bottoms reboiler). The calculated number of theoretical stages and tray efficiencies are as follows:

STAGE EFFICIENCY

Experimental Series	Estimated Number of Equilibrium Stages*	Actual Stages*	Tray Efficiency
Large Scale, Refinery C	6.3	10	63%
Small Scale, Refinery C	5.4	6**	90%
Small Scale, Synthetic II	9.0	6**	150%

*Excluding overhead condenser system.
**Five trays plus bottoms reboiler.

Obviously the 63 percent tray efficiency for the full-scale tower indicates the system is running well. The CREC questionnaire indicated most towers are in the 30-50 percent range. A check of the tray liquid and vapor loadings showed the tower to be operating in a range where efficiency should be optimum.

The efficiency of the small-scale unit on Refinery C water was even higher (i.e., 90 percent versus 63 percent) than the efficiency of the large-scale tower. This is not surprising since the small unit has tiny tray openings and gives better contact between liquid and vapor phases. In addition, it may have had significant wall effects due to the small column diameter.

The tray efficiency required to force a curve fit for the Synthetic II data is 150 percent. The difference in performance between the two waters in the same apparatus could not be explained. The vapor-liquid equilibrium data used in the calculations were originally obtained by Van Krevelen using similar synthetically prepared sour waters. This point definitely needs more study.

4. Equilibrium Data at High Concentrations

At the high concentrations of H_2S and NH_3 found in the reflux streams, the equilibrium data, as extrapolated by Beychok, predict liquid concentrations much higher than those observed (see Table 7). This discrepancy can be explained by two facts:

- recent equilibrium measurements by RDS at high partial pressures of NH_3 and H_2S indicate that ionic strength effects decrease solubilities to about half of what the extrapolated Van Krevelen data predict.

- o reflux condensate temperatures measured in both the small and full-scale strippers may not indicate the temperature at which liquid and vapor are in equilibrium, if they actually do approach equilibrium.

In particular, the measured temperatures could be too low due to subcooling of condensate.

E. Stripping Calculation Procedures

1. Beychok Procedure

Ultimately a calculational model is needed which takes into account all components present in refinery sour waters. Such a model is not generally available throughout the industry today. Further research is needed before this is possible. In the meantime, Beychok's calculation procedure can be successfully applied in most instances if allowance is made for the fixed ammonia.

Before initiating calculations, one should determine the fixed ammonia value using bench-scale apparatus. Several samples should be taken over a period of time to evaluate the effect of feed fluctuations. The fixed ammonia value chosen should be subtracted from the design feed concentration and tray-by-tray calculations conducted on the remainder. Then the fixed ammonia value must be added back to the calculated bottoms value. If this level is tolerable, a solution exists. If the value is too high, the steam rate and/or number of stages can be increased. Once these parameters are optimized and the bottoms NH_3 is still too high, pH adjustment must be considered.

2. Selection of Proper Bottoms NH_3 Concentration

A word of caution should be given at this point concerning selection of the proper stripper bottoms ammonia concentration to be used for design purposes. Start with the pounds per day NH_3 allowed in the plant effluent and back calculate the maximum concentration permissible in the stripper bottoms. Remember that the average for the worst (i.e., highest) consecutive 30 days must meet the permit conditions. Otherwise the permit may be met on a long-term average basis but contain some 30-day periods above the prescribed limits. Also, remember that although most effluent NH_3 in refineries comes from the sour water stripper, a significant amount may come from other dilute sources. An accurate effluent ammonia balance is needed for the entire plant. In addition, refineries with biological oxidation will need some NH_3 for nutrients in the biosystem. This generally averages about 4.4 pounds[5] of nitrogen per 100 pounds BOD_5 removed. Ammonia utilized in this manner will end up in the bacterial cell mass or be converted to nitrate. Very little ammonia removal is to be expected with conventional surface and submerged aeration unless the feed temperature is well above 100°F. Biocultures should not be exposed to basin water temperatures much above 105-110°F.[6]

F. Stripper Design Considerations

The last two sections of the Bechtel report cover the important topics of off-gas disposal and stripper design considerations. These sections prepared by Milton R. Beychok summarize the state of the art and offer several interesting observations. However, due to space limitations, it is not the author's intent to discuss the numerous items. Instead, only three will be mentioned.

First, requirements for low bottoms ammonia concentrations will increase steam stripping ratios unless more trays are utilized. Today's fuel shortage and high prices present special incentives to minimize steam usage. Boosting the stripping ratio one pound per gallon will require 288 M pounds per day additional steam for a 200-gpm unit. With an 80 percent boiler efficiency and a fuel with 5.9 MM Btu per barrel this amounts to 22,300 barrels of fuel per year. At $8 per barrel the added operating cost, considering only the steam, is $178,200. In addition, higher stripping ratios boost utility requirements on the overhead reflux condenser and increase the flow rate of water in the tower bottoms. From this illustration, it is obvious that additional trays are easily justified when building a new tower. In some instances, refiners may even find it advantageous to replace existing columns. On an industry-wide basis, proper tower design can save considerable fuel each year.

Secondly, turndown capability should be given special consideration during tower design. Sour waters come from several areas of the plant. At any given moment, all or part of these streams will be feeding the stripper. When some refinery units are down, such as during turnaround, it is necessary to continue efficient stripping of the remaining sour waters. Valve trays probably offer the best solution to this problem since turndown ratios of 3:1 are possible. Feed storage can also be considered if trace amounts of oxygen can be kept out of the system.

Finally, verbal reports from refiners confirm satisfactory recovery of stripper off-gases in Claus sulfur plants. Several plans indicated special burner designs are needed to ensure complete combustion of the ammonia. However, most plants would not discuss details of burner design due to proprietary reasons. Likewise, very little information could be obtained regarding system instrumentation and controls.

RDS 1974 STUDIES

During 1974 the Committee on Research Data and Information Services (RDS) sponsored an active program at Brigham Young University to obtain new vapor-liquid equilibrium data for refinery sour waters. The objective was to check some of the Van Krevelen NH_3-H_2S-H_2O data plus obtain new data points throughout the concentration and temperature ranges anticipated in well-designed refluxed units. In addition, some data were obtained to determine the effect of other components such as ethyl mercaptan,

hydrogen cyanide, and cresol. Results of this study are to be presented in a written report to API about midyear 1975.

CRE 1974 STUDIES

During 1974, Battelle Memorial Institute conducted corrosion studies on refluxed sour water strippers under the sponsorship of the Corrosion Subcommittee of the Committee on Refinery Equipment. Laboratory studies were to explor the effects of the following variables:

1. Velocity
2. Temperature and pressure
3. Phase (liquid, vapor, condensing, impingement)
4. Composition (H_2S, NH_3, Cl^- in H_2O)
5. Contaminants (cyanides, phenol, acids, caustics, etc.)
6. Materials (metals and coatings)
7. Inhibitors

A detailed report of the results will be submitted by Battelle to CRE in the fall of 1975.

FUTURE API STUDIES

API will continue a program of research on sour water strippers throughout 1975. Each of the three committees in 1974 experienced unexpected difficulties with portions of their programs. Attempts will be made to resolve these problems in 1975 and also explore new areas. CREC will concentrate on determination of proper methods of caustic injection, cyanide removal, plus further identification of components causing ammonia fixation. RDS will continue its program of expanding available equilibrium data. In addition, data will be gathered on systems containing CO_2 to assist in technology related to stripping sour water from synthetic fuel processes. CRE will continue its difficult task of defining corrosion mechanisms and potential corrective measures for refluxed strippers.

SUMMARY AND CONCLUSIONS

To date, the following conclusions have been reached as a result of the API Sour Water Stripper Studies.

1. Refinery sour waters frequently contain "fixed" ammonia which cannot be stripped out of solution unless the pH is adjusted. The amount of "fixed" ammonia varies considerably between plants and can be quite high.

2. Additional work is necessary to determine the best point(s) for caustic addition and the optimum bottoms pH.

3. Continuous flow bench-scale or batch boiling techniques can be successfully used to determine the amount of "fixed" ammonia in solution.

4. "Fixed" ammonia is due to the presence of acidic impurities. The Beychok calculation model does not take these additional components into consideration.

5. Phenols and cyanide do not appear to explain observed ammonia "fixation."

6. Exposure of sour waters to trace quantities of oxygen can slowly create oxidation products and cause some ammonia "fixation."

7. The Beychok calculation model appears to give satisfactory correlation with measured bench-scale and full-scale results down to the point the "fixed" ammonia value is approached.

8. Measured H_2S and NH_3 concentrations in the reflux drum are considerably less than predicted by extrapolation of the Van Krevelen data.

9. Development of a new multicomponent stripper calculation procedure is desirable with capability of handling external pH adjustments. This would take considerable new research effort.

10. The overhead system on refluxed strippers is subject to severe corrosion in many cases. Continued research is needed to fully understand the mechanisms and determine the best corrective measures.

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DISCUSSION

Milt Beychok: I have two comments to add concerning unknown acids found in the Bechtel work. First, I would like to emphasize that these acids affected only the ammonia. For those of you who are designing strippers and worrying about H_2S removal, there is no problem with the H_2S stripping. The acids fix only the basic ammonia. The second point was on Grant Wilson's work at Brigham Young University. His equations are theoretically more exact and he has much more data and better data than Van Krevelen did some 30 years ago. But in the region of most sour water strippers as compared to fractionators (that is where the molar ratio of ammonia to H_2S is 1-1/2 or higher) there doesn't appear to be very much difference at the usual concentrations levels of the 2-3,000 parts per million. When you get up to the 60,000 parts per million range, in the reflux accumulators Grant's data is much much better than Van Krevelen's. So I guess what I am really trying to say is that in the ordinary sour water stripper application other than very low ammonia, Van Krevelen's data is still usable because it is so much more simple than Grant's data which will require a computer to use.

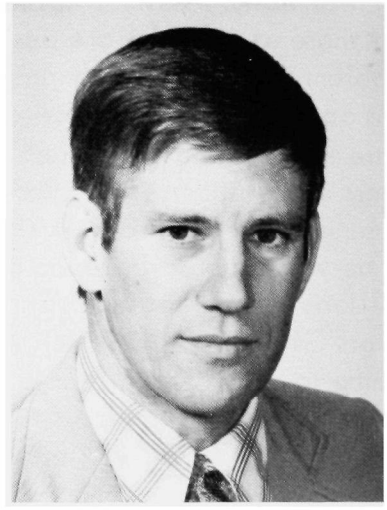
Bob Farnham: Did you look at chlorides in the stripper bottoms as a source of acidic material?

Ronald Gantz: As I recall we took very little data on chlorides.

Bob Farnham: I think people tend to ignore the fact that chlorides do get into refinery sour waters via such things as leaded gasoline that finds its way into processing units, chloride addition for catalyst activity, and materials such as neutralizing amines. I think chlorides could be one of the problems with the fixed ammonia. Another problem may be fixation of the ammonia due to exposure to air. Does that have anything to do with CO_2?

Ronald Gantz: Yes that could be a problem if air is allowed into the system. We have very little CO_2 data but obviously if ammonium carbonate were present you would have some ammonia fixation. However, most refinery sour water collection systems are blanketed with inert gas to prevent the entry of air.

BIOGRAPHY



R. G. Gantz is a Supervising Process Engineer in Continental Oil Company's corporate Process Engineering Department in Ponca City, Oklahoma. He currently directs activities of the Environmental Conservation Group which is involved with all phases of environmental engineering. Experience includes nine (9) years of assignments on a very wide variety of projects. Current responsibilities include preliminary and detailed process design work, pilot and bench-scale testing, plant technical services, stream surveys, and in-company consulting. Work areas include waste water treatment, air pollution abatement, and solid waste disposal for Conoco's Refining, Chemicals, and Natural Gas Departments. He is a member of API's Committee on Refinery Environmental Control and author of several technical publications. Mr. Gantz holds a B.S. degree in Chemical Engineering from Oklahoma State University. Prior experience includes product development work in DACRON textile fibers for the DuPont Company.

TABLE 1 - CREC - QEUSTIONNAIRE DATA ON NH_3 STRIPPING

		BOTTOMS NH_3 DATA			
	Total	Averaging 50 mg/l	Periodically Achieving 50 mg/l*	Averaging 100 mg/l	Periodically Achieving 100 mg/l*
Number Refluxed Towers Reporting	31	4	9	13	15
Number Nonrefluxed Towers Reporting	24	3	5	7	8
Totals	55	7	14	20	23

*Several questionnaires reported only average data. Numbers shown would probably be larger if minimum NH_3 had been reported in all cases.

TABLE 2 - SOUR WATER STRIPPERS WITH HIGH NH_3 REMOVAL

Questionnaire No.	Tower Media	Average Stripping Steam Pound/Gal. Fresh Feed	Average Feed	Average Bottoms	Minimum Bottoms	Bottoms pH
3 -Refluxed	10 Valve Trays	1.4	2,500	78	25	9.4
13B -Refluxed	8 Valve Trays	1.0	1,200	25	-	-
22A- Refluxed	30 Sieve Trays	1.1	1,720	68	-	-
22B -Refluxed	30 Sieve Trays	2.5	430	64	-	-
22C-Refluxed	24 Sieve Trays	0.6	74	63	-	-
23 -Refluxed	23 Sieve Trays	1.6	4,000	100	40	-
25 -Refluxed	52 Valve Trays	-	1,600	65	-	9.2
26A-Refluxed	5 Glitch Trays	7.8	5,410	45	19	8.4
26B- Refluxed	20'-3" Raschig Rings	1.3	3,550	-	37	9.3
27 -Refluxed	10 Flex Trays	1.8	2,000	200	25	9.0
34 -Refluxed	15'-3" Raschig Rings	1.5	1,400	80	7	-
36 -Refluxed	18 Trays	-	19,000	80	-	-
43 -Refluxed	20 Bubble Cap Trays	-	2,000	15	10	7.3
44 -Refluxed	12 Socony Trays	1.2	32,200	56	-	8.5
55 -Refluxed	20 Sieve Trays	-	1,600	25	7	9.0
7 -Nonrefluxed	8 Bubble Cap Trays	1.5	960	50	30	9.4
10 -Nonrefluxed	6 Shower Trays	0.3	1,850	96	-	-
32 -Nonrefluxed	15'-3" Raschig Rings	0.6	1,200	65	36	-
33 -Nonrefluxed	15'-3" Saddles	0.2	2,600	200	34	8.6
52 -Nonrefluxed	8 Valve Trays	1.9	5,450	56	-	8.6
53 -Nonrefluxed	28 Bubble Cap Trays	0.8	2,625	10	-	-
54A-Nonrefluxed	5 Valve Trays	0.4	215	76	-	9.3
58 -Nonrefluxed	8 Flex Trays	2.7	4,400	11	10	8.3

TABLE 3 - SOUR WATER STRIPPERS WITH POSSIBLE BOTTOMS NH_3 FIXATION

Questionnaire No.	Tower Media	Average Stripping Steam Pound/Gal. Fresh Feed	Average Feed	Average Bottoms	Minimum Bottoms	Bottoms pH
22A-Refluxed	30 Sieve Trays	1.1	1,720	68	-	-
22B-Refluxed	30 Sieve Trays	2.5	430	64	-	-
37A-Refluxed	35'-2" Raschig Rings	0.8	1,400	600	-	-
41 -Refluxed	16 Valve Trays	0.9	1,400	400	-	9.5
18 -Nonrefluxed	16'-3" Saddles	3.9	4.460	265	150	-
(a)21 -Nonrefluxed	9 Bubble Cap Trays	0.07	2,800		-	-
	15 Ballast Trays	0.5	-	300	200	-
47 -Nonrefluxed	19 Bubble Cap Trays	1.9	1,000	115	-	8.0
(a)48 -Nonrefluxed	20'-3" Raschig Rings	0.4	2,500	-	-	-
	12 V-Grid Trays	0.9	-	115	-	-

(a) 2-Stage Unit

TABLE 4 - DISPOSITION OF OVERHEAD GASES AND STRIPPER BOTTOMS

	NUMBER OF REPLIES	
Overhead Disposition	Refluxed	Nonrefluxed
Incinerated in Some Manner	19	19
Sulfur Plant	10	2
Vented to Atmosphere	0	6
Scrubbers	2	0
Gas Plants	0	1
	31	28*
Bottoms Disposition		
Desalter	14	11
Sewer	10	5
Biosystem	4	8
Cooling Towers	1	-
FCC Units	1	-
Oxidizers	1	-
	31	24

*Four units were 2-stage.

TABLE 5 - CHARACTERIZATION OF STRIPPER BOTTOMS SAMPLES

CONCENTRATION (mg/1) BASED ON ORIGINAL SAMPLE

Sample Source	Total Organic Carbon	Inorganic Carbon	Thiocyanate	Nonvolatiles*	Ash**
Refinery A	3,800	14	-	1,580	80
Refinery B	360	2	560	1,230	850
Refinery D	330	10	114	460	-

EMISSION SPEC SEMI-QUANT (mg/1)

Sample Source	Na	Fe	Ca	Mg	Si	Al
Refinery A	10	10	0.8	0.1	4	0.1
Refinery B	100	1	10	8	5	0.8

* Nonvolatiles are defined as the total materials (residue) remaining after evaporating samples to dryness.
** Material left after burning the residue.

TABLE 6 - EFFECT OF CAUSTIC ADDITION ON FIXED AMMONIA

Run	Sample	pH Initial	pH Final	Duration of Test***	Ammonia (mg/1)
		BEFORE BOILING**			
A-Raw	Refinery A	8.6	-	-	4,960
		AFTER BOILING			
A-1	Refinery A No Caustic	8.6	6.2	4 Hours	560
A-2	Product of A-1	9.0*	7.35	1 Hour	280
A-3	Product of A-2	9.0*	7.55	1 Hour	120
A-4	Product of A-3	9.0*	8.1	1 Hour	62
A-5	Product of A-4	9.0*	7.1	1 Hour	42
A-6	Product of A-5	9.0*	7.5	1 Hour	28
		BEFORE BOILING			
B-Raw	Refinery B	8.3	-	-	3,370
		AFTER BOILING			
B-1	Refinery B No Caustic	8.3	6.95	4 Hours	115
B-2	Product of B-1	9.0*	6.70	1 Hour	70
B-3	Product of B-2	9.0*	8.25	1 Hour	5

*pH adjusted to 9.0 by using caustic.
**All experiments conducted by batch boiling.
***Time considered to be in excess of that required to reach NH_3 residual level.

TABLE 7 - COMPARISON OF CALCULATED AND OBSERVED REFLUX COMPOSITIONS REFINERY C

Total Steam, Pound/Gallon Fresh Feed	REFLUX NH_3, mg/l		REFLUX NH_3, mg/l	
	Actual	Calculated*	Actual	Calculated*
1.20	32,600	65,800	16,300	47,400
1.41	36,300	90,800	30,600	73,300
1.58	42,600	102,000	28,600	83,100
1.76	26,300	61,900	17,700	42,100
1.90	30,300	73,300	8,600	54,900
2.23	10,000	78,200	9,200	58,500
2.87	52,300	103,200	12,500	86,500

*Actual operating conditions were used as a basis for all calculations.

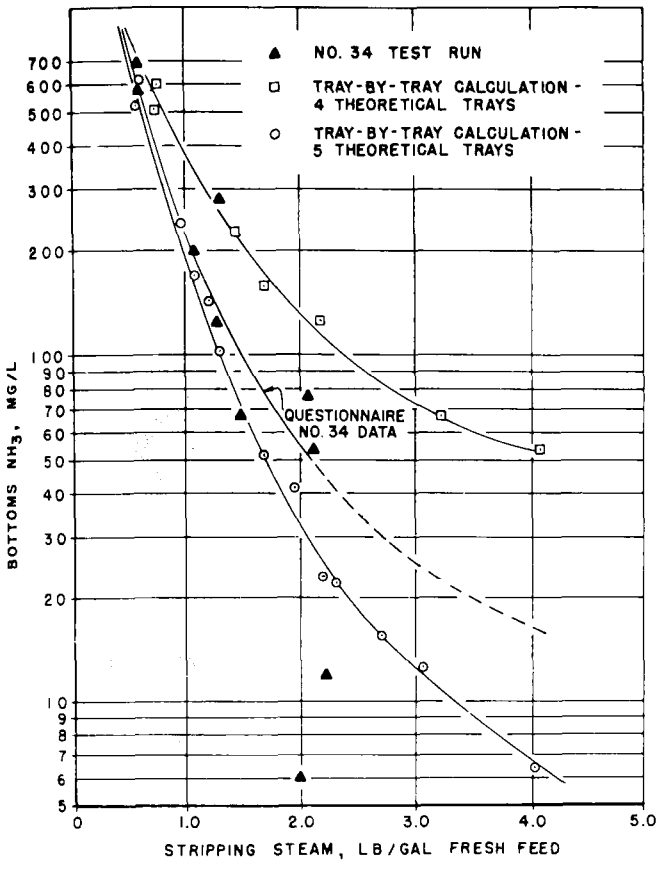


FIGURE 1. COMPARISON OF TRAY-BY-TRAY CALCULATIONS WITH QUESTIONNAIRE NO 34 STRIPPING CURVE

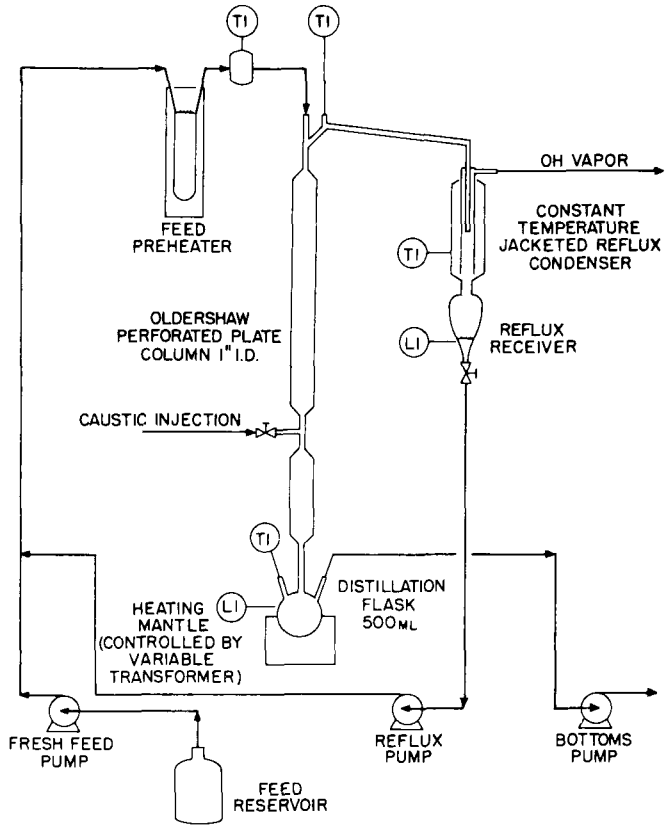


FIGURE 2. CONTINUOUS BENCH SCALE SOUR WATER STRIPPING APPARATUS

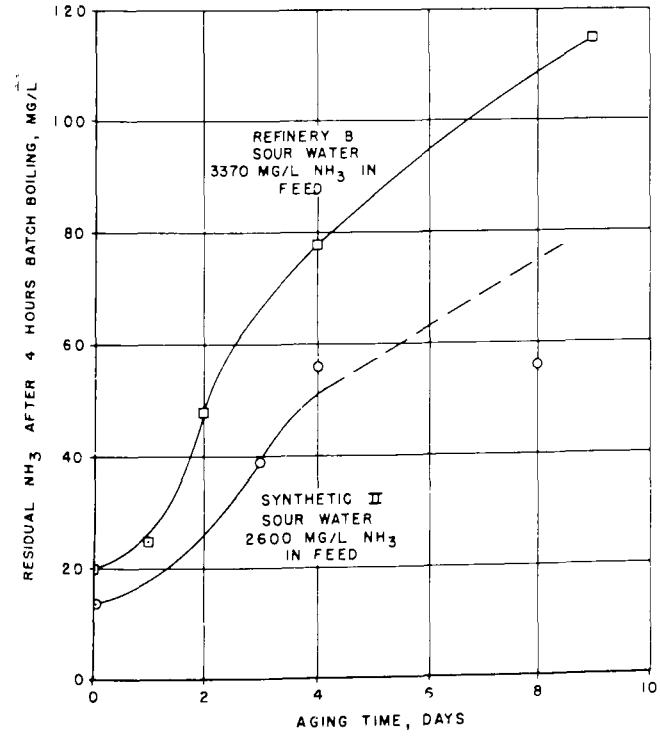
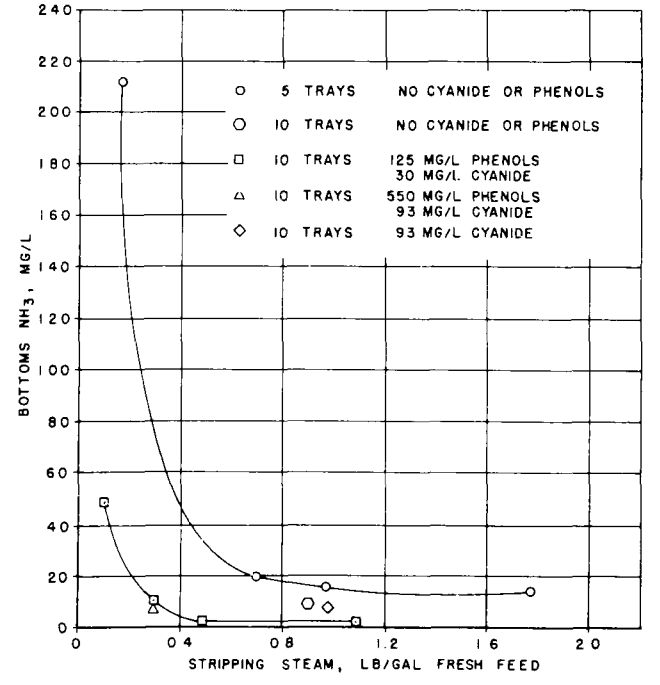
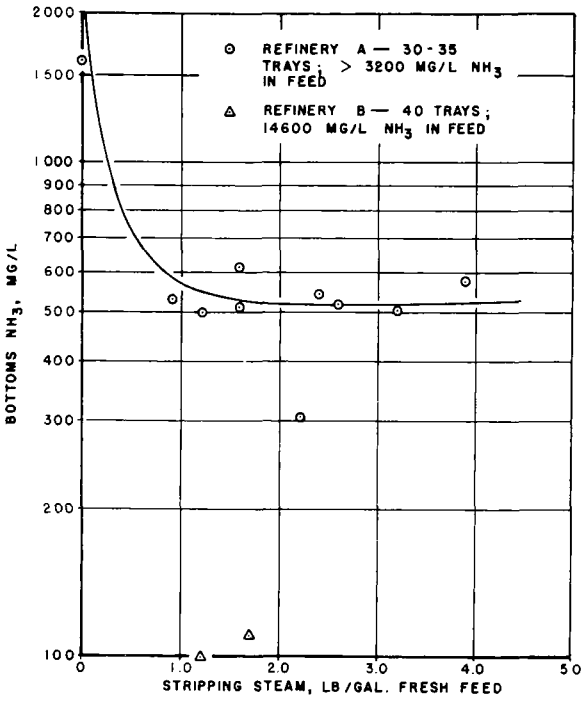


FIGURE 3. AGING EFFECTS ON SOUR WATER STRIPPING



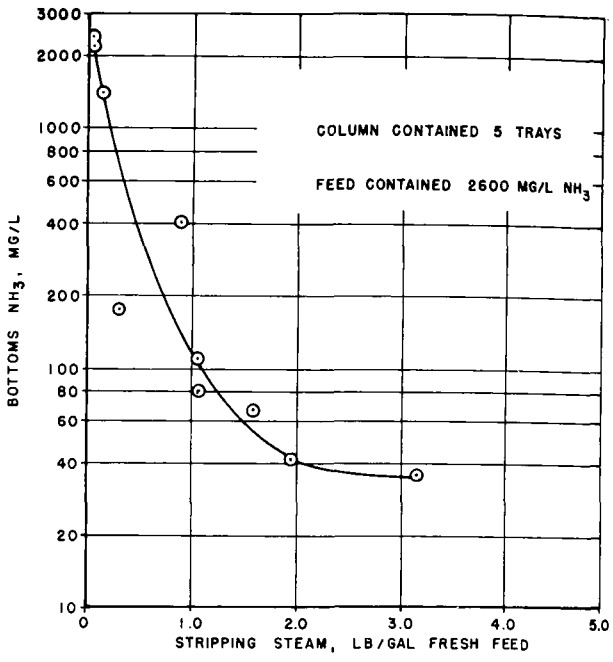
NOTES - COLUMN HAD BOTTOMS REBOILER AND OVERHEAD CONDENSER
- THE FEED CONCENTRATION OF NH_3 VARIED BETWEEN 2600 AND 5600 MG/L

FIGURE 4 BENCH SCALE STRIPPING OF SYNTHETIC II SOUR WATER



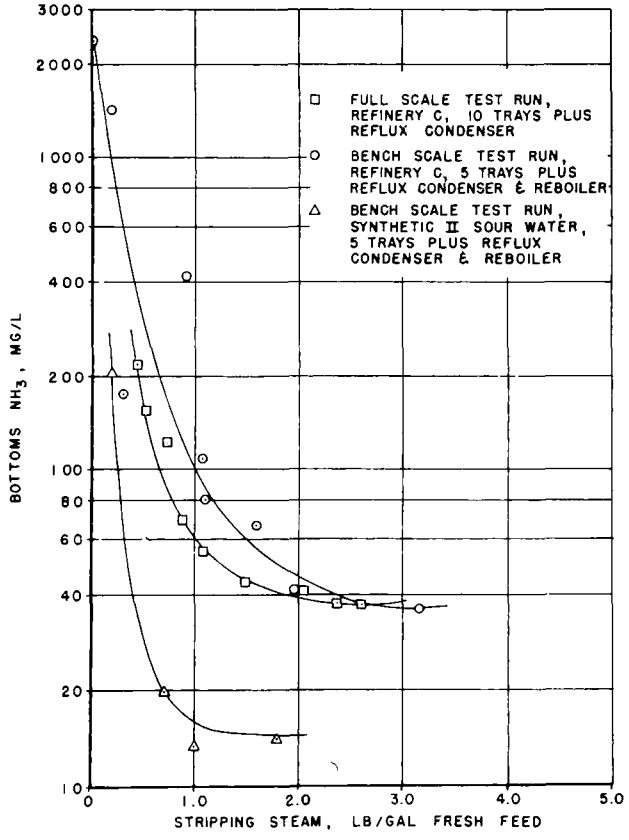
NOTE: COLUMN HAD BOTTOMS REBOILER AND OVERHEAD REFLUX CONDENSER.

FIGURE 5. BENCH SCALE STRIPPING RESULTS REFINERIES A AND B



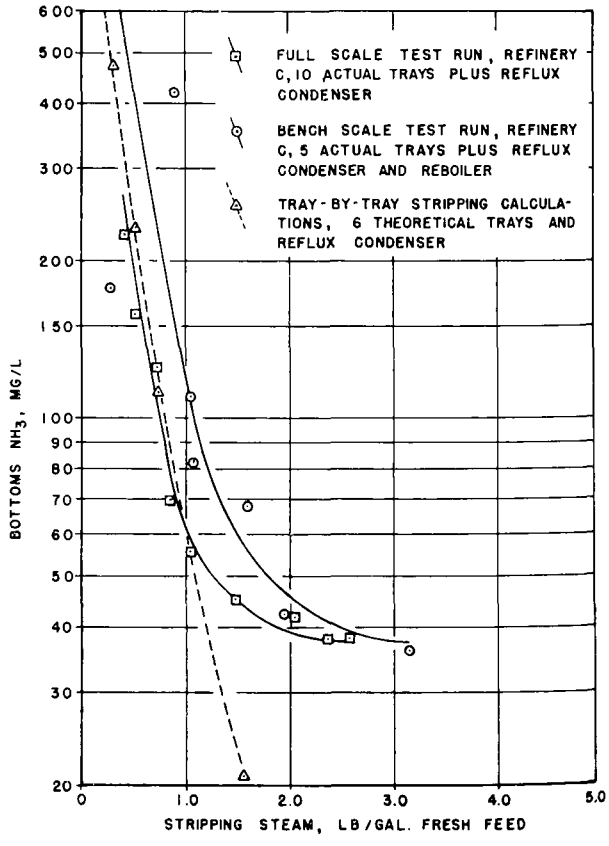
NOTE: COLUMN HAD BOTTOMS REBOILER AND OVERHEAD REFLUX CONDENSER

FIGURE 6. BENCH SCALE STRIPPING RESULTS REFINERY C



NOTE: APPROXIMATELY 2600 MG/L NH_3 IN FEED

FIGURE 7 SOUR WATER STRIPPING CHARACTERISTICS - REFINERY C



NOTE: APPROXIMATELY 2600 MG/L NH_3 IN FEED

FIGURE 8. COMPARISON OF TRAY-BY-TRAY CALCULATIONS WITH REFINERY C STRIPPING CURVES

SESSION VII

"FUTURE RESEARCH"

Chairman

Peter B. Lederman
Director, Industrial and Extractive Processes
U. S. EPA, Washington, D. C.

Speakers

Wilson K. Talley

"The EPA's Role in Future Research"

Arne E. Gubrud

"The Industry's Role"

Joseph F. Malina

"The University's Role in Future Research"

BIOGRAPHY Peter B. Lederman



Peter B. Lederman has just joined Research-Cottrell as Manager of Technical Development, where he is responsible for the Product Improvement, Warranty Service, and Gas Dynamics Departments. Prior to his current position, he spent four years with the United States Environmental Protection Agency as Director of Industrial and Extractive Processes. In that position, he was responsible at various times for planning, coordinating and implementing EPA's R&D program to develop improved technology for minimizing pollution from industrial and mining sources. Dr. Lederman holds B.S., M.S., and Ph.D. degrees in Chemical Engineering from the University of Michigan and is a Professional Engineer. He has published widely and has served on the faculties of the University of Michigan and the Polytechnic Institute of Brooklyn, as well as having industrial experience with Exxon, Shell and General Foods.

"THE EPA'S ROLE IN FUTURE RESEARCH"

Wilson K. Talley
Assistant Administrator, Research and Development
U.S. EPA, Washington, D.C.

I would like to talk about future research, more specifically, EPA's role. Let me preface my remarks by saying that it is my personal belief that the Nation's development of adequate, and even abundant, energy resources can be done in consonance with the protection as well as the enhancement of environmental quality. I think that that is a particularly appropriate thought to carry to this meeting because we are going to need more petroleum refineries in the future, not fewer, and they must be clean.

Before talking about any thrusts in research priorities, let me explain how the research arm of EPA functions. The first thing to recall is that EPA, when it was put together, was structured to be a regulatory agency. Its primary mission was not to be research and development. I would like to stress "primary," for we do need research and development, that is, we need the scientific and technological fruits of such labors. We do do research, but our rhrust in the research arm is to support the rest of the Agency. Ignoring for the moment whether standards and regulations not based on science and technology could stand legal tests, I don't believe that such arbitrary restrictions would serve the national interest. If they are too loose, they wouldn't protect the environment and such laxity is just no longer a publicly acceptable mode of operation. If they are too restrictive, they could cripple our struggle for new energy resources and this, by the way, might resound ultimately to the detriment of the environment itself: energy supplies, economic stability and growth, and environmental quality are now recognized as being inextricably intertwined. On the other hand, regulations and standards that are based on firm information as to health and ecological effects and on the existence of proven, adequate and effective technologies will prove, I think, acceptable to industry and to public alike. The question is how to develop that scientific and technological base.

I have been up on the Hill quite frequently in the last few months, engaged in discussions with Congress and with my fellow agencies on the proper structuring of research and development for regulatory agencies. One suggestion has been to "free" R&D from the regulatory mode. The examples that are given for this are our good friends in OSHA and NIOSH. The Occupational Safety and Health Administration is in the Department of Labor. It is supposed to be served by the research performed by the National Institute for Occupational Safety and Health in the Department of Health, Education and Welfare. There are some advantages to this separation, the most notable being the freedom to allow a research program to follow its own internal logic. There are also disadvantages, and I would like to mention just two, timing and feedback. If an R&D program yields its results months after the regulatory arm has had to make a decision, the late information may be worse than useless. The best you can hope for is confusion and loss of public confidence. And by feedback, I mean that the researchers, if they are separate, don't live with the same tempo as the regulators. The feeling of urgency in the researchers to solve actual problems, rather than interesting ones, isn't developed. If you have a more intimate contact, the problems that become interesting to the researchers are those that are vital

to the regulators. If they are solved, they will win for the researcher the gratitude and approbation of the regulators. The regulators become the first constituency ~~of the~~ researchers, and their fellow scientists and engineers a secondary constituency - an important one for peer review, but still secondary. Another extreme, which I haven't heard raised outside the Agency, is that all research should be directed, controlled, conducted - use any term you like - by the regulatory arm. Leaving aside the possibility that the rest of the world might view such research results as biased, there is a more dangerous and subtle disadvantage. Granted that we would have the tempo of the research geared absolutely to the temp of the regulatory program, the draw back is then that the researchers will adopt the same sense of time as held by the regulators. This is a disadvantage because regulators live in the present; they move from court-set dates to congressionally mandated time frames. The researchers, if they adopt this attitude, are likely to bury their noses in the present, with all of their time occupied by solving the immediate, the obvious problems. That will occupy all their time -- Parkinson's law codifies this -- the work will expand to take all their time and energy. Who then will look ahead to eliminate future problems, perhaps before they are even generally recognized?

EPA operates in a middle course. The Office of Research and Development is an independent Office within the Agency. As Assistant Administrator for Research and Development, I am co-equal with the Assistant Administrator for Air, the AA for Water, the AA for Enforcement and the like. In the Office of Research and Development, we set our own priorities, but we do it cheek to jowl with the rest of the Agency. If we more too far from their perception of their problems, they let us know it in no uncertain terms. We do back-stop them. Our research results may be the subject of litigation, and we have to be prepared to back them up as expert witnesses. This is in addition to facing the peer review as any other researcher does. Yet if all we did was to perform according to their needs, we would be failing the opportunity that we are given because we are an independent office. Edmund Burke said something to the effect that a representative owes his constituency more than the diligence of his labors on their behalf; he also owes them his judgment. I interpret this to mean that we owe the program offices the satisfaction of their perceived needs, but, if we see something that we feel is more important to them, we have the obligation to refuse to respond absolutely to their requests. We must reserve the right to act on our best judgment. That means we have to respond to them, but in a way to husband our resources so we can allow some work to anticipate what is going to happen. Another term is that we must perform "problem definition" research. If we can't spot a problem in the future and eliminate it so it never arises, at least we can flag it so that it doesn't arrive as an unheralded disaster. We know that it is coming and we can get ready for it. Now let me admit that all is not skittles and cream. If ORD does its job, there are but two options -- either we do our job well or we don't do it well. If we do it well, and in the main we do, we will produce solutions before the problems become critical or, better, we will eliminate problems in advance. In the main, that is what we do do. We are then hard pressed to justify our share of the Agency resources, because what have we done that is important to the Agency? On the other hand, if we fail to supply the technology, or cannot guarantee criteria based on unassailable dose-response functions, or the like, then we haven't helped the Agency, we're vilified and the result is the same: we are hard pressed to justify our resources. As I keep telling my people,

the best we can hope for is that we will be treated with, perhaps, benign neglect. Despite this, there is one advantage, a very important advantage, to our place in the organizational structure. We cannot be ignored when a decision is being made, especially one that has to be based upon science and technology. Were we totally removed, as NIOSH is from OSHA, then the regulatory side of the house could pick and choose selectively that information that supports their preconceived notions of what their decision should be. If we were completely captive to the regulatory side of the house, then we would have no voice at all.

Given the present organizational structure, how do we get the research done? Philosophically, I can see absolutely no reason to replicate with federal funds and people, resources that already exist in the private sector, in industry, and universities. It is a good thing that I have this attitude, because we don't have anywhere near the resources to even attempt that replication. We conduct a largely extramural program, out of necessity. Even if it were not, I would do it out of choice. We need and welcome participation from industry and other elements of the private sector. Roughly speaking, our budget is about $250 million. Of this, about $70 million is spent inhouse to support our own research staff. Another roughly $70 million is passed in interagency transfers to other federal agencies. The rest is let by contract and grant to industry, nonprofits, universities, and State and local governments.

Let me pause to mention our involvement with industry. There are some people who do not think it is a good thing for a regulatory agency to have part of its research conducted by people who may turn out to be part of the elements that are regulated. I don't subscribe to that. In the eleven years that I have been speaking and working in the environmental arena, I have yet to meet anyone whose primary purpose in life was to be a polluter. There aren't any all-black hats in this business. And there aren't any all-white hats, either. No one is pure; we all wear varying shades of grey. Given the opportunity to conduct his business or to live his life in a way that will achieve his basic goals, but will also protect the environment, I believe that anyone will opt for that choice. The remarkable thing is that industry and the public in general are willing to pay a penalty, to give up something in order to protect the environment.

I only require one thing when we go cooperative with an industry in a research program. There must be no suppression of data by either side. When research is done, it's got to be widely disseminated so that there is the possibility of examination by the rest of the research community. It is as simple as that.

Being debated by the National Academy of Sciences, the Office of Technology Assessment, the Congress, and the Agency is the subject of setting research priorities. Sometimes neglected is the problem of communicating those priorities to all interested parties, including not only the people who are going to receive the results of the research, but those who will take part in conducting the research, as well. If one can perform that communication and can allow feedback on the ordering of these priorities, the result may produce a better integrated and a more responsive R&D program. Success is not guaranteed, but if you set your priorities in splendid isolation, there is little chance that you are going to wind up with a research program that is acceptable in its performance or

acceptable in terms of delivery of the results. Let's begin my admitting that the budget is the ultimate arbiter of priorities. If you say that project X is your No. 1 priority but give it zero dollars, it is not your No. 1 priority. But the budget is not the sole measure of priorities. If all of our projects took less than a year to complete and if the development of the budget took long enough and was conducted in a way to allow enough interaction to take place, then the budget would serve as the appropriate vehicle to order our priorities. Unfortunately, our projects average longer than a year, and the "windows" available for observation while the budget is being prepared close very rapidly. Simply, I do not consider the budget an appropriate priority setting mechanism.

In the past the budget system has been the defacto system for setting priorities. However, this year - in fact in about 2 weeks - we are going to publish our first attempt at a five year plan: The Agency Research Statement or the ARS. While by no means perfect, it is the first and we hope it is perfectable. Each year we are going to produce a new ARS. It is a rolling plan, what is now the fifth year will become the fourth year, in the next version it will be the third year, the next the second, finally it will become the current year and guide the preparation of the budget. One sees that the "current year" will have been examined four times as it comes forward. While we will never reach the fifth year unchanged, and I suspect that you can't plan five years in the future, the decisions we make today will be based on our looking as far forward as we can. At least our decisions will have input other than the grim necessities and the urgencies of today.

All comments on the ARS are going to be welcome. Our object is to let the ARS become as detailed as possible, specifying as milestones the outputs of the research program: the years they will be available; how much it is going to cost to produce them. This has to be done with as much external and internal participation in the process as possible. I should add also that the ARS is our annual report to Congress. Another feature of the planning system is our "report card" to the Agency. Each year we have solicited satements of needs from the rest of the Agency. We have asked them what they would like in the way of research output, what problems they have. In the past that has been a one way street; the needs come in and sometimes they hear what has happened to them, more frequently not. From now on, when we send out the request for needs we are also going to say what we accomplished as contrasted to what we intended to do. In the subsequent years, I am going to try to get us to explain why we didn't solve or even attack some problems.

It is part of our obligation to try to explain in the ARS the rational for the research and development thrusts. For instance, I would like a debate on end-of-pipe pollution abatement technology versus process modification. My inclination is toward the latter. Simply put, as an engineer, I view end-of-pipe technology as a poor engineering solution. Since most of the waste stream is either the raw material -- that the manufacturer paid for -- or it is the finished product -- that he would like to sell on the market -- process modification that reduces that waste stream has got to be more profitable. (It's a return to the old conservation ethic -- use less, use it more efficiently -- and you will waste less. In these times of energy crises and material shortfalls, I think it is a good ethic to return to.) But I may be wrong, end-of-pipe has some advantages, and in some instances it may be the method of choice. Also, in some industries, the search for process modification

may be fruitless. Rather than commit budget dollars to a major shift to process modification, I would like to announce our intentions in advance and solicit advice, using the Agency Research Statement as the forum. That "straw man" characteristic is the main feature of the ARS. It is to serve as a guide to the budget only if the ideas and proposals contained in it withstand criticism. Without something specific down on paper, that you can react to, that includes resource estimates, it is just too easy to engage in generalized philosophical discussions about all the good things we might do. Frustratingly, we end up with everything as the No. 1 priority and budget totals that are beyond the realm of reason.

Let me illustrate by using the industrial waste program. It has been an effective government/industry cooperative effort. Public funds have served as seed money to produce new, economical abatement technology. The present pace places in serious doubt our ability to meet the 1983 standards, as most recently noted by the National Commission on Water Quality. Begin with that, and also note that R&D funds that are expended in 1981 and 1982 are going to do little toward achieving in-place technologies in 1983. Finally, note that if very large increases for funds for the program were to occur in fiscal year 1977, there is a good chance that there would be insufficient preparation for handling them correctly. One result might be the loss of the multiplier factor, the leverage that these monies have enjoyed. (By the way, I should point out to you that it is that leverage, the fact that Federal dollars aren't the only money in the game, that has persuaded OMB to allow us to continue this program. If that leverage is in jeopardy, the whole program becomes vulnerable.) In the ARS, we have suggested, and so noted to OMB, that the answer to all these issues may be a "spike" budget increase in 1978 and 1979. The amounts would be $45 million and $50 million respectively, better than a tripling of the projection we have for 1977. To get the money we will need input: will that amount be effective? Is it enough? Are there better ways to meet our national goals? By putting the issue into the ARS, we will have the time to debate it. We would welcome your help.

Let me turn toward a nearer future -- 1977. Our budget for research and development in EPA in the Office of Research and Development for 1977 comes in two portions. One is called the "base program" and the other is related to the environmental impact of new energy resources. The industrial program is within our base. Whether we're rising or shrinking depends on whether you look at the base or the energy portion and with what it is compared. In relation to the President's budget, delivered to Congress in January 1975, we are up $300,000 in the base program and down $16 million in energy. On the other hand, compared to what Congress appropriated for fiscal year 1976, we are down $7.3 million in base and down $3.6 million in energy. We believe at this point that we will be able to hold the 1977 industrial waste program at the $14 million level. This is our total industrial program, all industries, all media--air and water. We need assistance in developing the case for our budget. There is very little that outside people can do on a year to year basis, but with the Agency Research Statement, we are moving far enough into the future that external assistance can be useful. For example, OMB has not approved a tripling of the dollars for the industrial program, but they are willing to discuss the merits of the issue. I have put in three scenarios: a spike increase; the total program staying level; and a spike increase in the industrial program at the expense of

other elements of the research program. If industry, if the academic community, if knowledgeable people, feel that one or another of these modes of operation are reasonable, then that can be communicated to us, to Congress, to the Office of Management and Budget. That will be of great help when the budget issues are to be resolved.

My title is "Future Research: The Role of EPA," so let me pull the threads together. Our research program, as one of its functions, serves the intent of Public Law 92-500, the Federal Water Pollution Control Act of 1972. We cannot perform all the R&D alone. We need the active assistance of industry and other elements of the private sector, in particular academic institutions. We have conducted and we will continue to conduct a large extramural contract and grant R&D program. What is new is that we are attempting to develop a mechanism for an expansion of your assistance. This is to be an expansion of outside involvement into the planning, the setting of the priorities of the R&D effort. The potential benefits of success are high enough to make the attempt worthwhile.

In conclusion, meetings such as this, meetings that are reports of research in progress, are probably the most effective way to get research results into the hands of users. They are also a very good way for potential users to present their problems to researchers. The innovations we have made in planning are not intended to replace meetings such as this; they should rather supplement or complement such face-to-face dialogues. One of the drawbacks to my present position is that I seldom get to attend entire sessions and have to be content with reading the proceedings or the summaries. You miss a lot that way. However, I am grateful for the invitation and the chance to explain the role of EPA, the tacks we may be taking in the future, and how you can assist us in setting our research priorities.

DISCUSSION

Milt Beychok: Dr. Talley, you said I believe that the research office spends $100 million on extramural work outside contracted work. How much money is also spent on outside contracted work by the Office of Air Programs and in the Office of Water Programs - roughly?

W. K. Talley: I cannot say exactly.

Milt Beychok: Would it be the same order of magnitude or half of it?

W. K. Talley: No, I doubt it. The Agency has about 10,000 employees. We have about 2,000. The allocatable budget for the entire Agency is about $750 million. Against those numbers our budget is about $300 million. Hence, we represent about 40% of the allocatable funds and about 20% of the employees. 10% of the total budget of the Agency goes to pay the salaries of and the research conducted by that 20%, so I imagine that most of the money spent by the other program offices, goes to support salaries and fringe benefits of employees. I don't know how much they have left for outside studies and contracts, and they are not required to supply me with that sort of information.

Milt Beychok: We can assume they do spend some significant sums.

W. K. Talley: They spend some sums, I don't know how significant they are.

Milt Beychok: And that ERDA also does?

W. K. Talley: ERDA spends, in its environmental program, something on the order of $160 million. Recognize that most of that money was inherited from the Atomic Energy Commission so that that is primarily nuclear and Dr. Liverman, my counterpart in ERDA, is trying to reprogram to shift from nuclear to non-nuclear.

Milt Beychok: Even if a third of their $150 million is spent on non-nuclear it is half of what you spent in EPA.

W. K. Talley: I doubt that they spend as much as a third.

Milt Beychok: Well my real question is this, that with those three sources of funding, yours, ERDA and the Office of Air Programs and the Office of Water Programs, funding of contract research to support their development of regulations, has anyone ever considered a centralized liaison group to avoid redundancy which does exist and before any one of the three award outside contracts the other two must agree that it hasn't already been done or will be done shortly?

W. K. Talley: Yes, that has been considered - If you had asked that as the question at the beginning, I would have been able to give you the figure that the total amount estimated by the National Science Foundation spent by the Federal Government for research and development in the environmental area, is about $1.3 billion; of that, against the same base, I spent $300 million and in those figures you can forget about the Office of Air and the Office of Water, because they are in the noise level. While the federal government spends $1.3 billion, the total amount of money spent by industry dwarfs that. The question of coordination is a very important one and we are trying various means of doing it. I would like to point out that coordinating the existing programs is a very difficult task. It takes us, at best, six months to let a contract and it is quite easy for it to take nine months to a year. To then stick into that process the time to coordinate with 18 or 20 or 25 other agencies would mean that we would be taking two and three years to let contracts.

Up until now, we have never had a central planning document. No agency has made its projections other than for the budget year. For example, I have been reluctant to go see Dave Rauscher at the National Cancer Institute, with his $700 million budget, of which $100 million is in environmental carcinogenesis, and say, "Really, Dave, we ought to get our acts together," because I haven't been able to tell him what I would like him to do beyond the budget year. We hope that the ARS will serve as a focus for a constituency document. You raise a very important issue. I hold this job temporarily, but all my life I am going to be a taxpayer. I am very concerned that the government spend the money wisely. All my life I am going to be a consumer, I want the regulations that come forth from the government, that affect how industry operates and ultimately the price the consumer pays, to be adequate but not overly restrictive. I don't want to keep taking from one pocket of the taxpayer and the other pocket of the consumer.

Milt Beychok: Dr. Talley, I wasn't raising that question from the viewpoint of a taxpayer that is worried about efficiency in government, but you did make the point that the research arm's program should support the program's branches, and even try and think ahead of them to find the problems before they run into them, but so far I doubt very seriously if any of the regulations; both, air, water or noise that have been adopted have been based on contract reports other than those funded by the Office of Air and Water Programs themselves. Outside contract reports to support the guidelines and the new source performance standards have all been done by contract work funded by the Office of Air and Water Programs, or at least in large part.

W. K. Talley: That is not true with respect to effects research--human and environmental. It might be a true statement about the socio-economic research that we conducted, for we had a small minority of the economic analysis capability of the Agency, so that the program offices relied upon their own in-house staff.

Milt Beychok: The development documents for all of the effluent guidelines were written by outside contractors funded by the Office of Water Programs.

Peter Lederman: That is true, however, in writing the guidelines, the Office of Effluent Guidelines, Al Lynch's group, did use in addition to those development documents, any R&D developments that were available to them at that time or looked like they were successful and were viable. But they did use independent development contractors for a number of reasons. They felt that this was the way to go. However, the research results that were available over the last three years and were available on a timely manner, were utilized by them in setting criteria. Now how they used them may be another question, and I don't think it is one that we can address from the research arm.

W. K. Talley: I would like to mention that I know of three decisions that the Agency has made that were almost entirely the result of OR&D's function. One was the Administrator's decision that depended upon the possible production of sulfuric acid from oxidation catalysts on the 1975, 1976 and later model vehicles, that was based on the non-regulated emission program which we have been conducting for three years. Two others, fuels and fuel additives and equivalency regulations, those too, I know depend entirely upon OR&D because they are the only two regs that OR&D has.

Milt Beychok: I agree with you on the mobile sources, the automobiles and so forth, but in the industrial sector, the petroleum industry for example; I am sure that of the 634 law suits we spoke of the other day, that the defense of those in court will be done by the contractors who worked on the guidelines and air emissions and not the research department.

Doug Lofgren: I am very interested in the remarks you make, Dr. Talley, concerning looking ahead and the future research in areas that should be looked into. I assume for the moment that the Clean Air Amendments are passed as proposed with respect to the non-degradation regulations and that the requirements of zero discharge for 1985 are realized, could you comment a little bit on the proposed, how we are going to meet the national goal of energy independence?

W. K. Talley: Facetiously, the correct way to achieve it would be to have Congress repeal the first and second laws of thermodynamics, as was once done by a State legislature setting pi equal to 3.000.

Seriously, the last committee print on the Senate side of the Clean Air Act has more areas of uncertainty than certainty. They have been working for over a year, it's an election year, the coalitions seem to have little to do with political party, and so on. So I really don't think it is worthwhile to comment on the pending legislation because I don't know what is finally going to come out from that process.

Frank Martin: Dr. Talley, I would like to ask you to get down to something closer if your future program includes any work that would help the refiner reduce the amount of testing in order to stay within the permit? As has been pointed out many times it seems like the number of requirements are great and that the testing could be reduced for many people and I wonder if there was any work along this line.

Peter Lederman: We have nothing planned in detail in terms of reduction; we are trying to establish standard methods. I am sure that as these guidelines are utilized there will be efforts in this area and I think this is the type of information that is important for us in the planning area and then to work with API and the refineries or industry in general to determine what is realistic, what can be utilized, what is good enough and what is not onerous, but this is the type of interchange I think that is important and that we try to establish with the various industries and industrial groups.

Frank Martin: I have one more question. Recently, in fact last week in Houston, the President's White House Consumer Representation Plan had a meeting. There were a number of agencies, including the EPA there, that indicated that they were going to go out and go to the grass roots and get the consumers' ideas on what they needed and what was going to happen and so forth and so on. I realize, or at least one of the fears I had here is, that we are going to be listening to housewives and not industry in this because industry, although it is a consumer, is not really considered a consumer. I wondered if, how this information is going to reach your organization or the EPA or your department of the EPA on what the consumer wants?

W. K. Talley: What the consumer wants in the way of research?

Frank Martin: Yes, what the consumer wants in maintaining the environment and how effective it is going to be, how is this information going to get to you. For instance, you mentioned a budget and the budget is a big part of it and there were objections raised that many of the agencies there and not only the EPA but Agriculture and State and everybody else, figure up their budgets ahead of time and then they are going out and ask the consumer and it isn't going to do them any good to have somebody say we need something when the budget is already set.

W. K. Talley: I have to admit that the rest of the Agency has not generally adopted the point of view that we ought to look any further than the next budget year. But there are hopeful signs. One is that Dr. Andrew Breidenbach, the Assistant Administrator for Water and Hazardous Materials, in looking at our five year plan draft, told his people, "We

can't respond to a research plan five years into the future, unless we know what we want to do in water programs beyong next year or so." He is now exploring five year projections of the programs under his charge.

Industry, as you well know, has very effective and capable lobbyists in Washington. They serve a very useful function, they communicate with us directly, they are helpful, they are helpful, they are good contacts. My principal contacts are generally the vice presidents of research in companies. I get good feedback, early warnings of problems and so on.

We are all consumers, as you have mentioned. The initiative you described is an attempt on the part of the Administration to reach out after recognizing that there isn't any formal mechanism for contacting the average citizen. If you rely on those who write in and the like, then you are dealing with only a small activist corps. What Mr. Train has done, is to acquire a special assistant, a woman whose job it is to try to communicate with all organized constituency groups having to do with environmental affairs or consumer affairs. This initiative on the part of Mr. Train may or may not work, but at least he has made it. I can't predict how effective it's going to be, the decision to give her this responsibility was made very recently.

Umesh Mathur: EPA's approach to controlling industrial effluents into municipal treatment systems is to first designate an industry for control, then the pollutants to be controlled. Many of the larger industries are designated for control, but the contribution of a specific pollutant within an industrial category being controlled may be small compared to the pollution contribution of an industry not designated to be controlled. As an example, a toxic material discharged from the relatively unregulated electroplating and metal finishing industries may exceed that from a refinery which has been designated for control. When will we get guidelines from R&D documenting the state-of-the-art for effluent control? We would eventually like to know how the small industries who are discharging into sanitary sewers will be regulated?

W. K. Talley: Do you understand the division of responsibilities in the Agency? That the Office of Research and Development issues criteria (dose response functions, ecological effects or availability of technology), but that the issuance of standards and regulations comes from the Office of Water Planning and Standards.

The Office of Water Planning and Standards, through the Effluent Guidelines Division, is currently developing the technical information necessary to issue pretreatment standards.

Peter Ledeman: We are doing some work on the compatibility or incompatibility of heavy metals, and, I want to be very careful of the terminology I use, in joint treatment facilities. That work is going on right now. There is work going on and there will continue to be work. Of course one of the things about the effluent guidelines is in addition to what Joe Moore said the other day about a mid course correction.

W. K. Talley: Two things occur to me; one is that Cincinnati has always been the major

home of our municipal sewage research. We have now concentrated the responsibility for the industrial research program there also. This will effect a better communication between the municipal side, the ultimate recipients of what finally comes out of industrial discharges, and the people responsible for developing the industrial technology.

The other item serves to illustrate that we do re-examine problems. We are now re-examining the draft criteria document which ORD produced on land disposal of municipal sludge. If we can work out with USDA the issue of restricted land usage, rather than "any crop for all time," we can permit more land applications. As you know, it is the heavy metals, cadmium in the municipal waste, that are the major problem.

Umesh Mathur: The only reason why I brought this up is because I really believe that this has become a very critical question, particularly for the guys who are doing long term planning under things like Section 303 and 208. Unless we have some definitive answers to these problems we are going to be stuck with as many different local ordinances as there are cities in the country and each of them is unlikely to be enforced or administered at all well because the numbers they are putting in there are pulled out of the air, since there is no definitive guidance from EPA. Once the bad ordinance goes in and somebody goes in and builds a facility to comply with that ordinance and then you go back a few years later and say now that EPA has made up its mind, I want you to go back and now shoot for this target and of course two or three years later when you have your annual reviews or whatever you might have another ordinance and so obviously people will be shooting for moving targets and these are big bucks what you are talking about so I think the question should be answered definitively and quickly. I think the research has bee been done by Battelle because I have looked at that study and I am a chemical engineer and I feel that it is defensible; they have done an economic analysis which takes care of the size question and they did determine that some smaller industries may have to merge or in some ways consolidate themselves, otherwise they will have to go out of business. However, that is the principal behind the laws, if you pollute very badly and you can't afford to clean up, then you go out of business.

BIOGRAPHY



Dr. Wilson K. Talley was named Assistant Administrator for Research and Development at the U. S. Environmental Protection Agency in December 1971. In this position, Dr. Talley is responsible for planning, directing, and coordinating all EPA research activities covering air, water, pesticides, radiation, noise, and solid waste which are necessary in guiding national policy for environmental protection, developing pollution control strategies, and establishing adequate standards and regulations.

Prior to joining EPA, Dr. Talley was Study Director of the Commission on Critical Choices for Americans. He has served in a variety of academic and administrative positions with the University of California. In 1969 Dr. Talley was named a White House Fellow and served as Special Assistant to the Secretary of Health, Education, and Welfare until 1970. While at HEW he was detailed to the "Ash Council" to work on the study that led to the establishment of EPA. He has been a member of EPA's Hazardous Materials Advisory Committee since 1971.

A graduate of the University of California with an A.B. in Physics, Dr. Talley earned his S.M. in Physics from the University of Chicago and his Ph.D. in Nuclear Engineering at the University of California in 1963.

"THE INDUSTRY'S ROLE"

Arne E. Gubrud
Director, Environmental Affairs
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It is always an advantage to be second on a program like this, for one has the opportunity to respond to the earlier speaker. I would like to do that briefly before discussing API's programs. I was particularly heartened by the attitudes expressed by Dr. Talley regarding the need for open disclosure of research data, for cooperation, and for basing regulations on sound scientific information and demonstrated technology. All of these are principles that we in the oil industry have long espoused.

It is unfortunate that Dr. Talley can't speak for the EPA program offices, and that the attitude of objectivity that he put forward is not always reflected in the actions of those offices in the development of their regulations. To a large extent, the problems we in industry have with the Agency's regulatory policies are not all of EPA's making, but rather a result of rigid legislative deadlines and a regulatory framework which does not give the agency the flexibility it needs to regulate wisely in accordance with scientific principles and good economic principles. Unfortunately, this is a fact of life, and I am afraid the place where that problem will have to be solved is on Capitol Hill and not at the Waterside Mall, in Cincinnati, or down in Research Triangle Park.

Turning now to the field of water pollution control in refining, I think it is pretty clear that we have gone about as far as we can with research on that "add-on" technology Dr. Talley talked about. We know what the more sophisticated systems are and what they can do. We have the technological capability to discharge only distilled water, if we could stand the costs. So there is no lack of end-of-pipe technology, although the cost-effective technologies are, of course, limited.

End-of-pipe treatment is not the only answer, of course. There is a lot more that can be done by individual plants in better water management and in waste reduction to reduce the load imposed on the final treatment plant. Moreover, there may be refining process changes around the corner, revolutionary process changes, which will make possible new innovations.

While at the moment there does not seem to be much need for research on end-of-pipe treatment technology, this may change, because the rules of the water pollution game are changing and the concerns of the public and the Congress and those of us in the environmental field are changing.

We used to worry about overloading the assimilative capacity of receiving waters and depleting the oxygen needed to support sport fish and other biota. No longer. In fact, now-a-days we refuse to concede that receiving waters can assimilate wastes at all. The reason for the change in attitudes is the shift in focus in the 1972 amendments to the Federal Water Pollution Control Act. Today we are increasingly concerned about the possibility of more subtle, perhaps very long-term effects of very small quantities of substances about which we know very little.

I am pleased that the Office of Research and Development in EPA is going to research some of those problems, particularly in view of Dr. Talley's comments about the need to establish valid dose-response relationships, because we are surely going to confront regulation of some of these materials in the years ahead. With the passage of the Safe Drinking Water Act, the EPA Administrator has been given sweeping powers to take whatever action he deems appropriate whenever he discovers a threat to health through drinking water. Thus, industries have to be concerned about the contribution they may be making to the presence of harmful materials in sources of drinking water supplies.

The petroleum industry is concerned about this problem, and the API last year launched a very ambitious program which will probably continue for the next several years. In this program we are looking at the nature and quantities of these more exotic materials in refinery effluent following application of "best practicable treatment" and "best available treatment" as currently defined by EPA. At the same time, we are looking at the effluent from a well-managed and designed municipal waste treatment plant employing secondary treatment essentially to see what materials are present in such an effluent and compare them to those present in refinery effluent. We are also subjecting both of these effluents to chlorination to see what changes take place and whether chlorinated hydrocarbons are formed. A final report on Phase I of this work, which was a simple cracking refinery with reforming capacity, will be available in mid-1976. API plans to expand this study to look at other refineries with perhaps lube oil operations and petrochemicals. To do the job right, we feel we should eventually cover the whole broad spectrum of refinery categories, but this may take several years.

The API is also quite aware of the fact that so-called "toxic" pollutants are going to be receiving regulatory attention for the next several years and that toxicity of refinery effluent is a parameter which may be included in future permits. The biological-monitoring requirements in the Federal Water Pollution Control Act have yet to be implemented, so API has been working to develop a quick, simple bioassay method of determining gross toxicity in refinery effluent. We have several contracts with the Virginia Polytechnic Institute and State University to develop a series of tests which would be applicable to different situations: a coastal refinery discharging into an estuary, and inland refinery discharging into fresh water, and a refinery discharging into the ocean. We have already held several workshops to acquaint refinery waste-treatment personnel with one technique, which is now being used by a number of refineries in the country. We think that by gathering data from the users on the effectiveness and reliability of the techniques we are building the kind of data base which will support the adoption of one or more of these methods by government at some later date. So we are, I think, going to continue actively supporting research of this kind.

The focus of regulatory attention on small quantities of exotic materials and their potential toxicity both to aquatic forms of life and to human beings makes it all the more urgent it seems to me that the kind of objectivity that Dr. Talley spoke about be encouraged. As physicists -- and I was once a "would-be" physicist -- I think we both recognize the difference between an hypothesis which is as yet without data to support it but seems plausible and a theory, which is an hypothesis that has found support in data and has never been contradicted by data. A theory is a sound basis for predictive action

and for planning and policy, but an unproved hypothesis, however plausible, is not.

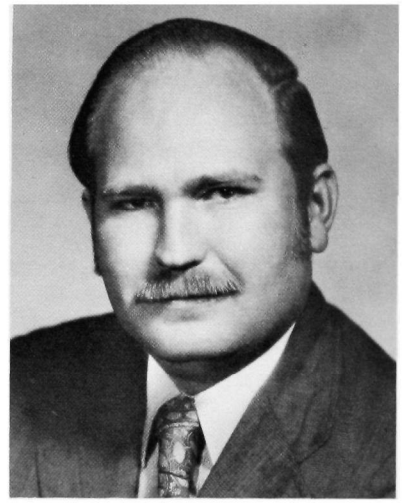
Unfortunately much environmental legislation ignores the distinction between hypothesis, as the basis for research, and theory, as the basis for policy. Thus, much environmental regulation is not based on logic, scientific principles, or anything but the fact that the law requires the Agency to act this way or that. The requirements may ignore the laws of thermodynamics or require government agencies to violate good scientific method, but the law must be obeyed. That is the bind that EPA finds itself in again and again. Those in the public sector who have to devise regulations which seem both to meet the requirements of the law and to be in the public interest and those in industry who have to comply should not be too critical of one another. I think we ought to work together to convince the Congress that we really do want to clean up the nation's air and waters, that we do want to have wholesome drinking water, that we do want to be responsible, and that we can do and are doing the job to the best of our ability. I think that this is true and that there is no question that the industry I represent and most major industries in this country are dedicated to doing the best job they can and still stay in business.

Yesterday, as I was on the plane coming to Tulsa, I sat next to a young man who is in shoe sales with a firm based in Maryland. He was writing a memo to his boss. Although I shouldn't have, I peeked at what he was writing and the first line read something like: "The figures below indicate that we have a considerable problem." Then he had three columns headed "promised", "actually ordered for production", and "deliveries". The figures were in hundreds of thousands, though I couldn't make out whether they were units of production, dollars, or what. Nevertheless, it was clear that deliveries were 50 per cent behind what had been promised to clients. He finished his memo with the statement, "I would be happy to discuss this with you" and then stuck it in his briefcase. After apologizing for reading the memo, I told him that he hadn't really finished the job. He had pinpointed a very real problem for his management, but hadn't offered any suggestions for a solution. I told him that the memo would upset his management and that since he was the source of the upset, they weren't going to be too happy with him. It is a first principle that one never bucks a problem upstairs without a recommendation. I asked whether he had any ideas about what was causing the problem and how it could be straightened out. He said the problem was in the manufacturing operation, so I asked whether he had talked to the person in charge of manufacturing. I suggested that if he could make a recommendation in his memo and say that he had discussed it with the manufacturing department, then he would really be performing a service for his organization rather than simply calling its attention to the fact that it was not performing well.

The point I want to make with this story is that the same advice I gave this young salesman applies in the current political situation surrounding the study of the National Water Quality Commission. The Commission will shortly submit its report to the Congress. It is to be hoped that this report will contain recommendations for action rather than simply an analysis of the problems with the present law. I would just say to my industry friends who are in the audience that if any of you or your companies are planning on submitting comments to the Commission's staff before the February 6 deadline, one of the

things you can and should urge is that the Commission not simply sidestep the issue of what legislative changes are needed to correct the problems it perceives in the present Act, but that it make affirmative recommendations as to what kinds of legislative changes are needed. If the Commission is unable or unwilling to make such recommendations, it will have failed to fulfill its mission.

BIOGRAPHY



Arne E. Gubrud is director of the American Petroleum Institute's Environmental Affairs Department. In this post, he supervises a staff of nine professionals. The function of the Department, whose annual budget for the past several years has ranged from two to three million dollars, is to conduct research and disseminate information about environmental conservation. Gubrud was deputy director of the Committee on Environmental Affairs from 1970 to 1973, when he assumed his present position.

Prior to joining API as an environmental writer in 1966, Gubrud had spent eight years with the American Water Works Association, starting as an assistant editor of the Association's Journal and rising to the post of assistant director of publications and public information.

Previously, he had been an editor of foreign language books and English translations of several journals of the Soviet Academy of Sciences.

Born in Redwood Falls, Minnesota, in 1934, Gubrud holds a Bachelor of Arts degree from the University of Chicago. He has also done graduate work in linguistics and physics at the University of Wisconsin.

Gubrud is a member of the Water Pollution Control Federation and the Air Pollution Control Association. He lives in Allview Estates, Maryland, with his wife and three children.

"THE UNIVERSITY'S ROLE IN FUTURE RESEARCH"

Joseph F. Malina, Jr., Gerard A. Rohlich, and Earnest F. Gloyna
Professors of Civil Engineering, College of Engineering,
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After hearing the proposed activities of the Federal government and industry in the area of future research related to management and pollution control of petroleum refinery wastewaters, there is some question as to what remains for the universities. However, if history repeats, a major role of the university will be to develop fundamental research programs leading to unique solutions to the environmental pollution abatement problems of the petroleum refinery industry. The universities have been involved in research related to pollution abatement in the refining industry for more than two decades. However, university efforts in the past were supported by industry and governmental agencies and in the future must not be carried out in a vacuum. The continued cooperation of the Federal government, industry, and the universities is essential to effective management of wastewaters and residuals generated at petroleum refineries.

The capabilities of universities to conduct research related to industry-wide problems have been recognized by the American Petroleum Institute, the Federal government through its past and present research components including the U.S. Public Health Service, the Federal Water Quality Administration, and currently, the Environmental Protection Agency, as well as by individual firms and installations through the support of a variety of research projects. The initial studies on the performance of oil-water separators and design of inlet devices for this unit process were performed by university personnel in laboratory studies and field evaluations under the sponsorship of API. Additional field studies on API separators were performed in cooperation with industry by the same university personnel at individual refineries. The effects of discharges of refinery wastewaters on receiving streams and some of the toxic effects of refinery effluents also were conducted by universities and funded by the API. More recent studies sponsored by the API at universities include for example:

"Bioassay of Refinery Effluents"
"Biological Effects of Pelagic Oil"
"Field Study on Effects of Oil on Marine Animals"
"West Falmouth Follow-up Studies"
"Fate of Oils in a Water Environment"
"Oyster Field Studies"
"Natural Biodegradation of Oil in Aqueous Environments"
"Clinical Studies of Toxicity of Oil in Water"
"Survey of Sub-Lethal Effects of Biota of Natural Chronic Exposure to Oil"

The EPA also has sponsored university research dealing with the treatment of petroleum refining wastewaters and the effects of effluents on ecosystems. The trend in EPA is away from extramural basic research in favor of in-house efforts, contracts, and demonstration grants. However, not all demonstration projects have been preceded by adequate laboratory studies, with the result that many pilot-scale or demonstration plant operations have met with difficulties and problems which often could have been identified and solved in bench-scale studies.

The design of some existing treatment facilities at refineries was based on research conducted by universities under grants funded by a particular company for a specific refinery. Therefore, it is likely that in the future the universities will be involved in research related to developing new solutions to another generation of environmental problems which face the petroleum refining industry.

One of the major roles of the university is in the education and training of people to carry out research at the universities, but more importantly, in industry and in governmental institutions. In the past, the support of this effort primarily was by the Environmental Protection Agency or its predecessor agencies. Students, mainly at the Master's level, received support and specialized in either air pollution control, water pollution control, or in solid waste management. At the completion of the university program, many of the trainees found employment in industry and became involved in design, operation, or research. However, the current trend in EPA is to limit training grants to individuals who are presently employed by regulatory agencies or who will seek employment in this type of agency after receipt of their advanced degree. If this trend continues, the number of qualified engineers and scientists trained specifically to direct their talents to environmental problems and available to industry will be markedly reduced. Industry then may be required to provide for education and training of individual employees in the area of environmental pollution abatement.

One of the difficulties facing universities at the present time is the curtailment of federal funds and to a certain extent, industrial support for advanced studies. This is particularly true for Ph.D. students who generally require a stipend for a period of three years. It is at the Ph.D. level that training in research is accomplished. Therefore, the university efforts require support through research grants or other means to assist in training Ph.D. students who will lead the way in developing unique solutions to existing and future problems.

Universities are uniquely suited to conduct research on problems which are of interest to the entire petroleum refining industry as well as to address specific industrial problems which may face a small facility. A wide range of talents are frequently available among the faculties and graduate students at the university. In Engineering for example, people in Chemical, Environmental, and Petroleum Engineering can be called upon in addition to individuals in Chemistry, Biology, and Microbiology. Universities also frequently are well-equipped with analytical instrumentation and supporting facilities to conduct fundamental research and bench-scale and pilot plant studies.

For example, at The University of Texas at Austin, the Environmental Health Engineering Labs at the Center for Research in Water Resources have been involved in bench scale and pilot scale studies related to the treatability of a variety of industrial wastewaters including petroleum refinery wastewaters. Efforts at the University of Tulsa through their Environmental Protection Projects program provide support for the education of undergraduate and graduate students in the College of Engineering and Physical Sciences.

The implications of PL 92-500, Water Pollution Control Act of 1972, and the Safe

Drinking Water Act, PL 93-523 lead to many areas where universities can make an impact in the immediate future. As long as the approach to the solution of the problem involves end of pipe treatment, treatability studies will have to be performed to develop more effective designs of facilities resulting in a more economical operation of the treatment plants.

Identification and quantification of organic and inorganic toxicants as well as techniques for ameliorating the effects of these materials is another area of industry-wide concern. The accumulation of toxic materials in sediments and in the food chain in the aquatic environment has not been established in sufficient detail. The entire question of quantifying toxicity is an area requiring considerable basic research. The toxicity bioassay procedure must be carefully evaluated especially in terms of selection of test organisms. The chemical species of materials discharged into the natural environment and interaction of the particular species with other components in the environment must be identified for many of the heavy metals discharged into natural systems. Some of these metals may react similar to mercury which when discharged into natural water can undergo conversion from the inorganic form to an organic compound more toxic than the inorganic form.

The Committee on Water Quality Criteria of the National Academy of Sciences and National Academy of Engineering (1) has defined some research needs. Universities will play an important role in these research efforts directed at establishing and mitigating the impact of industrial effluents on freshwater and marine aquatic life and wildlife. Concern for biological monitoring toxicity bioassays and assimilative capacity of receiving waters is a logical sequel to approaching the solution to the problem by end of pipe treatment. Some of the recommendations of the Committee report are pertinent to the topic under discussion and are quoted at this time.

> "...to undertake integrated studies of fresh water ecosystems in order to understand and ultimately predict the response of an ecosystem to various pollutants and to physical manipulation of the environment."
>
> "...biological scale models that can be manipulated in the laboratory provide a research tool that is convenient as well as productive. To deliberately control addition of pollutants to small unpolluted bodies of water has been used to great advantage in the past in determining the broad ecological impact of pollutants."

The report also directs comments to biological monitoring and bioassays.

> "The first concern of future efforts in biological monitoring should be development of standardized procedures having application to a diversity of aquatic systems. Such studies could most properly be conducted along with chemical analyses of water with the ultimate objective of identifying useful predictors of potentially toxic conditions."

"Research should be initiated to determine those species best suited for monitoring various kinds of pollutants."

"With such extensive use of bioassays there has developed a need for standardized procedures and methods for reporting particularly with regard to determining chronic and thermal effects in interactions of mixed toxic compounds. Also, yet to be resolved are questions of the comparability of results of bioassays involving different organisms and the applicability of laboratory data to the natural environment. Despite the progress that has been made bioassays have not yet been conducted for a number of important compounds."

"Research is needed to develop more effective bioassay methods for potential toxicants. The most sensitive marine organism should be identified and cultured on a generation-to-generation basis under laboratory conditions to provide genetic variability information on the test species and to form a basis for intercomparison of experiments and results."

"The effects on organisms of accumulation of sub-lethal levels of pollutants and the effects on man using these organisms in food should be investigated."

"Research is needed on the extent of bioaccumulation of various pollutants and the effects of transfer from organism to organism."

"It is essential to understand the interrelationships among organisms and between organisms including the highest trophic levels and their environment. This understanding is required for evaluation of the subtle and secondary effects which may be more important than the immediate and direct effects of an organism observed in a bioassay for acute toxicity."

"To make specific water quality recommendations for ecosystems it will be necessary to acquire information on the physical and chemical characteristics of the system, on distribution and abundance of species at all trophic levels, and on the normal variations in these characteristics over at least a representative annual cycle."

"Studies on the species diversities in a wide variety of marine ecosystems are needed as a basis for interpreting changes as indications of trends in overall water quality."

"The natural recovery potential of man stressed ecosystems as well as techniques for stimulating recovery require investigation in order to assess the permanence of damage and urgency in designating water quality for specific use."

The assimilative capacity of the ecosystem also must be defined.

> "Fundamental studies of the physical, chemical, and biological processes determining assimilative capacity are needed to develop methods of disposal that can be applied to a variety of locations. Each location however, will have some unique characteristic. Local conditions and the process operating there which determine the fate, concentration, and distribution of a pollutant must be studied in order to assure that a proposed rate of disposal not exceed levels harmful to the ecosystem."

> "The understanding of the rates of biological, chemical, and geological modifications is needed to evaluate the long-term impact of various pollutants on the marine ecosystem. Research is needed on the rates of biological degradation and decomposition, on the chemical reactions various compounds and elements undergo when introduced into seawater, and on the rates of absorption and precipitation to the sediments."

The non-living components of the marine ecosystem also must be considered.

> "Research is needed on the synergistic and antagonistic effects of seawater on organic and inorganic chemicals in the marine environment as well as on synergism or antagonism among the chemicals. A series of combinations and permutations should be tested under different conditions in both fresh water and seawater to understand more fully the mechanisms of synergism and antagonism."

On the topic of oils, the report mentions,

> "The presence of flowing oil in visible amounts is generally considered unsightly as well as harmful to aquatic life and wildlife. Nonetheless, invisible surface films of oil should be examined closely for adverse biological effects attributable to adsorption onto the body surface of organisms or to interference with the exchange that normally occurs at the air-water interface. The toxicity of oil dispersants of various crude and manufactured oils also require further investigation."

> "Sedimented oils pose a problem that demands more immediate attention in both fresh water and the marine environments because of their persistence and widespread occurrence. Safe levels of sedimented oils have yet to be determined and the impact's availability to concentrate other toxic substances is unknown."

The development of effective biological monitoring systems, more universally applicable bioassay procedures and a more complete understanding of the biological, chemical, and physical reactions and interrelationships in fresh water and marine ecosystems will require the cooperative efforts of industry, universities, and government agencies.

In areas other than end of pipe considerations future research activities at universities must be oriented to the industrial activities, specifically:

a) secondary recovery and reuse of raw materials;
b) process improvement to eliminate waste;
c) waste treatment with emphasis on liquid, solid, and gaseous waste; and
d) disposal of residuals and sludges.

A wide variety of organic solvents and detergents are used in secondary and tertiary recovery. The basic research on techniques to contain these materials and to minimize the effects on the enviroment still must be initiated. A great deal of effort has been expended on tertiary oil recovery with but little attention to the processes which would be required to make these operations environmentally acceptable.

Many of the companies involved in petroleum refining also are active in developing alternative energy sources. Many of these activities will require closer attention to their impact on the environment. Nuclear energy will require basic research directed at the disposal of spent fuels. Programs for developing effective methods of coal gasification are ongoing. But almost no information is available to the industry regarding the treatment or the disposal systems necessary to handle the liquid, solid, and gaseous wastes generated along with the usable product. It is in the development of unique solutions to these types of problems that the universities can make the most significant contribution.

A considerable amount of basic research also is required to modify unit processes involved in petroleum refining in order to eliminate, or at least minimize, the amount of waste generated. This type of problem can best be solved as a joint venture with the university and industrial personnel cooperating to develop a satisfactory solution using modern process control technology. Spills and leaks in process areas result in the loss of materials which find their way into waste ditches and eventually into the wastewater treatment system. Much of these materials are reusable in the refining process and in some cases are recovered and returned to the process areas.

The requirements for a higher quality effluent has led to the application of physical and chemical processes to treat effluents of biological treatment facilities. These processes result in increased sludge volumes which require disposal as well as in a higher total dissolved solids concentration in the effluent. A vast amount of basic research is needed to answer the myriad of questions that have been raised about the effects of toxicants on the biota in treatment plants and in receiving streams as well as on the methods of removal of these toxic substances. In many of the processes these toxicants are not destroyed but merely removed from the wastewater stream and concentrated as either a brine or in the sludge. The ultimate disposal of the brine or sludge requires basic research to define suitable methods of treatment or disposal of this material. This information is essential before large scale and industrial pilot plants are designed and constructed.

The area of solid waste management offers opportunities for much basic research. Solid wastes at a refinery range from plant trash to slop oils, tank bottoms, sludges, catalysts and other materials which are not carried away in the wastewater stream. Much of these materials are placed on the land, and in the case of slop oils, tank bottoms, and biological sludges, the soil bacteria are effective in decomposing the materials. However, a number of questions come to mind which require answers. This information can be

developed through a basic research program. Some of these questions include: a) At what levels are various toxicants present in the sludges? b) If toxicants are in the sludges, what is the rate of uptake of these toxicants by the crops grown on these lands? c) What is the mechanism by which the toxicants are transported from the sludge to the soil and possibly through the soil into groundwaters? d) What is the tolerance level of the soils for salts which may be present in the sludges? If the organic and inorganic toxicants can be transported from these sludges, and slop oils through the soil system, it is essential to define those characteristics of the soil which inhibit the transport of these materials so that proper site selection criteria can be developed.

There is no unified policy in the petroleum refining industry concerning solid waste management. In many cases, the problems of residuals handling and disposal are not clearly identified or understood. The characteristics of these residuals and their respective half-lives must be defined before any long-term solutions to this phase of waste disposal can be developed. Most universities have considerable capabilities for analyses and instrumentation which can be used to characterize various components of industrial waste.

Another problem which requires definition and quantification is that of non-point sources of pollutants. The run-off resulting from rainfall in process areas and product storage areas generally cannot be discharged directly into receiving streams. The characteristics of these materials must be quantified.

The problems of land use planning also require an objective review which may be considered as fundamental research. The approach to land use planning must be reasonable otherwise legislation may be forthcoming which will make it impossible to dispose of wastes generated by industry within the close proximity of industry. Land use legislation which does not recognize waste disposal as a reasonable use for certain lands will markedly affect the overall industrial efforts related to liquid, solid, and gaseous pollution abatement.

However, it should be emphasized once again that a primary function of the university will be to produce research engineers and scientists recognizing that these programs must continue as a cooperative effort with industry and agencies at all levels of government. In order to meet this responsibility universities will continue to be actively engaged in research related to industrial pollution abatement problems.

REFERENCE

(1) "Research Needs in Water Quality Criteria 1972", a report of the Committee on Water Quality Criteria to the Environmental Studies Board of the National Academy of Sciences, National Academy of Engineering, Washington, D.C., 1973.

DISCUSSION

Bob Huddleston: Just a comment - one of the problems that I have seen in looking at our Company's waste disposal problems, or waste treatment problems has been that we would like very much to not see variability in the material that we have to treat but we have

got to recognize the fact that it is there. One of the problems that we encounter is how to handle this variability and this is an area of research I think that needs to be looked into much more than it has in the past.

Joe Malina: I agree that variability will exist. However it is a matter of what degree of variability can be expected and to reduce the variability to something that is more or less predictable. Some work on equalization systems has been done at The University of Texas at Austin involving the types of models available to predict the size of basin needed based on the incoming variations, as well as the design of a facility for equalization which also provides some treatment in addition to equalizing the flow.

BIOGRAPHY

Joseph F. Malina, Jr. is Professor of Civil Engineering and Director of Environmental Health Engineering Laboratories at The University of Texas at Austin. He holds the Bachelor in Civil Engineering Degree from Manhattan College and M.S. and Ph.D. in Sanitary Engineering from the University of Wisconsin. He is registered as a professional engineer in the State of Texas, and has been with The University of Texas at Austin since 1961.



SUMMARY

"REVIEW OF OPEN FORUM"

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How does one review such a successful meeting? Obviously it is impossible to recapitulate the highlights of 32 presentations by experts far more learned and experienced than I. Let me start by thanking all those people who contributed so much to this open forum: -

1. You the participants of this open forum. Without your attendance this symposium would have been a disaster. Your excellent attendance, not only guaranteed the success, but also demonstrates the petroleum-refining industry's genuine concern for our environment.

2. Our speakers - all of them. I am sure the other 29 will forgive me if I make special mention of my old friends - Milt Beychok; Wes Eckenfelder; and Davis Ford - who have also contributed so much to my previous short courses.

3. The EPA for sponsoring this open forum. May I make special mention of my friends at the R. S. Kerr Laboratory in Ada, Oklahoma. Without Fred Pfeffer, Leon Myers, Bill Galegar and their colleagues there would have been no open forum.

4. The API and NPRA. The excellent attendance - over 300 - is due to Herb Bruck, NPRA and Arnie Gubund, API. They were the publicity.

5. Last but not least, my colleagues at T.U.: - Nick Sylvester, Katie Whisenhunt, Shirley Clymer and Paschal Twyman.

Please make no mistake about it. Many of you were kind enough to offer congratulations to me for "putting on such a success". With all due respect, my conscience insists that the whole truth be known. A successful open forum is not a one-man show. Of necessity it is a team effort. I merely had the privilege of coordinating their efforts with a lot of help from Fred Pfeffer.

To return to my original charge. How does one summarize this open forum? Let us content ourselves by discussing some of the major recurring themes: -

1. The large attendance and lively interchange of ideas constitutes "proof positive" that the petroleum-refining industry is a leader in preserving the environment. May I digress to offer two more "exhibits" in "evidence" of this concern for the environment: -

   (i) Since 1974, 14 petroleum and petroleum-related corporations have sponsored

the University of Tulsa's Enviromental Protection Projects program (UTEPP). Current UTEPP research includes: chromate removal from cooling tower blowdown; phenol removal from wastewater by carbon adsorption; phenol removal from wastewater; flocculation of oil-water emulsions; oil removal from wastewaters by induced air flotation; and oil removal from wastewaters by ultrafiltration. UTEPP was started after a two-year EPA Training Grant in oil-related water pollution control was terminated. UTEPP not only supports graduate and undergraduate education in oil-related pollution control; but also constitutes convincing evidence of the petroleum industry's concern for the environment. It is hoped that this cooperative research effort will not only grow but will also serve as a model for future research commitments by other industries at other universities. The Federal government should actively seek methods of participating in these joint efforts as this is a very efficient way of minimizing duplication of research efforts.

(ii) Since 1970 the petroleum industry has also supported 10 one-week short courses at T.U. on industrial pollution control as applied specifically to petroleum refining.

2. There has been a remarkable agreement among the views expressed - not only concerning the technologies but also the guidelines.

3. Sure there were differences in opinions and some keen arguments. These differences reflect honest attempts to state one aspect of our most complex task - optimizing the management of petroleum refinery wastewaters.

4. As Milt Beychok so eloquently noted, such dialogue between all the concerned parties is absolutely necessary. Progress will be made only if all parties are not only willing to state their viewpoints but also equally willing to allow their viewpoints to be cross-examined in depth. This adversary procedure is not the easiest on everybody's temper or nerves, and is not the least time-consuming; but is it not the "best available technology" for discovering "the truth, the whole truth, and nothing but the truth"?

Next let us sum up the "evidence" of the last 32 "witnesses". Some simple truths emerge: -

1. The petroleum refining industry should be justifiably proud of the technology it has developed. The technology described by Fred Weiss and Jim Grutch (to state just two examples) is second to none. Sure we can do even better and honest self-ctriticism is constructive. But there is no need for despair, no benefit in submitting quietly to unreasonable critics.

2. As Nick Gammelgard stated so forcefully it is senseless to strive blindly for "zero discharge" with no regard to any other variable. The "Energy Crisis" has forced us to step back and re-evaluate "the impossible dream" of zero discharge.

3. All our "expert witnesses" clearly demonstrated how complex it is to try to optimize

petroleum refinery wastewater management. We examined the subtleties in great detail - e.g.
Allen Cywin, Martha Sager, Joe Moore revealed the legal and political complexities.
Carl Schafer, Bob Silvus and Harless Benthul demonstrated the pitfalls of applying the legalities and politics!
Then after this introduction we reviewed at length the available technologies and speculated on the future advances.

4. This mass of evidence convinces me that rational optimization of wastewater management is achieved most readily if we use a model to help us. At the very least such a model should identify our problems. At best we get some useful results.

5. Please do not misunderstand me. I am NOT stating that all progress demands the largest computer. On the contrary, I am a most fervent believer in Occam's Razor. "Entia non sunt multiplicanda sine necessitate". In the current vernacular it is called, I believe, the KISS system; "Keep it simple, Stupid"!

6. Applying the KISS principle we must first determine what we are going to optimize. Very little thought is required to agree that we would like to minimize:
(i) the valuable natural resources consumed
(ii) the pollution load on the environment
(iii) the financial burden on the economy
(iv) the technical manpower required, etc.

7. Because we cannot simultaneously minimize all these objectives; trade offs are required. In other words we must convert or express "energy loss" or "pollution load" to $. This is a huge problem; and, in the long run, the "dollar value" or "conversion factors" must reflect public opinion. In many cases more research will be needed before we can say how bad a particular chemical is. The current activity in toxicity studies is addressing just such a facet of our objective function.

8. Next we must model our refinery. At a minimum we should know the energy consumed and pollution load generated first for a typical (say class A) refinery and second for each of the major operations, crude distillation, cracking, etc. This second-level detail would permit comparison and optimization of various modes of operation.

9. Please do not construe the previous ideas as a neglect of wastewater treatment technology. Such technology can perform wonders; but, it is only one alternative - another alternative may very well be - don't generate that particular pollutant, as Cyron Lawson observed. And, of course, the demand for refinery gas, heating oil, kerosene, etc., will also control plant operation.

10. Technical manpower can be minimized by concentrating on the bottlenecks and so avoiding spinning our wheels. Poor data or lack of data do not deserve a very detailed model and, of course, vice versa.

Please pardon this digression on modeling. But, I hope, that you experts will agree that this open forum has identified some key bottlenecks. At least we have discussed all the key ingredients for the model: -

- should the guidelines reflect a sensible trade-off between energy-consumption, economics, and technology?
- should the technology discussions help us improve our treatment processes?
- the recommendations on the direction for future research efforts should have helped us accelerate our treatment technology.

If this open forum has resulted in any of these goals it deserves to be labelled a success. At the very least it has encouraged and fostered 3-1/2 days of friendly and constructive dialogue - which is the ideal catalyst for progress.

To those impatient majority of you who restlessly seek to speed up in this optimization process, may I venture to calm you with the Latin proverb "festina lente" (hasten slowly). Rest assured the refinery industry can and will serve as leader for municipalities and other industries. Your interest in this open forum proves that you well realize the key for success. It is perhaps best stated in the State of Oklahoma's official motto, "Labor omnia vincit" (Work overcomes all obstacles).

BIOGRAPHY



Francis S. Manning is Professor and Chairman of Chemical Engineering at The University of Tulsa. He holds the following degrees in Chemical Engineering: - B. Eng. (Hons.) from McGill University and M.S.E., A.M., and Ph.D. from Princeton University. He is a professional engineer, registered in Oklahoma, Pennsylvania and Texas. Frank taught at Carnegie-Mellon for 9 years before joining the University of Tulsa in 1968. The author of 1 book and over 60 papers, Frank's current research interests lie in thermodynamics, reaction kinetics, and industrial pollution control. In 1969 he received the R. W. Hunt Silver Medal from the AIME.