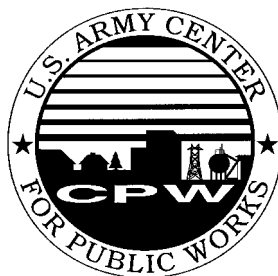


PUBLIC WORKS TECHNICAL BULLETIN 420-49-05
2 FEBRUARY 1998

**INDUSTRIAL WATER TREATMENT
PROCEDURES**



DEPARTMENT OF THE ARMY
U.S. Army Center for Public Works
7701 Telegraph Road
Alexandria, VA 22315-3862

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No. 420-49-05

2 February 1998

FACILITIES ENGINEERING
Utilities

INDUSTRIAL WATER TREATMENT PROCEDURES

1. Purpose. This Public Works Technical Bulletin (PWTB) transmits the Industrial Water Treatment Procedures handbook. The procedures provide information on the application, selection, procurement and implementation of water treatment procedures and chemicals required to properly operate boiler and cooling systems and maintain the waterside surfaces. The procedures improve maintenance, efficiency, reliability, treatment, system life and safety of boiler and cooling systems. The boiler and cooling systems include steam boilers, hot water boilers, chilled water systems, cooling towers and other industrial systems.
2. Applicability. This PWTB applies to all U.S. Army Public Works activities responsible for operating and maintaining boiler, cooling tower and HVAC systems.
3. References.
 - a. Army Regulation 420-49, Facilities Engineering, Utility Services, April 1997.
 - b. TM 5-650, Central Boiler Plants, October 1989.
 - c. TM 5-642, Operation and Maintenance Small Heating Systems, August 1990.
 - d. TM 5-671, Preventive Maintenance for Refrigeration, Air Conditioning, Mechanical Ventilation, and Evaporative Cooling, August 1958.
4. Discussion.
 - a. Many installations across the country are facing problems in industrial water systems (i.e., boiler and cooling systems). One of the most common problems is difficulty in preventing the formation of scale or the occurrence of corrosion in heating and cooling systems. As a result of these problems, system life, reliability, efficiency and safety are reduced. Many of these

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problems are preventable through proper boiler/cooling water chemistry maintenance and treatment.

b. Army policy requires generic chemicals for the treatment of central boiler plant system water. TM 5-650 provides basic guidance on the application of chemicals to steam and hot water boiler water. This PWTB amplifies the correct chemical treatment of boilers and adds required chemical treatment for cooling towers and chilled water systems. It also provides procedures for the economical, safe and efficient control of heating and cooling systems while setting specific standards for water treatment.

c. This PWTB provides one consolidated guide for chemical treatment of all HVAC systems.

5. Point of contact. Questions and/or comments regarding this subject, which cannot be resolved at the installation level, should be directed to:

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INDUSTRIAL WATER TREATMENT PROCEDURES

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Chapter 1

Introduction To Industrial Water Treatment

Section I Industrial Water Treatment Policy

1-1. Industrial water defined. Army policy requires in-house treatment of industrial water systems using generic chemicals or formulated products that can be bid on a generic basis from an approved water treatment service company. The term "industrial water," as used here, means the water used in Army heating, air conditioning, refrigeration, cooling, processing, and all other equipment and systems that require water in their operation. Industrial water is not the same as potable water. Industrial water is never to be consumed or used under situations that require a high degree of sanitation. Examples of industrial water applications are: boiler water (both steam and hot water boilers); cooling water circulated through cooling towers; evaporative condensers and evaporative coolers; diesel engine jacket water; and chilled water for air conditioning.

1-2. Problems encountered in industrial water systems. Problems found in industrial water systems are often caused by deposits, scale, algae growths, fungi, slime, corrosion of metals, and deterioration of wood or other parts of water-using equipment. These problems generally result in reduced system efficiency (higher operating costs), increased equipment replacement costs and reduced safety. At times they can be serious enough to cause complete system shutdown.

a. Deposits. Deposits are residues of insoluble materials, such as sludge, dirt, or

corrosion by-products, attached to pipe or equipment surfaces.

b. Scale. Scale is a specific type of deposit caused by precipitation of mineral salts from water, and is very adherent to the pipe or equipment surface.

c. Algae, fungi, and slime. Algae are microscopic plants that may grow in various industrial water systems, but most commonly appear on the distribution decks of cooling towers. Fungi are living organisms that may damage the wood parts of cooling towers through decay. Slimes are the accumulation of these biological contaminants and may foul the equipment.

d. Corrosion. Corrosion is the deterioration of a material, usually a metal, because of a reaction with water.

1-3. Objective of industrial water treatment. Industrial water is treated to prevent scale, corrosion and fouling, increase efficiency, prolong life, and reduce repair and replacement of water-using equipment. This requires an adequate and continuous supply of properly treated makeup water, which is normally from the installation's potable water distribution system. In addition, necessary steps should be taken to provide a backup supply. Every effort must be made to conserve water used in boilers, cooling towers, and other water-using equipment. This includes identifying and fixing leaks throughout the systems, minimizing boiler blowdown, reducing drift from cooling towers, and operating systems at the highest permissible cycles of concentration. Using less water also reduces the amount of treatment

chemicals required. This, in turn, eases operation of wastewater treatment facilities and reduces chemical handling and waste.

1-4. Responsibility for treatment.

a. Office responsible. The Director of Public Works (DPW) is responsible for treating and testing industrial water. Approved treatment programs are provided in this manual.

b. Organization assignments. Efficient and economical industrial water treatment and testing requires specific organizational assignments. The person assigned to industrial water treatment and testing is often assigned other duties, therefore, coordinate time to ensure that adequate and continuous attention is given to industrial water treatment and testing.

1-5. Unauthorized treatment.

a. Unnecessary treatment. Treatment of industrial water in excess of that which is required is unnecessary, expensive, and can lead to other problems. Chemicals authorized for treating water in one type of system are not necessarily desirable and may actually be detrimental in water intended for other industrial uses.

b. Use of premixed chemicals. The use of premixed proprietary chemicals in steam boilers is to be avoided. Such compounds, properly mixed for one type water, generally will not work effectively with a different type water. Since the compound is a fixed mixture of chemicals, there is no way to adjust the dosage of individual chemicals to maintain the proper amount of each in the boiler.

c. Use of Nonchemical Devices. Many nonchemical devices sold for industrial water treatment are purported to solve all water related problems including scale, corrosion,

slime, and odor. They are said to achieve remarkable results through natural forces (such as magnetism, electricity or radiation) either unknown to engineers or not disclosed. Often it is stated that the nonchemical devices require little or no attention and no chemicals. Generally, they have not proven effective. Therefore, the use of these nonchemical treatment devices on Army systems either regularly or on a test evaluation basis, is prohibited.

1-6. Protecting health. Many of the chemicals used to treat industrial water may be harmful to the health of the operator and other installation personnel, unless they are handled and controlled properly.

a. Protecting potable water supplies. Protection of potable water supplies as it applies to an industrial water system is summarized as follows:

(1) A cross-connection is a physical connection between a potable water supply system and a nonpotable system (such as an industrial water system) through which contaminated water can enter the potable water system. Cross-connection must be avoided to maintain the safety of potable water supplies. To prevent cross-connections where potable water is supplied to industrial water systems, backflow prevention devices must be installed.

(2) Only Class III backflow prevention devices (air gap or reduced pressure principle devices) are permitted between a potable water supply system and an industrial water system which is from a source of nonpotable water, or to which chemicals have been added for any purpose.

(3) If potable makeup water is supplied to a tank or other type of open system, an air gap must be provided between the water inlet

and the maximum overflow level of the tank, device, or system.

b. Restrictions on direct steam use.

Neutralizing amines added to protect the condensate lines from corrosion makes the steam and condensate unfit for consumption or other uses normally reserved for potable water. Do not use treated steam in direct contact with food, heating of food trays, or for humidification. For these applications use steam-to-steam heat exchangers to provide amine-free steam. Guidance is provided in AR 420-49, section 6-5.

c. Ban against sodium chromate.

Sodium chromate, an excellent corrosion inhibitor, historically has been used extensively in the treatment of cooling towers and closed systems. After it was identified as a human carcinogen (cancer causing), the Environmental Protection Agency (EPA) prohibited its use in comfort cooling towers because of unacceptable health risks. Also, chromates have to be handled and disposed of as hazardous materials. Army policy prohibits the use of chromates for treatment of industrial water systems.

1-7. Record keeping requirements.

Industrial water treatment and testing procedures may vary from one installation to another. This is because of the water quality at the site and the type and size of the systems. These are governed by local factors, such as the installation's mission, geographical location, and climate. Industrial water treatment and testing logs and records should reflect the minimum entries needed for control of the treatment program and for operating records. Sampling and testing frequencies for various industrial water systems are provided in chapter 6.

a. Control charts. Develop control

charts showing the treatment chemicals used, the amount to add, the limits to maintain in the system, testing required, and the information peculiar to the system for the larger boilers and cooling towers.

b. Operating logs:

(1) Large Steam and Water Boilers. Keep boiler water treatment records on DA Form 4367 (Repair and Utilities Operation Log, Boiler Water Treatment) or an equivalent form. Logs should be maintained in plants operating above 15 psig steam or 30 psig water with an output capacity above 3.5 MBtu/hr or 100 horsepower. The log provides a record of boiler, makeup and condensate water treatment and test results. One log should be maintained for each boiler and one for plant makeup water data.

(2) Cooling Towers. Keep local organized operating logs on all operating cooling towers. These logs should contain results (including dates) of all chemical tests, calculated cycles of concentration, amounts of chemicals added, and the amount of blowdown performed.

(3) Other Systems. Local organized operating logs should also be kept for low pressure steam boilers, high temperature hot water (HTW), medium temperature hot water (MTW) and low temperature (LTW) boilers, and for closed chilled water systems. These logs should contain results (including dates) of all chemical tests, amounts of chemicals added, and the amount of blowdown, where applicable.

c. Local records. Keep the maintenance and history of industrial water treatment, other than that which must be entered on the log form or data accumulated for log form entries, in a historical record book for each system.

(1) This record should be at least letter-size, and may be larger. It should be a

bound book, not a loose-leaf binder.

(2) This record should contain a historical record (including dates) of system start-up and shut-down, occurrences of corrosion and scale, major maintenance performed on the system, replacements of piping and equipment, accidents, outages, changes in methods of operation and treatment used, and other pertinent data.

1-8. Support available:

a. Boiler/Cooling water quality assurance program. Army Regulation 420-49, Apr 97, section 6-4 requires samples from certain heating systems be submitted to an adequately equipped laboratory for analysis. The primary purpose for the check analysis program is to ensure that treatment chemical concentrations are, in fact, what the in-plant test results show. If in-plant tests are in error, the treatment levels in the boiler may be out of control limits, resulting in inefficient operation or damage to the boiler system. Water chemistry limits that are out of control are a major cause of boiler failures and damage. The contract laboratory, under contract to USACPW (CECPW-ES), will provide the following support:

(1) Perform analyses on water samples submitted from Army installations.

(2) Provide, on request, condensate corrosion testers.

(3) Analyze test rings from condensate corrosion testers after exposure.

(4) Analyze scale or deposit samples from any industrial water system submitted from Army installations.

(5) Evaluate results of analyses and provide to the submitting installation a written report including appropriate technical comments and recommendations. In overseas commands where shipment of samples to the

United States is not feasible or expeditious, samples will be sent to a central laboratory established by the command. Sampling requirements under the check-analysis program are provided in chapter 6, paragraph 6-1.

b. Other support. Matters concerned with Army policy, request for staff visits to troubleshoot industrial water systems, training of water treatment personnel, and general technical questions should be addressed to USACPW, ATTN: CECPW-ES, Sanitary and Chemical Division, 7701 Telegraph Rd., Alexandria, VA 22315-3862.

Section II Safety And First Aid

1-9. Safety considerations. Chemicals used in water treatment and related maintenance activities range from highly toxic to mildly irritating to the persons handling them. Handle all water treatment and testing chemicals with care, following any special instructions prescribed by the manufacturer. Keep areas where chemicals are handled or stored clean and free of debris to minimize the chances for accidents. Personnel handling these chemicals should attend educational sessions, refer to material safety data sheets (MSDS's) for additional information, and use proper respirators and protective equipment recommended by the installation environmental engineer.

a. Handling acid. Avoid splashing acid. If acid does contact the eyes, skin, or even clothing, flush immediately with water. Refer all cases of acid burns, especially to the eyes, to a doctor. When diluting any acid, never add water to the acid because this may cause a violent reaction or splattering. Always pour acid into the water. Wear Occupational Safety

and Health Agency (OSHA) approved goggles, face shield, rubber gloves, and a rubber apron when handling acid.

b. Handling caustic soda (sodium hydroxide). Caustic soda is a strong alkali that can cause severe burns when contacted in either the liquid or solid form. If caustic soda does contact the eyes, skin, or even clothing, flush immediately with water. When water is added to caustic soda, a great deal of heat may be generated which can cause splattering or boiling of the solution. The dust or mist from caustic soda may cause injury to the upper respiratory tract if inhaled. When handling caustic soda wear close fitting OSHA approved industrial goggles, rubber aprons and gloves, and coveralls that fit snugly at the neck and wrist.

c. Handling other chemicals. Many of the other chemicals used in water treatment, including amines, soda ash, lime, sodium aluminate, sulfite, biocides, and algicides, may cause some irritation on contact with the skin. Handle all chemicals with caution, following the manufacturer's recommendations. Immediate flushing with water is generally recommended for any contact of a chemical with the skin. Review the material safety data sheets (MSDSs) that are available for the chemicals being handled for any special precautions that should be taken.

d. Chemical spill kits. Each area where acids, caustic soda, or other hazardous materials are used or stored must be equipped with appropriate chemical spill kits. Kits for cleaning up acids, bases, and solvents are commercially available. It is best to be prepared for a spill that never happens.

1-10. First aid information:

a. Eyewash fountain. An eyewash fountain or a ready source of running tap

water (a bubbler drinking fountain or hose with a soft flow of water) must be readily available to wash out or flush the eyes. If even minute quantities of acid or caustic soda enter the eyes, immediately flush the eyes with large amounts of water for at least 15 minutes.

b. Safety shower. A readily accessible, well marked, rapid-action safety shower must be in the area where acid or caustic soda is being handled.

c. Safety inspection. Regularly inspect all safety equipment to ensure it is in good working condition. Operate safety shower and eyewash weekly to prevent accumulation of rust. Place clearly marked signs containing concise instructions on their use near the emergency eyewash fountain and the safety shower.

Section III Disposal Of Industrial Water Wastes

1-11. Disposal procedures. Coordinate the treatment and disposal of liquid and solid (sludge) wastes from industrial systems with the installation environmental engineer (coordinator).

a. New chemicals. The use of a new water treatment chemical must be reviewed by an environmental engineer to determine if it can be safely disposed of by the existing procedure or if new procedures must be developed.

b. Discharge pretreatment. Pretreatment of water discharges refers to a treatment procedure that is applied to the water before it is discharged to the base treatment systems. The installation environmental engineer is responsible for determining when pretreatment is required and what methods are to be used.

c. Discharge requirements. The discharge of industrial water treatment system wastes may be regulated by the installation environmental engineer. The discharge may be controlled in the following ways:

(1) The location of the discharge should be set by the configuration of the water treatment system and available sewers. The location of discharge for occasional discharges should be established through the installation engineer. Normal practice may include discharge into either the sanitary or industrial wastewater treatment system.

(2) The maximum rate of discharge to the designated sewer system should be established through the installation environmental engineer. There are two factors of importance in setting a maximum rate: the hydraulic capacity of the sewer, and the strength (chemical concentration) of the waste.

(3) The time when a discharge is allowed from a water treatment system unit may be established by the installation environmental engineer.

1-12. Regulations that may apply:

a. Installation directives.

The water treatment system operator is responsible for complying with the procedures and policies established at the installation, including the directives on waste disposal from the installation environmental engineer. The compliance of the installation directives with government environmental regulations is the responsibility of the installation environmental engineer.

b. Environmental regulations.

There are numerous environmental regulations that may apply at the installation level. These have been established by law. Current regulatory information is available from the

installation environmental engineer.

(1) Toxic Substances Control Act authorizes the US Environmental Protection Agency (EPA) to control all new and existing chemical substances determined to cause unreasonable risk to the public health or environment.

(2) Clean Water Act (CWA) includes the Federal Water Pollution Control Act and amendments. The CWA establishes limits for the discharge of pollutants to navigable waters, regulations on specific toxic pollutants in wastewater discharges, and control of oil and hazardous substance discharges.

(3) Safe Drinking Water Act provides for protection of underground sources of drinking water and establishes primary and secondary drinking water standards.

(4) Federal Insecticide, Fungicide, and Rodenticide Act requires that all pesticides be registered with the U.S. EPA.

(5) Resources Conservation and Recovery Act (RCRA) addresses the control of solid waste. Defined hazardous wastes are controlled under RCRA by a complex manifest system designed to track a waste from its generation to final disposal.

(6) Occupational Safety and Health Act establishes health and safety requirements for the work place including handling and labeling requirements, safety precautions, and exposure limits to work place contaminants.

(7) Comprehensive Environmental Response, Compensation, and Liability Act (also commonly referred to as Superfund) establishes the responsibilities and procedures for the response to existing uncontrolled hazardous waste sites.

Chapter 2

Makeup Water

Section I General Information

2-1. Industrial water.

Industrial water systems at most Army installations use recirculating water systems. Fresh water added to replace water lost by blowdown, evaporation, wind drift, leaks, or withdrawal in these systems is referred to as makeup.

2-2. Sources of makeup water. The usual source of makeup water is the installation's potable water supply. This represents a treated water that usually is of a very uniform quality on a day-to-day basis. Other sources of makeup water could include well water, surface water, or holding ponds that are not treated to the extent that the potable water source is treated. The quality of this makeup water may vary slightly, depending on its source.

a. Groundwater. Groundwater generally contains high dissolved minerals but are more uniform in quality. Where the groundwater is treated before use by a system, there may be some fluctuations in quality due to variations in treatment efficiency.

b. Surface water. Surface water supplies may vary with the season and also the weather, with higher turbidity and suspended solids possible during wet weather. Where these waters are treated, the quality generally will be more uniform than for untreated surface waters.

2-3. Source selection factors to consider. The source of water used in industrial water

systems should be both reliable and uniform in quality. There should also be a backup source available to the operator.

2-4. Reasons and criteria for treating makeup water:

a. Reason for treating makeup water. Makeup water is treated to remove or reduce the concentration of any undesirable impurity. This may include impurities that will cause corrosion in the industrial water system, create a deposit or scale in the system, or otherwise interfere with the operation of the system.

b. Criteria for treating makeup water:

(1) Cooling towers. Because impurities do not become highly concentrated, pretreatment of makeup water for cooling towers is normally not required. Special conditions may require treatment.

(2) Steam boilers. Water softeners (usually "zeolite" units) should be installed at boiler plants. New steam boilers normally require makeup water with less than 1 ppm hardness, however, the manufacturer's recommendations should be followed.

(3) Hot water systems. Softening is recommended for high-temperature, high-pressure hot water systems when the total hardness of the makeup water exceeds 10 ppm (as CaCO_3).

(4) Other systems. Softening of makeup water is generally recommended in chilled water systems, dual purpose (hot or chilled) systems, and in hot water boilers treated with nitrite-borax, or molybdates if the makeup water total hardness exceeds 250 ppm (as CaCO_3). Makeup water in hot water boilers treated with sodium sulfite and caustic

soda, and diesel jacket systems should be softened when its total hardness exceeds 50 ppm (as CaCO_3).

c. Measurement of makeup water.

Makeup rates are required to calculate proper operating data on cooling towers and steam boilers. They may be estimated by recording the time it takes to fill a container of known volume, or preferably, measured with a appropriate makeup meter to provide more accurate values and to reduce labor requirements.

Section II

Methods Of Treatment

2-5. General discussion. Treatment of industrial water falls into two categories - external treatment and internal treatment. External treatment involves the pretreatment of makeup water to remove hardness, alkalinity, dissolved gases, or other impurities before the water enters the particular water system, e.g., steam boiler, cooling tower, closed hot or chilled system. Internal treatment involves the introduction of chemicals directly into the water system. Some waters may require one or both methods.

a. External treatment. External treatment equipment and chemicals are available to remove impurities from the makeup water before they enter the internal system. Removing impurities before they enter a system, particularly a steam boiler, is the most effective way to protect the system, to reduce water problems, and to improve operating efficiency. The treatment methods and equipment required are determined by the impurities that need to be removed from the makeup water. Various external treatment methods available to remove typical impurities

found in makeup water are shown in table 2-1. The effects of these treatment methods on raw water are illustrated in figure 2-1. Treatment may be applied to only a part of the makeup water which is then blended with raw (untreated) water to achieve a desired quality. This is known as split stream treatment. External treatment methods are briefly described in paragraph 2-6 through 2-18. External water treatment is generally required for only steam boilers and high temperature hot water (HTHW) systems, but may be justified for use in other industrial water systems as well. Although several types of treatment may be available, sodium zeolite softening (ion exchange) is the most common method used at Army installations for treating makeup water. A guide for selecting external treatment methods/equipment for steam boilers is provided in table 2-2.

b. Internal treatment. The purpose of internal treatment is to prevent any problems in the internal water system that might be caused by the impurities remaining after external treatment. Essentially all industrial water systems require internal water treatment. Internal water treatment methods approved for use on Army installations are covered in chapters 3, 4, and 5.

2-6. Aeration. Some waters, in particular well water, contain low levels of dissolved iron (1 to 5 ppm). Although these quantities seem small, they will produce voluminous precipitates when they come in contact with air. If these precipitates are deposited in lines, they will restrict flow. When deposited in heat exchangers, they will restrict heat transfer. Iron in the makeup water can be removed by contact with air to cause it to precipitate, and then by removing the precipitate by filtration.

a. Aerators are usually of the coke tray or

TABLE 2-1
MAKEUP WATER TREATMENT METHODS FOR REMOVING IMPURITIES

Impurity	Method
Hardness (calcium & magnesium)	Lime-soda softening Sodium ion exchange Hydrogen ion exchange Reverse Osmosis Evaporation
Alkalinity (bicarbonate & carbonate)	Lime-soda softening Hydrogen ion exchange(followed by degasifying) Dealkalization (chloride ion exchange)
Suspended solids	Filtration
Dissolved solids	Electrodialysis Evaporation Reverse Osmosis Demineralization (deionization)
Dissolved iron	Aeration (converts to precipitated iron) Sodium ion exchange (iron will foul the resin)
Dissolved gases (carbon dioxide, hydrogen sulfide, methane)	Aeration Degasifying

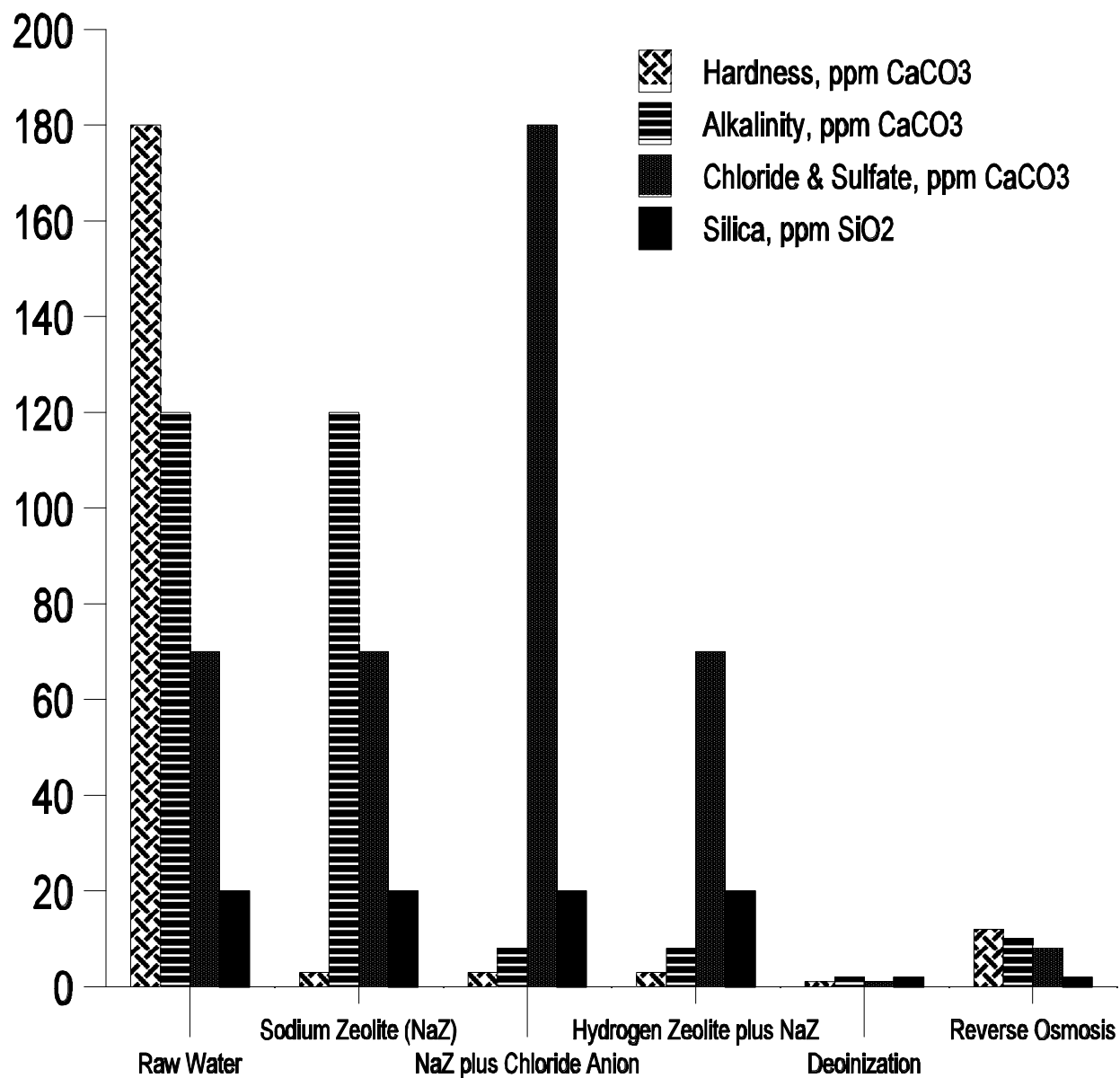
TABLE 2-2
GUIDE FOR SELECTION OF EXTERNAL TREATMENT EQUIPMENT

Makeup Requirements	Steam Pressure	Alkalinity	Turbidity	Recommended External Treatment Equipment
G.P.M.	PSIG	PPM-CaCO ₃	PPM	
All	Less than 15	All	Less than 10	Normally internal treatment only.
			Over 10	Filtration plus internal treatment.
Less than 100	15-200	Less than 75	Less than 10	Sodium zeolite.
			Over 10	Filtration plus sodium zeolite.
		Over 75	Less than 10	1.Sodium zeolite plus hydrogen zeolite (3). 2.Sodium zeolite plus chloride/anion exchange. 3.Hydrogen zeolite (3,5).
			Over 10	1.Filtration plus sodium zeolite plus hydrogen zeolite. 2.Hydrogen zeolite (3,5).
	200-650	Less than 35	Less than 10	Sodium zeolite.
			Over 10	Filtration plus sodium zeolite.
		Over 35	Less than 10	1.Sodium zeolite plus hydrogen zeolite (3). 2.Demineralization.
			Over 10	1.Filtration plus sodium zeolite plus hydrogen zeolite. 2.Filtration plus demineralization.
Over 100	15-200	Less than 75	Less than 10	Sodium zeolite.
			Over 10	1.Filtration plus sodium zeolite. 2.Hot-lime soda.
		Over 75	Less than 10	Sodium zeolite plus hydrogen zeolite (3).
			Over 10	1.Filtration plus sodium zeolite plus hydrogen zeolite (3). 2.Filtration plus demineralization.
	200-650	All	Less than 10	1.Sodium zeolite plus hydrogen zeolite (3). 2.Demineralization.
			Over 10	1.Filtration plus sodium zeolite plus hydrogen zeolite (3). 2.Filtration plus demineralization. 3.Hot-lime hot-sodium zeolite. Above psig.
All	Over 650 (Normally superheated)	All	Less than 10	Demineralization.
			10-400	Filtration plus demineralization.
			Over 400	1.Filtration plus demineralization. 2.Reverse osmosis. 3. Electrodialysis.

NOTES

1. The above chart provides general guidelines only. Final choice of treatment system must be based upon complete raw water analysis, feedwater requirements, and overall economics, including both external and internal treatment and blowdown. External treatment may be desirable to reach recommended levels of TDS without exceeding other parameter limits for causticity, silica, or suspended solids.
2. Separate deaeration is required to all boilers over 15 psig pressure, except where lime-soda softeners are designed to provide adequate deaeration as well as softening.
3. Degasification is required after hydrogen zeolite treatment.
4. Filtration process may require clarification and aeration.
5. Flows less than 10 g.p.m. or very low sulfate plus chloride content.

FIGURE 2-1
EFFECTS OF TREATMENT ON RAW WATER



wood slat design. Coke tray aerators consist of a series of coke-filled trays through which the water percolates. Aeration is supplied during the percolation and the free fall from one tray to the next. Wood slat aerators are similar to small atmospheric cooling towers with the slats staggered to break the free fall of the water and, therefore increase the surface contact with air. Wood slat aerators can also be equipped with a forced draft fan to increase their efficiency.

b. In addition to oxidizing iron, aeration can also remove undesirable dissolved gases such as carbon dioxide, hydrogen sulfide, and methane.

2-7. Filtration:

a. **Standard filtration.** Suspended solids in makeup water can be removed by filtration. These solids may include soluble iron that has been precipitated or residual calcium carbonate particles. These solids must be removed from the feed to ion exchange units or reverse osmosis units.

(1) A typical filter is a bed of sand or anthracite below a set of distribution headers and resting on a support of coarse rock. Below the bed is the collection header through which the clarified water is drawn. Water flows through the filter bed either by gravity or by pressure.

(2) The sand or anthracite does not actually remove the suspended solids. Instead, a layer of suspended solids is laid down on top of the bed and this layer of filter cake does the actual removal.

(3) As the thickness of the filter cake builds up, the water flow decreases. When the flow becomes too small to be useful, the water flow is reversed and the filter is backwashed to remove the buildup of suspended solids. The filter is then returned to service and the cycle repeated.

(4) Filtration rates are typically 3 gallons per minute per square foot (gal/min/ft^2). Backwash rates are 12 to 15 gal/min/ft^2 for sand filters and 8 to 12 gal/min/ft^2 for anthracite filters.

2-8. Lime-soda softening. The lime-soda process is a common method of treating water for potable and industrial uses.

a. Hydrated lime (calcium hydroxide) and soda ash (sodium carbonate), added to the water in a reaction tank, reduces hardness due to calcium and magnesium by precipitation. The solids formed are allowed to settle for removal as a water sludge. The settled water is passed slowly from the tank and filtered for use as makeup.

b. The addition of lime and soda ash at normal temperature is referred to as the cold lime-soda process. There also is a process where the lime and soda ash are reacted with the water at temperatures greater than 212 degrees Fahrenheit ($^{\circ}\text{F}$), called the hot lime-soda process. This is used to remove a greater amount of the hardness in water.

2-9. Ion exchange process - general. Ion exchanger units (water softeners) are used extensively at Army installations. An ion exchanger is a vessel containing several cubic feet (ft^3) of ion exchange material resting upon a gravel support. The direction of water flow is down. Most Army units operate under pressure, but gravity flow units are available. Flow rates vary with the make of equipment but are in the range of 6 to 8 gal/min/ft^2 of ion exchange material surface. The type of ion exchange materials determines the type of system. A backup ion exchange unit and surge tank are typically included in these systems to permit an uninterrupted supply of softened water. The manufacturer's recommendations should be posted near the softening unit. A

typical ion exchanger unit is illustrated in figure 2-2.

2-10. Sodium ion exchange.

The Softening process used on most Army installations is sodium ion exchange. It is preferred to other softening processes because it is compact, easy to operate, relatively inexpensive and produces a suitable makeup water for industrial water systems.

a. Service cycle. This is the normal operating cycle during which hardness is removed from the makeup water flowing through the softener.

(1) The sodium ion exchange process depends upon the exchange of sodium ions from certain minerals and synthetic ion exchange resins for calcium and magnesium ions in the water.



(2) The softening capability of an ion exchange material is usually given in kilograins per cubic foot (kgr/ft³). A kilograin is 1,000 grains and there are 7,000 grains in a pound. The volume of water that a given ion exchange material can soften is determined by the capacity of the material and the hardness in the water.

Example 2-1:

1. The capacity of ion exchange material is 20 kgr/ft³. (That means that one cubic foot of it can remove 20,000 grains of hardness from water.) The water being treated has 257 ppm hardness.
2. How much will it treat? (17.1 ppm equals one grain per gallon)

$$\text{Removal} = \frac{\text{Capacity, kgr/ft}^3}{\text{Hardness, ppm}} \times 1,000 \times 17.1$$

$$= \frac{20,000}{257} \times 17.1 = 1,331 \text{ gal/ft}^3$$

(3) The operator needs to know how much water can be softened before regeneration is necessary. This can be estimated by multiplying the cubic feet of ion exchange material by the number of gallons each cubic foot can soften.

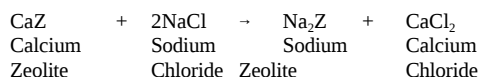
Example 2-2:

1. There are 10 cubic feet of material in the ion exchanger in example 2-1.
2. Since each cubic foot can soften 1,331 gallons, then $10 \times 1,331 = 13,310$ gallons can be softened before the material is completely spent.

(4) In practice, it is necessary to check the outlet water at regular intervals. The hardness of the outlet water should be less than 1 ppm. When the hardness approximates 1 ppm, the material must be regenerated.

b. Regeneration cycle. The regeneration cycle is a number of steps during which the softener is taken off line, backwashed, the resin regenerated and then rinsed.

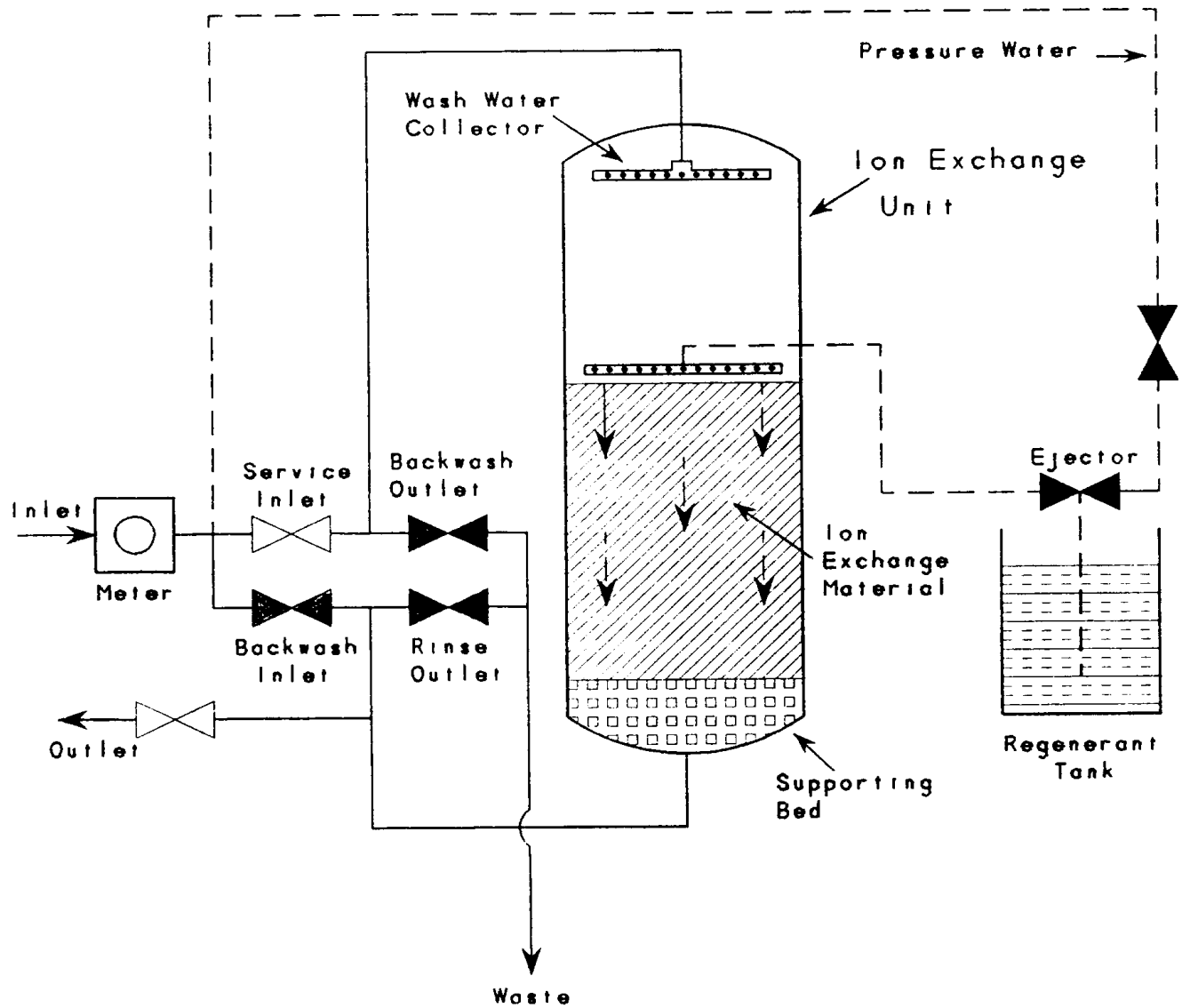
(1) When the spent ion exchange material or calcium zeolite is in contact with a strong salt solution, the material is regenerated by the calcium being exchanged for sodium.



The completeness of regeneration depends upon the strength of the salt solution (brine) used. After the material is regenerated, it can be used again to remove hardness from water.

(2) Before the bed is regenerated, it must be backwashed by flowing water from bottom to top. The flow rate must be

FIGURE 2-2
TYPICAL ION EXCHANGE UNIT



adequate to remove any suspended solids which have been caught on top of the bed. The bed will need to expand by about 50 percent due to the backwash flow rate. The rate should be controlled so that it will not sweep ion exchange material out of the softener into the lines. A backwash rate of 4 to 6 gal/min/ft² of bed surface for about 10 minutes is normal, but the manufacturer's recommendations should be followed.

(3) Next comes the brining. A 10 percent solution of salt brine is slowly added downflow at a rate of 0.5 to 1.0 gal/min/ft³ of bed volume for about 30 minutes. Rock salt is preferred to granulated salt because it is just as effective and less prone to cake. Some installations may start with concentrated brine which must be diluted. The salt required and the capacity regenerated is shown for a typical resin in table 2-3. However, the manufacturer's instructions should be followed, if available.

(4) A slow rinse follows the brining. One to three bed volumes of freshwater are used to remove the brine from the bed. This is equal to 7.5 to 22.5 gal/ft³ of bed volume.

(5) Finally, a fast rinse is used to remove any traces of the regenerant. This is done at a rate of 1.5 to 2.0 gal/min/ft³ of bed volume until the discharge is free of hardness; 35 to 100 gal/ft³ of bed volume is required.

(6) The unit is now ready for another service cycle.

c. Testing and record keeping.

Feedwater should be tested for hardness weekly and the outlet water should be tested for hardness every shift (3 times a day) for systems that require frequent regeneration. Accurate records should be kept of these tests along with the gallons of water treated during each service cycle, and the salt used during each regeneration cycle.

d. Operating problems. There are several

common problems sometimes encountered with softener operation.

(1) There will be a normal decrease in capacity of about 5 percent per year. Any decrease greater than this should be investigated. Incomplete softening is another indication of trouble.

(2) A common cause of capacity loss is iron fouling. Soluble iron will exchange for sodium during the service cycle, but sodium will not exchange for iron during the regeneration cycle. There is a simple test to determine iron fouling. A pinch of iron-fouled ion exchange material added to 10 percent hydrochloric acid in a test tube will cause the hydrochloric acid to turn yellow.

(a) An iron-fouled material may be treated with dilute hydrochloric acid or sodium hydrosulfide. This procedure is followed by a standard brine regeneration.

(b) Check the manufacturer's recommendations before using the above regeneration procedure. Do not attempt with a galvanized or unlined steel tank. The tank must be all reinforced plastic or rubber, or plastic lined with no breaks in the lining.

(3) Improper backwash is the other common cause of trouble. Too high a backwash rate can wash the ion exchange material out of the unit. The bed depth can be checked by probing with a steel rod until the underdrain material can be felt. Normal bed depth is usually 30 to 36 inches. The bed volume in cubic feet (ft³) can be calculated by the following formula:

$$\text{Volume, ft}^3 = (\text{Radius, ft})^2 \times (\text{Depth, ft}) \times 3.14$$

(a) Check the bed depth at 10 points and use the average value. If there is much difference in the thickness of different points (say as much as 15 percent), channeling can be occurring. This can be caused by too low a

TABLE 2-3
SALT REQUIRED FOR REGENERATION OF A COMMONLY USED
CATION RESIN

Pounds Salt Used per Cubic Foot of Ion Exchange Material	Capacity of Ion Exchange Material, Kilograins Hardness per Cubic Foot
5.0	19
7.5	24
10.0	27
15.0*	32*

* Practical upper limit for exchange capacity. This upper limit and the actual dose per capacity relationship may vary with the resin; the manufacturer's instructions should be followed.

backwash rate.

(b) If the calculated bed volume is less than the volume given by the manufacturer, material has been lost. The lost material should be replaced, and the backwash rate carefully watched to ensure material is not being washed out.

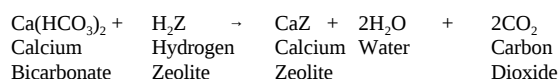
(c) If the cause of malfunction cannot be determined, consult the manufacturer's service representative.

(4) The resin in the ion exchanger should be replaced when the resin capacity or softening efficiency has decreased by 25 percent and cannot be almost completely restored by cleaning and special procedures recommended by the manufacturer. Based on a normal decrease of one to five percent per year, the typical ion exchange resin should last from five to twenty-five years.

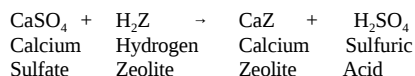
2-11. Hydrogen ion exchange. The hydrogen ion exchange process is essentially the same as the sodium ion exchange process except the regenerant is an acid (sulfuric or hydrochloric) rather than salt. The hydrogen

ion exchange process will reduce the total dissolved solids and the alkalinity of the treated water. These impurities may need to be reduced further for boiler makeup water.

a. The hydrogen ion process is based on the ability of certain minerals and synthetic resins to exchange hydrogen with calcium, magnesium, and sodium.



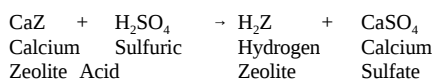
The carbon dioxide and water products do not contribute to the total dissolved solids. The alkalinity from the calcium bicarbonate has been destroyed. The reaction with calcium sulfate is:



Sulfuric acid will further destroy alkalinity by reacting with sodium bicarbonate.

b. The spent ion exchange material is regenerated by contact with dilute sulfuric acid. Hydrochloric acid may also be used, but

no other acid.



c. The hydrogen ion exchanger is much the same as the sodium ion exchanger, except that the tank is made of or lined with acid resistant material.

d. The regeneration cycle is also much the same, except that sulfuric acid is used instead of salt. Before using sulfuric acid, be sure to review available information on safety and first aid. Handling and safety instructions should be posted near sulfuric acid equipment.

e. Troubleshooting is also much the same, although iron fouling does not occur in hydrogen ion exchangers.

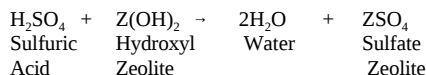
f. The outlet water is acidic and cannot be directly used as boiler makeup. The water can be mixed with the outlet of a sodium ion exchanger. The acid in the hydrogen ion exchange water will be neutralized and at the same time a portion of the alkalinity in the sodium ion exchange water is destroyed. The proportion of the water mix depends upon the analysis of the water being treated, but typically it is approximately half and half.

g. Carbon dioxide is produced in the hydrogen ion exchange process and is also produced when the water from hydrogen and sodium ion exchange is mixed. It can be removed from the water in a degasifier or a deaerator.

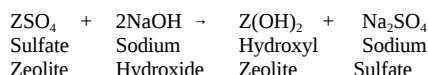
2-12. Anion exchange. Sodium and hydrogen ion exchangers remove the positively charged ions (cation exchange). Ion exchange materials also have been developed which remove negatively charged ions (anion exchange). Demineralization uses both cation and anion exchange to remove all ions from the water. A typical deionization process is illustrated in figure 2-3.

a. The cation exchange is described in

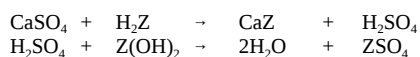
paragraphs 2-10 and 2-11. The anion exchange reactions involve:



b. The spent ion exchange material (ZSO₄) is regenerated with sodium hydroxide (caustic).



c. When the anion exchange is combined with hydrogen exchange, the resulting water will contain no minerals. It has become deionized (also referred to as demineralized).

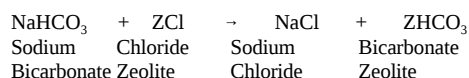


d. The two reactions can take place in separate vessels (a "two bed" deionizer), or the two ion exchange materials can be combined in a single vessel (a "mixed bed" deionizer).

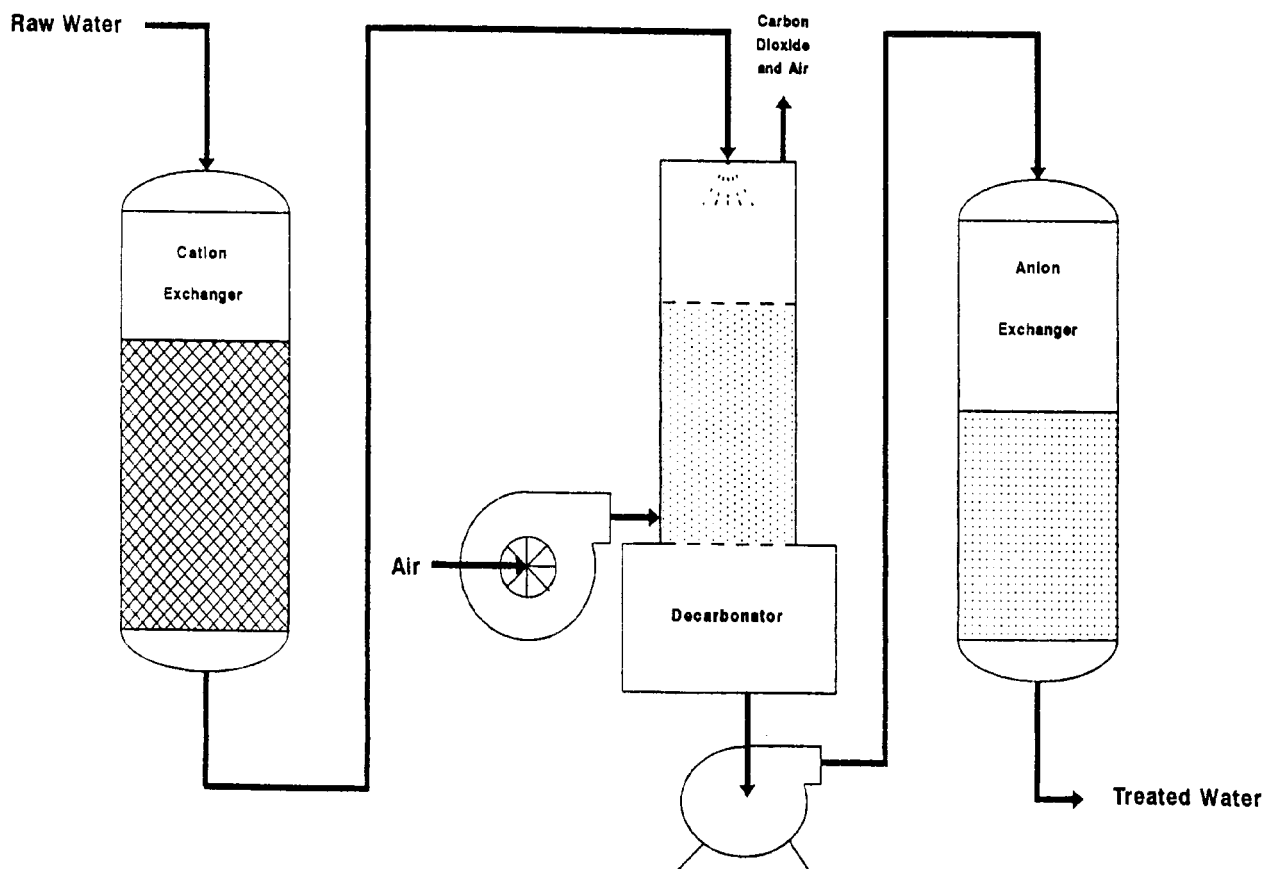
e. The deionization process has limited application at an Army installation. It is required mainly for high pressure boilers.

2-13. Dealkalization:

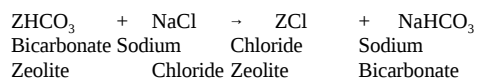
a. Anion dealkalization. It may be necessary to treat water with a low hardness and high alkalinity to reduce the alkalinity before it is used in boilers. There is an anion exchange process called anion dealkalization which will remove alkalinity and also remove sulfates and nitrates. In almost all cases, the anion dealkalizer should follow a softener. Bicarbonate is exchanged for chloride as illustrated by the following reaction:



**FIGURE 2-3
DEIONIZATION PROCESS**



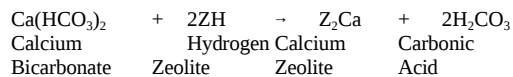
(1) The system is regenerated with sodium chloride (salt) as shown below:



(2) The equipment and operation of such a system is much the same as for a sodium ion exchange material system described in paragraph 2-10. This process is illustrated in figure 2-4.

b. Split stream dealkalization. In split

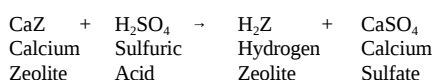
stream dealkalization, the water is split into two parallel streams, one passing through a strong acid cation exchange (dealkalizer) and the other through a sodium zeolite softener. Blending the two product streams produces a soft water low in alkalinity. The alkalinity reduction is described by the following equation:



The carbonic acid dissociates into CO_2 and H_2O . The CO_2 must be released into the atmosphere.

(1) The cation exchange resin also reacts with sodium, calcium and magnesium chlorides, sulfates and nitrates, and other salts to produce free mineral acids (FMA). pH adjustment is necessary to balance alkalinity with acidity (FMA) to form neutral water.

(2) The system is regenerated with sulfuric acid as shown below:



(3) The exchanger tank is made of or lined with an acid resistant material.

(4) Since blending also produces CO_2 , a decarbonator is normally used to reduce CO_2 concentration to 5-10 ppm or less. A typical split stream process is shown in figure 2-5.

2-14. Decarbonation. Carbon dioxide is produced during hydrogen exchange and also when the waters from hydrogen ion exchange and sodium ion exchange are mixed. Carbon dioxide dissolved in water can cause corrosion in water lines, pump impellers, and vessels. As discussed in chapter 3, carbon dioxide must be kept as low as possible in boiler water and steam condensate lines.

a. Free carbon dioxide is commonly removed in a degasifier, which is a wooden vessel through which the water trickles over slats or packing. Air is blown into the bottom of the vessel and strips out the carbon dioxide. In steam and high temperature water systems, removal of the CO_2 is achieved in the deaerator rather than with a separate degasifier unit. This changes a portion of the bicarbonate alkalinity in the makeup water to carbonate alkalinity and increases the pH.

b. By analyzing for the hydrogen ion concentration (pH) and total alkalinity (M) of a water, the free carbon dioxide content can be

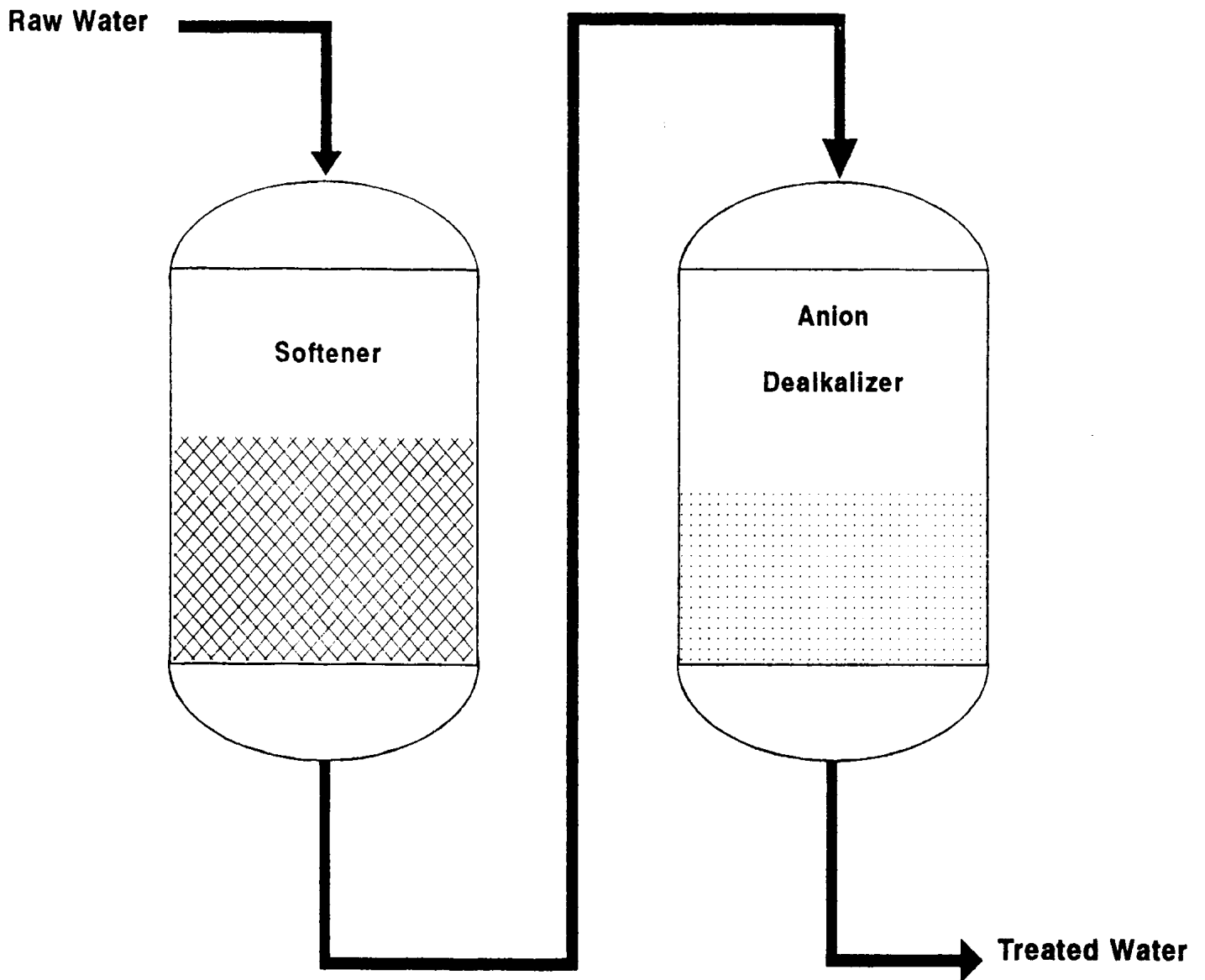
estimated from table 2-4.

2-15. Evaporation. In this process, water is heated to produce relatively pure vapor, which is then condensed and used for boiler feed. Evaporators are of several different types, the simplest being a tank of water through which steam coils are passed to heat the water to the boiling point. To increase efficiency, the vapor from the first tank may pass through coils in a second tank of water to produce additional heating. Another type of evaporator operates under a partial vacuum causing a lowering of the boiling point of water and evaporation at lower temperatures. Evaporators may be economical where steam as a source of heat is readily available. They also have an advantage over deionization when the dissolved solids in the raw water are very high.

2-16. Reverse osmosis. If salt water and distilled water are separated by a semi-permeable membrane, the distilled water will tend to diffuse through the membrane to the salt water. This flow is in one direction—from the more dilute to the more concentrated. The distilled water will continue to permeate through the membrane until equilibrium is established and both waters will be salty. The direction of flow is determined by the osmotic pressure of the system. If a pressure exceeding the osmotic pressure is exerted on the salt water side of the membrane, the flow will be reversed and distilled water can be produced from salt water. This process is illustrated in figure 2-6.

a. Pretreatment. Material that can potentially foul the membrane will interfere with the process and must be removed by pretreatment. Foulants include suspended and colloidal solids, iron, metal oxides, scale, and biological materials.

FIGURE 2-4
ANION DEALKALIZATION PROCESS



**FIGURE 2-5
SPLIT STREAM DEALKALIZER**

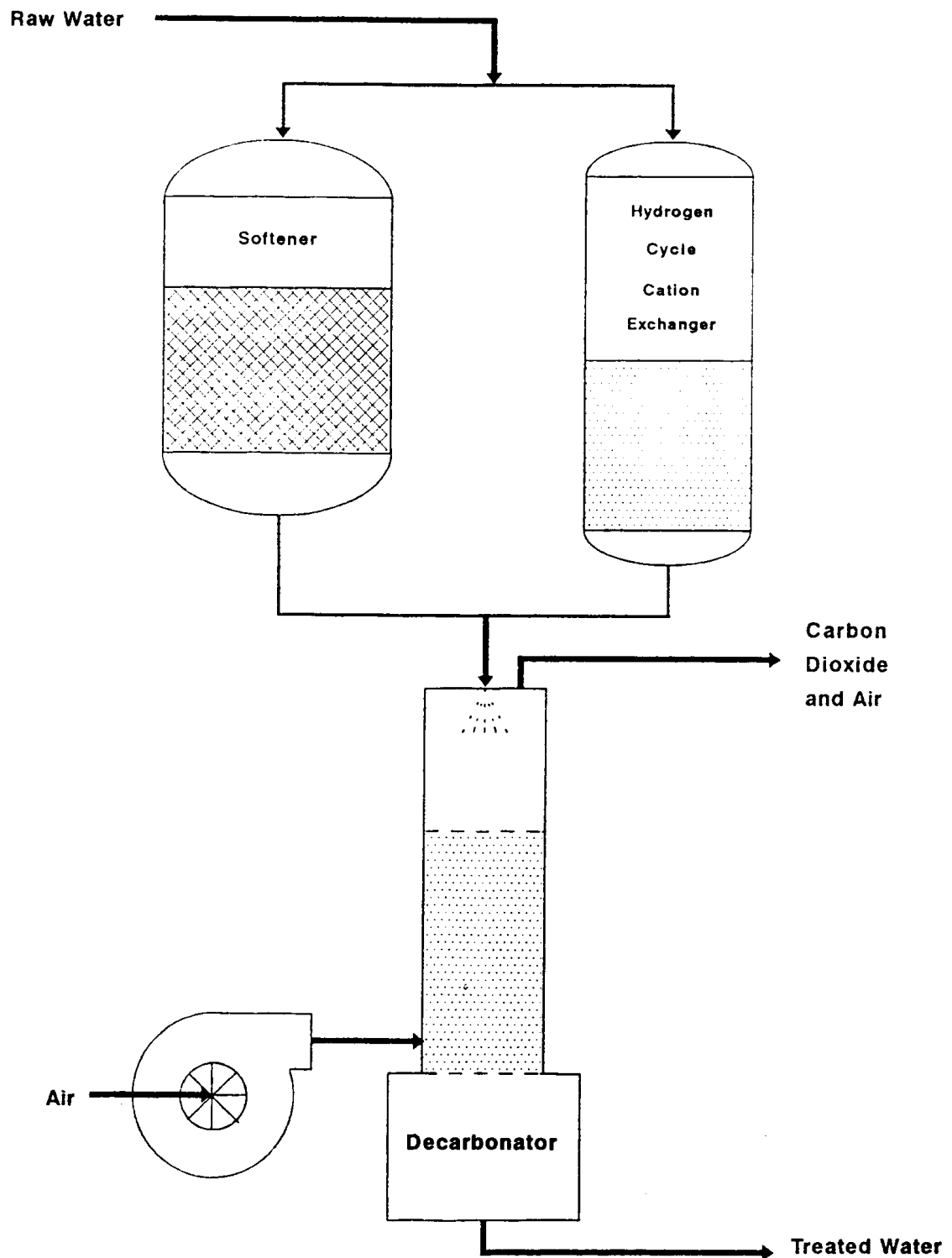


TABLE 2-4
CARBON DIOXIDE CONTENT OF WATER VERSUS pH.
(ppm CO₂ as CO₂ PER ppm M ALKALINITY as CaCO₃)

pH	CO ₂	pH	CO ₂	pH	CO ₂
5.4	4.40M	6.6	0.45M	7.3	0.099M
6.0	1.94M	6.7	0.38M	7.4	0.079M
6.1	1.58M	6.8	0.31M	7.5	0.062M
6.2	1.23M	6.9	0.24M	7.6	0.050M
6.3	0.92M	7.0	0.19M	7.7	0.040M
6.4	0.75M	7.1	0.15M	7.8	0.033M
6.5	0.62M	7.2	0.12M	7.9	0.026M

NOTE: At pH levels 8.0 or higher, the free CO₂ content is negligible.

i

Example 2-3:

1. Total alkalinity (M) of an inlet water to a degasifier is 100 ppm and the pH is 6.8. CO₂ content = Value x M = 0.31 x 100 = 31 ppm
2. The outlet pH is 7.9, so the CO₂ content will be: (let M = 80, since some alkalinity was removed as CO₂) CO₂ content = 0.026 x 80 = 2.1 ppm
3. The carbon dioxide removal is: 31 - 2.1 = 28.9 ppm. The efficiency of CO₂ removal in a deaerator is related to its operating conditions, shown in table 3-3.

(1) Suspended solids can be removed by filtration, usually a sand filter followed by a cartridge filter. The addition of filter aids may be necessary. In certain instances, coagulation and clarification may be required before the

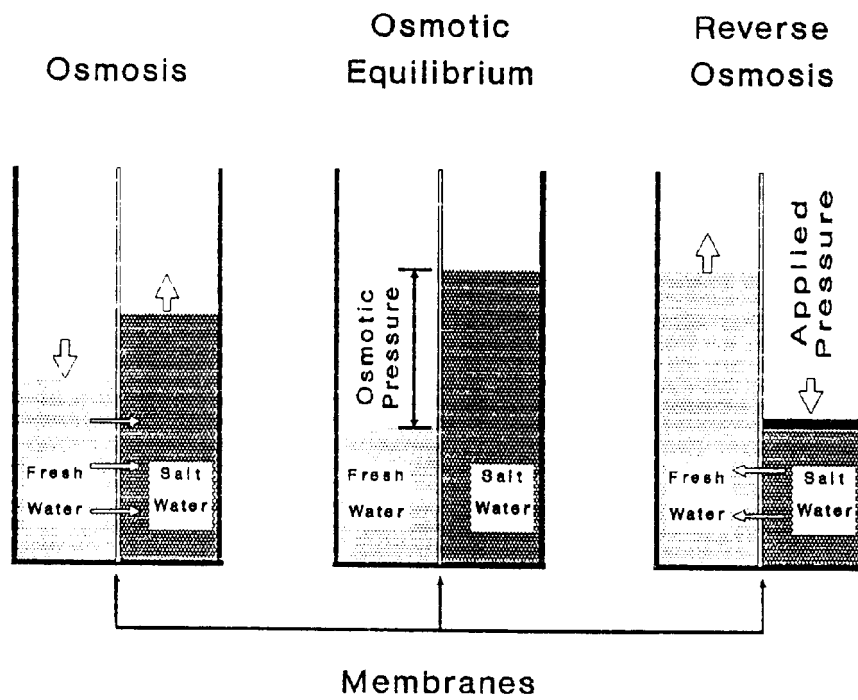
filtration step.

(2) Iron oxides are the result of the oxidation of dissolved ferrous salts or they could come from corrosion of the equipment. The first can be controlled by aerating the water ahead of the filter; the second by threshold treatment with sodium hexametaphosphate.

(3) Scale-forming salts are concentrated in reverse osmosis just as they are in an evaporative process. To keep scale forming salts in solution adjust the pH between 5.0 and 6.5 and add a solubilizer such as sodium hexametaphosphate or any of the phosphonates (HEDP or AMP). The solubility of scale-forming salts controls the rejection rate, i.e., blowdown.

(4) Biological fouling can best be controlled by chlorination. Since chlorine can damage the membrane, the water must be

FIGURE 2-6
REVERSE OSMOSIS PROCESS.



dechlorinated with a reducing agent or with activated carbon before the reverse osmosis feedpoint.

b. Membrane configuration. There are three basic membrane configurations; tubular, spiral wound or scroll, and hollow fine fiber.

(1) The tubular configuration is simply a porous tube supporting a membrane. Feedwater is introduced into the tube, product water permeates the membrane and reject water exits from the far end of the tube.

(2) The spiral configuration is a sheet membrane supported on each side by a porous material which provides flow distribution and is rolled into a spiral or "jelly roll" configuration.

(3) The hollow fiber configuration consists of small (85 mm diameter) tubes whose outside is semi-permeable. A large number of these tubes are placed in a shell, similar to a heat exchanger. Water, under pressure, on the outside permeates through tubes and is collected from the tube interiors.

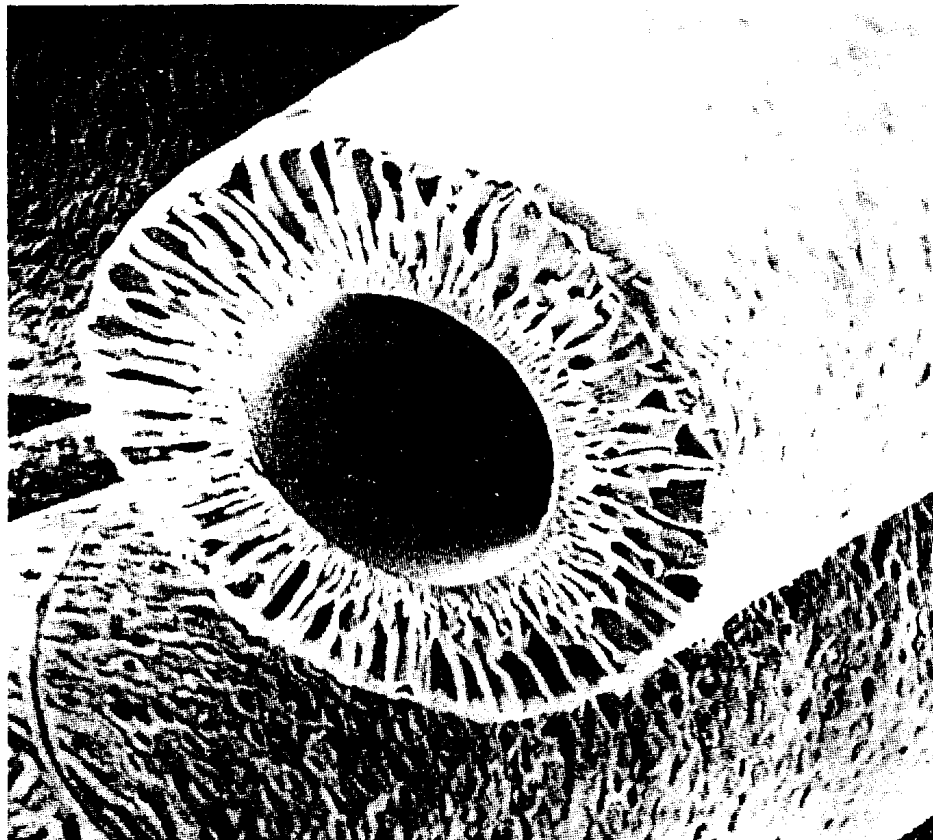
c. Reverse osmosis technology is particularly useful when feedwater is high in dissolved solids or when the source is brackish water or sea water. When used ahead of a deionizer, the chemical requirements for the deionizers are reduced and resin life extended.

2-17. Ultrafiltration. Ultrafiltration is also a pressurized membrane process in which particulate, colloidal and high molecular weight material is filtered from a fluid. It is similar to reverse osmosis in that a semipermeable membrane is used to remove the filterable solids, except that it is more porous. Figure 2-7 is a photomicrograph of a hollow fiber membrane used in ultrafiltration. The feedwater flows through the inside of the fibers, permeates through the membrane and is removed as product from the shell side. The filtered solids are continuously removed from the other end of the fiber in a reject stream that

is typically 5 to 10 percent of the feed.

2-18. Electrodialysis. This process will remove minerals from water by attracting the ions in water through membranes using oppositely charged electrodes. When the water is high in dissolved minerals as in brackish water that contains more than 2,500 ppm total dissolved solids, it may be more economical than the ion exchange methods. Under some circumstances, it may remove enough minerals to make sea water usable in industrial water systems.

FIGURE 2-7
PHOTOMICROGRAPH OF HOLLOW FIBER MEMBRANE



Chapter 3

Steam Boiler Systems

Section I General Information

3-1. Boiler system defined. A boiler is an enclosed vessel with an external heat source that produces steam or hot water. Steam boilers are discussed in this chapter (hot water boilers are addressed in chapter 5). Two types of boilers are commonly used on Army installations. There are the fire tube boilers, where the hot combustion gas passes through tubes with the water surrounding the tubes. This type of boiler is common for package boilers. There also are water tube boilers, where the water is converted to steam within the tubes and the hot combustion gases pass on the outside. Most Army installations will have a central boiler plant containing several steam and hot water boilers in addition to boilers located in and serving individual buildings. Central boiler plants should be equipped with external treatment systems to reduce the sludge and scale potential of the boiler water, and with deaerators capable of delivering feedwater with low oxygen content at all operating loads. Where external treatment is not available, special precautions must be taken to blowdown the boiler sufficiently to keep suspended solids at a low level, prevent sludge from forming on boiler surfaces and keep silica concentrations low enough to prevent deposits.

a. Boiler classification. For the purpose of water treatment, the categories of high pressure (above 15 psig) and low pressure (15 psig and below) are sufficient. Boiler capacity rating is given as horsepower, pounds of steam per hour, or British Thermal Units (BTU) per

hour. One boiler horsepower reflects the energy to convert 34.5 pounds of water to steam from (and at) 212°F at sea level, which is equivalent to 33,479 BTU per hour. The actual steam produced, however, will vary depending on the boiler operating pressure and altitude with respect to sea level.

b. Treatment program for high pressure steam boilers. Water for high-pressure steam boilers is generally treated for scale control, sludge conditioning, corrosion (oxygen and carbon dioxide), and foaming (steam drum).

c. Treatment program for low pressure steam boilers. Low pressure boilers are usually installed for single unit heating or to provide process steam for industrial purposes. The installations are comparatively simple and may require very little makeup due to small steam and condensate losses. These boilers may need only corrosion control. However, if significant makeup is required these systems will need a complete water treatment program.

3-2. Components of a steam boiler. The design of a steam boiler is based on a variety of engineering and service factors. The typical components that may be included at a specific unit are illustrated in figure 3-1 and briefly described below.

a. External water treatment. Makeup water for a boiler represents the added amount from a completely external source. The treatment of makeup water is discussed in chapter 2. A storage tank may be provided for the treated makeup as part of the boiler system. The makeup is combined with the condensed steam returned from the

distribution system (called the condensate return) to become the boiler feedwater. The feedwater typically will be deaerated, with preheating sometimes used before the deaerator. The feedwater may be contacted with steam in the deaerator to strip out noncondensable gases, followed by a storage section. Oxygen scavengers should be added before the storage section. An intermittent discharge from the lowest point of the storage section should be provided to remove any accumulated solids. (See paragraph 3-13 for more information on deaerators.)

b. Inside the steam boiler (circulation section). The circulation section consists of tubes and an external boiler shell. The fire tube boiler passes the hot combustion gases through the tubes, which are surrounded by the water. The water tube boiler passes the hot combustion gases around the tubes in which the water is converted to steam. The circulation of water, in the water tube boiler may be natural, or the water may be pumped through the heating circuit (forced circulation). Usually a mud drum is provided at the lowest point in the circulation section in order to remove any sludge accumulations. **c** .

Steam drum. The mixture of steam and water is separated in the steam drum. This may include mechanical devices to assist in removing entrained water from the steam. Steam from the drum may be heated further in some boilers to generate superheated steam. Usually the feedwater is added to the steam drum. Chemical feed for internal boiler water treatment also may be added to the steam drum. The continuous blowdown is the discharge of the boiler water to maintain the required operating condition in the boiler. In some cases the blowdown will be discharged to a flash drum where lower pressure steam is recovered (possibly for use in the deaerator).

Continuous blowdown water may also be used to preheat the makeup water by means of a heat exchanger.

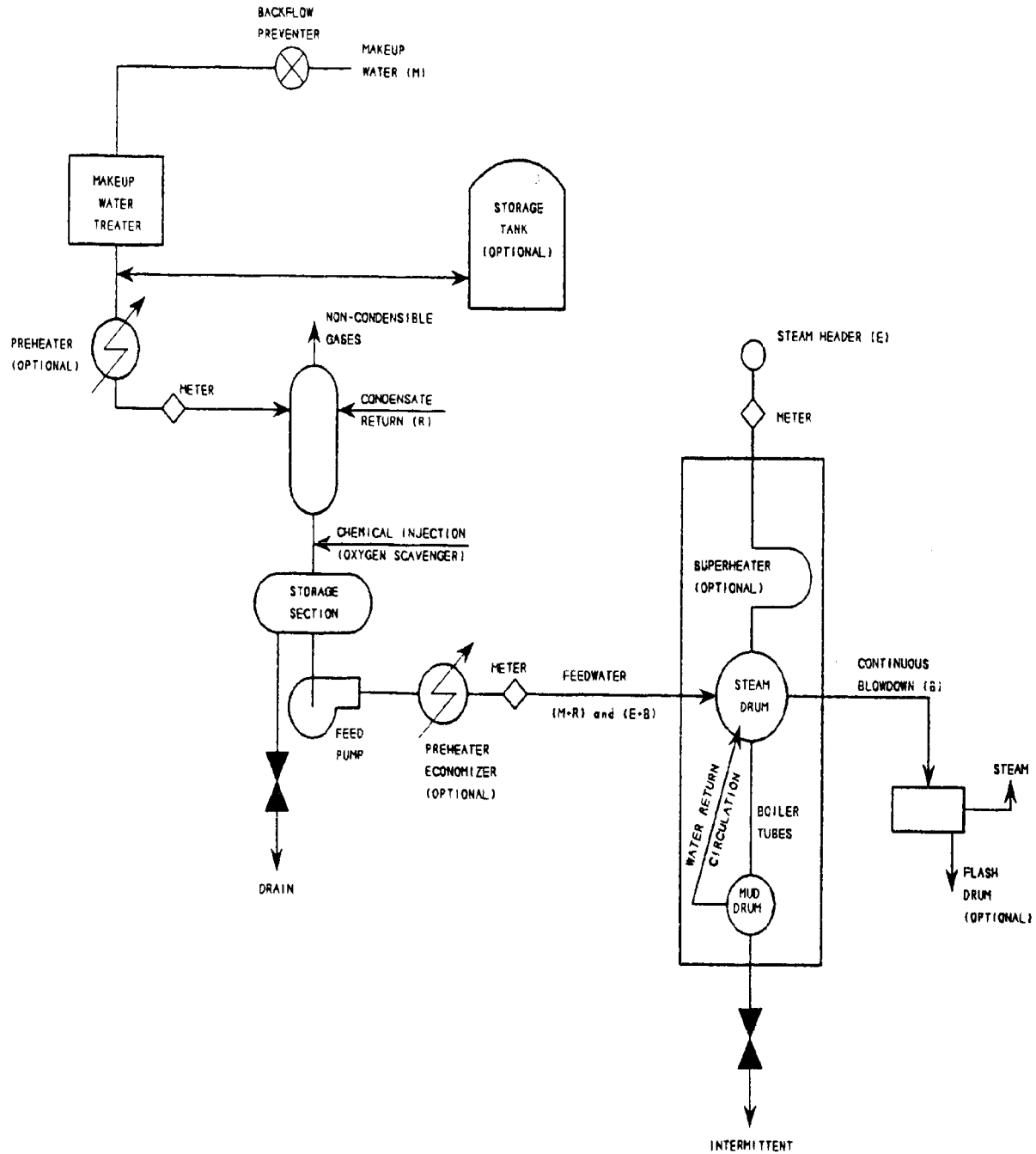
d. Steam header. The steam generated by the boiler is discharged to a header. This feeds the steam distribution system. The steam is consumed by process equipment; lost through leaks; lost from valves, fittings, or steam traps; or condensed for return to the deaerator.

e. Metering. To determine the proper water treatment of a steam boiler requires information on the quantity of steam, feedwater, blowdown, makeup and condensate in the system. As a minimum, flow meters are required in the makeup water line, the feedwater line and in the steam header. Condensate and blowdown values can be calculated as described in paragraph 3-4.

3-3. Total dissolved solids (TDS) and alkalinity:

a. TDS in a boiler. TDS in a boiler is one of the parameters used to control the water treatment program. Dissolved solids are continually added to the boiler with the makeup. Also, chemicals added to treat the boiler water add to the TDS levels. These solids do not evaporate with the steam; as a result, the water in the boiler becomes more concentrated in TDS as the steam is generated. The level to which the TDS will concentrate is determined by the amount of these solids removed in the blowdown. Control of TDS level is critical in boiler operation. Higher TDS levels can result in higher boiler efficiency with corresponding savings of energy, treatment chemicals and water, but TDS levels that are too high will interfere with boiler operation. Conversely, carrying lower TDS levels than the optimum will result in the use of more makeup water, more chemicals to

**FIGURE 3-1
SIMPLE STEAM BOILER**



treat the additional water, and loss of energy required to heat the additional water. In certain cases the TDS may be limited by the water quality, such as makeup water with high silica content. Total dissolved solids may be controlled by the continuous blowdown, which typically is removed from the steam drum, or by manual blowdown. Guidelines for maximum TDS levels in boilers operating at various steam pressures are shown in table 3-1. It is advisable to keep the TDS in the boiler water just below the maximum allowed in order to save fuel, water and treatment chemicals. Because of the time it takes to determine the TDS by evaporation, the TDS is calculated from the water's conductivity. The relationship between TDS and conductivity varies depending on the water quality. For boilers that use synthetic polymers as a sludge dispersant, a factor of 0.7 times the neutralized conductivity (in μmhos) may be used. For boilers that use Quebracho tannin, the factor will vary from 0.7 to 1.0 depending on the amount of tannin in the water.

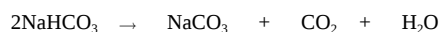
b. Alkalinity in a boiler. Alkalinity in boiler water essentially results from the presence of hydroxyl and carbonate ions. The relationship of the various forms of alkalinity is covered in paragraph 6-14.

(1) Hydroxyl alkalinity (causticity) in boiler water is necessary to protect the boiler against corrosion. Proper dosage of sodium hydroxide is covered in paragraph 3-19. Too high a causticity causes other operating problems, such as foaming. Excessively high causticity levels can result in a type of caustic attack of the boiler called "embrittlement".

(2) With the phosphate control program phosphate in the boiler water combines with calcium to precipitate calcium phosphate, removing calcium from the boiler water. Calcium phosphate, under proper

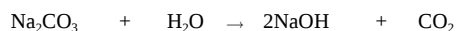
conditions, forms a finely divided, fluid sludge, which can be carried by the boiler circulation and can, in general, be readily removed by blowdown. Because calcium phosphate is the least soluble of the calcium salts in boiler water, phosphate control prevents formation of other calcium scales, such as calcium carbonate, calcium sulfate, or calcium silicate. The pH in the boiler must be kept above 11.0 to prevent possible formation of a sticky sludge that adheres to the boiler surfaces.

(3) Causticity in boiler water is the result of the addition of sodium hydroxide (NaOH) or the breakdown of bicarbonate alkalinity in the feedwater under the influence of heat to produce sodium carbonate, carbon dioxide and water:



Sodium Bicarbonate	Sodium Carbonate	Carbon Dioxide	Water
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Carbonates react with the hot boiler water, although not as fast or as complete as the bicarbonate reaction, to form carbon dioxide and sodium hydroxide which increases the causticity in the boiler and the acidity of the steam.



Sodium Carbonate	Water	Sodium Hydroxide	Carbon Dioxide
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3-4. Boiler blowdown calculations. TDS in the boiler is controlled by the rate of blowdown from a boiler.

a. The water added to the boiler must equal water loss from the boiler.

where:

F	= E + B
F	= feedwater, pounds / hour (lb/hr)
E	= steam generated, lb/hr
B	= blowdown, lb/hr

TABLE 3-1
TOTAL DISSOLVED SOLIDS (TDS) AND CONDUCTIVITY LIMITS FOR
STEAM BOILERS

Pressure Range (psig)	Maximum TDS (ppm)	Maximum Conductivity (1) (µmho)
0-15	3,500	5,000
16-149	3,500	5,000
150-299	3,500	5,000
300-449	3,000	4,300
450-599	2,500	3,500
600-749	2,000	2,800
750	2,000	2,800

NOTE: (1) Conductivity taken after sample has been neutralized.

b. The blowdown can be related to the feedwater using the cycles of concentration (COC):

where: $C = F \div B$, or $F = B \times C$
 C = COC, no units
 F = feedwater, lb/hr
 B = blowdown, lb/hr

It is common to express blowdown as a percent:

$$\%B = \frac{100}{C}$$

c. The relationship between feedwater, blowdown, steam generation, and COC is represented as (terms are as defined above):

- (1) $F = B \times C$ from b. above
- (2) $F = E + B$ from a. above
- (3) $B \times C = E + B$ replacing F in equation 2) with equation (1)
- (4) $B \times C - B = E$ rearranging equation (3)
- (5) $B \times (C-1) = E$ rearranging equation (4)
- (6) $B = E \div (C-1)$ rearranging equation (5)

d. Blowdown is rarely metered, but it can be calculated if any two of the feedwater,

COC, or steam generation quantities are known. Steam is usually metered. The COC can be calculated by measuring the conductivity or TDS in the boiler water and in the feedwater (note that the blowdown TDS is the same as the boiler TDS):

$$C = \frac{B_{TDS}}{F_{TDS}} \quad \text{or} \quad \frac{B_{\mu mho}}{F_{\mu mho}}$$

where: C = COC, no unit
 B_{TDS} = blowdown TDS, ppm
 F_{TDS} = feedwater TDS, ppm
 $B_{\mu mho}$ = blowdown conductivity, micromhos
 $F_{\mu mho}$ = feedwater conductivity, micromhos

3-5. Determining feedwater requirements.

The blowdown calculations in paragraph 3-4 can be used to determine feedwater requirements. Note that feedwater means the

water that is fed to the boiler from the deaerator and includes makeup plus condensate return.

Example 3-1:

1. A 250 psig boiler operates at a conductivity level of 5,000 μmho (see table 3-1 for the maximum allowable level). The boiler feedwater has a conductivity of 250 μmho . The COC is calculated as follows:

$$C = \frac{B_{\mu\text{mho}}}{F_{\mu\text{mho}}} \text{ or } \frac{5,000}{250} = 20$$

2. The percent blowdown is:

$$\%B = \frac{100}{C} = \frac{100}{20} = 5\%$$

3. If the boiler is producing 40,000 pounds of steam per hour, the blowdown must be:

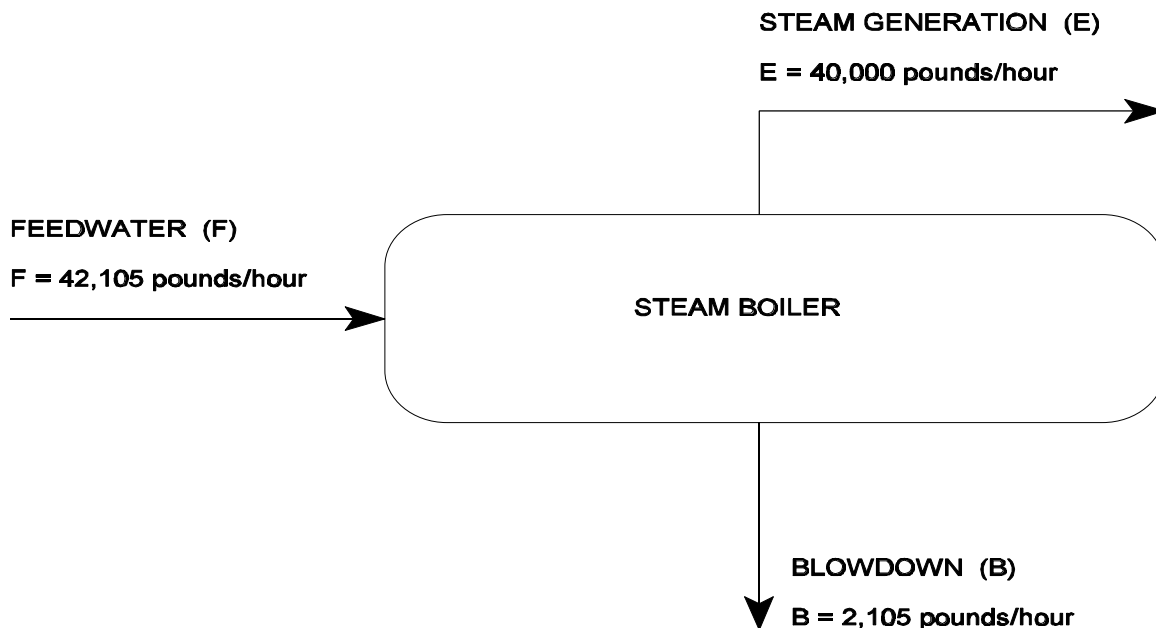
$$B = E \div (C - 1) = 40,000 \div (20 - 1) = 2,105 \text{ lb/hr}$$

4. The feedwater is calculated to be:

$$F = E + B = 40,000 + 2,105 = 42,105 \text{ lb/hr}$$

This is equivalent to 5,054 gal/hr (8.33 lbs/gal). This example is illustrated in figure 3-2.

**FIGURE 3-2
EXAMPLE OF BOILER FEEDWATER, STEAM GENERATION
AND BLOWDOWN RELATIONSHIPS**



3-6. Determining makeup requirements.

Makeup is the water from the external water treatment system provided to the deaerator. The amount or percentage makeup required in a boiler is affected by blowdown, steam leaks, consumption of steam in process equipment and condensate leaks. In a tight system where steam is not used in process equipment, about 5 to 10 percent makeup would be desirable. However, some poorly controlled or maintained systems can approach 100 percent makeup. The criteria for treating makeup is covered in paragraph 2-4b.

a. Makeup is the difference between the condensate return and the feedwater.

$$\begin{aligned} \text{where: } M &= F - R \\ M &= \text{makeup, lb/hr} \\ F &= \text{feedwater, lb/hr} \\ R &= \text{condensate return, lb/hr} \end{aligned}$$

b. The condensate will not contain any appreciable level of dissolved solids (or conductivity) unless there is a source of contamination within the system. This allows the determination of percent makeup using the equation:

$$\%M = \frac{F_{\mu\text{mho}}}{M_{\mu\text{mho}}} \times 100$$

where: $\%M$ = percent makeup
 $F_{\mu\text{mho}}$ = Feedwater conductivity, micromhos
 $M_{\mu\text{mho}}$ = makeup conductivity, micromhos

Example 3-2:

1. Makeup conductivity is 900 μmho for the boiler in example 3-1. The percent makeup is calculated:

$$\%M = \frac{F_{\mu\text{mho}}}{M_{\mu\text{mho}}} \times 100 = \frac{275}{900} \times 100 = 30\%$$

2. This means that the makeup is 30 percent of the feedwater. The condensate return percent is calculated:

$$\%R = 100 - \%M = 100 - 30 = 70\%$$

3. The quantity of makeup is calculated:

$$M = \frac{\%M}{100} \times F = \frac{30}{100} \times 42,105 = 12,632 \text{ lb/hr}$$

4. The condensate return quantity is calculated:

$$R = F - M = 42,105 - 12,632 = 29,473 \text{ lb/hr}$$

c. The difference between steam produced and the condensate returned represents both steam and condensate losses in the system. These losses may include steam leaks, consumption of steam by the process equipment and condensate leaks. The total losses can be calculated as follows:

$$\begin{aligned} L &= E - R \\ \text{where: } L &= \text{total steam and condensate losses, lb/hr} \\ E &= \text{steam generated, lb/hr} \\ R &= \text{condensate return, lb/hr} \end{aligned}$$

Example 3-3:

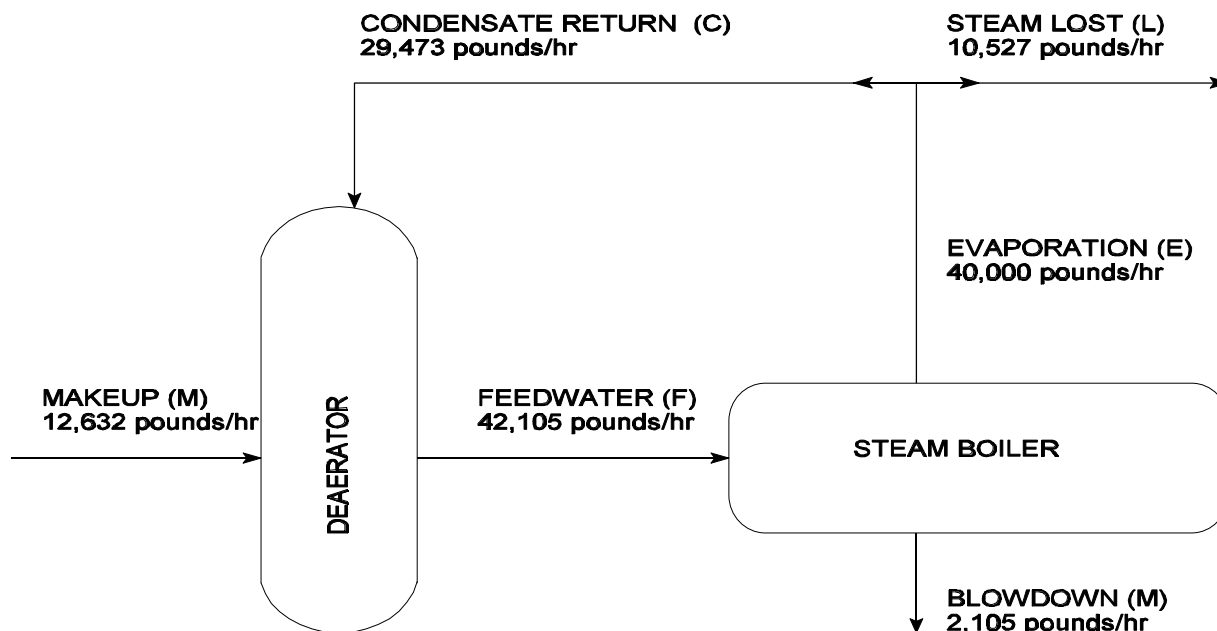
1. The steam losses for the boiler described in examples 3-1 and 3-2 can be calculated:

$$L = E - R = 40,000 - 29,473 = 10,527 \text{ lb/hr}$$

2. This relationship and the information from the previous examples are presented in figure 3-3.

d. Monitoring the system for conductivities and steam generated, and performing these calculations on a regular interval will give a basis for evaluating boiler system performance. An increase in steam loss may indicate the development of a new leak or an increase in existing leaks. On the other hand, these calculations can provide a good basis for estimating steam savings from maintenance efforts.

**FIGURE 3-3
EXAMPLE OF BOILER CALCULATIONS**



3-7. Determining chemical treatment required. Chemical treatment programs involve selecting the type of chemical to be used and establishing a treatment level. These factors are discussed in sections II and III. Blowdown calculations can be used to determine the amount of chemical that needs to be added to meet the treatment objectives.

Example 3-4:

1. The boiler in examples 3-1, 3-2, and 3-3 is to be operated with a phosphate level of 60 ppm (as PO_4) in the boiler water. The blowdown has been determined to be 2,105 pounds per hour. The required phosphate addition of a daily basis must equal the phosphate that is discharged with the blowdown plus that used up in precipitating calcium phosphate.

Phosphates required to replace that lost in blowdown is calculated as follows: (complete chemical requirement calculations are covered in section III.)

$$\begin{aligned}
 \text{Phosphate Loss} &= B \times \text{Level} \\
 &= \frac{(2,105 \text{ lb/hr}) \times (24 \text{ hr/day}) \times (60 \text{ ppm})}{1,000,000} \\
 &= 3.03 \text{ lb/day phosphate}
 \end{aligned}$$

2. The treatment chemical selected is sodium hexametaphosphate which contains 90.5 percent phosphate. This means there is 0.905 pounds phosphate per pound chemical:

$$\begin{aligned}
 \text{Chemical Required} &= \text{Phosphate loss} \div 0.905 \\
 &= 3.03 \div 0.905 = 3.35 \text{ lb/day}
 \end{aligned}$$

Section II Boiler Water Treatment

And Control

3-8. Deposit formation. The dissolved solids in boiler water tend to concentrate as steam is generated. The dissolved solids can come out of solution and form scale. The dissolved solids also can form a sludge in the boiler which can form a deposit.

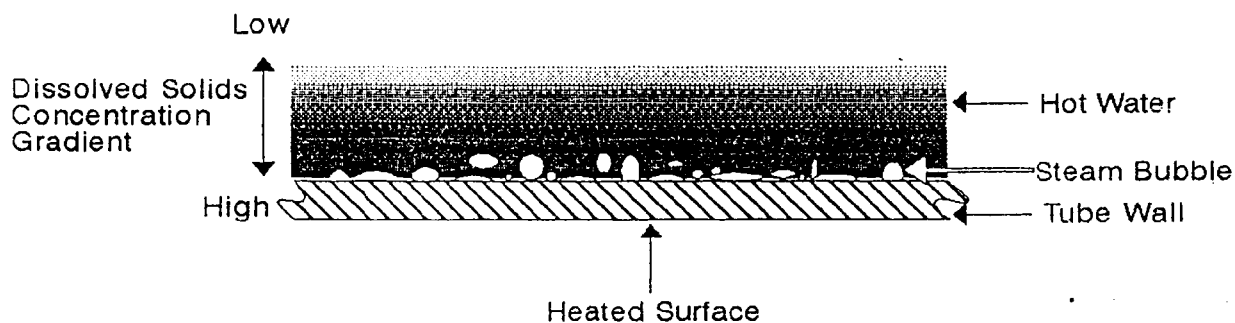
a. Some dissolved solids become less soluble as the water temperature increases. This includes the salts of calcium and magnesium [CaCO_3 , CaSO_4 , MgCO_3 , Mg(OH)_2]. As a result of this property, these materials will tend to form scale in the hotter

areas of the boiler.

b. Scale can occur locally due to evaporation as illustrated in figure 3-4. When a steam bubble forms on a heated surface, a thin film of water between the bubble and the tube wall becomes more concentrated with the dissolved materials. This thin layer also can be as much as 30°F hotter than the average boiler water temperature. These local conditions can cause the precipitation of the solids and the local formation of scale.

c. Sludge deposits can form when the precipitated materials in the boiler water become attached to surfaces.

**FIGURE 3-4
LOCALIZED SCALE FORMATION PROCESS**



3-9. Problems caused by scaling. Normally the steam boiler uses an external heat source much hotter than the boiler water. The metal tubes in the boiler are kept cool by the boiler water. When scale forms, it acts like an insulating material between the water and the metal. This results in the metal tubes operating at a higher temperature. The greater the thickness of scale, the greater the insulating effect and the higher the temperature of the tubes. At sufficiently high temperatures, the tube can lose tensile strength and rupture. The insulating property of a scale can act in any part of the boiler system to reduce the heat transfer capacity of affected areas.

3-10. Common scales found in boilers. The most common scales consist of calcium and magnesium salts and iron oxide.

a. Calcium carbonate. Calcium carbonate is caused by the breakdown of calcium bicarbonate by heat. It is found in untreated boilers, or improperly treated boilers.

b. Calcium sulfate. Calcium sulfate (gypsum) is found in boilers using high hardness, low alkalinity water, without proper treatment.

c. Calcium phosphate. Calcium phosphate is formed when the calcium in the feedwater reacts with the phosphate used for treatment. With proper treatment, this will form a sludge which can be removed in the blowdown. However, calcium phosphate can deposit as scale if the pH of the boiler water is below 11.0 and a sludge condition is not used.

d. Magnesium phosphate. Magnesium phosphate is caused by the reaction of magnesium salts in the feedwater with the phosphate used in the treatment. It will form only if the hydroxide content and the silica content of the boiler water are low.

e. Magnesium silicate. Magnesium silicate is formed from the magnesium and silica in the feedwater if the pH is above 11.0 and the silica level is more than half the phosphate level. Normally, it forms as a sludge that can be removed in the blowdown, but it may deposit on tubes as scale if a sludge conditioner is not present.

f. Iron oxide. Iron oxide is formed from the dissolved iron in the feedwater and hydroxide in the boiler water. Usually, the dissolved iron comes from the condensate return. This also should occur as a sludge which can be removed in the blowdown, but iron oxide can deposit as a scale on the boiler tubes if a sludge conditioner is not present.

3-11. Internal treatment of boiler water. Internal treatment of boiler water refers to the addition of chemicals to prevent scale formation and to prevent sludge deposits from forming due to precipitation of these materials.

a. Prevention of scale formation. The best method is to remove hardness from the makeup in a water softener. Hardness that enters the boiler has to be treated with chemicals which react with the hardness to form a sludge rather than scale.

(1) Low Pressure Boilers: (15 psig and less) In low pressure systems with no makeup or blowdown, sodium hydroxide (caustic) is added to maintain a pH between 10.5 and 11.5 to help prevent corrosion. Total alkalinity (M-alkalinity) levels greater than 50 ppm (as CaCO_3) in the feedwater will normally provide sufficient causticity in the boiler without the need to add sodium hydroxide. If there are high makeup requirements, treat the same as for high pressure boilers. (2) High Pressure Boilers: (greater than 15 psig) Phosphate, properly added, will react with both calcium and magnesium to form a sludge.

Sodium hydroxide may be required to maintain the appropriate hydroxyl alkalinity (causticity).

(a) Sodium hexametaphosphate is preferred because it generally cost less and has a higher phosphate level. Sodium tripolyphosphate (hydrated or anhydrous) also may be an economical choice. The relative cost of the alternative phosphate chemicals can be evaluated by comparing the cost per pound of phosphate (PO_4) provided by each chemical (see table 3-8).

(b) Sodium hexametaphosphate or tetrasodium pyrophosphate may be added to the feedwater, or directly to the steam drum. Disodium phosphate may also be added to the steam drum, but not to the feedwater because it will cause calcium phosphate scale to form in the line.

b. Prevention of sludge deposits. The hardness carried into both low and high pressure boilers with the feedwater will precipitate. To avoid forming sludge deposits, natural or synthetic organic compounds are added that will neutralize the charges on the sludge particles and provide sites for precipitation. The organic also will distort the crystal structure of scales, which helps to prevent their formation. A natural organic compound, Quebracho tannin, has traditionally been used in Army boilers with satisfactory results and may still be used, particularly in low pressure boilers. Tannin also helps in corrosion control since it absorbs a small amount of dissolved oxygen and forms a protective film on steel. Synthetic polymers recently developed have been shown to be more effective than tannins. Polyacrylates or a copolymer of methacrylate and sulfonated styrene are the preferred dispersants for minimizing the formation of scale in boilers. The copolymer is best for feedwater with iron concentrations exceeding 0.1 ppm.

3-12. Water carryover in steam. The steam produced from the evaporation of boiler water should not contain any contaminating materials or water. However, there commonly will be water droplets carried into the steam, due to several processes:

a. Mist carryover. A fine mist is developed as water boils. The process is illustrated in figure 3-5. A bubble of water vapor (steam) reaches the water surface and bursts leaving a dent in the water. The water surface in the dent rises as liquid fills it. The center of the dent will rise at a faster rate than the edges. This results in a small droplet that necks off at the center of the dent, and this is thrown off as a fine mist. This mist is removed to a great extent in the dry portion of the boiler. However, any mist that remains entrained in the steam will have the same level of dissolved solids as the boiler water and will contaminate the steam.

b. Foaming carryover. The alkalinity, TDS and suspended solids can interact to create a foam in the boiler. A light foam will reduce the problem of misting to some extent. However, a heavy foam layer is another source of liquid carryover into the steam. Normally, foaming can be controlled to a reasonable level by maintaining the total alkalinity less than 20 percent of the TDS and the total suspended solids (TSS) less than 8 percent of the TDS. Antifoam agents can be added to the boiler water to help control foaming.

c. Priming carryover. This is caused by liquid surges into the steam drum that throw water into the steam space where it is carried into the steam header. Priming is always caused by a mechanical problem or mechanical properties such as oversensitive feedwater controls, steam surges or incorrect blowdown procedures. There is no chemical control method available.

d. Silica carryover. Silica in the boiler water can volatilize and enter the steam, independent of water carryover. The silica may form a deposit when it condenses. These problems are controlled by maintaining a low silica level in the boiler water. The suggested limits are shown in table 3-2.

e. Determining the amount of carryover. The best way to determine carryover is to measure the steam condensate

conductivity. If less than about 25 micromhos carryover is probably insignificant.

(1) A high conductivity measurement in the steam condensate means there is either carryover or leakage into the steam/condensate system. The hardness must also be checked in the latter case. If hardness is found, the contamination of the condensate is due to raw water leakage into the

**FIGURE 3-5
MIST FORMATION DUE TO WATER BOILING**

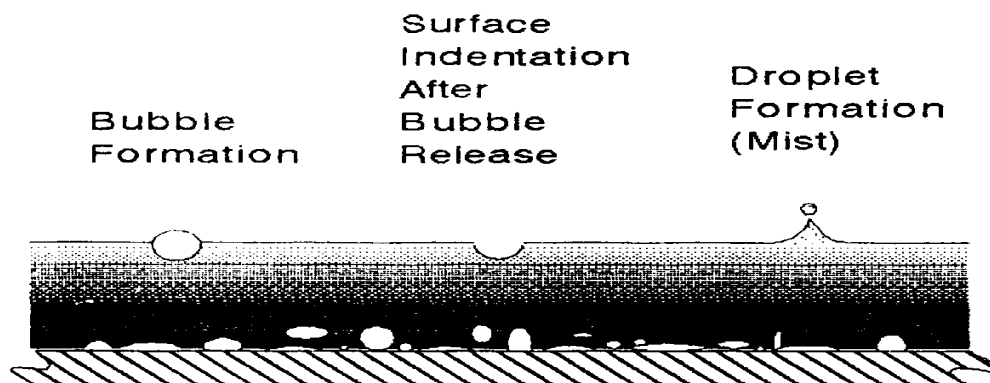


TABLE 3-2
SILICA LEVELS ALLOWED IN BOILER WATER

Boiler Pressure	Allowable Silica (as ppm SiO₂)
0-15	150
16-149	150
150-299	150
300-449	90
450-599	40
600-749	30
750	20

condensate system rather than, or in addition to, carryover. This is because the carryover of boiler water should be at a very low hardness due to chemical treatment.

(2) Any deposits found in the steam or condensate systems should be analyzed to determine the cause. Deposits that are mostly magnetic iron oxide are due to corrosion of iron. This can be controlled by using neutralizing amines (covered in paragraph 3-14). If the deposits are mostly silica, they can be reduced by increasing the blowdown or by removing silica from the makeup water. If the deposits are mostly sodium salts (sodium hydroxide, sodium carbonate, sodium sulfate, sodium phosphate), the cause is probably carryover. Additional antifoam should be added and the equipment inspected for any mechanical causes for carryover.

3-13. Removal of oxygen from feedwater. A mixture of oxygen and water is a very corrosive combination. This corrosivity

doubles with every 18°F increase in temperature. Oxygen corrosion can be recognized by pits, typically found in the top of the steam drum or at the waterline. Oxygen can be removed from feedwater by mechanical and chemical deaeration; and combination of these methods is commonly used.

a. Mechanical removal. Mechanical removal requires a deaerating heater in which the makeup water and condensate return are contacted with live steam using trays, sprays, or both. This heating literally boils the oxygen and other noncondensable gases out of the water. The oxygen is vented, along with a small amount of steam.

(1) There are two key operating controls that must be watched. First, the deaerator vent must be checked to see that a plume of steam is always flowing. Second, the pressure of the deaerator and the temperature of the outlet water must be controlled. Deaerators should operate at plus 3 psig or more. At any given pressure, the temperature

should be within 2°F of the temperatures shown in table 3-3 based on the elevation of the installation. If there is low or no steam flow or a low water temperature, the deaerator is not operating properly. This should be recorded and fixed immediately.

(2) A mechanical deaerator can reduce the oxygen content of feedwater to a fraction of a ppm. Complete removal requires chemical treatment.

b. Chemical removal. Chemical removal at Army installations uses either catalyzed sodium sulfite, or straight sodium sulfite, depending on the particular boiler system.

(1) The chemical reaction will consume 7.88 pounds of pure sodium sulfite per one pound of oxygen. In practice, about 10 pounds per pound of oxygen are added to carry a small excess of sulfite in the boiler water. The excess that should be carried is based on the boiler pressure, according to the levels shown in table 3-4.

(2) Higher sulfite residuals should not be carried because it is a waste of chemical and a waste of money. Also, sulfite can breakdown and cause condensate to become corrosive.

TABLE 3-3
DEAERATOR WATER OUTLET TEMPERATURE FOR BOILER SYSTEMS
AT VARIOUS PRESSURES AT SEA LEVEL (SEE NOTE).

Deaerator Pressure (psig)	Deaerator Water Outlet Temperature (°F)	Deaerator Pressure (psig)	Deaerator Water Outlet Temperature (°F)
0	212.0	11	241.6
1	215.3	12	244.4
2	218.5	13	246.4
3	221.5	14	248.4
4	224.4	15	250.3
5	227.1	16	252.2
6	229.8	17	254.1
7	232.2	18	255.3
8	234.8	19	257.0
9	237.1	20	258.8
10	239.4		

NOTE: For every 500 feet in elevation from sea level, subtract 1°F from the listed temperature.

TABLE 3-4
LEVELS OF SULFITE TO BE CARRIED IN BOILER WATER.

Boiler Pressure (psig)	Sulfite Residual (as ppm SO ₃)
0-15	20-40
16-149	20-40
150-299	20-40
300-449	20-40
450-599	20-40
600-749	15-30
750	15-30

3-14. Condensate corrosion and control.

The two impurities that promote corrosion are oxygen and carbon dioxide. Oxygen corrosion is prevented by removing it at the boiler and preventing leaks into the condensate.

a. Estimating carbon dioxide in steam.

(1) Any free carbon dioxide (CO₂) in the feedwater is removed by the deaerator, however, combined carbon dioxide can enter the boiler as carbonates and bicarbonates in the feedwater. Under the influence of heat and pressure, this combined CO₂ will create free CO₂ which leaves the boiler with the steam.

(2) CO₂ levels in the steam can be estimated from the bicarbonate and the carbonate in the feed water as follows:

$$\begin{aligned} \text{CO}_2 &= [\text{Bicarbonate} \times 0.79] + [\text{Carbonate} \times 0.35] \\ &= [(M - 2P) \times 0.79] + [2P \times 0.35] \end{aligned}$$

where: CO₂ = carbon dioxide estimate, ppm as CO₂
M = total (methyl orange) alkalinity, ppm as CaCO₃
P = phenolphthalein alkalinity, ppm as CaCO₃

Example 3-5:

1. Measured P = 2 ppm, M = 15 ppm
2. Bicarbonate CO₂ contribution [15 - (2 x 2)] x 0.79 = 8.7
3. Carbonate CO₂ contribution (2 x 2) x 0.35 = 1.4
4. Carbon dioxide estimate CO₂ = 8.7 + 1.4

= 10.1 ppm CO₂ in the steam

(3) CO₂ corrosion can be recognized by the thinning of condensate lines, particularly at the bottom of the pipe, and at pipe threads.

b. Control by neutralizing amines.

(1) Control Limits: CO₂ in the steam boiler systems can be controlled by neutralization with volatile amines. Sufficient amines are added to maintain the pH in all condensate return systems between 7.5 to 8.0. Condensate pH should not be allowed to fall below 7.5 anywhere in the return system. These amines are generally fed separately from other chemicals into the boiler steam drum, where they vaporize and pass over with the steam. Continuous feed is recommended for adding the amines.

(2) Amines Approved for Use:

Morpholine, diethylaminoethanol (DEAE), and cyclohexylamine are the three neutralizing amines approved for use in Army boilers. However, these amines are not to be used when the steam is used directly for cooking or humidification (refer to paragraph 1-6b.). Physical and chemical properties of these amines are shown in table 3-5. Because each of these amines have different vapor-liquid

distribution ratios, which is the tendency to condense with the steam condensate, they will not work equally well in all systems. Optimum results are obtained by choosing the appropriate amine or combination of amines on a system-by-system basis. A neutralizing amine selection chart is provided in table 3-6.

(a) Morpholine: Morpholine, with a low vapor-liquid distribution ratio, will drop out of the steam early, making it suitable for protecting short to moderate length condensate return systems. Morpholine can only be used in high pressure systems because of its high boiling point. However, very little morpholine is lost in deaerators from returning condensate.

(b) Diethylaminoethanol (DEAE): DEAE has a vapor-liquid distribution ratio between that of morpholine and cyclohexylamine. This makes DEAE a good choice for protecting moderate length systems

where either morpholine or cyclohexylamine used separately would not provide complete protection. The low boiling point of a DEAE and water mixture makes DEAE suitable for use in low pressure boilers as well as high pressure boilers.

(c) Cyclohexylamine:

Cyclohexylamine, with a high vapor-liquid distribution ratio, is best suited for protecting the extremes of long systems. It is necessary to also treat long systems with morpholine to protect the early part of the system where steam starts condensing. Cyclohexylamine can also be used in low pressure systems. Cyclohexylamine should not be used in systems when the feedwater alkalinity exceeds 75 ppm because of the low solubility of cyclohexylamine bicarbonate. The likely area for formation of these deposits is in low flow areas at the far end of the condensate return

TABLE 3-5
PHYSICAL AND CHEMICAL PROPERTIES OF NEUTRALIZING AMINES

	Morpholine	DEAE	Cyclohexylamine
Boiling Point, °F (100% amine)	264	325	273
Boiling Point, °F (Amines/water azeotrope)	--	210	205
Decomposition Temperature, °F	644	794	626
Vapor-Liquid Distribution Ratio	0.4	1.7	4.7
Specific Gravity (100% amine)	1.002	0.88	0.86
pH, 100 ppm Solution	9.7	10.3	10.7
Amount of Amine (ppm) Required to Maintain pH of 8.0 in Water Containing 10 ppm CO ₂	37	22	15

TABLE 3-6
NEUTRALIZING AMINE SELECTION CHART.

Amine	Low Pressure (below 15 psig)	High Pressure Systems (above 15 psig)		
		Short System (< 800 ft) ⁽²⁾	Medium System (< 1 mile) ⁽²⁾	Long System (> 1 mile) ⁽²⁾
Morpholine		X		
DEAE	X		X	X
Cyclohexylamine ⁽¹⁾	X			
Cyclohexylamine/ Morpholine Mixture			X	X

NOTES: (1) Not for use in systems having a feedwater alkalinity more than 75 ppm.
(2) These systems lengths are for classification only and are not absolute. For example, a medium length system may have more of the characteristics of a long system if lines are poorly insulated or because of poor design. The characteristics of a condensate return system are best determined by a condensate pH survey.

system. This problem can be avoided by reducing feedwater alkalinity or by using DEAE.

(d) **Morpholine/ Cyclohexylamine:**
A mixture of morpholine and cyclohexylamine can also be used to provide full protection in medium and large systems. The optimum blend of these amines is determined by measuring the actual pH at various locations in the condensate return system. If samples from far sections have a lower pH than other samples, increase the cyclohexylamine in the mixture and vice versa. Another pH survey should be done whenever the ratio is changed. An initial blend of one part cyclohexylamine and three parts morpholine is a good starting point. **c. Control by filming amines.** CO₂ corrosion can also be controlled with 0.7 to

1.0 ppm of a filming amine such as octadecylamine. This chemical will coat the condensate pipe and prevent the CO₂ in the water from coming into contact with the pipe wall. Because they coat the metal, filming amines may also be appropriate for use if there is a high in leakage of air. However, they are not recommended in condensate systems that have had corrosion problems in the past. They must be added directly to the steam header through a quill instead of to the steam drum. Inadequate dosages can result in accelerated pitting type corrosion due to incomplete surface coverage. Filming amines are not authorized for use in Army boilers without written approval from USACPW (CECPW-ES).

Section III Putting It All Together

3-15. General information:

a. A complete program for boiler water may need to include softening of the makeup water and treatment of the internal system for controlling scale formation, sludge conditioning, corrosion control (oxygen and carbon dioxide), foam control and boiler blowdown control. The treatment methods authorized for meeting these needs include:

(1) Softening of makeup water to remove calcium and magnesium.

(2) Phosphate addition (for boilers with blowdown and makeup requirements) to prevent the formation of calcium carbonate and calcium sulfate scales.

(3) Synthetic polymer addition to ensure formation of sludge with proper characteristics.

(4) Alkalinity addition (sodium hydroxide), if required, to prevent magnesium phosphate scale formation and corrosion.

(5) Sulfite addition to prevent oxygen corrosion.

(6) Amine addition to prevent carbon dioxide corrosion in the condensate return system.

(7) Antifoam agent to control foaming in the steam drum, if required.

(8) Blowdown adjustment to ensure:

(a) The silica content is low enough to prevent carryover.

(b) The TDS level (or conductivity) is low enough to minimize foaming.

(c) The causticity (alkalinity) and suspended solids are low enough to prevent foaming or carryover (this is seldom the reason for adjusting blowdown but must be monitored).

b. Table 3-7 provides guidelines on limits for an effective program based on boiler pressure. These guidelines apply for deposit

control as well as steam quality. However, maximum limits for a specific boiler system may vary because of such factors as boiler design, rating, water level, load characteristics, or type of fuel. The maximum levels possible for a specific boiler are usually determined from experience. The boiler should be operated at or near the maximum levels of TDS or silica (depending on which is the controlling parameter). This will save water, treatment chemicals and energy.

c. The development of a treatment program should be approached on a step-by-step basis. A recommended procedure for developing this program is described in paragraphs 3-16 through 3-22, and summarized in paragraph 3-23.

3-16. Determining blowdown required.

Minimum blowdown is controlled by either the level of TDS (or conductivity) or the level of silica in the boiler water. The calculations used to develop a blowdown estimate based on the levels of these materials are described in paragraph 3-4.

Example 3-6:

1. A boiler operates at 150 psig. The feedwater contains 4 ppm silica and 225 ppm TDS.
2. The limits for silica and TDS in the boiler water are determined from table 3-7 to be:

Silica = 150 ppm, maximum

TDS = 3,500 ppm, maximum

3. Maximum allowable COC are determined to be (note that the blowdown level is the same as the maximum level allowed in the boiler water):

$$\text{Silica COC} = \frac{\text{Blowdown, ppm}}{\text{Feedwater, ppm}} = \frac{150}{4} = 37.5 \text{ COC}$$

TABLE 3-7
LIMITS ON BOILER WATER CONDITIONS
FOR AN EFFECTIVE TREATMENT PROGRAM

Boiler Pressure (psig)	Maximum TDS (ppm)	Maximum Silica (ppm)	Range Sulfite (ppm SO ₃)	Range Ortho- Phosphate (ppm PO ₄)	Range Hydroxyl Alkalinity (Causticity) (ppm as OH)
0-15	3500	150	20-40	30-60	20-200
16-149	3500	150	20-40	30-60	20-200
150-299	3500	150	20-40	30-60	20-200
300-449	3000	90	20-40	30-60	15-200
450-599	2500	40	20-40	30-60	13-180
600-749	2000	30	15-30	30-60	13-180
750	2000	20	15-30	30-60	13-100

Silica = 40 ppm, maximum
TDS = 2,500 ppm, maximum

$$\text{TDS COC} = \frac{\text{Blowdown, ppm}}{\text{Feedwater, ppm}} = \frac{3,500}{225} = 15.6 \text{ COC}$$

- The COC based on TDS is lower, so it will be the controlling factor in setting blowdown requirements. The boiler blowdown always will be adjusted to maintain the TDS at less than 3,500 ppm. This will be adequate to maintain silica at less than 150 ppm.

Example 3-7:

- A boiler operates at 450 psig. The feedwater contains 4 ppm silica and 225 ppm TDS as in example 3-6.
- The limits for silica and TDS in the boiler water are determined from table 3-7 to be:

- The maximum allowable COC are determined to be (note that the blowdown level is equal to the maximum level allowed in the boiler water):

$$\text{Silica COC} = \frac{\text{Blowdown, ppm}}{\text{Feedwater, ppm}} = \frac{40}{4} = 10.0 \text{ COC}$$

$$\text{TDS COC} = \frac{\text{Blowdown, ppm}}{\text{Feedwater, ppm}} = \frac{2,500}{225} = 11.1 \text{ COC}$$

- The COC based on silica is lower, so this will be the controlling factor in setting blowdown requirements. The boiler blowdown must be adjusted to maintain the silica at less than 150 ppm.

5. It is easier to measure TDS (or conductivity) than silica in boiler water. Therefore, it will be more convenient to control the TDS to be always lower than the TDS level that would occur at 10.0 COC. The TDS level at 10 COC can be calculated:

$$\begin{aligned}\text{Boiler TDS, max.} &= \text{feedwater TDS} \times \text{COC} \\ &= 225 \text{ ppm} \times 10.0 = 2,250 \text{ ppm}\end{aligned}$$

6. The same calculation can be performed using conductivity data. (Note that when measured properly, for boilers using synthetic polymers, neutralized conductivity = $\text{TDS} \div 0.7$.)

$$\begin{aligned}\text{Neutralized} \\ \text{Conductivity, max.} &= \text{TDS, maximum} \div 0.7 \\ &= 2,250 \text{ ppm} \div 0.7 = 3,214 \text{ micromhos}\end{aligned}$$

Example 3-8:

1. The 150 psig boiler in example 3-6 produces 40,000 pounds of steam per hour. The blowdown is calculated based on the maximum COC of 15.6 as follows (paragraph 3-4c covers the relationship between steam generated and blowdown):

$$B = E \div (C - 1) = 40,000 \text{ lb/hr} \div (15.6 - 1) = 2,740 \text{ lb/hr}$$

2. The blowdown in lb/day = $24 \times 2,740 = 65,760$
3. The blowdown in gal/day = $65,760 \div 8.33 = 7,894$ (where 8.33 = lb/gal of water).

Example 3-9:

1. The 450 psig boiler in example 3-7 produces 40,000 pounds of steam per hour. The blowdown required to operate the boiler is calculated based on the steam generated (40,000 lb/hr) and the maximum COC 10.0 using the relationship:

$$B = E \div (C - 1) = 40,000 \text{ lb/hr} \div (10.0 - 1) = 4,444 \text{ lb/hr}$$

2. The blowdown in lb/day = $24 \times 4,444 = 106,656$.
3. The blowdown in gal/day = $106,656 \div 8.33 = 12,804$ (where 8.33 = lb/gal of water).

3-17. Determining phosphate required to replace blowdown loss.

For systems that require phosphate, the recommended range to carry in the boiler water is 30 to 60 ppm (as orthophosphate, PO_4). The amount of chemical to add is the sum of phosphate lost in the blowdown and the phosphate that reacts with the hardness in the feedwater. The type of phosphate chemical selected for use will determine the actual amount of chemical to add (see paragraph 3-11a which give information on selecting the chemical). The preferred chemical is sodium hexametaphosphate because of the relatively low cost and high phosphate level. The use of sodium tripolyphosphate (hydrated or anhydrous) also may be an economical choice due to local conditions. The amount of chemical to add depends upon the concentration of phosphate in the chemical that is used (table 3-8).

Example 3-10:

1. The 150 psig boiler in example 3-6 will require a phosphate chemical, preferably sodium hexametaphosphate. The amount of phosphate required to maintain 60 ppm in the boiler water is calculated based on the blowdown loss (65,760 lb/day, per example 3-8):

$$\begin{aligned}\text{Phosphate Loss} &= 65,760 \text{ lb/day} \times 60 \text{ ppm} \div 1,000,000 \\ &= 3.95 \text{ lb/day}\end{aligned}$$

2. If the chemical selected is sodium hexametaphosphate, table 3-8 shows the

phosphate (PO_4) content to be 90.5 percent. The required daily feed of this chemical to replace the phosphate lost in the blowdown is:

$$\begin{aligned}\text{Feed, hexametaphosphate} &= \frac{\text{phosphate lb/day}}{\% \text{ phosphate}} \times 100 \\ &= \frac{3.95}{90.5} \times 100 = 4.36 \text{ lb/day}\end{aligned}$$

3. If the chemical selected is anhydrous disodium phosphate, table 3-8 shows the phosphate to be 65.7 percent. The required daily feed is:

$$\begin{aligned}\text{Feed, anhydrous disodium phosphate} &= \frac{\text{phosphate lb/day}}{\% \text{ phosphate}} \\ &= \frac{3.95}{65.7} \times 100 = 6.01 \text{ lb/day}\end{aligned}$$

Example 3-11:

1. The 450 psig boiler in example 3-7 will require a phosphate chemical based on the discussions in segment 3-11a. The amount of phosphate required to maintain 60 ppm in the boiler water is calculated based on the blowdown loss (106,656 pounds water/day, per example 3-9):

$$\begin{aligned}\text{Phosphate} &= 106,656 \text{ lb/day} \times 60 \text{ ppm} \div 1,000,000 \\ &= 6.40 \text{ lb/day}\end{aligned}$$

2. If the chemical selected is sodium hexametaphosphate, table 3-8 shows the phosphate to be 90.5 percent. The required daily feed of this chemical to replace the phosphate lost in the blowdown is:

$$\begin{aligned}\text{Feed, hexametaphosphate} &= \frac{\text{phosphate lb/day}}{\% \text{ phosphate}} \times 100 \\ &= \frac{6.4}{90.5} \times 100 = 7.07 \text{ lb/day}\end{aligned}$$

3. If the chemical selected is anhydrous disodium phosphate, table 3-8 shows the phosphate to be 65.7 percent. The required daily feed is:

$$\begin{aligned}\text{Feed, disodium phosphate} &= \frac{\text{Phosphate lb/day}}{\% \text{ phosphate}} \times 100 \\ &= \frac{6.40 \times 100}{65.7} = 9.74 \text{ lb/day}\end{aligned}$$

3-18. Determining phosphate required for hardness reaction.

Any calcium or magnesium hardness in the feedwater will react with the phosphate added to form a precipitate. Additional phosphate required to react with the hardness is presented in table 3-8 as the pounds of phosphate chemical required per 1,000 gallons feedwater per ppm hardness. The total phosphate dose in the feedwater is the sum of the requirements for maintaining the 30 to 60 ppm level (paragraph 3-17) and the hardness reaction. The chemical dose should be gradually increased or decreased as necessary (about 10 percent per day) to maintain the desired level.

Example 3-12:

1. The 150 psig boiler in example 3-6 produces 40,000 pounds of steam per hour. It was determined in example 3-8 that the blowdown is 2,740 pounds per hour. The total feedwater quantity is calculated:

$$\begin{aligned}F &= E + B = 40,000 + 2,740 = 42,740 \text{ lb/hr} \\ &= 42,740 \times 24 \text{ hr/day} \\ &= 1,025,760 \text{ lb/day} \\ &= 1,025,760 \div 8.33 \text{ lb/gal} \\ &= 123,140 \text{ gal/day}\end{aligned}$$

2. The feedwater contains 5 ppm hardness. The selected phosphate chemical is sodium hexametaphosphate. From table 3-8, the required addition per 1,000

TABLE 3-8
PHOSPHATE, CAUSTIC & POLYMER ADDITION REQUIREMENTS FOR BOILERS

Chemical Name	Formula	Percent Phosphate as PO ₄ ⁽¹⁾	Pounds Phosphate Chemical Required to Treat 1,000 Gallons Feedwater per ppm Hardness	Pounds Sodium Hydroxide (Caustic) Required per 100 Pounds Phosphate Treatment	Pounds 100% Active Polymer Required per Pound Phosphate ⁽²⁾
Disodium Phosphate, Dodecahydrate	Na ₂ HPO ₄ ·12H ₂ O	26.0	0.02	11	0.03
Disodium Phosphate, Anhydrous	Na ₂ HPO ₄	65.7	0.0082	28	0.07
Trisodium Phosphate, Dodecahydrate	Na ₃ PO ₄ ·12H ₂ O	25.1	0.021	0	0.03
Trisodium Phosphate, Monohydrate	Na ₃ PO ₄ · H ₂ O	52.0	0.01	0	0.06
Sodium Tripolyphosphate, Hexahydrate	Na ₅ P ₃ O ₁₀ ·6H ₂ O	61.1	0.0088	33.6	0.07
Sodium Tripolyphosphate, Anhydrous	Na ₅ P ₃ O ₁₀	76.4	0.0068	43.5	0.09
Tetrasodium Pyrophosphate, Anhydrous	Na ₄ P ₂ O ₇	71.0	0.0072	30.08	0.08
Tetrasodium Pyrophosphate, Decahydrate	Na ₄ P ₂ O ₇ ·10H ₂ O	42.7	0.012	17.9	0.05
Sodium Hexametaphosphate	(NaPO ₃) ₆	90.5	0.0056	78.4	0.10

1) The percent phosphate in chemicals commonly is reported as either PO₄ (phosphate) or P₂O₅ (phosphorus pentoxide) (%P₂O₅ x 1.34 = %PO₄).

2) The values shown are for "100% polymer". The product is obtained as a solution containing less than 100%. The pounds polymer required must be divided by the decimal percent active polymer in product. The supplier must supply the information on percent active. For example: If the polymer to be used is a 50% solution of polyacrylic acid, and the phosphate form is sodium hexameta phosphate, the amount of polymer to be used is .10 ÷ .50 = 0.2 pounds per pound of sodium hexameta phosphate.

gallons feedwater for hardness removal is:

$$\begin{aligned}\text{Chemical} &= 5 \text{ ppm H} \times 0.0056 \text{ lbs/1,000 gallons/ppm H} \\ &= 0.028 \text{ lb/thousand gallons}\end{aligned}$$

3. Additional chemical for the hardness reaction is calculated:

$$\text{Chemical per day} = 0.028 \text{ lb/thousand gal.} \times \frac{123,140}{1,000} = 3.4 \text{ lb/day}$$

4. The chemical added to maintain the 60 ppm PO₄ level was calculated in example 3-10 to be 4.36 lb/day. The total sodium hexametaphosphate requirement is calculated:

$$\text{Sodium hexametaphosphate} = 4.36 + 3.45 = 7.81/\text{day}$$

3-19. Determining sodium hydroxide (caustic soda) required. The boiler water hydroxyl alkalinity (causticity) must be maintained at the levels in table 3-7 to help prevent corrosion and the formation of magnesium phosphate sludge which will adhere to the surface. The amount of sodium hydroxide required for each of the phosphate chemicals is shown in table 3-8. When softened water is used as makeup, sufficient alkalinity may be present to provide the required causticity in the boiler without adding sodium hydroxide.

Example 3-13:

1. The 150 psig boiler in example 3-12 will require 7.81 pounds of sodium hexametaphosphate per day.
2. Table 3-8 shows that 78.4 pounds sodium hydroxide is required per 100 pounds of phosphate treatment. Sodium hydroxide (NaOH) needed is calculated:

$$\text{NaOH} = 7.81 \text{ lb chemical/day} \times \frac{78.4 \text{ lb NaOH}}{100 \text{ lb chemical}}$$

$$= 6.12 \text{ lb sodium hydroxide/day}$$

Example 3-14:

1. The 450 psig boiler in example 3-11 will require 9.74 pounds per day of anhydrous disodium phosphate to replace the loss in the blowdown.
2. Table 3-8 shows that 28 pounds sodium hydroxide is required per 100 pounds of phosphate chemical. Sodium hydroxide (NaOH) needed is calculated:

$$\begin{aligned}\text{NaOH} &= 9.74 \text{ lb chemical/day} \times \frac{28 \text{ lb NaOH}}{100 \text{ lb chemical}} \\ &= 2.73 \text{ lb/day}\end{aligned}$$

3-20. Determining synthetic polymer dosage. There is no easy test method currently available for determining the concentration of polymers in boiler water. To ensure that there is always an adequate level of polymer in the boiler, the polymer is mixed and fed with phosphate in the ratio of 0.1 pounds of polymer per pound of available PO₄ in the phosphate used. The amount of active polymer to add to various types of phosphate to achieve the desired 0.1 ratio is provided in the last column of table 3-8.

Example 3-15:

1. The 150 psig boiler in example 3-12 requires 7.81 lb/day of sodium hexametaphosphate.
2. Table 3-8 shows that 0.10 pounds of active polymer per pound of sodium hexametaphosphate.

$$\text{Synthetic polymer} = 7.81 \times 0.10 = 0.78 \text{ lbs/day of 100\% polymer}$$

3. Assume the polymer used is only 50% active, then the amount of polymer required is:

$$0.78 \times \frac{100}{50} = 1.56 \text{ lb/day}$$

3-21. Determining sulfite dosage. Sulfite at levels shown in table 3-4 is required to remove oxygen from the feedwater. More

sulfite is needed to maintain these levels when there is no deaerating heater. The initial dosage should be calculated for the middle of the range in table 3-4 and then adjusted to maintain the desired level.

Example 3-16:

1. The 150 psig boiler in example 3-8 needs 20 to 40 ppm sulfite (as SO_3). The sulfite dosage is initially selected at the midpoint level of 30 ppm. The blowdown is 65,760 lb/day as determined in example 3-8. The sulfite required is calculated based on chemical lost in the blowdown:

$$\text{Sulfite} = 65,760 \times 30 \div 1,000,000 = 1.97 \text{ lb/day}$$

2. There is one pound of sulfite per 1.575 pounds sodium sulfite. The amount required is calculated:

$$\text{Sodium sulfite} = 1.97 \times 1.575 = 3.10 \text{ lb/day}$$

Example 3-17:

1. The 450 psig boiler in example 3-9 needs 20 to 40 ppm sulfite (as SO_3). The midpoint of 30 ppm is initially selected. The blowdown is 106,656 pounds per day as determined in example 3-9. The required sulfite is calculated based on chemical lost in the blowdown:

$$\text{Sulfite} = 106,656 \times 30 \div 1,000,000 = 3.20 \text{ lb/day}$$

2. There is one pound of sulfite per 1.575 pounds sodium sulfite. The addition required is calculated:

$$\text{Sodium sulfite} = 3.20 \times 1.575 = 5.04 \text{ lb/day}$$

3-22. Determining amine dosage. The procedure for estimating the neutralizing and filming amine requirements in the feedwater is presented in paragraph 3-14. These chemicals are consumed in the distribution system, so the

dose is based on the feedwater rate rather than the blowdown.

3-23. Summary of required calculations.

The step-by-step procedure for developing the chemical feed program for Army boilers that use makeup and blowdown includes the following:

a. Estimate the blowdown rate for the boiler based on the COC and the steam rate (paragraph 3-16).

b. Determine the phosphate required to maintain a level of 30 to 60 ppm (as orthophosphate) in the boiler, based on the chemical lost in the blowdown (paragraph 3-17).

c. Determine the phosphate required to react with the hardness in the feedwater (paragraph 3-18).

d. Determine the sodium hydroxide (caustic) required, based on the total phosphate added to the system, including blowdown loss and the hardness reaction (paragraph 3-19).

e. Determine the synthetic polymer required (paragraph 3-20).

f. Determine the sulfite dose, based on the blowdown loss (paragraph 3-21).

g. Determine the amine dose required, based on feedwater rate (paragraph 3-22) and the amine level (paragraph 3-14).

Example 3-18:

1. An Army boiler operates as follows:
Boiler Pressure: 150 psig
Steam Production: 40,000 lb/hr
Feedwater: TDS = 225 ppm
Silica = 4 ppm
Hardness = 5 ppm
2. COC = 15.6, based on TDS controlling (example 3-6).

3. Blowdown = 65,760 lb/day (example 3-8).
4. Feedwater = 123,140 gal/day (example 3-12).
5. Phosphate dosage = 7.81 pounds of sodium hexametaphosphate/day (example 3-12).
6. Sodium hydroxide dosage = 6.12 lb/day (example 3-13).
7. Polymer dosage = 1.56 lb/day (example 3-15).
8. Sodium sulfite dosage = 3.10 lb/day (example 3-16).
9. The proper mixture of treatment chemicals for this boiler should include sodium hexametaphosphate, polymer, and sodium sulfite. The sodium hydroxide should not be included in a blend because it is more likely to vary. It should be added separately. The proper mixture concentrations are developed:

$$\begin{aligned}\text{Sodium hexametaphosphate} &= \frac{\text{lb chemical}}{\text{lb total}} \times 100 \\ &= \frac{7.81}{7.81 + 1.56 + 3.10} \\ &= \frac{7.81}{12.47} \times 100 = 62.6\%\end{aligned}$$

$$\text{Polymer} = \frac{1.56}{12.47} \times 100 = 12.5\%$$

$$\text{Sodium sulfite} = \frac{3.10}{12.47} \times 100 = 24.9\%$$

10. The initial feed rate for this boiler using this mixture should be 12.47 pounds per day.
11. The operator should adjust the feed rate of the mixture to maintain the recommended levels. When any of the recommended levels cannot be maintained within 10 percent of the

target level with the mixture, a new mixture should be considered.

h. Information on chemical mixing and feeding is provided in chapter 7.

Section IV Boiler Layup Requirements

3-24. General information. An Army boiler that is to be out of service for more than four calendar days will require special treatment to prevent internal corrosion. Boiler layup can be either dry or wet. The advantages of wet layup are that it provides better corrosion protection and the boiler can be brought on-line much faster than when dry layup procedures are used.

3-25. Dry layup. Boilers with manholes may be laid up in one of two ways depending on the length of storage and conditions in the boiler room.

a. Open method. This is recommended for short term storage, 30 to 150 days, where the boiler room is dry and well ventilated.

(1) Take the boiler out of service and drain it completely while still warm. Make sure the water walls and gage columns are not overlooked. Open the boiler and wash the inside of all loose scale and sediment by flushing with strong water pressure. Use a stiff brush to clean all internal surfaces that can be reached. Break the feedwater and steam connections to the boiler and blank off connections if other boilers in the plant are operating.

(2) Leave boiler open to the atmosphere.

b. Quicklime or silica gel method. This procedure is recommended for storage over

150 days or for less than 150 days when the boiler room is not dry and well ventilated.

(1) Take the boiler out of service and drain completely while still warm. Make sure that water walls and gage columns are not overlooked. Open the boiler and wash the inside of all loose scale and sediment by flushing thoroughly with strong water pressure. Use a stiff brush to clean all internal surfaces and blank off the connections if other boilers in the plant are operating.

(2) Start a very light fire in the furnace. Maintain this fire for at least two hours or until inspection shows no moisture on internal sections of the boiler.

(3) Place quicklime (not hydrated lime) or silica-gel in one or more metal or fiber trays in the boiler. Place the trays on wood blocks so air can circulate under them. The amount of lime or silica-gel required is about 50 pounds per 3,000 pounds of steam per hour boiler capacity.

(4) Seal the boiler.

(5) Open and inspect the boiler every two months. Replace wet lime or silica-gel with dry material. Carefully reseal immediately after the inspection.

3-26. Wet layup. This method means that the boiler is completely full of treated water. This method is easier to check, and the boiler can be put back in service more quickly. This method should not be used if the boiler is subject to freezing temperatures.

a. Layup without draining (operational boilers). This is most common where a boiler is to be shutdown for a period of four to thirty calendar days. Often the boiler must be maintained in a standby condition. Corrosion will result in the boiler unless the water level and the chemicals in the boiler are increased. Recommended procedures for layup of a boiler without cleaning are:

(1) About four hours before the boiler is to be shutdown, add enough sodium hydroxide (caustic) to increase the hydroxyl alkalinity (causticity) to slightly higher than the upper limit given in table 3-7 for the pressure of the boiler to be laid up. Add sodium sulfite to increase the sulfite residual to 200 ppm (as Na_2SO_3).

(2) Put out the fire to the boiler. Add water to completely fill the entire boiler until the water runs out of the safety valve. When the boiler is completely cool, add more water to ensure it is full. Maintain a pressure of 5 to 10 psig during layup.

(3) Check the boiler frequently to make sure no water has leaked out. Analyze the water once per month to make sure the chemical residuals are being maintained.

b. Layup of drained boilers.

Recommended procedures for boilers that have been emptied for cleaning or repair before layup are:

(1) Drain the boiler completely and remove scale or deposits. Remove connections to other active boilers, feedwater, and steam systems.

(2) Fill the boiler with deaerated water if available, and add enough sodium hydroxide (caustic) to give a hydroxyl level of about 200 ppm (as OH). Add sodium sulfite to give a sulfite residual of 200 ppm (as Na_2SO_3).

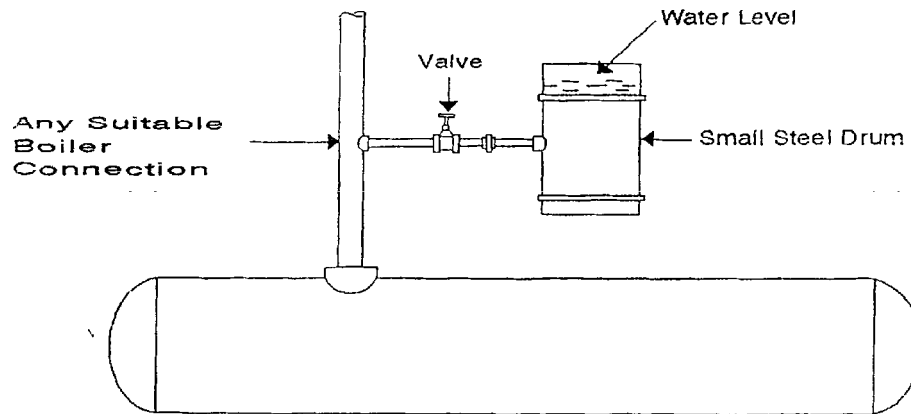
(3) Circulate chemicals in the boiler by careful boiling for two hours. Be sure to fill the boiler to replace any losses during this treatment.

(4) Put out the fire to the boiler. Add water to completely fill the entire boiler until the water runs out of the safety valve. When the boiler is completely cool, add more water to ensure it is full. Maintain a pressure of 5 to 10 psig during layup.

(5) Inspect the boiler on a regular basis and replace any water losses. To facilitate inspections, a small steel tank equipped with a gage can be installed above the top of the boiler as shown in figure 3-6. Fill the tank

with water and connect to a steam takeoff tap, vent, or safety valve connection. A glance at the water level in the small drum will quickly tell whether or not the boiler is completely filled.

**FIGURE 3-6
WET STORAGE METHOD**



Chapter 4

Cooling Towers

Section I General Information

4-1. Open recirculating system defined:

a. Definition. An open circulating water system includes the units where heat is to be removed, the cooling water distribution, the return system, and the cooling tower. Heat, picked up in the recirculating water, is transferred from the cooling water to the atmosphere in a cooling tower. This requires the exposure of the water to a great quantity of air. The water also is cooled to a lesser extent, by conduction; that is, by the difference in temperature between the water and the air. Additional water (called makeup) must be added to replace the water lost through evaporation to maintain a constant operating volume of water in the cooling system. A portion of the cooling water must be discharged to the sewer as waste (called blowdown) to maintain an adequate quality of water. Makeup water added to the cooling system must also replace this loss. The cooling system will operate most efficiently when the recirculating water is properly treated on a regular basis. This will result in reduced operating, maintenance, and replacement costs.

b. Type of cooling towers:

(1) Natural draft towers: Air flow through the tower is achieved without fans. Air flow across the falling water depends on the wind conditions. Injecting water into the tower with spray nozzles improves efficiency by bringing more water drops in contact with air.

(2) Forced draft towers: These

towers use one or more fans to blow air up through the tower fill against the flow of falling water. Drift eliminators are installed to prevent water entrained in the air from leaving the system.

(3) Induced draft towers: These towers use one or more fans to draw air across the falling water. The air flows either cross-flow or counter-flow to the falling water drops. Drift eliminators are also installed.

c. Typical cooling towers at Army installations. Cooling towers at Army installations are mostly the induced draft cross-flow variety. They typically range in size from 25 to 200 ton capacity.

4-2. Fundamental parts of a cooling tower. A simple cooling tower is shown in figure 4-1. The major parts of the tower include:

a. Basin and cold well. The basin is the portion of the tower below the cooling section or the coil section used for collecting and retaining circulating water and adding makeup water. The cold well is a deepened portion of the basin that contains distribution pumps.

b. Louvers. These are members installed horizontally on the sides of a tower wall to provide openings through which air enters the tower. These are usually at an angle to the direction of air flow.

c. Fill. The fill is the part of a tower which intercepts the downward fall of water at regular intervals, forming splash surfaces which cause the water to breakup into smaller droplets for the air-water contact. The tower fill commonly includes mist eliminators which are internal structures designed to prevent

transport of the fine water droplets out of the tower.

d. Distribution and fan deck. The deck on top of a cooling tower is used to distribute return flow to the tower fill and to support the fan housing. The stack is the structure (typically a cylinder) that encloses the fan discharge of an induced draft tower.

e. Cell. This is the smallest subdivision of a complete cooling tower that can operate as an independent unit.

4-3. Objective of cooling water treatment:

a. The open circulating cooling-tower system has a greater potential for all types of problems associated with deposits, corrosion and microbiological organisms. These problems are magnified in an open system for several reasons, including:

(1) Generally higher water temperatures exist in the water system promoting scale deposition and corrosion.

(2) The cooling tower acts as a huge air scrubber, introducing microorganisms, dust and dirt in the circulating waters which enhance the potential for fouling and corrosion.

(3) Makeup water brings in more scale, deposit, and corrosion forming constituents.

(4) Oxygen is continuously added to the water as it passes through the cooling towers increasing the potential for corrosion of steel and other metals in the system.

b. Regardless of the size and type of cooling tower used, the system problems are similar, varying only in degree, and are dependent on the water used and the materials of construction. All problems fall into three main categories - deposit formation, biological deposition, and corrosion. While problems caused by these occur primarily in the system

heat exchangers, they can also occur in all water-carrying lines, in the cooling tower, and in other system components that come in contact with the cooling water. Solutions to these three problem areas are covered in sections III, IV, and V of this chapter, respectively.

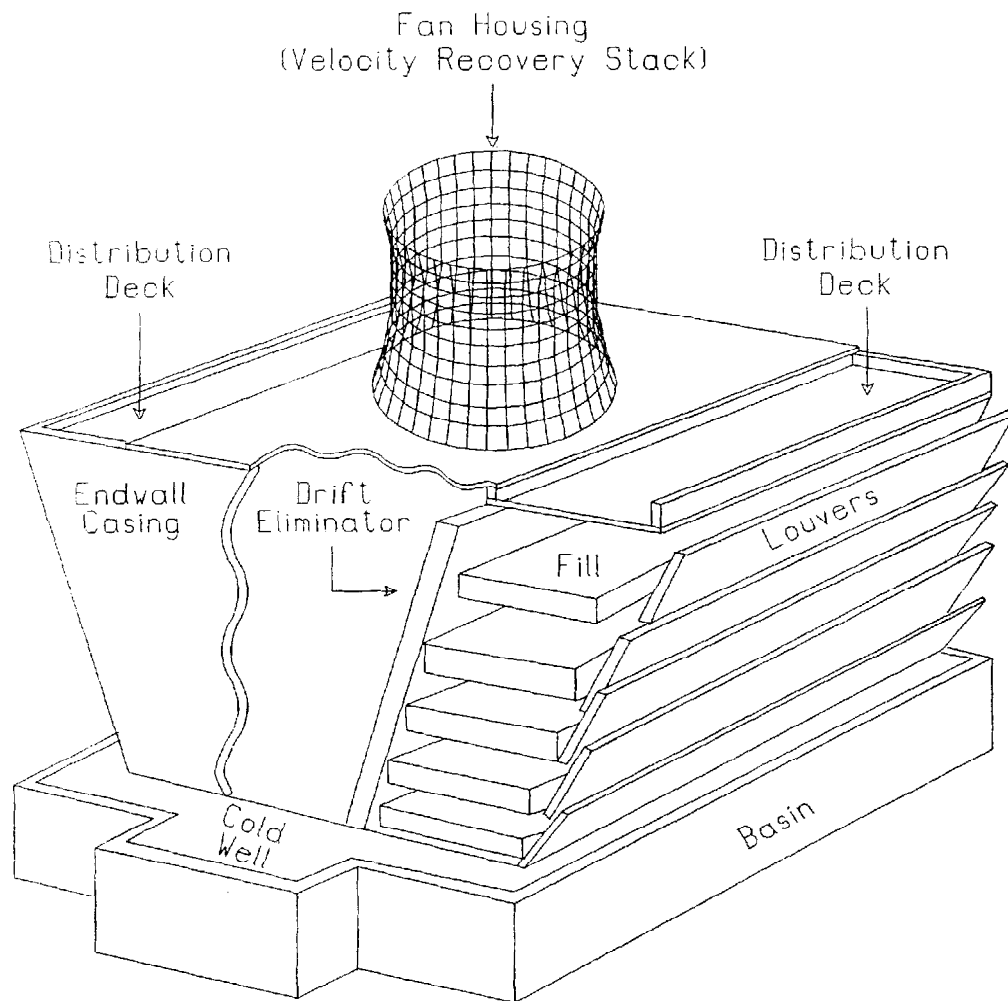
c. Knowing the water quality is an essential element in determining the type of treatment to use in a recirculating cooling water system. Before beginning a water treatment program, the makeup water should be analyzed to determine its potential for scaling or corrosion in the system. Several scaling indices have been developed to predict a water's scaling tendency. These are explained in paragraph 4-11 and appendix B.

Section II

Cooling Tower Operating Calculations

4-4. Principles of cooling tower operations. The only function of a cooling tower is to cool warm water. The cooling water circulates to operating units where it picks up heat while cooling or condensing one or more process streams and the resulting warm water is returned to the cooling tower. The warm water is cooled by intimate contact with air as it flows down through the tower. Two processes are involved. Conduction transfers sensible heat from water to the cooler air, cooling the water and warming the air. This accounts for 20 to 30 percent of the total cooling. The remaining cooling is the result of evaporation of about 1 to 2 percent of the recirculating water. It takes approximately 1,000 BTU to evaporate one pound of water. These BTU are supplied by the main body of water. If this amount of heat is extracted from 1,000 pounds of water, the temperature of the

FIGURE 4-1
TYPICAL COOLING TOWER



recirculating water will drop 1°F. If it is extracted from 100 pounds of water, the water temperature will drop 10°F. This accounts for the remaining 70 to 80 percent of the total cooling. The water lost by evaporation must be replaced. Water also has to be added to replace water lost through tower drift (loss of water from the tower as a fine mist), leaks in the system, and water discharged as blowdown. Water added to the cooling tower to replace all these losses is known as makeup. A simple cooling system is shown in figure 4-2 with makeup water and system losses indicated.

4-5. Relationship between evaporation, blowdown, and makeup. The operation of cooling towers can be described by the relationship between evaporation, blowdown, and makeup. Makeup must equal blowdown plus evaporation to maintain a constant operating level in the system, or:

where: $M = B + E$
 M = makeup water, gallons per day (gpd)
 B = blowdown, gpd
 E = evaporation, gpd

NOTE: Blowdown (B) includes discharge to sewer, drift loss, and consumption in the system.

4-6. Cycles of concentration. A common term used in describing the performance of cooling tower water systems is the cycles of concentration (COC). This term gives the relationship between the makeup water quantity and blowdown quantity.

a. Definition. COC is defined as:

$$C = M \div B$$

where: C = COC, no units
 M = makeup water, gpd
 B = blowdown losses, gpd

b. Measuring COC. Both the makeup and blowdown must be known to determine COC. However, COC can be estimated from the conductivity of the recirculating water and the conductivity of the makeup (note the blowdown will have the same conductivity as the recirculating water). The COC can be estimated using other water characteristics such as chlorides. The relationship is:

$$C = \frac{B_{\mu\text{mho}}}{M_{\mu\text{mho}}} \text{ or } \frac{B_{\text{cl}}}{M_{\text{cl}}}$$

where: C = COC, no units
 $B_{\mu\text{mho}}$ = conductivity of blowdown (recirculating water), micromhos (μmho)
 $M_{\mu\text{mho}}$ = conductivity of makeup water, μmho
 B_{cl} = chlorides in blowdown, ppm
 M_{cl} = chlorides in makeup water, ppm

Example 4-1:

1. The measured conductivity of the blowdown (recirculating water) is 800 micromhos; with the makeup 300 micromhos.
2. The COC is:

$$C = \frac{B_{\mu\text{mho}}}{M_{\mu\text{mho}}}$$

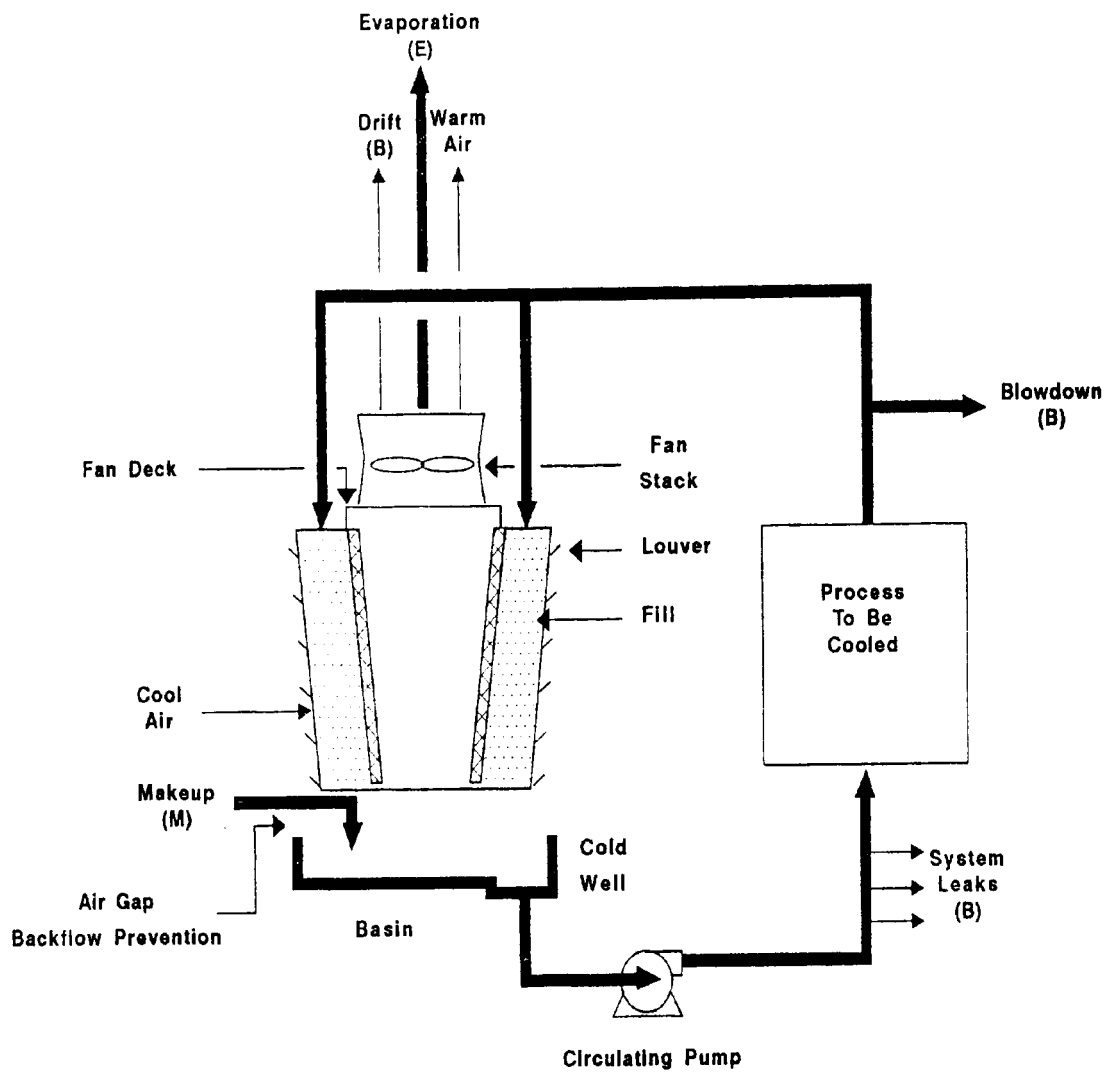
$$C = \frac{800}{300} = 2.67$$

c. Controlling COC. A simple rule sometimes overlooked:

- (1) To increase COC, decrease blowdown.
- (2) To decrease COC, increase blowdown.

d. Relationship between COC and makeup. The COC and makeup requirements are related to the temperature drop across a cooling tower and the recirculating rate of the tower. This is shown in figure 4-3 for a recirculating tower with temperature drops of 10°F, 20°F, and 30°F. The significance of

FIGURE 4-2
SIMPLE COOLING SYSTEM WITH MAKEUP AND LOSSES



these curves is to show that the makeup requirement decreases very rapidly as the COC is increased to about 4 or 5, with lower incremental reductions at higher COC.

4-7. Relationship between blowdown, evaporation, and cycles of concentration.

The cooling water evaporation loss is used to calculate the blowdown rate that needs to be maintained in order to operate at a desired COC.

a. The relationship between blowdown, evaporation, and COC is as follows:

$$B = E \div (C - 1)$$

where: B = blowdown, gpd (or gpm)
E = evaporation, gpd (or gpm)
C = COC, no units

b. This formula is derived as follows:

- | | |
|--------------------------|--------------------------|
| (1) $M = B + E$ | from paragraph 4-5 |
| (2) $C = M \div B$ | from paragraph 4-6a |
| (3) $C = (B + E) \div B$ | from equation (1) |
| (4) $C = 1 + (E \div B)$ | rearranging equation (3) |
| (5) $(C - 1) = E \div B$ | rearranging equation (4) |
| (6) $B = E \div (C - 1)$ | rearranging equation (5) |

c. If evaporation is known, the blowdown required for a given COC can be calculated. The evaporation can be estimated using simple rule of thumb estimates:

(1) For a typical recirculating water system, approximately 1 percent of the cooling water is evaporated for every 10°F temperature drop in the cooling water as it passes through the tower.

$$E = 0.01 \times \text{recirculating rate} \times \text{T-drop } ^\circ\text{F} \div 10^\circ\text{F}$$

Example 4-2:

1. A cooling system operates at 5,000 gpm. The temperature drop through the tower is 14°F.
2. The evaporation estimate is:

$$E = 0.01 \times 5,000 \text{ gpm} \times 14^\circ\text{F} \div 10^\circ\text{F} = 70 \text{ gpm}$$

(2) For an air conditioner cooling tower, the evaporation rate is approximately:

(a) One and one-half (1.5) gallons per hour per ton (gal/hr/ton) for centrifugal or reciprocating air conditioners.

(b) Three (3) gal/hr/ton for an absorption air conditioners.

Section III Deposit Formation & Control

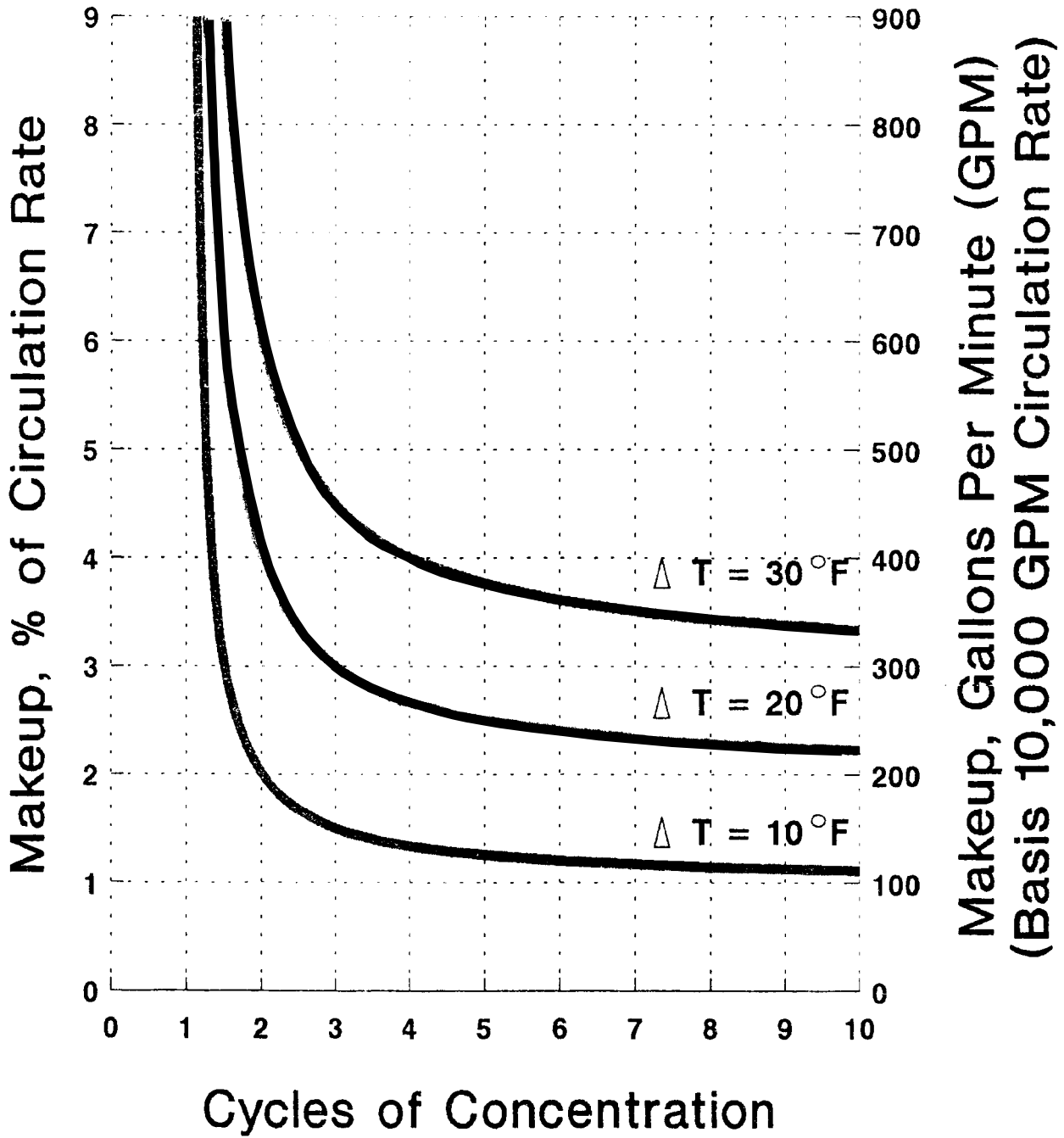
4-8. **Types of deposits.** Deposit problems are usually divided into two categories - scale and fouling. Deposits of both types interfere with heat transfer in the heat exchanges, thereby reducing their efficiency.

4-9. **Causes of scale.** Scale is the deposition on heat transfer surfaces and in flow lines of material normally in solution in water. As water is evaporated in a cooling tower, the dissolved solids concentration becomes greater until the solubility of a particular salt is exceeded. When this happens in an untreated cooling water system the salt will crystallize on any surface in contact with the water, especially on heat transfer surfaces.

a. The most common scaling materials are calcium phosphate, calcium carbonate, calcium sulfate, and silica, not necessarily in that order. Magnesium silicate scale is also possible under certain conditions. Most salts, including silica, are more soluble in hot water than in cold. However, most calcium salts, including calcium phosphate, calcium sulfate, and calcium carbonate, are more soluble in cold water than in hot. The water temperature will increase as recirculating water passes through the cooling system. As a result scale may form anywhere in the system, but most likely on heat exchanger surfaces.

b. The concentration of salts in the makeup

FIGURE 4-3
EFFECT OF CYCLES OF CONCENTRATION ON MAKEUP REQUIREMENT



water can be measured. Also, it is possible to calculate the evaporation in the system. By selecting an upper limit for the concentration of solids in the system (as reflected by conductivity), it is possible to calculate the optimum COC of an untreated system. Blowdown then can be estimated to maintain this level using the relationship between COC, evaporation, and blowdown.

4-10. Determining scaling limits. The upper limit for dissolved solids to prevent scaling in an untreated system must be set based on the types of scales that can form. The amounts of dissolved materials should be maintained as close to this level as possible in order to minimize the system blowdown. This is controlled by maintaining the COC in the system at a level that is equal to the lowest COC allowable for any one of the salts. The operating COC can be increased with proper cooling water treatment.

a. Calcium carbonate COC. The prediction of calcium carbonate scale depends on the alkalinity and calcium hardness of the makeup.

$$C \equiv \sqrt{\frac{110000}{TA \times M_{ca}}}$$

where: C = COC
TA = total (M) alkalinity (as CaCO₃) in makeup, ppm
M_{ca} = calcium hardness (as CaCO₃) in makeup, ppm

b. Calcium phosphate COC. When greater than 5 ppm of orthophosphate are present in the circulating water, the COC at which calcium phosphate scale will form can be calculated:

$$C \equiv \frac{(105) \times (9.8 - B_{pH})}{M_{ca}}$$

where: C = COC, no units

B_{pH} = measured pH in blowdown, pH units
M_{ca} = calcium hardness (as CaCO₃) in makeup, ppm

c. Calcium sulfate COC. The COC at which calcium sulfate scale will form can be calculated:

$$C \equiv \sqrt{\frac{1250000}{M_{ca} \times M_{su}}}$$

where: C = COC, no units
M_{ca} = calcium hardness (as CaCO₃) in makeup, ppm
M_{su} = sulfate (as SO₄) in makeup, ppm

d. Silica COC. The solubility of silica is about 150 ppm at the temperature range encountered in most cooling towers. The allowable COC is:

$$C \equiv \frac{150}{M_{si}}$$

where: C = COC, no units
150 = solubility of silica, ppm
M_{si} = silica (as SiO₂) in the makeup, ppm

e. Determining the COC that control operation. In untreated systems the smallest calculated COC, using the relationships for these salts, is the controlling factor. This is due to the fact that, as the system operates, the material that has the lowest calculated COC will be the first to come out of solution, and therefore, is the most likely to form a scale deposit in the system. The COC in the system must be kept at a level that is lower than the smallest COC calculated for calcium carbonate, calcium phosphate, calcium sulfate, and silica to prevent these materials from forming a deposit.

Example 4-3:

1. A cooling tower makeup has the following composition:

Calcium Hardness 100 ppm
Total (M) Alkalinity 60 ppm
Sulfate 60 ppm
Silica 14 ppm

At what COC can the system operate without water treatment?

2. Based on calcium carbonate:

$$COC = \sqrt{\frac{110000}{60 \times 100}} = 4.3$$

3. Based on calcium sulfate:

$$COC = \sqrt{\frac{1250000}{100 \times 60}} = 14.4$$

4. Based on silica:

$$COC = 150 \div 14 = 10.7$$

5. The COC determined for calcium carbonate is lowest at 4.3, and this therefore controls the system operation. Scaling should not occur provided the system is operated without water treatment at less than 4.3 COC. Use of a phosphonate or a polymeric antiscalant will increase the number of allowable COC for calcium carbonate. The COC and hence the blowdown will then be determined by a calculated "scaling index".

4-11. Use of scaling indices. The most common scale found in cooling tower systems is calcium carbonate in the form of calcite. The solubility of calcium carbonate, which decreases with an increase in temperature, is a complex function of temperature, total dissolved solids (TDS), calcium hardness, total alkalinity, and pH. To predict if scale would

form in the hotter sections of a cooling water system, researchers have over the years developed scaling indices.

a. Langelier and Ryznar indices. W.F. Langelier derived a method to calculate the calcium carbonate scale-forming or scale-dissolving tendency of a water. The method is based on determining the saturation pH (pH_s), the pH at which calcium carbonate will start to come out of solution. If the measured pH of the water is greater than its pH_s , the water has a scale-forming tendency; if it is less than its pH_s , it has a scale-dissolving tendency. The formula pH minus pH_s is known as the Langelier Index or Langelier Saturation Index (LSI). A positive value indicates a scale-forming tendency. A negative value indicates a scale-dissolving tendency. J.W. Ryznar later devised a more sensitive formula, $2pH_s - pH$, known as the Ryznar Index or the Ryznar Stability Index (RSI). A value of 6 indicates a stable water. A value less than 6 indicates a scale-forming tendency and greater than 6 indicates a scale-dissolving tendency. The indices have also been used to try to estimate the degree to which calcium carbonate will form. The more positive the LSI, the greater the scale formation. For the RSI, however, the smaller the index, the greater the scale formation. In some cases, the LSI and RSI can give conflicting predictions with the same water.

b. Practical (Puckorius) scaling index. Paul R. Puckorius and J. Maxey Brooke developed a modified version of the RSI to give a better and more consistent indication of scaling conditions of cooling water. Known as the Practical Scaling Index (PSI), it takes into consideration the effect that the total alkalinity of the cooling water has on the measured pH value. Since pH is often buffered by other ions, it does not always relate correctly to

bicarbonate alkalinity. Rather than using the measured pH in calculating the PSI, an adjusted or equilibrium pH (pH_{eq}) is used: $PSI = 2pH_s - pH_{eq}$. As with the RSI, a PSI of 6 indicates a stable water and a value lower than 6 indicates a scale-forming tendency. Without the use of a scale control treatment, a cooling tower with a PSI of 6 to 7 should operate scale free. However, a PSI of greater than 6 indicates that corrosion may occur. Information on calculating the PSI is provided in appendix B.

4-12. Scale control. There are three basic methods for preventing the formation of scale in cooling water systems:

- 1) Remove the scaling material from the water prior to use,
- 2) Keep the scale-forming materials in solution, and
- 3) Allow the scaling material to precipitate as a removable sludge, rather than as hard deposits.

All three methods are authorized for use on Army installations. Inhibition of calcium scales, those most common in cooling tower systems, can be achieved by lowering the pH of the recirculating water (with the addition of acid), or by the addition of a calcium scale inhibitor (HEDP or AMP) which allows the PSI to be carried at a lower value (higher COC) without scaling occurring, or both. Because of the hazards associated with handling strong acids and the potential damage from an acid spill, the use of acid in cooling towers is not recommended. If the characteristics of a water at a specific location indicate the need to use acid, contact USACPW (CECPW-ES) at Fort Belvoir, Virginia, for guidance.

a. Calcium carbonate control. Calcium carbonate normally results from the

breakdown of calcium bicarbonate, a naturally occurring soluble salt. The degree of scaling depends primarily on the levels of calcium hardness and bicarbonate alkalinity in the cooling water. The breakdown of calcium bicarbonate increases with temperature. Two phosphonates most frequently used for calcium carbonate control in recirculating cooling tower systems are AMP (Aminotri methylenephosphonic acid) and HEDP (1-Hydroxyethylidene 1,1-Diphosphonic acid). The chemical reaction of both are similar, however, HEDP is more stable at chlorine levels normally found in cooling towers. The use of 3 to 5 ppm HEDP will increase the solubility of calcium carbonate by a factor of three. Rather than operating at a PSI of 6.0 as in an untreated system, the cooling tower will be able to operate at a PSI of 4.0 without potential scaling (refer to paragraph 4-11 and appendix B). However, the use of HEDP in the absence of calcium and magnesium hardness (or at very low levels), can increase the corrosion of both mild steel and copper.

b. Calcium phosphate control. Calcium phosphate scale is common in cooling water systems treated with a phosphate-based corrosion inhibitor program. Calcium phosphate is also less soluble at higher pH and temperatures. If the calcium hardness is 500 ppm and the pH is above 7.0, it is likely to cause scaling even at the low level of 5 ppm phosphate. Calcium phosphate solubility can be increased by a factor of a little less than three with the addition of 4 ppm phosphonate (HEDP).

c. Calcium sulfate control. Calcium sulfate results from high concentrations of calcium and sulfate ions in the recirculating water. Calcium sulfate is the most soluble of the scale-forming calcium salts found in cooling towers (calcium chloride is extremely

soluble). This means that calcium sulfate scale will not form unless some calcium hardness remains after it reacts with all the carbonate in the water. Still, calcium sulfate scale may occur when the recirculating water contains calcium hardness in the range of 300 to 500 ppm as CaCO_3 and sulfate in the range of 500 to 700 ppm SO_4 . The addition of 3 to 5 ppm of a phosphonate (HEDP) or other appropriate calcium inhibitors will allow almost three times the level of calcium sulfate to remain in solution.

d. Magnesium silicate control. Formation of magnesium silicate is possible under certain conditions. Magnesium first reacts with hydroxyl ions (OH^-) to form magnesium hydroxide, which then reacts with dissolved or colloidal silica to form magnesium silicate. Since silica solubility increases with temperature, this scale will usually form in the coldest portion of the system.

e. Silica control. Nothing can be done to increase the solubility of silica above 150 ppm. Since silica is more soluble in hot water than in cold water, it will first deposit on the cooling tower slats rather than in the heat exchanger. The slats will become coated with a white, sometimes sparkling deposit. If this occurs, increase blowdown, which decreases cycles of concentration. This should stop additional scale formation. If the concentration of silica in the makeup water is above 30 ppm, it usually controls the operation of the system (maximum 5 COC). If it is too high for efficient cooling tower operation, it can be reduced in or removed from the makeup water by treatment (chapter 2).

4-13. Causes of fouling. Fouling is the deposition, usually on heat transfer surfaces, of materials normally in suspension. Such materials include silt and other suspended solids brought into the system with the

makeup water; dust and pollen scrubbed out of the air passing through the tower; product leakage; corrosion products; and both living and dead microbiological materials.

Slime-producing organisms can be particularly serious as a source of fouling. They can multiply and grow until they completely plug a heat exchanger in a matter of days if conditions are favorable for the organisms.

4-14. Fouling control. Fouling by nonliving matter can be controlled by the addition of a dispersant such as polyacrylate. The addition of about 4 ppm will keep foulants in suspension and prevent them from depositing on heat transfer surfaces. Prevention of fouling by living matter is discussed in paragraph 4-16.

Section IV

Microbiological Deposits And Control

4-15. General information.

Microbiological problems are generally referred to as slime deposits. They result from the presence of microorganisms such as algae, bacteria, and fungi. These can grow within a cooling system, coating all pipe and heat exchanger surfaces. The gelatinous slimes produced by many microorganisms can trap sediments, thus encouraging fouling and scale. Even corrosion can be caused by certain organisms that produce corrosive byproducts.

a. Algae: Tiny green plants, usually found growing in masses on top and on sides of cooling towers. They are not harmful until they die. Then they will slough off, become part of the suspended matter in the circulating water, and may cause fouling. Algae also may provide a breeding place for bacteria.

b. Bacteria: Microscopic one-celled organisms. Most bacteria are suspended in the cooling water and do not harm the cooling

system. However, some can cause fouling and corrosion.

(1) **Slime-forming bacteria:** Bacteria that can grow in colonies on almost any surface covered by the water. These slime colonies can grow so large that they can restrict water flow and heat transfer. They also may promote corrosion. The presence of slime-formers can be tested by feeling inside the cooling tower just below the water level. If there is slime in the system, it can usually be felt there.

(2) **Sulfide-producing bacteria:** Bacteria that can grow under slime masses. They can produce hydrogen sulfide which is very corrosive. They may be detected in a system where the underside of the slime layer is a metallic black color, or the odor of rotten eggs is present.

c. Fungi: Microscopic plants that do not require sunlight. They can attack wood in cooling towers. Their control requires special treatment of the wood, usually before the construction of the tower. Their control in an operating system requires special techniques.

4-16. Microbiological control. Chemical treatment is the method used on Army installations for microbiological control. Biocides used to control microbiological growth fall into two broad categories - oxidizing and nonoxidizing. The choice between these two depends on various factors. A major consideration is limitation on discharge of toxic substances. Also, operating parameters of the cooling tower, such as temperature, pH, and system design, must be considered in a decision involving oxidizing and nonoxidizing biocides. Control programs aim for 99 percent reduction of organism populations. This is done by using one or more biocides, sometimes including the combination of both oxidizing and

nonoxidizing biocides. The use of oxidizing biocides requires careful control of their addition to cooling water. If this cannot be assured, it may be best to eliminate their use to avoid problems, such as delignification of wood. Besides being capable of killing a large percentage of microorganisms, the selection of biocides must also consider cost. The primary factor affecting cost is the frequency of application to provide the desired control. Normal slug dosage should be applied an average of one to three times a week, unless fouling is particularly severe. The most important aspect of biofouling control is to match the biocide to the problem organism.

a. Algae control. Algae can be controlled by preventing their growth or by destroying the plants that have grown.

(1) Algae need light to survive because they are plants. They often can be kept under control by covering the upper decks of the towers.

(2) Calcium hypochlorite sprinkled on the upper deck will kill algae. However, it will add calcium to the circulating water increasing the possibility of scale and could attack the wood.

b. Bacteria control.

(1) **Bacteria control with chlorine:** Chlorine is the most familiar and effective industrial biocide. When chlorine gas is introduced to water, it hydrolyses to form hydrochloric and hypochlorous acid. It is the latter that is an oxidizing biocide, provided there is little or no deionization. The hypochlorous acid state is favored by low pH. At a pH of 5.0, there is very little ionization; at a pH of 7.5 there are approximately equal amounts of hypochlorous acid and the ion. Chlorine is less effective as a biocide at pH of 9.5 or greater, because of the total lack of ionization. Generally, a pH range of 6.5 to 7.5 is considered practical for chlorine, or chlorine

based microbial-control programs, since a lower pH would increase system corrosion. Because of safety concerns when handling gaseous chlorine, controlling the feed of the gas, and the increasing concern for the environmental effects of escaping residual chlorine, gaseous chlorine is seldom used on Army installations for treating cooling towers.

(2) Alternatives to chlorine: Some of the many biocides available, other than chlorine, are listed in table 4-1. Selection of a biocide (or combination of biocides) should be based on the chemical treatment program used and on local factors. This may include biocides that are not on the list in table 4-1, provided they are approved by the installation environmental engineer.

c. Ozone (O₃). Ozone is a very strong oxidizing biocide which would provide effective control of microorganisms in cooling tower systems, if properly applied. However, because of safety and operational problems associated with its manufacture and use, and the resulting high cost, it is not an economical method for microbiological control in cooling towers. Unsubstantiated claims have been made that ozone provides total protection against scale, fouling and microbiological problems in cooling towers. Its use on Army installations is not authorized (refer to paragraph 4-26).

4-17. Legionnaires' disease.

Legionnaires' Disease (Legionellosis) is a respiratory disease (atypical pneumonia) which strikes certain individuals exposed to a mist of water laden with the bacteria *Legionella Pneumophila*. There is a possibility that a cooling tower at an Army installation could become infected with the bacteria. The presence and density of *Legionella Pneumophila* cannot be detected with normal microbiological testing done at installation

level. Samples need to be sent to a laboratory with the capability to conduct such tests. If infection of a tower is suspected, the installation's medical officer will identify the need and procedures to disinfect the cooling tower. A typical procedure is to add a gallon of chlorine release agent (sodium hypochlorite) and a pound of trisodium phosphate (or a nonfoaming household detergent) to the cooling tower sump for every 100-ton capacity. This should be done every 2 days for a total of 6 days.

Section V

Corrosion In Cooling Systems

4-18. Definition of corrosion.

Corrosion is the deterioration of a metal that may occur because it is in contact with the cooling tower water. The corrosion occurs when an electric current flows from one part of the metal (anode) through the water (electrolyte) to another part of the metal (cathode). Corrosion takes place where the current leaves the metal (at the anode). Forms of corrosion associated with industrial water systems are illustrated in figure 4-4.

a. Galvanic corrosion. When two different metals are coupled together the metal higher on the galvanic series becomes the anode and will corrode. In the case of steel and copper, for example, the steel becomes the anode and corrodes. If steel and zinc are coupled together at temperatures normally found in cooling tower systems, the zinc becomes the anode and corrodes. One of the most common causes of galvanic corrosion found in cooling water systems is the combination of steel and copper alloy metals in contact with each other. Dissolved copper resulting from copper corrosion can plate out on steel surfaces setting up a galvanic cell. Pitting corrosion is the result. Since it is

TABLE 4-1
BIOCIDES FOR COOLING TOWERS

Appendix F Reference No.	Biocide
3.	Methylenebis (thiocyanate)
4.	2,2-Dibromo-3-nitrilopropionamide
5.	Dodecylguanidine hydrochloride plus Bis(tri-n-butyltin)oxide
6.	n-Alkyldimethylbenzylammonium chloride plus Bis(tri-n-butyltin)oxide
7.	Poly[oxyethylene(dimethyliminio)ethylene- (dimethyliminio)ethylene dichloride]
8.	Disodium cyanodithioimidocarbonate plus potassium n-methyldithiocarbamate
9.	1-Bromo-3-chloro-5,5-dimethylhydantoin

- NOTES: (1) Biocides 3, 4, and 5 in table 4-1 are liquids and can be used in cooling towers where the water pH is less than 7.5. Biocides 6, 7, and 8 are liquids that can be used in cooling towers where the pH is greater than 7.5. Biocide 6 may cause foaming but it is usually not serious. Biocide 8 can be corrosive to copper alloys unless a copper corrosion inhibitor is used. All biocides listed in table 4-1 are nonoxidizing except number 9.
- (2) Biocide 9 in table 4-1 is a solid that comes in granular, stick and briquette form and is so slow dissolving that it can be used in a bypass feeder or hung in a nylon net bag in the cooling tower sump. It can be used at all pH levels and is especially useful in small or remote towers.
- (3) To be effective it is very important to follow the manufacturer's application instructions. It is a good idea to keep two different biocides on hand and alternate their use on a regular basis.

difficult to protect the steel from the plating action, it is necessary to treat the copper to keep it from corroding.

b. Crevice corrosion. A crevice can exist at many locations in a cooling tower, such as at the contact point of two steel plates bolted together. Flow is restricted in a crevice, and as a result, oxygen is consumed faster than it can be replenished. The metal in the crevice then becomes the anode and corrodes. This is a form of concentration cell corrosion.

c. Deposit corrosion. The underside of a deposit caused by fouling, bacterial slime, or even debris acts in much the same way as the inside of a crevice. The metal under the deposit may become anodic and corrode. This is another form of concentration cell corrosion.

d. General corrosion. Even a single piece of steel will have cathodic and anodic areas due to differences in impurities and stresses. Further, a cathodic area will periodically change to anodic and vice versa, causing the steel to corrode at a more or less uniform rate.

4-19. Corrosion rates. Corrosion rates are measured in mils per year (mpy). A mil is one-thousandth of an inch. An assessment of corrosion rates in cooling water systems is provided in table 4-2. Some factors that can cause an increase in corrosion rates and their potential for control by the water system operator are shown in table 4-3.

4-20. Methods of corrosion control:

a. Galvanic and crevice corrosion. Galvanic and crevice corrosion are design problems and cannot be entirely eliminated by the water system operator. However, a properly operated water treatment program will help reduce these types of corrosion.

b. Deposit corrosion. Deposit corrosion is controlled by keeping the system clean. Fouling is prevented by the use of dispersants

as discussed under deposit control. Bacterial slime is prevented by the use of biocides as discussed under microbiological control. Debris can be kept out of the system by the use of screens in the cooling tower sump.

c. General corrosion. General corrosion is controlled by the use of inhibitors. These are chemicals which form a film on the cooling tower metal. The film must be thick enough to insulate the metal from the water to prevent the current flow, but thin enough not to significantly interfere with the heat transfer through the metal.

(1) Anodic inhibitors such as orthophosphate, nitrite, molybdate, and silicates coat the anode and directly control corrosion by preventing the reaction that results in corrosion. Cathodic inhibitors such as zinc, polyphosphates, and polysilicates, coat the cathode and indirectly prevent corrosion by interfering with the link required between the cathode and anode.

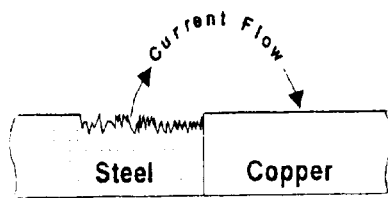
(2) Using only an anodic inhibitor will not give complete protection from corrosion because inhibitors do not always give 100 percent coverage. The unprotected areas will corrode at a much faster rate than the larger areas, resulting in pitting attack.

(3) The best way to control general corrosion is to add both a cathodic and an anodic inhibitor.

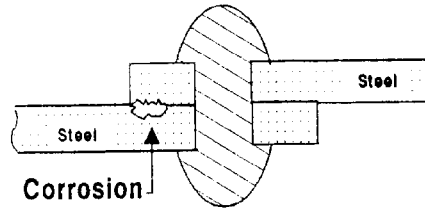
d. Special corrosion control for copper and copper alloys. The protection of copper and copper alloys requires the use of tolyltriazole (TT), which can be added to the system separately or in a blend of other treatment chemicals. The recommended application rate is 0.1 pound per day per 100 ton capacity of the tower.

Section VI Putting It All Together

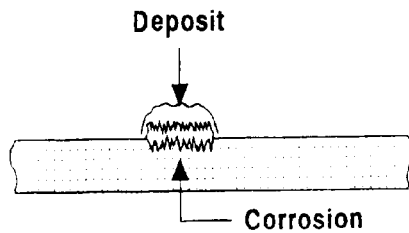
**FIGURE 4-4
FORMS OF CORROSION**



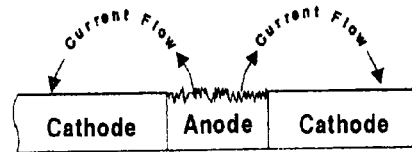
(A) Galvanic Corrosion



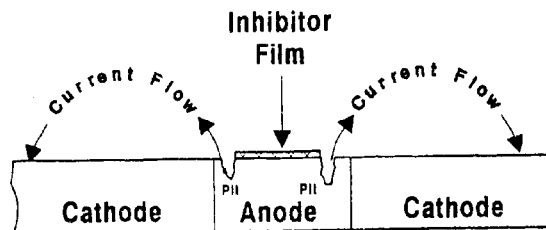
(B) Crevice Corrosion



(C) Deposit Corrosion



(D) General Corrosion



(E) Pitting Attack

TABLE 4-2
ASSESSING CORROSION IN COOLING WATER SYSTEMS

METAL	MPY	COMMENTS
Mild Steel Piping in Open Systems	<1 1 to 3 3 to 5 5 to 10 >10	Excellent Good Fair Poor Unacceptable
Mild Steel Heat Exchanger Tubing in Open Systems and Piping in Closed Systems	<0.2 0.2 to 0.5 0.5 to 1.0 >1.0	Excellent Good Fair Unacceptable
Copper and Copper Alloys	<0.1 0.1 to 0.2 0.2 to 0.3 0.3 to 0.5 >0.5	Excellent Good Fair Poor Unacceptable
Stainless Steel	<0.1 >0.1	Acceptable Unacceptable

TABLE 4-3
FACTORS AFFECTING CORROSION IN COOLING TOWERS

FACTOR	POTENTIAL FOR OPERATOR CONTROL
Temperature increase	Very limited-design factor
Flow rate increase	Very limited-design factor
Dissolved O ₂ increase	Very limited-design factor
Increase in foulants	Possible-water treatment program
Use of wrong inhibitor	Possible-water treatment program
Decrease in inhibitor content	Possible-water treatment program

NOTE: The control of foulants may require dispersants. Inhibitor selection is addressed in paragraph 4-20c.

4-21. General information. A complete treatment program for cooling water may need to include treatment of the makeup water and for the recirculating water.

a. Treatment of makeup water. It is normal practice to use water from the installation supply for cooling tower makeup without additional treatment. There are special conditions where the treatment of makeup might be warranted, such as high levels of iron, hardness, silica, or dissolved solids. Makeup treatment should be used when such treatment will significantly reduce the cost of internal treatment, or when improved protection of the system warrants the cost. However, in general, there will not be an advantage to using treated water if the COC that can be carried by the system using untreated water is calculated to be greater than three.

b. Treatment of recirculating water. Treatment programs for cooling tower recirculating water can be divided into two basic categories; small towers (less than 25 ton capacity) and larger ones, e.g., medium size towers (25 to 100 ton) and large size towers (greater than 100 ton). In addition to controlling scale by adjusting the cycles of concentration through blowdown (covered in paragraph 4-22), recirculating water in these towers generally needs chemical treatment for control of scale formation, fouling, corrosion, and microbiological growth. Treatment chemicals and methods are individually covered in previous sections. Complete chemical programs are covered in paragraphs 4-23 and 4-24.

4-22. Scale control by adjusting COC. The COC of small, medium, and large cooling towers may be controlled by blowdown to avoid high levels of silica and calcium salts that

can lead to their precipitation. This is done by monitoring the blowdown and makeup conductivity to maintain the tower at a COC less than the smallest allowable COC for these materials (paragraph 4-10). This technique of scale control applies to both treated and untreated towers. The difference is that rather than operating an untreated tower at a PSI of 6.0, for example, it would be possible to operate the tower at a PSI of 4.0 (with a corresponding higher COC), if properly treated.

4-23. Treatment program for small cooling towers. A small cooling tower at an Army installation typically will have a rating of less than 25 tons. The treatment used for small towers also may be applied to isolated medium towers that must operate with very little operator control.

a. Treatment. Small systems can be treated by placing a nylon mesh bag containing about 15 to 20 pounds of a slowly soluble phosphate chemical in the cooling tower sump. If microbiological problems exist, a biocide such as item 9 in table 4-1 may be added.

b. Testing. The bag with chemical treatment should be checked weekly to ensure that chemical remains available. The frequency for replacing the bag will vary, but 1 to 2 months is typical.

4-24. Treatment programs for medium and large cooling towers. The chemical treatment program for a large tower (typically greater than 100 tons) should include control of scale, fouling, microbiological growth, and corrosion. The treatment program for a medium tower (25 to 100 tons) should include these controls where possible, or the treatment procedures in paragraph 4-23 for isolated systems. The optimum chemical treatment

program for cooling towers on an Army installation depends on the quality of water available, operating conditions of the tower and the environmental constraints placed on zinc and other treatment chemicals in the blowdown. Three treatment programs found to be effective for typical cooling tower conditions are provided below. These treatment programs provide for scale control, fouling control, and corrosion control (both ferrous metals and copper alloys). The cooling towers will also most probably need biocides for microbiological control (refer to section IV of this chapter). Conditions at a particular Army installation may require variation in the quantity or mix of the chemicals prescribed.

a. Zinc-Phosphonate program. This program can be used when zinc is allowed in the blowdown. It is best to limit the hardness of the makeup water to 140 ppm (as CaCO_3) and the COC to about 3, although the program will still provide some protection with higher hardness makeup water. Keeping the pH of the system below 8.0 will help prevent formation of zinc hydroxide. The program will still be effective at a higher pH but may require

more zinc. Operating limits and approximate amounts of chemicals required to maintain these limits are shown in Table 4-4:

b. Zinc-Molybdate program. This program can be used when zinc is allowed in the blowdown. Keeping the pH below 8.0 will help prevent formation of zinc hydroxide. However, the program will still be effective at a higher pH but may require more zinc. Zinc-stabilizing polymers may also be used. Operating limits and approximate amounts of chemical required to maintain these limits are shown in Table 4-5:

c. Phosphonate-Polymer program. This program can be used where zinc, molybdate or other heavy metals are not allowed for environmental reasons. Keep the pH for this program between 7.5 and 8.5 for best results. Operating limits are approximate amounts of chemicals required to maintain these limits are shown in Table 4-6:

d. Specifications. Treatment chemical specifications for these programs are provided in table 4-7.

TABLE 4-4
DOSAGES FOR ZINC-PHOSPHONATE PROGRAM

Limits	Estimated Chemical Requirement Pounds Per Day Per 100 Ton Tower Capacity at 3 COC & 10°F t
3-5 ppm phosphonate	0.1 HEDP
1-2 ppm zinc (as Zn)	0.1 zinc sulfate
3-4 ppm polymer	0.1 polyacrylate
1-2 ppm TT	0.1 tolyltriazole

TABLE 4-5
DOSAGES FOR ZINC-MOLYBDATE PROGRAM

Limits	Estimated Chemical Requirement Pounds Per Day Per 100 Ton Tower Capacity at 3 COC & 10°F t
10-15 ppm molybdate as Mo	0.9 sodium molybdate as $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
2-3 ppm zinc (as Zn)	0.1 zinc sulfate
2-3 ppm phosphonate	0.1 HEDP
3-4 ppm polymer	0.1 polyacrylate
1-2 ppm TT	0.1 tolyltriazole

TABLE 4-6
DOSAGES FOR PHOSPHONATE-POLYMER PROGRAM

Limits	Estimated Chemical Requirement Pounds Per Day Per 100 Ton Tower Capacity at 3 COC and 10°F t
3-5 ppm phosphonate	0.1 HEDP
3-4 ppm polymer	0.1 polyacrylate
1-2 ppm TT	0.1 tolyltriazole

TABLE 4-7
TREATMENT CHEMICALS FOR COOLING TOWERS

Inhibitor	Chemical Name
Phosphonate	HEDP (1-hydroxyethylidene 1,1-diphosphonic acid), 60% active
Phosphate	Slowly soluble polyphosphate, glassy plate or lump
Polymer	Sodium polyacrylate or polyacrylic acid, molecular weight 2000-4000, 50% active
Tolyltriazole	Sodium tollyltriazole, 43% active as TT
Zinc	Zinc sulfate, $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
Molybdate	Sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$

e. Potential problems. The three treatment programs specified above use calcium scale inhibitors to solubilize calcium salts in cooling water systems. The operator should be aware that severe scaling will occur rapidly, almost instantaneously, should these chemicals be lost from the cooling water. Continuous and uniform feed is essential.

4-25. Treatment chemical calculations:

a. Determining amount of chemicals required. The calculation of blowdown, makeup, evaporation, and COC (covered in section II of this chapter) is important in estimating water use and treatment chemical requirements.

(1) Chemical Requirements: Chemical requirement can be estimated based on:

(a) The desired level in the cooling system.

(b) The sum of chemical loss in the blowdown, chemical consumed by reaction, and other losses in the system. The key factor

in operating the system is that the chemical added must equal chemical loss:

$$\begin{aligned} \text{where: Treatment} &= \text{Loss} \\ \text{Treatment} &= \text{chemical added, pounds per day (lb/day)} \\ \text{Loss} &= \text{chemical loss, lb/day (lb/day chemical in} \\ &\quad \text{blowdown + lb/day reacted + lb/day other} \\ &\quad \text{losses)} \end{aligned}$$

(c) In practice, the reaction losses and other losses are determined by experience with the system. The chemical addition calculated from blowdown losses is increased gradually by an amount that will replace these other losses.

(2) Blowdown Loss: The blowdown loss can easily be calculated as follows:

$$\begin{aligned} \text{where: Blowdown Loss} &= \text{B} \times \text{Level} \times \text{Conversion Factor} \\ \text{Blowdown Loss} &= \text{chemical in blowdown, lb/day} \\ \text{B} &= \text{blowdown, gallons per minute (gpm)} \\ \text{Level} &= \text{concentration of chemical in blowdown, ppm} \\ \text{Conversion Factor} &= 8.33 \text{ pounds per gallon (lb/gal)} \times 1,440 \\ &\quad \text{minutes per day (min/day)} \div \\ &\quad 1,000,000 \text{ gal} \\ &= 0.012 \end{aligned}$$

Example 4-4:

1. A cooling tower with 5,000 gpm recirculation has an 8°F temperature drop. The conductivity of the blowdown (recirculating water) is 1,200 micromhos and that of the makeup water is 300
2. Determine the evaporation in the system (paragraph 4-7c).

$$E = 0.01 \times \text{recirculating rate} \times (T \text{ drop } ^\circ\text{F}) \div 10^\circ\text{F} \\ = 0.01 \times 5,000 \text{ gpm} \times 8^\circ\text{F} \div 10^\circ\text{F} = 40 \text{ gpm}$$

3. Determine COC in the system using the conductivity data (paragraph 4-6b).

$$\text{COC} = \frac{B_{\mu\text{mho}}}{M_{\mu\text{mho}}} = \frac{1200}{300} = 4.0$$

4. Estimate system blowdown, based on COC and evaporation (paragraph 4-7a).

$$B = E \div (C - 1) = 40 \text{ gpm} \div (4 - 1) = 13.3 \text{ gpm}$$

5. Determine makeup water (paragraph 4-5).

$$M = B + E = 40 \text{ gpm} + 13.3 \text{ gpm} = 53.3 \text{ gpm}$$

6. Determine treatment chemical required. The chemical added to the system must equal the chemical lost in the blowdown. The calculated chemical level might need to be increased in practice to account for chemical reaction and other losses, until the desired level is reached.

$$\text{Blowdown} = \text{Loss} \times \text{Level} \times \text{Conversion Factor} \\ = 13.3 \text{ gpm} \times 100 \text{ ppm} \times 0.012 \\ = 16.0 \text{ lb/day}$$

b. Feeding treatment chemicals. The individual chemicals identified in the three treatment programs (paragraph 4-24) may be mixed in the proper proportions and added as a blend (mixture), preferably with a continuous feed system. The cooling tower will probably

micromhos. It is desired to maintain 100 ppm treatment in the system. What is the required blowdown? What will be the makeup? How much chemical must be added each day?

also need biocides (refer to section IV of this chapter).

Example 4-5:

1. A cooling tower is treated with program (1): 5 ppm phosphonate (HEDP), 2 ppm zinc, 4 ppm polyacrylate, and 2 ppm tolyltriazole.
2. For a 100 ton tower this requires:

HEDP	0.1 lb/day (approximately)
Zinc Sulfate	0.1 lb/day (approximately)
Polyacrylate	0.1 lb/day (approximately)
Tolyltriazole	0.1 lb/day (approximately)

These components are sold in various solution strengths. Later adjustments in quantities may be necessary.

3. The proper mixture concentrations (percent by weight) are:

$$\text{HEDP \%} = \frac{\text{lbs}}{\text{lbs total}} \times 100 \\ = \frac{0.1}{0.1+0.1+0.1+0.1} \times 100 \\ = \frac{0.1}{0.4} \times 100 = 25\%$$

$$\text{Zinc Sulfate} = \frac{0.1}{0.4} \times 100 = 25\%$$

$$\text{Polyacrylate} = \frac{0.1}{0.4} \times 100 = 25\%$$

$$\text{Tolyltriazole} = \frac{0.1}{0.4} \times 100 = 25\%$$

4. Cooling towers on Army installations are normally fed continuously from a 55 gallon drum or tank. To prepare a 3 percent chemical solution add the following to fifty gallons (416.5 pounds) of water:

3% x 416.5 = 12.50 total pounds of chemicals consisting of:

25% x 12.5 = 3.1 pounds HEDP
25% x 12.5 = 3.1 pounds Zinc Sulfate
25% x 12.5 = 3.1 pounds Polyacrylate
25% x 12.5 = 3.1 pounds Tolyltriazole

5. The blend is fed initially at 0.3 lb/day for each 100 ton capacity of a cooling tower operating at 3 COC.
6. Adjust the feed rate of the mixture to maintain the recommended levels. When any of the recommended levels cannot be maintained within 10 percent of the target level with the mixture, consider the use of a different mixture.
7. Add appropriate biocides for microbiological control (refer to section IV of this chapter).

4-26. Use of ozone (O₃) in cooling towers:

a. Ozone, a strong oxidizing agent, is an unstable form of oxygen in which three oxygen atoms are combined to form an ozone molecule, O₃. It has had limited use since the early 1900's as a disinfectant for municipal water supplies. The first significant use of zone for treatment of cooling towers was done in 1976 by the Jet Propulsion Laboratory in California. Test results alleged the ozone not only was an effective biocide but also effective in removing scale and maintaining a clean system.

b. Because ozone is an unstable molecule quickly reverting to oxygen (O₂), it (ozone) must be generated on-site. The most practical way to generate ozone is to pass oxygen (either air or pure oxygen) through a corona discharge produced by applying high voltage across two electrodes with a dielectric and an air gap between. These systems can produce from 1 to 3 percent ozone when air is used, and from 2 to 6 percent when oxygen is used to feed the generator. The ozone gas is

injected into the circulating cooling tower water at an appropriate location in the system.

c. Ozone has been used successfully for treatment of cooling tower water a number of times since 1976. Ozone has been very effective for replacing cooling tower biocides. However, ozone can increase corrosion. Excess ozone feed is especially corrosive. Ozone may not have any affect against scale. Scale and corrosion control chemicals may still be required. Ozone systems are not inexpensive and maintenance of ozone systems can be a problem. Cooling water characteristics and equipment maintenance plans must be carefully reviewed before a decision is made to implement ozone treatment.

4-27. What to look for as a cooling tower operator.

Problems associated with scaling, corrosion and fouling in a cooling tower system, if detected early, can be minimized by corrective action. There are certain things that the operator should look for when on-site.

a. Cooling tower distribution deck.

(1) Plugged water distribution holes: This will cause an uneven water flow through the tower, lowering tower efficiency.

(2) Green slime: Indicates algae growth, usually found in areas not shielded from sunlight.

b. Cooling tower fill, air intake slats, and basin.

(1) Scale can form on cooling tower fill. Scale can range in color from white to gray or reddish depending on the scale composition. Calcium carbonate is white, but in a cooling tower may be gray due to dirt and other impurities. Scale usually occurs on heat transfer surfaces and is not visible in the bulk circulating water. Scale formation on the cooling tower fill usually indicates a severe

scaling situation. If possible, obtain a sample of the scale.

(2) Scale will often form on the air intake slats of a cooling tower. This buildup is mostly due to evaporation and generally does not indicate a serious problem.

(3) Slime deposits (microbiological) can sometimes be detected by feeling the bottom of the distribution deck and walls of the tower basin. Most microbiological growth will have a slimy feel.

(4) The purpose of a dispersant is to keep particulate solids in suspension and to prevent them from settling out or adhering to heat transfer surfaces. They are removed with the blowdown. The tower water will be turbid if the dispersant is doing its job.

c. Corrosion test coupons.

(1) Scale formation can occur on corrosion test coupons. This usually indicates a fairly severe scaling situation since no heat transfer is involved. Heat exchangers probably will be worse. Always note the visual appearance of corrosion coupons when removed.

(2) Suspended solids can deposit on corrosion coupons. This may indicate the need for more dispersant. It is important to be present, if possible, when the corrosion coupons are removed.

(3) Inside surface of heat exchanger tubes:

(a) Scale deposits, typically tightly adherent to the tube surface, range in color from white to gray or reddish depending on the makeup of the scale. Any scale present should be no more than paper thin, and may be visible when the tube has dried. It is important to inspect heat exchanger tubes at least once per year, or whenever scale formation is suspected.

(b) Fouling type deposits may look similar to scale deposits. Unlike scale, these

deposits are usually loosely adherent to the tube surface.

(4) Chiller Performance: Degradation of chiller performance or efficiency may be a strong indication of scale or fouling problems in the chiller.

Chapter 5

Other Industrial Water Systems

Section I Hot Water Boiler Systems

5-1. Description of hot water boilers. Some boilers are designed to produce hot water rather than steam. Hot water boilers include high temperature water (HTW) systems (pressurized systems with water temperatures more than 350°F), medium temperature water (MTW) systems (pressurized systems with water temperatures from 250 to 350°F), and low temperature water (LTW) systems (water temperatures below 250°F). Hot water boilers can be either direct fired (heated with gas, oil or coal), or unfired (heated by steam from a steam boiler, by hot water from a higher temperature hot water system or by a solar system). For many applications, hot water boilers may be preferred over steam boilers because of lower makeup requirements, less costly and easier to control chemical treatment programs, lower manpower requirements for operation, and less maintenance.

5-2. Description of hot water systems. A typical hot water system is illustrated in figure 5-1. Hot water boilers (fired and unfired) differ from steam boilers discussed in chapter 3 in that they:

- a. Do not have deaerating heaters. These are not required because there is very low makeup requirements.
- b. Require recirculating pumps to distribute the heated water to the processing equipment.
- c. Require expansion tanks that contain a cushion of steam or nitrogen.
- d. Do not have a condensate return because there is no steam generated.

- e. Do not have a blowdown. Rather, they operate as a closed system to the greatest extent possible.

5-3. Treatment of hot water boiler systems:

a. Makeup water. The makeup water required for a hot water boiler should be very low unless there are leaks in the system. In general, do not drain closed systems (fired or unfired) unless there is evidence of a real need to remove dirty water, or suspended matter. Refilling closed systems brings in oxygen which can cause increased corrosion. Carefully monitor the makeup water quantity. If there is an increase in the quantity of makeup water, determine the cause and correct it.

b. Treatment type. The three basic water treatment programs used in fired and unfired hot water boilers are sulfite-caustic soda, nitrite-borax, and molybdate-caustic soda. The choice of which chemistry system to use is primarily based on the temperatures and metals in the system, and the relative cost of the treatment program at the specific installation. Factors influencing the cost of chemical treatment include the size of the system (volume of water), amount of makeup required, and environmental and/or health restrictions imposed by the installation. Generally, the sulfite-caustic soda program is the least expensive, however, it requires greater attention, control and more frequent testing and is normally used with HTW and MTW systems because of their large capacity and temperature requirements. Mild steel can be treated effectively with all three treatments.

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FIGURE 5-1
SIMPLE HOT WATER BOILER SYSTEM

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If copper alloys are present, all three treatments must be supplemented with tolyltriazole.

c. Sulfite-Caustic soda program. Treat the initial fill of the boiler using water from the installation potable water system with sodium hydroxide (caustic soda) to a pH of 9.5 and with sodium sulfite to sulfite level of 100 ppm (as SO_3). This program is suitable for temperatures up to 550°F. Sulfite dosing calculations are discussed in paragraph 3-21. However, the dosage will be based on the water volume in the system rather than on makeup. Maintenance of this system is as follows:

(1) Soften makeup water unless there is a very low hardness in the makeup supply (typically less than 10 ppm, as ppm CaCO_3). The makeup water should be dealkalized if the makeup supply alkalinity is high (typically greater than 200 ppm, as CaCO_3).

(2) Add sodium sulfite to maintain 50 to 100 ppm sulfite (as SO_3).

(3) Add the appropriate chemical to maintain a pH of 9.0 to 10.0. A pH less than 9.0 can be raised by adding sodium hydroxide (caustic soda). A pH of more than 10.0 can be lowered by adding sodium bisulfite.

(4) If copper is in the system, add a copper inhibitor such as tolyltriazole.

(5) Test daily to maintain pH and sulfite levels.

d. Nitrite-Borax program. This program is not recommended for temperatures exceeding 250°F. Treat the initial fill of these systems (from a potable water supply) with a nitrite-borax compound to a nitrite level of 1,000 ppm (as NO_2). This will require about 17 to 18 pounds nitrite-borax per 1,000 gallons of water in the system. The stock listed nitrite-borax powder form compound is a premixed blend containing approximately 68 percent sodium nitrite, 10 percent borax, 17

percent sodium carbonate (soda ash) and 5 percent copper corrosion inhibitor. Test the initial fill for pH and adjust to 9.0 with sodium carbonate (soda ash). This chemical treatment program is compatible with ethylene glycol used for freeze protection. Maintenance of the system is as follows:

(1) Soften makeup water if it has very high hardness (over 250 ppm as CaCO_3).

(2) Add sodium nitrite-borax blend to maintain a nitrite level of 600 to 1000 ppm (as NO_2) in the system.

(3) Add sodium carbonate to maintain a pH range of 8.5 to 9.5.

(4) Test after chemical addition and then monthly for pH and nitrite levels.

e. Molybdate-Caustic soda program. This treatment can be used with systems containing copper alloys and where temperatures do not exceed 250°F. The stock listed molybdate-caustic soda compound is a premixed blended liquid containing approximately 10 percent sodium molybdate, 3 percent caustic soda, and 3 percent copper corrosion inhibitor. Treat the initial fill to a molybdate level of 125 ppm (as MoO_4) and adjust the pH to 9.0 with sodium hydroxide (caustic soda). Be aware that there may be some concern about disposal of molybdate. This chemical treatment program is compatible with ethylene glycol. Maintenance of the system is as follows:

(1) Soften makeup water if it has very high hardness (over 250 ppm as CaCO_3).

(2) Add the molybdate-caustic soda compound to maintain a molybdate level of 100 to 125 ppm (as MoO_4).

(3) Add sodium hydroxide (caustic soda) to maintain a pH of 8.0 to 9.0.

(4) Test monthly for proper pH and molybdate levels.

5-4. Procedures for layup of hot water

boilers.

Do not drain these systems. Follow the procedure for wet layup of operational boilers discussed in paragraph 3-26.

a. Completely fill the hot water generator and expansion tank. Where nitrogen pressurization is used for the system, the expansion tank does not need to be filled.

b. For all steel systems using the sulfite-caustic soda program, increase the pH to 11.7 with sodium hydroxide (caustic soda). Add sodium sulfite to a level of 200 ppm (as Na_2SO_3).

c. Treat systems using the nitrite-borax or molybdate-caustic soda treatments with appropriate chemicals to maintain levels required for normal operation.

d. Monthly, test for treatment chemicals and check water levels.

Section II Chilled Water & Brine Systems

5-5. Description of systems.

Chilled water systems and chilled brine systems are closed systems with very little water loss, and therefore, require very little makeup. Do not drain them unless necessary.

a. **Chilled water systems.** Chilled water systems circulate water that may contain treatment chemicals. A typical chilled water system is illustrated in figure 5-2.

b. **Chilled brine systems.** Chilled brine systems may involve a calcium chloride brine, sodium chloride brine, sodium chloride and calcium-magnesium brine, or an ethylene glycol brine.

5-6. Treatment for corrosion control.

Operating systems should be treated to inhibit

corrosion. Softening of makeup water for these systems normally is not required because of the low quantity required. However, when hardness exceeds 250 ppm (as CaCO_3), treat or blend the makeup to reduce the hardness to below 200 ppm as CaCO_3 .

a. **Nitrite-Borax program.** Treat the initial fill for these systems (from potable water supply) with a nitrite-borax compound to a nitrite level of 1,000 ppm (as NO_2). This will require about 17 to 18 pounds of nitrite-borax blend per 1,000 gallons of water in the system. The stock listed nitrite-borax powder form compound is a premixed blend containing approximately 68 percent sodium nitrite, 10 percent borax, 17 percent sodium carbonate (soda ash) and 5 percent corrosion inhibitor for copper. Treat the initial fill for pH and adjust to 9.0 using sodium carbonate (soda ash). Maintenance of the system is as follows:

(1) Soften the makeup water if it has very high hardness (over 250 ppm in CaCO_3).

(2) Add sodium nitrite-borax blend to maintain a nitrite level of 600 to 1,000 ppm (as NO_2) in the system.

(3) Add sodium carbonate to maintain a pH range of 8.5 to 9.5.

(4) Test monthly for pH and nitrite levels.

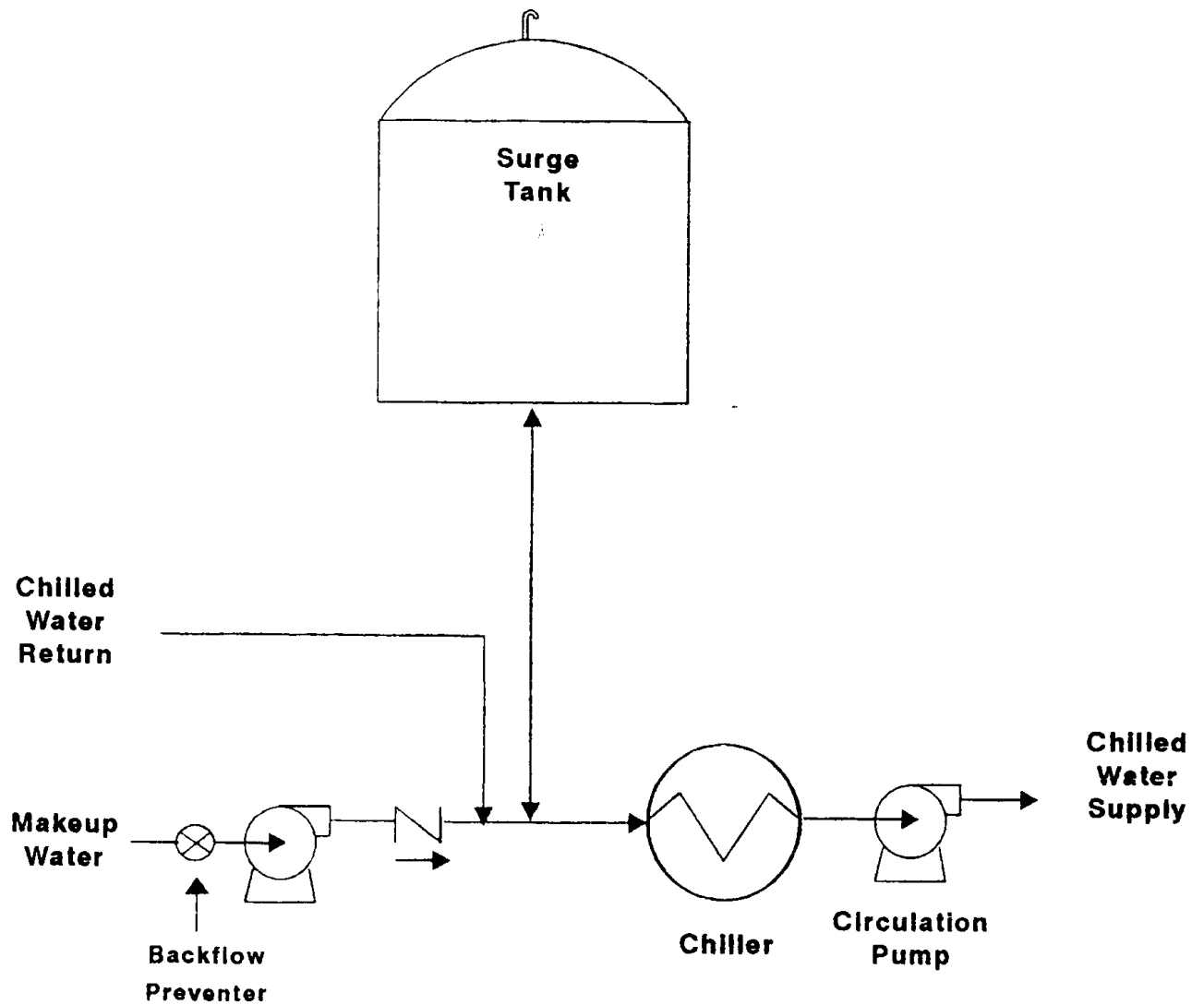
NOTES:

1. It may be necessary to add a biocide that is compatible with the system pH to prevent bacterial attack of the nitrite.

2. This program can be used in systems with ethylene glycol antifreeze.

b. **Molybdate-Caustic soda program.** This treatment can be used with systems containing copper alloys. The molybdate-caustic soda compound is a premixed blended liquid containing approximately 10 percent sodium molybdate, 3 percent caustic soda, and 3 percent copper corrosion inhibitor. Treat

**FIGURE 5-2
TYPICAL CHILLED WATER SYSTEM**



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the initial fill with the sodium molybdate compound to a molybdate level of 125 ppm (as MoO_4) and adjust the pH to 8.5 with sodium hydroxide (caustic soda).

(1) Soften the makeup water if it has very high hardness (over 250 ppm as CaCO_3).

(2) Add the molybdate-caustic soda compound to maintain a molybdate level of 100 to 125 ppm (as MoO_4).

(3) Add sodium hydroxide (caustic soda) to maintain a pH range of 8.0 to 9.0.

NOTES:

1. This program can be used with ethylene glycol antifreeze.
2. Test monthly for proper pH and molybdate levels.

5-7. Determining leaks in the system. The presence of leaks in the system can be checked by testing the inhibitor concentration in the circulating fluid. Measure and record the inhibitor concentration once per month. When the inhibitor concentration has dropped to 98 percent of the original value, about 2 percent of the system water will have been lost. If the lapsed time for this 2 percent loss is less than 4 months, the system leakage is excessive and should be investigated and corrected.

NOTE:

Two percent loss over 4 months is equivalent to 0.5 percent loss per month. However, due to the accuracy of analysis of these tests, it is better to use a longer time for confirming this loss rate. If the rate for any month exceeds 1 percent, it is advisable to repeat the test and then investigate if the results still indicate large amounts of leakage.

Example 5-1:

1. The initial molybdate concentration of chilled water system is 125 ppm. After 3 months, the concentration is 123

ppm. Is the water loss excessive?

$$\text{Loss} = \frac{\text{initial} - \text{final}}{\text{initial}} \times 100 = \frac{125 - 123}{125} \times 100$$

$$= 1.6 \% \text{ after 4 months}$$

2. The monthly loss based on the 4 month result is calculated:

$$\text{Monthly Loss} = \frac{1.6}{4 \text{ months}} = 0.8\% \text{ per month}$$

This loss is less than 0.5 percent and not excessive.

3. If the concentration had dropped to 123 ppm after 2 months, the loss would be:

$$\text{Loss} = \frac{125 - 123}{125} \times 100 = 1.6 \text{ percent after 2 months}$$

4. The monthly loss is calculated:

$$\text{Monthly Loss} = \frac{1.6}{2 \text{ months}} = 0.8\% \text{ per month}$$

This loss is greater than 0.5 percent, and the system should be inspected for leaks.

Section III Combined Hot And Chilled Water Systems

5-8. Description of systems.

Some systems serve the dual purpose of heating and cooling by circulating hot water during the cold season and chilled water during the hot season.

5-9. Treatment required. Keep the makeup to these systems to a minimum by controlling leaks and avoiding consumptive use. Treat the makeup with a zeolite softener when hardness exceeds 250 ppm (as CaCO_3). The nitrite-borax treatment or the molybdate-caustic soda treatment program is recommended as described in paragraphs 5-3d and e. Monthly testing of these systems is usually adequate.

Section IV

Diesel Engine Jacket

Cooling Systems

5-10. General information. Diesel engines may be operated continuously or they may be on a standby basis. These systems are usually closed systems, except where surge tanks may be partially open to the atmosphere. The heat transfer from the circulating water is usually through a heat exchanger or similar device. These systems have very low losses, and the makeup requirements are close to zero. Chemical treatment of these systems requires infrequent makeup, but the variety of metals in these systems may cause some corrosion problems. There are three types of systems:

a. Air cooled systems. Air cooled systems are used on small engines and sometimes on large engines. The jacket water is circulated through a radiator that is cooled by air. Antifreeze must be used in these systems in freezing areas because the radiators are exposed to the atmosphere.

b. Water cooled systems. Water cooled systems are used on large engines. The jacket cooling water passes through a heat exchanger, where a separate cooling water system removes the heat from the jacket cooling water. These systems commonly will use antifreeze. The separate cooling water system may require treatment.

c. Vapor-Phase cooling systems (also called ebullient systems). Vapor-phase cooling systems operate by heating the water to boiling temperature (or greater, for pressure systems). Steam is formed from the water, which removes heat from the system. The steam often is used for space heating as a method for recovery and reuse of waste heat. This type of system will require makeup of both water and treatment chemicals.

5-11. Treatment required.

Normally, diesel engine cooling systems require little makeup. Since scale formation must be prevented, softening of makeup water is recommended when the hardness exceeds 50 ppm (as CaCO_3). Demineralization may be required where saline water (such as seawater) is used.

a. Corrosion control in continuously operated systems. Special corrosion control may not be required for small systems where makeup water is rarely required and an inhibited antifreeze is used. Adjust the makeup for these small systems with sodium carbonate (soda ash) to maintain the pH in the system between 7.5 and 8.5. Large, continuously operated diesel engines may also use an inhibited antifreeze. If necessary, they can be treated and controlled with the sodium nitrite-borax treatment program (paragraph 5-3d) or the molybdate-caustic soda treatment program (paragraph 5-3e). If operating systems are not treated and monitored, replace the antifreeze every year.

b. Corrosion control in standby units. Normally, those systems that use an inhibited antifreeze will not require additional treatment. If necessary, the sodium nitrite-borax treatment or the molybdate-caustic soda treatment program can also be used for additional corrosion control.

c. Systems without antifreeze. Treat systems (operating or standby) that do not use an inhibited antifreeze with a nitrite-borax program or a molybdate-caustic soda program.

d. Testing required. Monthly testing to monitor pH and nitrite or molybdate levels is usually adequate.

Chapter 6

Sampling And Testing Of Industrial Water Systems

Section I General Information

6-1. Requirement for sampling and testing:

a. Purpose of sampling and testing.

Regular, representative sampling and accurate testing are essential parts of a sound industrial water treatment program. Each treated industrial water system must be tested often to show whether the proper chemical levels are being maintained and whether the pH of the water is within the set range. Sampling and testing frequencies outlined in this chapter will ensure an effective industrial water treatment program. Safety considerations must be a priority when sampling any industrial water system and when conducting laboratory tests.

b. Quality assurance sample analysis.

Sampling requirements for the quality assurance program described in paragraph 1-8 are as follows:

(1) Each operating boiler plant equipped with hot water or steam boilers with one or more boilers of 3.5 MBTU/hr or 100 horsepower or greater capacity must submit a sample for quality assurance each month.

(2) Each operating boiler plant equipped with hot water or steam boilers of less than 3.5 MBTU/hr or 100 horsepower capacity shall submit a sample for quality assurance once every three months.

(3) Sample size will be 32-ounce, or as required by the contract laboratory, for all high pressure (15 psig or greater) boilers and low pressure boilers treated with caustic, phosphate, tannin, and sodium sulfite.

(4) Sample size will be 4-ounce for low pressure boilers (less than 15 psig) treated

with caustic only.

(5) Sample size will be 32-ounce, or as required by the contract laboratory, for hot water boilers.

(6) Sample shipping containers and bottles for submission of boiler water for check analyses are obtained by direct request to the contract laboratory. In overseas areas when the command has established a central laboratory for the analysis of boiler water, sample containers and bottles should be obtained from that source. Containers for high-pressure boiler water samples are designed for shipping a 32-ounce plastic bottle. Containers for water samples from low-pressure boilers treated with caustic soda are designed for shipping a 4-ounce plastic bottle. Pack the bottle carefully so that it will not leak in shipment. A data sheet is enclosed in each sample container. Completely fill out the data sheet and ship it with the sample.

6-2. In-plant testing. Army installations are required to obtain test chemicals and equipment from commercial sources, usually as test kits. Test procedures will be furnished with the test kits.

Section II Sampling And Testing Cooling Towers

6-3. Methods of sampling. Collect cooling tower water samples in clean glass or plastic bottles, cap immediately, and test without delay. Do not take the sample immediately after treatment chemicals are added, but when the chemicals have mixed with the system water. Samples of the recirculating water can

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be dipped from the cold well or taken from the recirculating pump discharge. If these locations are inaccessible, another location may be used. Possible sampling points for a typical open recirculating system are shown in figure 6-1. It is best to always collect the sample for each system in the same manner and from the same location.

6-4. Frequency of samples.

Sample the recirculating water in small tower (less than 25 tons) once per week; medium sized towers (25 to 100 tons) at least two times per week; and large towers (more than 100 tons) daily. Establish a routine schedule for sampling these systems that is designed to meet these goals. Usually, the makeup water is the same for all or many of the cooling towers and one sample per week of each

makeup source is adequate.

6-5. Testing requirements. Test samples from recirculating water systems for pH, methyl orange (M) alkalinity, conductivity, inhibitor content, and calcium hardness. Also, follow any testing requirements established by the manufacturer of a special chemical treatment process, where appropriate. Test the makeup water sample for M alkalinity, conductivity, and calcium hardness. The testing requirements and frequency are summarized in table 6-1 according to the source of sample. Periodic testing for chlorides in the recirculating water and in the makeup water may be required to calculate the most accurate COC in an operating system.

TABLE 6-1
SAMPLE FREQUENCY AND TESTING REQUIREMENTS FOR
COOLING TOWER SYSTEMS ACCORDING TO SOURCES OF SAMPLES

	pH	M Alkalinity	Conductivity (or TDS)	Calcium Hardness	Inhibitor
Makeup	--	1/W	1/W	1/W	--
Small CT < 25 ton (1)	1/W	1/W	1/W	1/W	1/W
Medium CT 25-100 ton (1)	2/W	2/W	2/W	2/W	2/W
Large CT > 100 ton	1/D	1/D	1/D	1/D	1/D

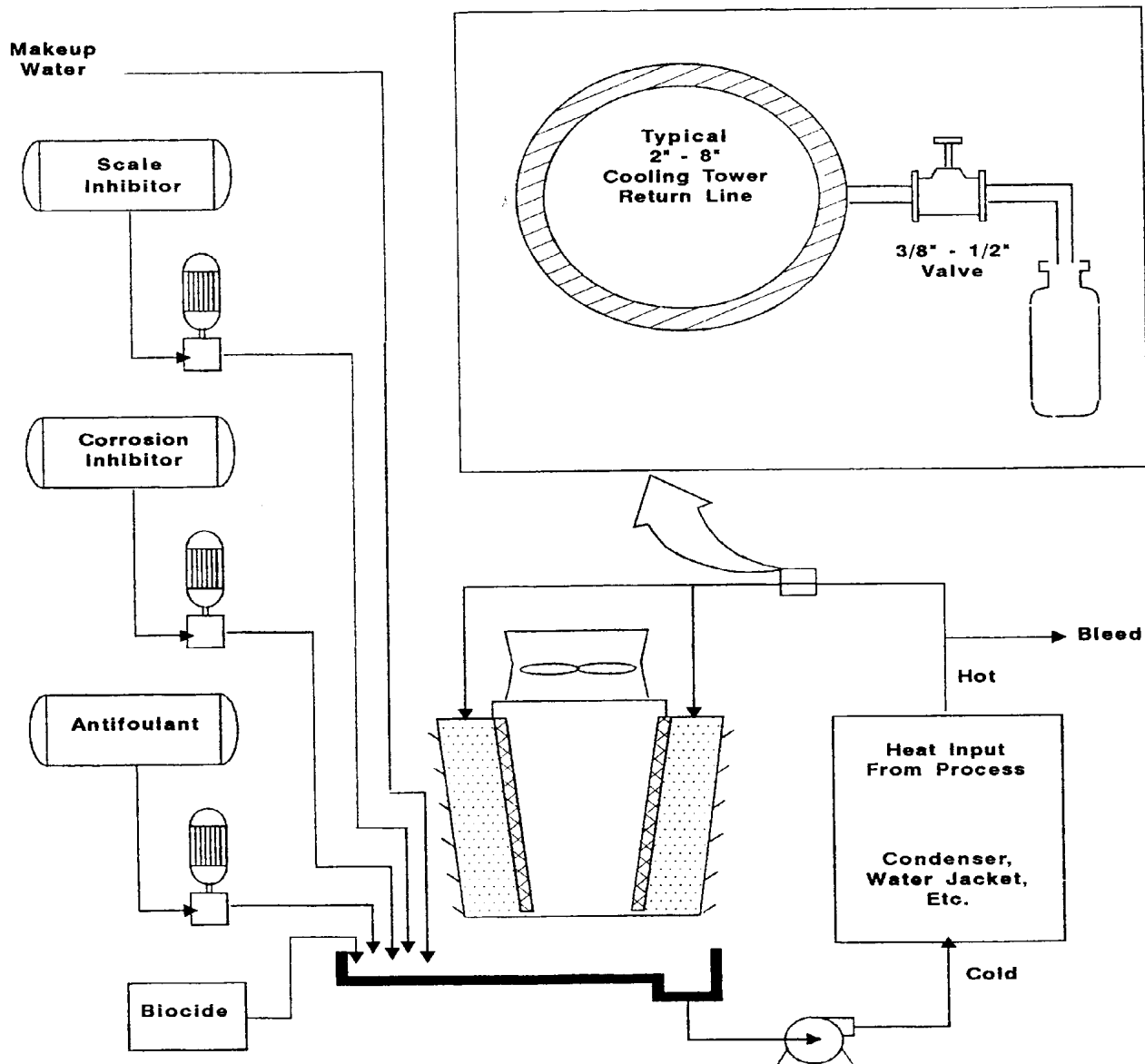
NOTES: CT = Cooling Tower

W = Week (for example, 1/W = once per week)

D = Day (for example, 1/D = once per day)

(1) = Slowly soluble polyphosphate chemicals used in treatment of small and medium cooling towers should be checked weekly and replaced as necessary.

FIGURE 6-1
POSSIBLE SAMPLING POINTS FOR A TYPICAL OPEN
RECIRCULATING COOLING SYSTEM



Section III

Sampling & Testing Boilers

6-6. Method of sampling. Boiler water will be hot and under pressure. If the water is not cooled as it is sampled, part of the water will flash off as steam and the remaining sample will not be representative of the system. The resulting sample will show lower oxygen and carbon dioxide readings than actual levels in the boiler. Other values will generally be higher because of less water in the test sample for the same amount of solids. Use of a sample cooler described below will greatly reduce the chance of the operator getting burned, and the possibility of obtaining a nonrepresentative sample.

a. Sampling cooler. Use a commercially available sample cooler when collecting a sample. If not available, then use a 15 to 20 foot coil of copper or stainless steel tubing to cool the sample. The coil can be immersed in a permanent cooling jacket as shown in figure 6-2, or it may be immersed in a bucket of cold water; when this does not interfere with operation of the system or create a hazard. The flow of the sample through the coil must be slow enough so that the cooled sample is not more than just warm to the hand (approximately 100°F).

b. Sampling procedures. Turn on the cooling water to the cooling coil before taking the boiler water sample and turn it off after the sample is collected. Flush the coil with several times its volume before taking the sample. Then extend the end of the sample coil to the bottom of the sample bottle and allow at least one volume of the bottle to overflow from the container during the collection process. The bottle can be glass, but plastic bottles are preferred. Do not use glass bottles if the

boiler is silica limited, or if high silica is suspected.

c. Sampling locations. See figure 6-3 for typical locations for water sampling points in a steam boiler system. Each sampling point should have a separate cooling coil. Two or more sampling points manifolded to the same cooling coil is not a desirable situation because it is almost impossible to know if one of the valves has a leak that might contaminate the sample being taken.

(1) The makeup water sample does not have to be cooled. The sample location typically will be the output of an ion exchange unit or some other water softening unit.

(2) The boiler feedwater sample is a combination of makeup and condensate return. Take the sample from the discharge of the boiler feed pump. It may be a hot sample.

(3) The boiler water will be very hot. It is best to take this sample from the continuous blowdown line between the boiler and the regulating valve. It can be taken from a gauge-glass connection, if necessary.

(4) The steam condensate will be hot. For small systems, take the sample from a line that enters the deaerating heater if possible. Also, for medium and large systems, it may be necessary to take condensate samples at two or more locations in the system to calculate the proper treatment level. It is sometimes necessary to take condensate samples from various locations in the system when attempting to find a leak.

(5) Steam samples are rarely taken. For sampling methods see the American Society of Mechanical Engineers (ASME) Performance Test Code.

6-7. Frequency of samples and testing. The sample and testing frequency for steam boiler systems is summarized in table 6-2.

FIGURE 6-2
DIAGRAM OF A BOILER OR CONDENSATE SAMPLE COOLING COIL

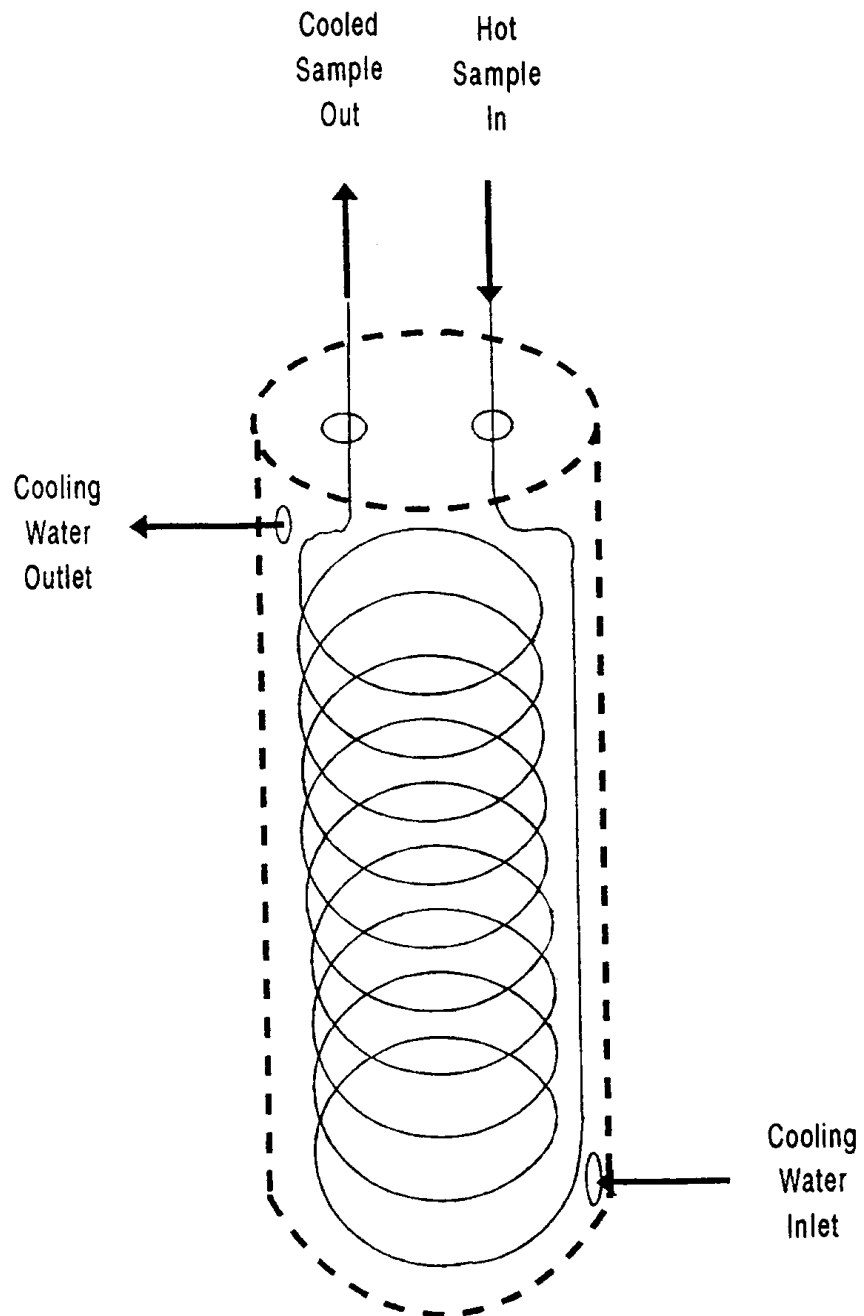


FIGURE 6-3
TYPICAL LOCATIONS FOR WATER SAMPLING POINTS IN A
STEAM BOILER SYSTEM

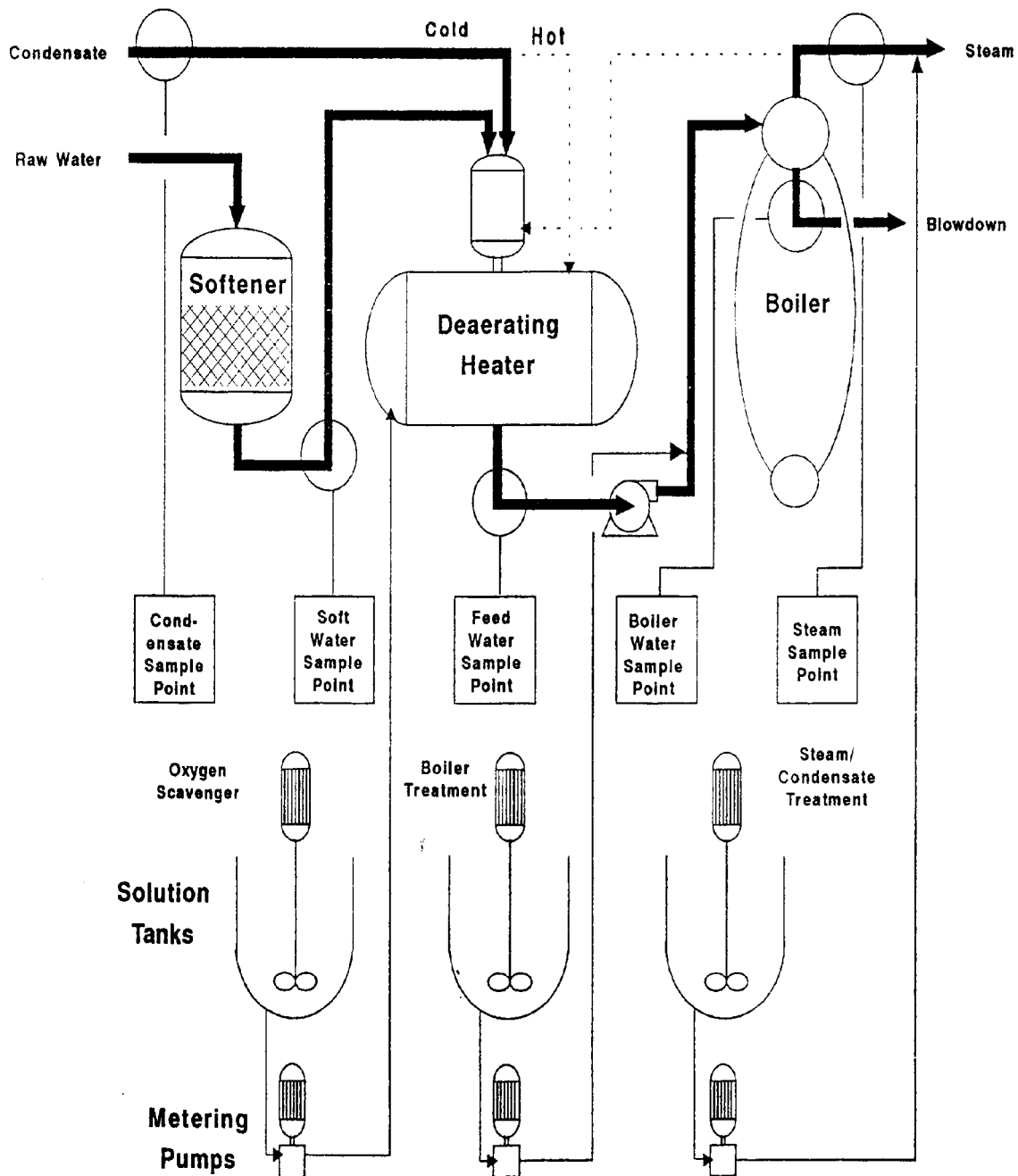


TABLE 6-2
SAMPLE FREQUENCY & TESTING REQUIREMENTS FOR
BOILER WATER SYSTEMS

	pH	Total Alkalinity ⁽¹⁾ (M)	Hydroxyl Alkalinity (Causticity)	Calcium Hardness	Total Dissolved Solids (TDS)	Copper and Iron	Ortho-phosphate	Sulfite
Makeup water	--	1/W	--	1/W	1/W	--	--	--
Feedwater, small boilers (<25 hp)	--	1/W	--	1/W	1/W	--	--	--
Feedwater, medium boilers (25-150 hp)	--	2/W	--	2/W	2/W	--	--	--
Feedwater, large boilers (>150 hp)	--	1/D	--	1/D	1/D	--	--	--
Boiler water, small boilers (<25 hp)	1/W	--	1/W	--	1/W	--	1/W	1/W
Boiler water, medium boilers (25-150 hp)	2/W	--	2/W	--	2/W	--	2/W	2/W
Boiler water, large boilers (>150 hp)	1/D	--	1/D	--	1/D	--	1/D	1/D
Condensate Return (small boilers)	1/W	--	--	As needed	1/W	1/Q	--	--
Condensate Return (medium boilers)	2/W	--	--	As needed	2/W	1/Q	--	--
Condensate Return (large boilers)	1/D	--	--	As needed	1/D	1/Q	--	--

NOTES: W = Week (for example, 1/W = once per week)
D = Day (for example, 1/D = once per day)
Q = Quarter (for example, 1/Q - once per 3 months)
(1) = Feedwater alkalinity only for boilers that use dealkalizers

a. Feedwater sample. Take feedwater samples once a week for small boilers (less than 25 hp); at least two times per week for medium boilers (25 to 150 hp); and daily for large boilers (more than 150 hp). Test the samples for M alkalinity, conductivity, and calcium hardness.

b. Condensate sample. Take condensate samples once a week for small boilers (less than 25 hp); at least two times a week for medium boilers (25 to 150 hp); and daily for large boilers (more than 150 hp). Test for pH and conductivity. If the conductivity is greater than 35 micromhos, test for calcium hardness. Test the condensate for iron and copper, if applicable, on a quarterly basis.

c. Blowdown sample. Take blowdown samples for small boilers (less than 25 hp) once per week; for medium boilers (25 to 150 hp) at least two times per week; and for large boilers (more than 150 hp) daily. Test for hydroxyl (OH) alkalinity (causticity), neutralized conductivity, orthophosphate, and sulfite.

Section IV Sampling And Testing Other Water Systems

6-8. Hot and chilled circulating water. The testing frequency for these systems is summarized in table 6-3 with additional information provided below.

a. Makeup water to hot water boilers, chilled water circulation systems, and diesel engine jackets usually comes from an ion exchange unit or a dealkalizer (see paragraph 6-9).

b. Test recirculating water from HTW systems and systems using the sulfite-caustic soda treatment program (paragraph 5-3c) once per day for pH and sulfite.

c. Test recirculating chilled and hot water treated with the nitrite-borax or molybdate

programs (paragraphs 5-3d and e) once per month for either molybdate or nitrite depending upon the chemical in use. Also test the system pH once per month and after chemical addition.

6-9. Ion exchangers and dealkalizers. The testing frequency for these systems is summarized in table 6-3 with additional information provided below.

a. Test ion exchange influent water once per week for total hardness. Test dealkalizer influent water once per week for total (M) alkalinity.

b. Test the effluent water from these systems for total hardness either once per day or once per shift (three times a day) depending on the frequency of regeneration. Cycle length will depend upon feedwater hardness, bed size, resin type, strength of regenerant, and flow rate.

c. The location of the sample point is important to ensure that the proper sample is obtained. Care must be taken to avoid collecting a sample that is a mixture of influent and effluent water on ion exchange units that use automatic regeneration and multiport valves.

d. The operator must mix the brine used for regeneration. In some cases, the brine should be sampled and tested with a hydrometer to measure its strength. The brine should be as near 100 percent saturation as possible (approximately 28%).

Section V Testing Procedures

6-10. Purpose of testing. Water testing is performed to provide the proper control of recommended treatments. Testing is not only for the purpose of record keeping, although good records will aid in the analysis of long-term effectiveness of treatment methods. Test

TABLE 6-3
FREQUENCY AND TESTING REQUIREMENTS FOR OTHER SYSTEMS

System	pH	Sulfite	Nitrite	Molybdate	Total Hardness	Total Alkalinity
HTW Caustic-Sulfite	1/day	1/day	--	--	--	--
Closed Hot Water Nitrite-Borax	1/mo	--	1/mo	--	--	--
Closed Hot Water Molybdate	1/mo	--	--	1/mo	--	--
Chilled Water & Brine; Molybdate	1/mo	--	--	1/mo	--	--
Chilled Water & Brine Nitrite-Borax	1/mo	--	1/mo	--	--	--
Diesel Jackets Molybdate	1/mo	--	--	1/mo	--	--
Diesel Jackets Nitrite-Borax	1/mo	--	1/mo	--	--	--
Ion Exchange Feedwater	--	--	--	--	1/week	--
Ion Exchange Outlet	--	--	--	--	3x/day	--
Dealkalizer Feedwater	--	--	--	--	--	1/week
Dealkalizer Outlet	--	--	--	--	--	3x/day

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results that do not agree with the results expected for the treatment method being used should be acted upon immediately. This can involve reanalysis and checking of the test reagents. If the test results are correct, the treatment program should be evaluated. Section VI discusses interpretation of test results.

6-11. Water sample testing procedures.

Water test procedures will be provided with the test kits obtained from commercial sources. Test kit requirements will generally include tests for:

- a. Alkalinity-Phenolphthalein (P); Alkalinity-Methyl Orange (M) or Total; Alkalinity-Hydroxyl (OH) or Causticity
- b. Conductivity
- c. Tannin
- d. pH
- e. Hardness (total, calcium, magnesium)
- f. Phosphate (orthophosphate, total phosphate)
- g. Sulfite
- h. Nitrite
- i. Chloride
- j. Molybdate

6-12. Corrosion testing. A positive way to determine if corrosion is occurring is to place corrosion test specimens in the system. Army installations are strongly encouraged to test for possible corrosion in large or critical heating and cooling systems.

a. There are two corrosion test specimens commonly used. These are listed below.

(1) Corrosion test coupons for use in open and closed cooling systems, closed hot water systems, and domestic water systems (refer to appendix C).

(2) Corrosion pipe inserts for use in steam condensate return systems (refer to appendix D). The inserts are captive in an assembly of 3/4" pipe.

b. Corrosion test coupons and analysis of exposed coupons are available from a number of commercial sources. Pipe insert assemblies for steam condensate systems and analytical evaluation of the test inserts are available from the quality assurance laboratory under contract with USACPW. Guidance covering corrosion testing is provided in appendices C and D.

c. Corrosion test results are usually reported as a rate of corrosion penetration into the metal given in mils penetration per year (mpy). A mil is one-thousandth (0.001) inch. Thus, the corrosion rate of 10 mpy means that the thickness of a piece of metal is reduced by $10 \times 0.001 = 0.01$ inches per year. If the metal being studied is 1/16 or 0.0625 inches thick, this means that it will be completely destroyed in just over 6 years. Corrosion rates may also be expressed in millimeters per year (mmpy) penetration. The relationship between mpy and mmpy is: 1 mpy = 0.0254 mmpy; 1 mmpy = 39.4 mpy.

d. Corrosion also may be given as a weight loss in milligrams per square decimeter per day (mdd). For steel, the relationship between penetration and weight loss is: 1 mdd = 0.2 mpy or 1 mpy = 5 mdd.

e. There are a variety of electrical instruments available which monitor and record corrosion rates. These are installed and maintained by specialists.

Section VI Interpretation Of Tests

6-13. General information. Many water treatment systems require that a specific level of a treatment chemical be carried in the water. This applies to nitrites, phosphates, sulfites, molybdates, and to any specialized chemicals used in the treatment program. When a test indicates that a chemical is not within the limits required for the treatment program, confirm

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that the test was performed properly and is valid. (Check test methods, including the chemical reagents, on a routine basis even when treatment levels are being maintained.)

a. When the valid test results indicate a level that is too low, evaluate the chemical addition program and make the appropriate adjustment. This normally means increasing the chemical feed rate by 10 percent or less. If adjustments to the treatment program do not correct the situation, then evaluate the system in total to determine the nature of the problem. Outside assistance can be obtained through the USACPW (CECPW-ES).

b. When the valid test results indicate a level that is too high, evaluate the chemical addition program. Care should be used in reducing chemical feed rates based on a level that is too high. Do not reduce the chemical feed rate more than 5 to 10 percent at any one time.

c. When the test for hardness indicates levels in the system that are higher than the desired level, investigate the makeup treatment system for problems. Also investigate other possible sources of hardness in the system.

6-14. Alkalinity relationships:

a. **Sources of alkalinity.** The three basic sources of alkalinity in water are: alkalinity resulting from the bicarbonate ion (HCO_3^-), the carbonate ion (CO_3^{2-}), and the hydroxyl ion (OH^-). The amount of each of these in water can be determined by titrating with an acid to certain pH levels (end points) using phenolphthalein (P alkalinity) and a methyl orange (M alkalinity) end points. The relationship between pH and these alkalinities is shown in figure 6-4.

b. **Relationship of P, M and OH alkalinities.** Test procedures for determining the P and M alkalinities are included in commercially available test kits. The OH alkalinity can be determined by a specific test

or it can be calculated from the P and M alkalinities. The OH alkalinity is the result of the hydroxyl ion (OH^-) in the water, and is also known as "caustic alkalinity" or "causticity". The relationship between the measured P and M alkalinities and level of hydroxyl, carbonate, and bicarbonate forms of the alkalinity is shown in table 6-4 and is discussed below.

Example 6-1:

P = 86 ppm, M = 118 ppm; situation 2 exists ($P > 1/2M$);

Hydroxyl = $2 \times 86 - 118$
= 54 ppm

Causticity = hydroxyl alkalinity $\div 3$
= $54 \div 3 = 18$ ppm

Carbonate = $2 \times (118 - 86)$
= 64 ppm

Bicarbonate = 0 ppm

Check: Total = $54 + 64 + 0 = 118$ ppm

(1) The tests for P alkalinity and M alkalinity may give the same result. This means that all of the alkalinity is due to hydroxyl ions. There is no carbonate or bicarbonate present. (This is rare, but occurs when a caustic solution unexposed to air).

(2) The P alkalinity may be greater than one-half of the M alkalinity. This indicates that there is hydroxyl and carbonate alkalinity, but no bicarbonate alkalinity.

(3) The P alkalinity may be equal to one-half of the M alkalinity. This indicates that all the alkalinity is due to carbonate. There is no bicarbonate alkalinity, and the hydroxyl alkalinity is insignificant.

(4) The P alkalinity is less than one-half of the M alkalinity. This indicates that carbonates and bicarbonates are present.

(5) The P alkalinity is zero. The M alkalinity is due to bicarbonates only.

FIGURE 6-4
ACIDITY & VARIOUS TYPES OF ALKALINITY & THEIR pH RANGES

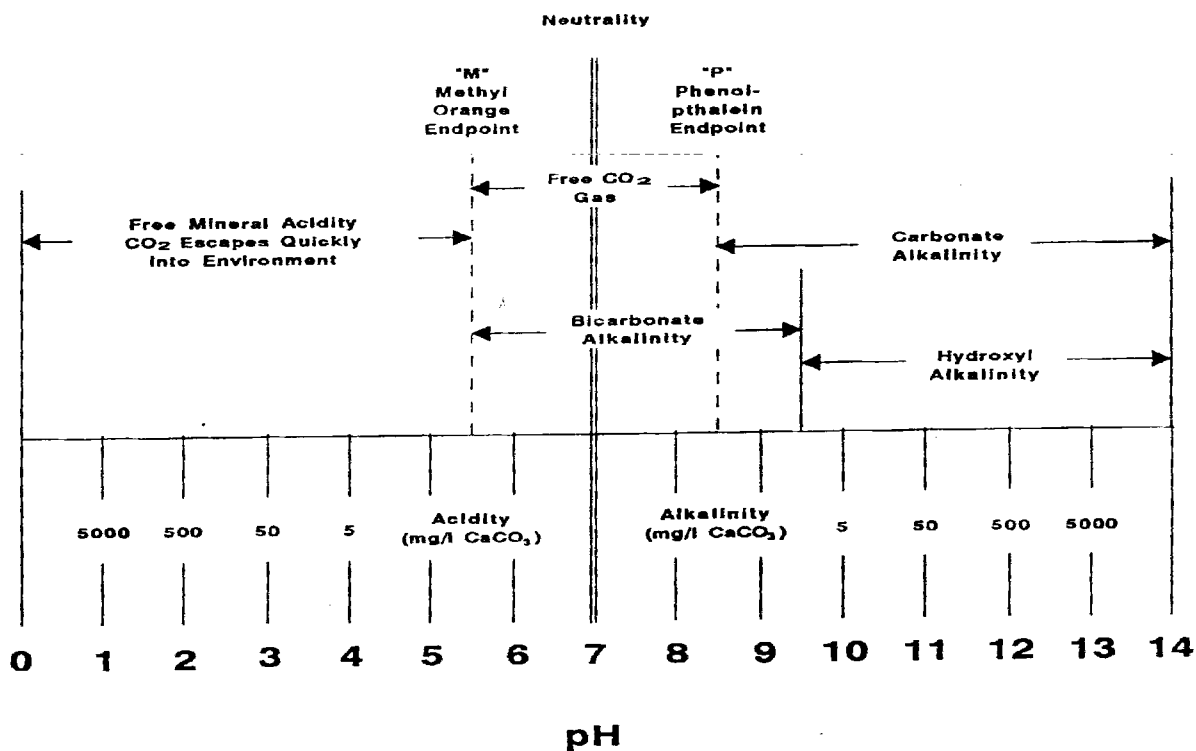


TABLE 6-4
ALKALINITY RELATIONSHIP BASED ON P AND M TESTS

Situation	Hydroxyl	Level of Alkalinity Contributed by Carbonate	Bicarbonate
1. $P = M$	M	0	0
2. $P > 1/2M$	$2P - M$	$2 (M - P)$	0
3. $P = 1/2M$	0	M	0
4. $P < 1/2M$	0	$2P$	$M - 2P$
5. $P = 0$	0	0	M

**6-15. Hydrogen ion concentration (pH):
a. Meaning of pH.**

The pH is a measure of the acidity or alkalinity of the water. (The test specifically measures the concentration of hydrogen ion in the water). A neutral water will have a pH of 7. Values less than 7 are considered acidic. Values greater than 7 are considered alkaline.

(1) Common pH values for materials on the acid side include spinach with a pH of about 5.5, orange juice, and most soft drinks with a pH of about 3.5, lemon juice with a pH of about 2.2, and 0.1 N sulfuric acid with a pH of 1.2.

(2) Common pH values of materials on the alkaline side include sodium bicarbonate with a pH of about 8.4, milk of magnesia with a pH of about 10.5, household ammonia with a pH of about 11.5, and 0.1 N sodium hydroxide with a pH of 13.0.

(3) The pH scale is logarithmic. A pH of 4 is 10 times as acidic as a pH of 5 and a hundred times as acidic as a pH of 6. This is important to consider when adding a strong acid to a system, because 0.1 N sulfuric acid will have more than 100,000 times the acidity of neutral water.

b. Relationship to causticity. When the pH of a water exceeds about 9.6 to 9.8, a measurable concentration of hydroxyl ions (OH⁻) begins to appear. As the hydroxyl alkalinity (causticity) increases, the pH of the solutions also increases. The relationship between causticity and pH is shown in table 6-5.

6-16. Conductivity and total dissolved solids.

In neutral or alkaline waters, there is no consistent relationship between conductivity and TDS. If alkaline water is acidized to the phenolphthalein end point with an organic acid such as gallic acid (which neutralizes causticity but does not contribute conductivity), the TDS

is approximately equal to two-thirds the neutralized conductivity in micromhos. At Army installations, a factor of 0.7 will be used for water treated with synthetic polymers as a sludge dispersant, and from 0.7 to 1.0 for water treated with Quebracho tannin, depending on the amount of tannin in the water. Conductivity and TDS are used to determine the COC and the potential for scale formation (chapter 3).

**Section VII
In-plant Laboratory
Requirements**

6-17. General data. Provide the water analyst with a separate laboratory space to perform the routine control tests that are required. The space preferably should be set off from the industrial plant by walls. Include a suitable bench, sink and cabinet, a distilled or deionized water source, and have ventilation and comfort heating and cooling. Provide standard lighting at reading intensity with white fluorescent lamps. A record file for test results and references should be located in the laboratory.

6-18. Laboratory equipment recommended. Select the equipment at each location to perform all of the tests routinely performed. Provide sufficient quantities of standard materials such as beakers, test tubes, graduated cylinders, and casseroles so that the tests can be performed efficiently. The equipment required for each test will be included with the appropriate test kit.

6-19. Chemical reagents. Maintain a master list of reagents that are stocked, their reference number, the quantity of stock, and the test for which the reagent is used. The minimum stock level should be defined, and the reagent

TABLE 6-5
RELATIONSHIP BETWEEN CAUSTICITY AND pH

pH	Hydroxyl Alkalinity, ppm		pH	Hydroxyl Alkalinity, ppm	
	as CaCO ₃	as OH		as CaCO ₃	as OH
9.0	0.5	0.17	11.1	63	21.4
9.5	1.6	0.54	11.2	79	26.9
10.0	5	1.70	11.3	100	34.0
10.2	8	2.72	11.4	126	42.8
10.5	16	5.44	11.5	158	53.7
10.6	20	6.80	11.6	199	67.7
10.7	25	8.50	11.7	250	85.0
10.8	33	11.2	11.8	315	107
10.9	40	13.6	11.9	397	135
11.0	50	17.0	12.0	500	170

ordered when that level is reached. The chemical reagents required for field tests will be included with the appropriate test kit. Material Safety Data Sheets (MSDS) must be

provided by the supplier for each of the chemical reagents. The MSDS must be kept in the vicinity of the test area in case of an emergency.

Chapter 7

Chemical Mixing, Feeding, And Control Devices

Section I General Information

7-1. Chemical mixing. The mixing of chemicals is necessary when dissolving dry chemicals or when reducing the concentration of liquid chemicals.

a. Liquid chemicals. A liquid chemical can be adjusted to a lower concentration by adding water. This should be done with care for acids and alkalis. The concentration of purchased chemicals may need to be reduced when only a small quantity of chemical is to be fed. Better control of the treatment program is possible by feeding a lower concentration chemical at a higher and easier to control flow rate.

b. Dry chemicals. Dry chemicals frequently must be added as a solution to the water system. Dry chemicals are dissolved in water to make a known concentration of the chemical. Specific instructions on mixing a dry chemical are normally provided with the chemical.

c. Chemical mixture. A chemical mixture can be procured (such as nitrite-borax) or developed at the installation for a specific application to reduce the effort required to add several chemicals to a water system. The mixture can be developed using either liquid or dry chemicals, or by supplementing an existing mixture with a specific chemical. The chemicals in a mixture must be at the proper proportions to match the treatment needs of the system. The chemicals also must be compatible, not react in the mixture and not come back out of solution.

7-2. Chemical feeding. Feed chemicals to

the water treatment system on the basis of the treatment program requirements and the results of the test program.

a. Feed options. If the test program results indicate that the chemical residual levels are either too low or too high, increase or decrease the addition of the treatment chemical. The options for changing a feed program are listed below. The selection of one option depends on the type of feed equipment.

(1) The rate at which the chemical solution is fed to the system can be changed to be either higher or lower.

(2) The concentration of the chemical in the feed stream can be increased by adding the concentrated chemical to the mixing tanks, or decreased by diluting the chemical with water in the mixing tanks.

(3) The frequency or quantity of chemicals added on an intermittent basis may be changed.

b. Feed methods. The method of chemical feed is dependent upon the type of water treatment system and the reasons for adding the chemical. The common methods of feeding are described below:

(1) Continuous feed systems involve the addition of chemicals at a constant rate. This rate may be a constant flow of materials into the water system, or the rate may be automatically adjusted according to a system parameter such as pH or flow rate.

(2) Intermittent feed systems may be operated either manually, or they may be automatically operated on a timer basis, or they may be based on a system parameter such as blowdown.

(3) Slug feed systems involve the addition of chemicals in excess of the amount required to just meet the level required in the system. The timing and quantity of a slug feed is adjusted in order to always maintain a level of at least the minimum required in the water system.

(4) Shock feed is a special chemical feed method used for microbiological control in cooling water systems. A high level of chemical is added on an infrequent basis in order to shock the system and provide the necessary "kill" effect.

7-3. Chemical control. The control of chemical levels in treated water systems generally involves one of three methods.

a. Continuous testing. Continuous testing can be used in large systems where the service requirement justifies continuous control or the cost of the chemical feed warrants close control. This technique requires monitoring devices external to the system with probes and transmitters sending a signal to the monitoring device. These systems often are linked directly to the chemical feed system to provide automatic control of the chemical feed.

b. Manual testing. Manual testing is most common. This technique is effective where the treatment chemical levels in the system are not expected to vary widely in short periods of time, or the treatment chemical feed can be linked to the makeup water flow rate. Normally, the results of the manual testing are used to manually adjust the chemical feed rates.

c. No testing. No testing is used only where there is a chemical feed system that is not controlled from day to day, or there is no treatment. This technique is used, for example, at remote cooling towers where a slowly soluble chemical is suspended in the

cold well. Even for such systems, an occasional test for treatment chemical level is recommended.

Section II

Chemical Mixing Procedures

7-4. Dissolving dry chemicals.

Fill the chemical vat about one-half full of softened water (or condensate). Turn on the mixer and add the chemical slowly into the vortex of the mixing action. After a few minutes, fill the vat with softened water to the proper level and continue mixing for 10 to 15 minutes.

a. Improper location of the mixer shaft may cause difficulties in dissolving chemicals. Locate the shaft on one side of the tank and slanted into the water. The contents of the vat should move in a circular pattern.

b. Solutions greater than about 5 percent concentration may be difficult to attain for some chemicals. Review the guidance provided in chemical data sheets for each chemical to determine any special mixing problems.

c. The amount of chemical to add can be determined from the desired concentration and the volume of the vat. The concentration of a solution can be calculated from the amount of chemical added and the volume of the vat.

Example 7-1:

1. A solution of sodium hexametaphosphate is to have a 5 percent phosphate (PO_4). This is to be added to a boiler at a rate of 3.95 pounds per day of phosphate to replace blowdown (example 3-10). The mixing vat volume is 1,000 gallons.
2. The total pounds of phosphate to add to the vat is calculated:

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$$\text{Phosphate, lb} = \text{Percent}/100 \times \text{Vat Volume, gal} \times 8.33 \text{ lb/gal} \\ = (5 \div 100) \times 1000 \times 8.33 = 417 \text{ lb}$$

3. Sodium hexametaphosphate contains 90.5 percent phosphate (table 3-8). The total pounds of sodium hexametaphosphate to add to the vat is calculated:

$$\begin{array}{lcl} \text{Sodium} & & \\ \text{hexametaphosphate, lb} & = & \text{Phosphate, lb} \div \text{Percent}/100 \\ & = & 417 \div 0.905 = 461 \text{ lb} \end{array}$$

4. Note the chemical feed rate of the 5 percent phosphate solution must be 3.95 lb/day of phosphate (PO_4). The gallon per day feed is calculated:

$$\begin{array}{lcl} \text{Feed,} & = & \text{Phosphate,} \div (8.33 \text{ lb/gal} \times \text{Percent} / 100) \\ \text{gal/day} & \text{lb/day} & \text{Phosphate} \\ & = & 3.95 \div (8.33 \times 0.05) \\ & = & 9.5 \text{ gal/day} \end{array}$$

5. The vat will need to be replenished in about 105 calendar days (1,000 gallon $\div$ 9.5 gal/day).

Example 7-2:

1. Boiler treatment program requires 3.95 pounds/day of phosphate (example 3-10). It is desired to establish a 60 day supply of the mixed chemical. The required amount of phosphate is calculated:

$$\begin{array}{lcl} \text{Phosphate, lb} & = & \text{Supply, day} \times \text{Phosphate, lb/day} \\ & = & 60 \times 3.95 = 237 \text{ lb} \end{array}$$

2. Sodium hexametaphosphate is available in 100 pound bags at a concentration of 90.5 percent phosphate (PO_4). Therefore, three bags are to be added to the vat. The amount of phosphate added in the three bags is calculated:

$$\begin{array}{lcl} \text{Phosphate, lb} & = & \text{Bags} \times \text{Pounds/Bag} \times \text{Percent Phosphate}/100 \\ & = & 3 \times 100 \times 0.905 = 272 \text{ lb} \end{array}$$

3. The vat is 1,000 gallons. The concentration of phosphate in the vat is calculated:

$$\begin{array}{lcl} \text{Concentration, percent} & = & (100 \times \text{phosphate, lb}) \div (8.33 \text{ lb/gal} \\ & & \times \text{Volume, gal}) \\ & = & (100 \times 272) \div (8.33 \times 1,000) \\ & = & 3.3 \text{ percent} \end{array}$$

7-5. Diluting liquid chemicals.

Dilute a liquid chemical to a lower concentration by adding softened water. Add the concentrated chemical to a partially filled vat, and then bring the vat to a full level with more softened water. Turn on the mixer before adding the chemical. Careful mixing is required when a volatile chemical is being diluted, such as the amines used for condensate corrosion control in steam boilers. The calculations for mixing liquid chemicals are similar to the mixing of dry chemicals except that volumes are used.

7-6. Changing concentration in a tank. It is common to add the dry or liquid chemical to a tank that is not completely empty. It also may be desired to adjust the concentration of the chemical to meet different treatment objectives or to make the addition of chemicals easier to control.

a. It is convenient to express the chemical in the tank in terms of pounds per inch (lb/in). This can be calculated by dividing the total amount of chemical by the liquid depth of the full tank.

b. The total amount of chemical required in the full tank, minus the chemical remaining in the partially filled tank, equals the amount of chemical to add to the system. The amount of chemical remaining in the tank is computed by multiplying the level in the partially full tank times the chemical per inch.

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Example 7-3:

1. The chemical vat in example 7-2 has a diameter of 6 feet and a full depth of 56 inches, for a full volume of 1,000 gallons. The 3.3 percent phosphate in the full tank represented 272 pounds of phosphate, based on three 100 pound bags of sodium hexametaphosphate. The phosphate per inch is calculated:

$$\begin{aligned}\text{Phosphate, lb/in} &= \text{Phosphate, lb} \div \text{Full Level, inches} \\ &= 272 \div 56 = 4.9 \text{ lb/in}\end{aligned}$$

The level in the tank is 20 inches. The amount of phosphate remaining in the tank is calculated:

$$\begin{aligned}\text{Phosphate, lb} &= \text{Level, inch} \times \text{Phosphate, lb/in} \\ &= 20 \times 4.9 = 98 \text{ lb}\end{aligned}$$

2. The desired concentration in the full tank is 2.0 percent. The total phosphate required in the full tank is calculated:

$$\begin{aligned}\text{Phosphate} &= \text{Percent}/100 \times \text{Vat Volume, gal} \times 8.33 \text{ lb/gal} \\ &= 0.02 \times 1000 \times 8.33 = 167 \text{ lb}\end{aligned}$$

3. Phosphate to add to the vat is 69 pounds (167 - 98). The sodium hexametaphosphate contains 90.5 percent phosphate. The chemical to add is calculated:

$$\begin{aligned}\text{Chemical, lb} &= \text{Phosphate, lb} \div \text{Percent}/100 \\ &= 69 \div 0.905 = 76 \text{ lb}\end{aligned}$$

4. The chemical comes in 100 pound bags, so the actual phosphate added is 91 pounds (100 lb $\times$ 0.905 lb PO₄/lb). The total phosphate in the full tank is 189 pounds (98 + 91). The new phosphate per inch is calculated:

$$\begin{aligned}\text{Phosphate, lb/in} &= \text{Phosphate, lb} \div \text{Full Level, inches} \\ &= 189 \div 56 = 3.4 \text{ lb/in}\end{aligned}$$

5. The actual concentration of phosphate in the tank is calculated:

$$\begin{aligned}\text{Concentration, percent} &= (100 \times \text{Phosphate, lb}) \div (8.33 \text{ lb/gal} \times \text{Volume, gal}) \\ &= (100 \times 189) \div (8.33 \times 1,000) \\ &= 2.27 \text{ percent}\end{aligned}$$

Section III

Feeding Devices

7-7. Metering pumps:

a. Feed pumps tied to pulsing makeup meters, or some other type of proportional feed system are recommended for most systems, especially large steam and cooling water systems and unmanned small systems. Also, if these systems have a metering pump instead of a proportional system, the metering pump can be set to a short stroke or speed to feed smaller amounts of chemical over a long period of time. This avoids large upswings and downswings in system chemical levels.

b. Pumps of various types can take suction from chemical solution tanks and inject a solution of a chemical into a line, a boiler drum, or a cooling tower basin. Pump types include piston pumps, spring-loaded diaphragm pumps, hydraulically actuated diaphragm pumps, peristaltic pumps, and gear pumps. Piston pumps, or to a lesser degree, diaphragm pumps, have trouble with valves sticking or plugging if there are solids in the stream being pumped. Peristaltic pumps do not have this problem since they have no valves. They are especially recommended for feeding sulfuric acid, but they cannot pump against much pressure.

7-8. Bypass feeders. The typical bypass feeder is useful for feeding a solid to a water stream. A bypass feeder will operate across an orifice plate, a partly closed valve, or any other restriction in the line. Bypass feeders are not

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recommended for steam boiler systems, cooling tower systems, or systems that require much makeup water.

7-9. Slowly dissolving chemical packages.

Nylon mesh bags containing slowly dissolving chemicals can be hung in the cold well of a cooling tower. This method of chemical addition is useful for small remote cooling towers that require little attention.

7-10. Eductor chemical addition systems.

The regenerant for ion exchangers is usually fed to the exchanger by an eductor. This is an enclosed unit where the regenerant feed rate is set by the manufacturer. The sales representative should be contacted in case of a malfunction.

7-11. Other systems. Chemical drip pots, even those with a constant head, are not recommended.

7-14. Flow proportioning control. The addition of treatment chemical proportional to makeup water flow is common for cooling towers. This should be done on an automatic basis based on the volume of makeup or on a continuous analysis of one of the control parameters. The addition of treatment chemicals proportional to the boiler feedwater or hot water system makeup flow rate also is common. A typical proportional feed system is illustrated in figure 7-1.

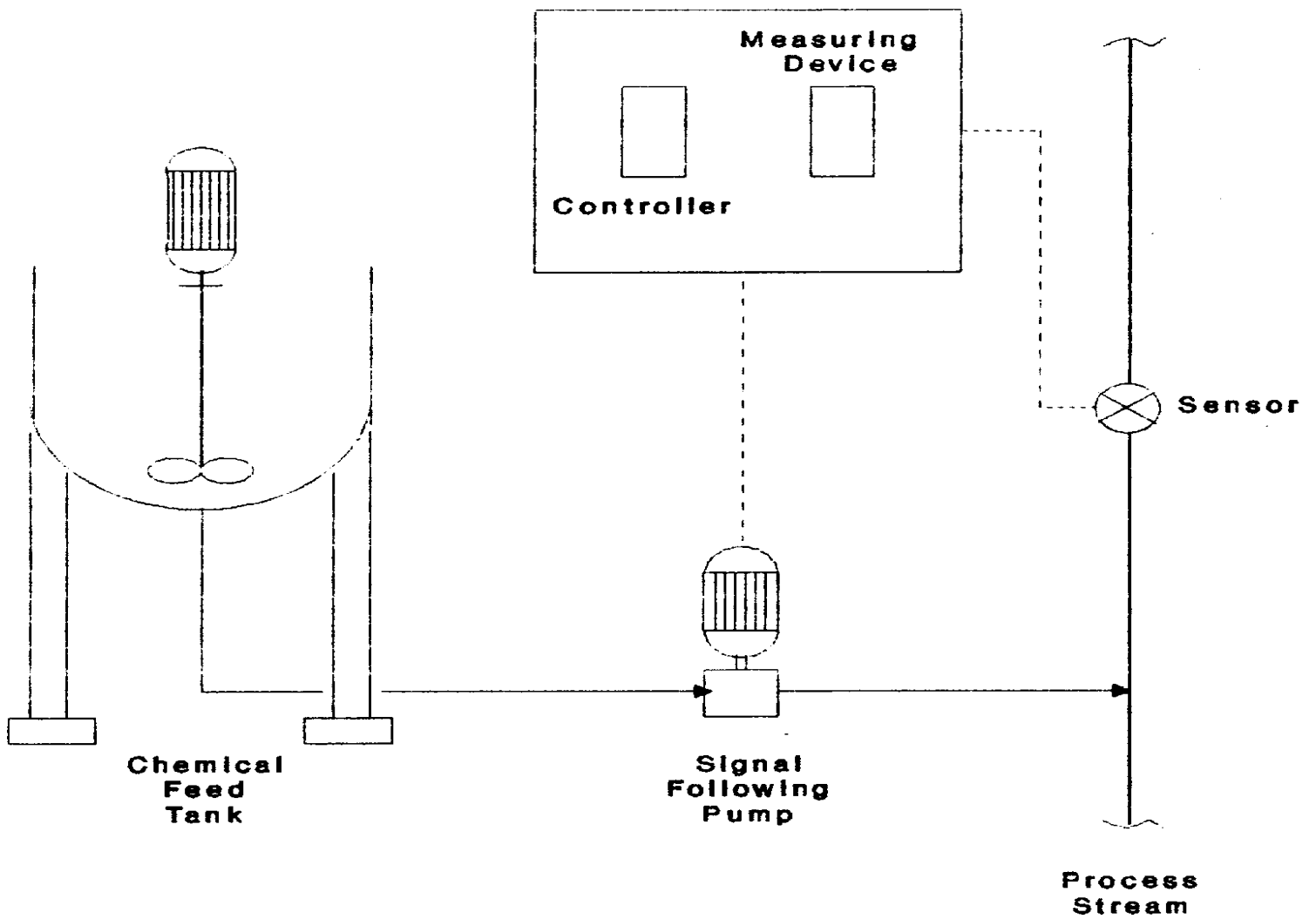
7-15. Timer control. A programmed timer can be used to control chemical feed to water treatment systems. This technique is applied where a regular application of chemical is critical, for example in microbiological control.

Section IV Control Devices

7-12. Conductivity control. This is used in both cooling and heating systems to control the dissolved solids level in the system. The controller can be set at the desired upper level for conductivity with the system blowdown mechanism operating in response to the detection of the upper limit. The signal that controls the blowdown from the system also can be used in cooling towers to control the addition of the treatment chemical.

7-13. Controlling pH. Cooling systems require control of pH within preset limits to prevent corrosion and scaling. Automatic pH controllers for acid or caustic addition are commonly used on major systems.

FIGURE 7-1
TYPICAL PROPORTIONAL FEED SYSTEM



Chapter 8

Chemical Cleaning

Section I General Information

8-1. General guidance.

Chemical cleaning is required to remove mill scale, oil, grease and other debris resulting from installation of new equipment or maintenance and repair of old equipment, and to remove scale and deposits accumulated during system operation. Chemical cleaning of existing systems is not a normal or routine procedure. In fact, the need to chemically clean a boiler in a manned heating plant indicates a need to improve the chemical treatment program.

a. New boilers should be thoroughly cleaned with an alkaline solution at elevated temperature (boilout) to remove oils and greases left from construction. A typical cleaning solution consists of 24 pounds caustic soda, 24 pounds trisodium phosphate (TSP) or disodium phosphate, 8 pounds sodium nitrate and 0.5 pounds wetting agent in 1,000 gallons water. Boilout is generally done by the contractor installing the boiler.

b. Information and procedures in this chapter are general in nature and need to be modified to fit specific applications.

c. The chemical cleaning of an industrial water system should never be attempted by inexperienced personnel. For some cleaning jobs, such as large boilers and cooling towers, it may be advisable to engage a service company specializing in chemical cleaning. If the cleaning is contracted out, it is vital that adequate lines of communications be established, and that safety procedures employed by the service company comply with Army regulations. An orientation meeting

should be scheduled between Army and service company representatives. At that time, the scope of the work can be defined, proper procedures initiated, the nature of the hazards thoroughly discussed and users of the facility notified. Many times proprietary cleaning chemicals may be involved and disclosure of these chemicals should be made at the orientation meeting. Army policies and restrictions can also be explained.

8-2. Reason for cleaning.

Consistent application of a good water treatment program is essential to minimize scale and corrosion problems in industrial water systems. However, scale and deposits which may form will require maintenance cleaning (descaling). If not removed, these scale and deposits may impair the safety of operating personnel, interfere with heat transfer and cause excessive damage to or destruction of the equipment. Cleaning is not appropriate for the removal of deposits when corrosion of the system has advanced to the point where a large number of leaks may be created.

8-3. Types of deposits:

a. The deposits encountered in water systems can be inorganic mineral salts and corrosion products as well as those that are organic or biological in nature. Deposits range from very dense crystalline structures, to very porous, loosely bound materials, to gelatinous slimes. Most water-formed deposits consist of corrosion products such as iron and copper oxides, mineral scales or mixtures.

b. Waterside deposits in heat exchangers are usually carbonate-based scales, while

steam side deposits may be a mixture of metallic oxides and organic residuals from lubricating oil, particularly where reciprocating type engines are used. In steam systems, the oxides are usually iron and copper resulting from aggressive condensate. Microbiological deposits may form in cooling systems from bacterial or algae growths, or from decomposition products of various microorganisms.

c. Boiler deposits may take various forms. In low pressure boilers using a relatively hard feedwater, deposits are essentially calcium and magnesium, silicates, sulfates, carbonates, phosphates and hydroxides, plus some organics. Deposits may also contain considerable amounts of silica, iron, and copper. The characteristics of such deposits can run from spongy, porous to relatively hard, glass-like deposits. The latter deposits occur where silica is present in appreciable quantities in the boiler water. Deposits in medium to high-pressure boiler systems usually are mixtures of iron and copper oxides and phosphates. Dense deposits may tend to form in high heat transfer areas. Considerable quantities of "sludge type" accumulations may be found in downcomers, mud drums, waterwall headers, crossover tubes and areas of low water circulation in the boiler.

Section II

Cleaning Procedures

8-4. Cleaning methods:

a. The oldest techniques of deposits removal utilize mechanical methods. To do an adequate mechanical cleaning job, the equipment may need to be partially or entirely dismantled. Even when equipment is dismantled, some areas may be extremely difficult to reach. Chemical cleaning has

largely replaced mechanical cleaning of process equipment as the most satisfactory method of removing deposits. However, mechanical methods such as wire brushing, tumbling, scraping and abrasive blasting with sand, grit, etc. are still employed in special applications.

b. Cleaning agents may be broadly classified as acid, alkaline, organic or solvent cleaners. There is no general or universal cleaner to remove all deposits. The selection of a solvent or cleaning agent must be based on the material's ability to remove or dissolve the deposit, on cost considerations, safety hazards and the effect of the cleaning material on the metals involved.

c. General guidance and procedures for preparing solutions of hydrochloric (muriatic) acid and sulfamic acid are provided in paragraphs 8-5 and 8-6.

8-5. Hydrochloric (muriatic) acid.

Inhibited hydrochloric (muriatic) acid in strengths of 5 to 20 percent is a very effective scale remover. However, for most applications, a 10 percent solution is adequate. The following formulation is for a 10 percent hydrochloric acid solution. It is designed for removing scale consisting primarily of carbonates with lesser amounts of phosphates, sulfates and silicates typically found in a steam boiler system containing copper alloys and treated with a phosphate base program. Depending on the specific descaling application some of these ingredients can be omitted from the formulation. For example, diethylthiourea does not need to be added if there is no copper in the system. Where there is only carbonate scale to be removed, ammonium bifluoride may be omitted. A wetting agent is preferable but not absolutely necessary.

a. To make one thousand (1,000) gallons of

a 10 percent solution:

(1) Add two hundred eighty-five (285) gallons concentrated (36% strength) hydrochloric acid, Federal Specification O-H-765, to about 600 gallons of water.

(2) Add an amount of corrosion inhibitor, Military Specification MIL-1-17433, recommended by the manufacturer to the diluted acid solution. The inhibitor must be compatible with hydrochloric acid and must not precipitate under any condition during the cleaning operation.

(3) In a separate tank containing about 75 gallons water:

(a) Add eighty-five (85) pounds of one, three (1,3) diethylthiourea to complex any copper and keep it from depositing. Do not use the diethylthiourea as the corrosion inhibitor required in (2) above.

(b) Add one hundred-twenty (120) pounds of ammonium bifluoride, technical grade, to help dissolve certain iron and silica scales.

(c) Add 1 gallon of wetting agent, Military Specification MIL-D-16791.

(4) Add the dissolved diethylthiourea, ammonium bifluoride, and wetting agent to the diluted acid solution. Add sufficient water to obtain 1,000 gallons.

b. Carbonate deposits dissolve rapidly in hydrochloric acid with evolution of free carbon dioxide. The escaping carbon dioxide tends to create some circulation or agitation of the acid, which insures the continual contact of fresh acid with the scale. Once the carbonate has been dissolved from a mixed deposit, a loose, porous structure may be left behind, which disintegrates or can be effectively removed from the equipment by washing with high pressure water or by mechanical means.

c. The removal of phosphate deposits can usually be affected by hydrochloric acid. However, phosphate deposits have a tendency

to go into solution rather slowly. To keep the total cleaning time within reason, a higher temperature usually is necessary to remove a predominantly phosphate scale.

d. Most metallic oxides that might be found in deposits can be removed with hydrochloric acid. The rate of the dissolution is a function of temperature and solution velocity.

e. Heavy silica and sulfate scales are almost impossible to remove with hydrochloric acid. Special chemicals and procedures are required to remove these scales.

f. Hydrochloric acid should not be used to clean stainless steel because the chloride ion may cause pitting or stress corrosion cracking. Also, hydrochloric acid should not be used for removing scale from galvanized steel surfaces since the zinc in the galvanizing is corroded by it.

8-6. Sulfamic acid.

Sulfamic acid is an odorless, white, crystalline solid organic acid readily soluble in water. An inhibited sulfamic acid compound, in a dry powder form, is available under Military Specification MIL-B-24155. A 5 to 20 percent solution (5 to 20 pounds to about 10 gallons water) is generally used for removing scale from metal surfaces.

a. Carbonate deposits are dissolved in sulfamic acid in a similar manner as in hydrochloric acid. All the common sulfamate salts (including calcium) are very soluble in water.

b. The dry powder form of sulfamic acid is safer to handle than hydrochloric acid. Aqueous solutions of sulfamic acid, however, are generally much slower in action and requires heating to provide effective scale removal. To obtain the same fast cleaning time achieved with hydrochloric acid at room temperature the sulfamic acid solution must be heated to 130 to 160°F. One exception is

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sulfate scale. Sulfamic acid is more effective on sulfate scale than hydrochloric acid.

c. Inhibited sulfamic acid used at temperatures up to 110°F will not corrode galvanized steel, and is recommended for removing scale in cooling towers, evaporative condensers, and other equipment containing galvanized steel. In general, sulfamic acid can be applied to equipment while operating, but should be drained from the system after a few hours.

d. Commercially prepared descaling compounds consisting of concentrated or diluted inhibited acid (containing 7 to 28 percent of the acid and inhibitor) may be purchased under various trade names at prices 4 to 30 times the costs of the ingredients when purchased as generic chemicals.

(1) Advertisements of some of these products may claim that cotton clothes and skin are not attacked by the acid. These claims are usually based on the use of such a dilute solution of the acid that attack on clothes and skin is minimal, however, the economics of scale removal is seriously affected. Recognize that the handling of acid in any strength must be performed with considerable care and caution.

(2) Since the cost of diluted acid is expensive, Army personnel are encouraged to purchase the concentrated acid under government specifications, dilute to usable strengths, and add necessary corrosion inhibitors (see paragraph 8-5). Users of small quantities (possibly less than 10 gallons of diluted acid per year) may not be able to justify the purchase of undiluted acid and the spending of time, cost and effort to prepare the cleaning solution. Therefore, consider your own requirements before ordering.

8-7. Preparation for cleaning.

The unit to be cleaned must be isolated from

other parts of the system. For systems which cannot be isolated by closing valves, isolation may be accomplished using rubber blankets, wooden bulkheads with seals, inflatable nylon or rubber bags, rubber sponge-covered plugs, blind flanges and steel plates with rubber seals. Long lines may require auxiliary connections for chemical cleaning.

a. Decide whether to clean by a soaking process, or by circulation of the cleaning solution (see paragraph 8-8). In either case, temporary piping or hose lines will be required from the cleaning solution mixing tanks or trucks to the unit, with return lines to tanks or drains. Proper precautions and adequate provisions must be made to protect equipment, isolate control lines, replace liquid level sight glasses with expendable materials and provide suitable points for checking temperatures. It may be mandatory to remove certain system components which cannot stand up under the cleaning cycle.

b. Complete cleaning procedure must be worked out in detail before starting chemical cleaning operations. Some of the factors to be considered are methods for controlling temperatures, means of mixing, heating and circulating the chemical solution, proper venting of dangerous gases from equipment to a safe area, and means for draining, filling and flushing under inert atmospheres. Sampling points, test procedures and control limits also need to be engineered.

8-8. Methods for removing scale.

Removal of scale may be done by circulating the inhibited acid solution through the equipment or by soaking the equipment in a tank of the inhibited acid. Before starting any descaling process the acid descalant must be checked to make sure it is properly inhibited. This is done by placing a mild steel coupon into a breaker containing the prepared diluted

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acid. No reaction should be noticed around the coupon. If a reaction generating hydrogen gas bubbles around the coupon is observed, additional inhibitor must be added.

a. Recirculating process for boilers. The following procedures are applicable for cleaning small boilers or other systems that can accommodate a hot recirculating acid solution.

(1) Fill the boiler or system with preheated 160 to 170°F dilute acid solution.

(2) Allow the dilute acid solution to soak for 8 hours. Circulate the acid solution for about 15 minutes each hour at a rate of about 50 gal/min.

(3) Keep the temperature of the acid solution between 160 and 170°F. Measure and record the temperature at least every 30 minutes.

(4) Check and record the acid strength (see paragraph 8-9) at least every hour.

(5) Drain the system by forcing out the acid solution with 40 to 50 psi nitrogen; Federal Specification BB-N-411, Class 1. If leaks develop when the system is under nitrogen pressure, an alternate method for removing the acid must be used such as pumping.

(6) Fill the boiler with preheated 150 to 160°F water and soak at this temperature for 15 minutes.

(7) Drain under nitrogen pressure at 40 to 50 psi.

(8) Prepare a mild acid rinse solution as follows: Add 2 gallons of hydrochloric acid (Federal Specification O-H-765) for each 1,000 gallons water. Also add corrosion inhibitor, Military Specification MIL-1-17433, in the amount recommended by the manufacturer.

(9) Fill the boiler with the preheated 160 to 170°F mild acid rinse solution and soak for 30 minutes.

(10) Drain the mild acid rinse under nitrogen pressure at 40 to 50 psig. Maintain nitrogen on the boiler to prevent air from leaking inside.

(11) Prepare passivating solution as follows: To each 1,000 gallons of distilled water (or other water with less than 50 ppm total hardness (as CaCO_3)), add 80 pounds of passivator compound, Military Specification MIL-P-24183, 0.5 percent by weight sodium nitrite (Federal Specification O-S-639), and 0.25 percent by weight monosodium phosphate (Military Specification MIL-S-13727).

(12) Fill the boiler with the passivating solution preheated to 150 to 160°F, circulate for 10 minutes, and hold in boiler at 150 to 160°F for an additional 30 minutes.

(13) Drain and rinse boiler until the pH of the rinse water is between 8 and 10.

b. Circulating method without heat. A typical process for descaling smaller type equipment, such as enclosed vessels or hot water heater coils, without heating the acid solution is as follows:

(1) Note that an acid cleaning assembly may consist of a small cart on which is mounted a pump and a 5 to 50 gallon steel or polyethylene tank with a bottom outlet to the pump.

(2) Install sill cocks at the bottom of the water inlet of the heat exchanger and at the top of the water outlet so that a return line can be connected directly from the acid pump and from the heat exchanger to the acid tank.

(3) Prepare an inhibited acid cleaning solution (see paragraph 8-5 or 8-6).

(4) Pump acid solution into the heat exchanger through the hose connection. Continue circulation until the reaction is complete as indicated by subsidence of foaming or depletion of the acid.

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(5) If the scale is not completely removed, check the acid strength in the system (see paragraph 8-9). If less than 3 percent, add fresh acid solution and continue circulation until the remaining scale is removed. Usually an hour of circulation is adequate.

(6) Drain the heat exchanger.

(7) Neutralize remaining acid by circulating a 1 percent sodium carbonate (soda ash) solution (about 8 lb/100 gal) for about 10 minutes.

(8) Rinse thoroughly with water until the pH of the rinse water is between 8 and 10.

c. Fill and soak method:

(1) Prepare an inhibited dilute acid solution (see paragraph 8-5 or 8-6) in a suitable size container.

(2) Depending on the item being cleaned and the types of scale involved, it may be desirable to place an agitator (mixer) in the tank or install a pump outside the tank to circulate the acid solution. Also, a method to heat the acid may be required such as the use of a steam coil. All equipment must be explosion proof and acid resistant.

(3) Immerse the item to be cleaned in the dilute acid solution. Continue soaking until the reaction is complete as indicated by the subsidence of foaming or depletion of the acid.

(4) If the scale is not completely removed, check the acid strength (see paragraph 8-9). If less than 3 percent, add additional acid and continue soaking the items until the remaining scale is dissolved. Usually one to two hours of soaking is adequate.

(5) Remove item from tank.

(6) To neutralize remaining acid, immerse the item in a 1 percent sodium carbonate (soda ash) solution (about 8 lb/100 gal) for about 2 to 3 minutes.

(7) Thoroughly rinse with water.

8-9. Checking strength of acid solution.

The initial strength of the dilute acid will vary from about 5 to 20 percent, although about 10 percent is typical. As the acid is consumed in dissolving scale, the strength of the acid is decreased. Periodically, during a cleaning operation the strength of the acid solution should be measured. When it falls below about 3 percent, the solution may be discarded since most of its scale dissolving capability will have been used. The procedure to check the acid strength is as follows:

Apparatus:

Burette, 25 ml Automatic (for sodium hydroxide solution)

Bottle, w/Dropper, 2 oz. (for phenolphthalein indicator solution)

Graduated Cylinder, 10 ml

Casserole, Porcelain, heavy duty, 210 ml capacity

Stirring Rod

Reagents:

Sodium Hydroxide Solution, 1.0 N

Phenolphthalein Indicator Solution, 0.5 percent

Method:

1. Measure 10 ml of the acid solution accurately in the graduated cylinder.
2. Pour into the casserole.
3. Add 2 to 4 drops of Phenolphthalein Indicator Solution to the casserole and stir.
4. Fill the automatic burette with the 1.0 N Sodium Hydroxide Solution, then allow the excess to drain back into the bottle.
5. While stirring the acid solution constantly, add Sodium Hydroxide Solution from the burette to the casserole until color changes to a permanent faint pink. This is the endpoint. Read the burette to the nearest 0.1 ml.

Results:

1. For Hydrochloric Acid:

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Percent Hydrochloric Acid = ml of
1.0 N Sodium Hydroxide x 0.36

2. For Sulfamic Acid:

Percent Sulfamic Acid = ml of 1.0
N Sodium Hydroxide x 0.97*

Appendix A

REFERENCES

Government Publications

Department of the Army

- AR 420-49 Utility Services
- TM 5-650 Central Boiler Plant
- TM 5-660 Maintenance and Operation of Water Supply, Treatment, and Distribution Systems.

Nongovernment Publications

- National Association of Corrosion Engineers (NACE)
 - TPC Publication 1; Cooling Water Treatment Manual
- American Society of Mechanical Engineers (ASTM)
 - Performance Test Codes

Appendix B

Practical (Puckorius) Scaling Index (PSI)

B-1. Development of PSI.

a. Historically, the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI) have been used to predict the tendency of a water to be scale forming or scale dissolving. Both are based on the pH of saturation (pH_s) for calcium carbonate under a specific water condition. Both indices use the measured pH of the cooling water.

(1) $\text{LSI} = (\text{measured pH}) - (\text{pH}_s)$. A positive value indicates scale; a negative value, no scale.

(2) $\text{RSI} = (2 \text{ pH}_s) - (\text{measured pH})$. A value below 6 means scale; above 6, no scale.

b. Use of LSI and RSI sometimes gave inconsistent or even conflicting results. Based on a long term study relative to calcium carbonate scale formation when applying both the LSI and RSI, P.R. Puckorius and J.M. Brooke developed a new index that gives much better and more consistent indication of scaling conditions of cooling water. The new index, the Practical Scaling Index (PSI), or sometimes called the Puckorius Scaling Index, is based on correction of the system pH to match the total alkalinity of the water being evaluated. This is necessary because the pH is often buffered, causing the pH to not relate correctly to the bicarbonate alkalinity, one of the factors in the pH_s calculation. To calculate the PSI, the pH_s is determined in the same manner as for the LSI and RSI. Next, an adjusted or equilibrium pH (pH_{eq}) is obtained from a total alkalinity/pH chart (paragraph B-3 and table B-5). The value of pH_{eq} rather than measured pH is used in the

following formula:

$$\text{PSI} = (2 \text{ pH}_s) - (\text{pH}_{\text{eq}})$$

A value below 6 means scale; above 6, no scale.

B-2. Calculating pH of saturation (pH_s).

The pH of saturation (pH_s) can be determined from the relationship between various characteristics of water. The following factors and formula are used in determining the pH_s :

(1) Factors Needed to Calculate pH_s :

A = Total Dissolved Solids

(ppm), table B-1

B = Temperature ($^{\circ}\text{F}$), table B-2

C = Calcium Hardness (ppm as CaCO_3), table B-3

D = Total Alkalinity (ppm as CaCO_3), table B-4

$$(2) \text{pH}_s = 9.30 + A + B - (C + D)$$

(3) Example B-1: Water from a cooling tower has a TDS of 1,000 ppm, calcium hardness of 500 ppm (as CaCO_3), total alkalinity of 100 ppm (as CaCO_3) and measured pH of 8.2. The hottest temperature on the waterside of the heat exchanger is 120°F .

$$\text{pH}_s = 9.30 + A + B - (C + D)$$

$$\text{pH}_s = 9.30 + 0.20 + 1.57 - (2.30 + 2.00) = 6.77$$

B-3. Calculating equilibrium pH (pH_{eq}).

Puckorius and Brooke developed the improved relationship between total alkalinity and pH after studying hundreds of cooling systems over some 20 years. The pH_{eq} values shown in table B-5 for the total alkalinity measured in the cooling water are used for calculating the PSI.

TABLE B-1
FACTOR "A" FOR TOTAL DISSOLVED SOLIDS

Total Solids, ppm	Value of "A"
50	0.07
75	0.08
100	0.10
150	0.11
200	0.13
300	0.14
400	0.16
600	0.18
800	0.19
1000	0.20
1500	0.21
2000	0.22
2500	0.23
3000	0.24
4000	0.25
5000	0.26

TABLE B-2
FACTOR "B" FOR TEMPERATURE*

deg F	deg F, units				
tens	0	2	4	6	8
30	--	2.60	2.57	2.54	2.51
40	2.48	2.45	2.43	2.40	2.37
50	2.34	2.31	2.28	2.25	2.22
60	2.20	2.17	2.14	2.11	2.09
70	2.06	2.04	2.03	2.00	1.97
80	1.95	1.92	1.90	1.88	1.86
90	1.84	1.82	1.80	1.78	1.76
100	1.74	1.72	1.71	1.69	1.67
110	1.65	1.64	1.62	1.60	1.58
120	1.57	1.55	1.53	1.51	1.50
130	1.48	1.46	1.44	1.43	1.41
140	1.40	1.38	1.37	1.35	1.34
150	1.32	1.31	1.29	1.28	1.27
160	1.26	1.24	1.23	1.22	1.21
170	1.19	1.18	1.17	1.16	--

* Find value of "B" in appropriate units column. Example: For water at 86°F, B = 1.88

TABLE B-3
FACTOR "C" FOR CALCIUM HARDNESS (as ppm CaCO₃)*
Zero to 200 ppm

ppm	ppm, units									
tens	0	1	2	3	4	5	6	7	8	9
0	--	--	--	0.08	0.20	0.30	0.38	0.45	0.51	0.56
10	0.60	0.64	0.68	0.72	0.75	0.78	0.81	0.83	0.86	0.88
20	0.90	0.92	0.94	0.95	0.98	1.01	1.02	1.03	1.05	1.06
30	1.06	1.09	1.11	1.12	1.13	1.15	1.16	1.17	1.18	1.19
40	1.20	1.21	1.23	1.25	1.25	1.25	1.26	1.27	1.28	1.29
50	1.30	1.31	1.32	1.33	1.34	1.34	1.35	1.36	1.37	1.37
60	1.38	1.39	1.39	1.40	1.41	1.42	1.42	1.43	1.43	1.44
70	1.45	1.45	1.46	1.47	1.47	1.48	1.48	1.49	1.49	1.50
80	1.51	1.51	1.52	1.53	1.53	1.53	1.54	1.54	1.55	1.55
90	1.56	1.56	1.57	1.57	1.58	1.58	1.58	1.59	1.59	1.60
100	1.60	1.61	1.61	1.61	1.62	1.62	1.63	1.63	1.64	1.64
110	1.64	1.65	1.65	1.65	1.65	1.66	1.67	1.67	1.67	1.68
120	1.68	1.68	1.69	1.70	1.70	1.70	1.70	1.71	1.71	1.71
130	1.72	1.72	1.72	1.73	1.73	1.73	1.74	1.74	1.74	1.75
140	1.75	1.75	1.75	1.76	1.76	1.77	1.77	1.77	1.77	1.78
150	1.78	1.78	1.78	1.80	1.80	1.80	1.80	1.80	1.80	1.80
160	1.81	1.81	1.81	1.81	1.82	1.82	1.82	1.82	1.83	1.83
170	1.83	1.84	1.84	1.84	1.84	1.85	1.85	1.85	1.85	1.85
180	1.86	1.86	1.86	1.86	1.87	1.87	1.87	1.87	1.88	1.88
190	1.88	1.88	1.89	1.89	1.89	1.89	1.89	1.90	1.90	1.90
200	1.90	1.91	1.91	1.91	1.91	1.91	1.92	1.92	1.92	1.92

TABLE B-3 continued

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FACTOR "C" FOR CALCIUM HARDNESS (as ppm CaCO₃)*
200 to 990 ppm

ppm	ppm, tens									
100's	0	10	20	30	40	50	60	70	80	90
200	--	1.92	1.94	1.96	1.98	2.00	2.02	2.03	2.05	2.06
300	2.08	2.09	2.11	2.12	2.13	2.15	2.16	2.17	2.18	2.19
400	2.20	2.21	2.23	2.25	2.25	2.26	2.26	2.27	2.28	2.29
500	2.30	2.31	2.32	2.33	2.34	2.34	2.35	2.36	2.37	2.37
600	2.38	2.39	2.39	2.40	2.41	2.42	2.42	2.43	2.43	2.44
700	2.45	2.45	2.45	2.47	2.47	2.48	2.48	2.49	2.49	2.50
800	2.51	2.51	2.52	2.52	2.53	2.53	2.54	2.54	2.55	2.55
900	2.56	2.56	2.56	2.57	2.57	2.58	2.58	2.59	2.59	2.60

* Use upper portion to find values of "C" for 3-209 ppm calcium hardness, lower portion for 210-990 ppm. Example: For 144 ppm calcium hardness (as CaCO₃), C = 1.76

TABLE B-4
FACTOR "D" FOR ALKALINITY (as ppm CaCO₃)*
Zero to 200 ppm

ppm	ppm, units									
tens	0	1	2	3	4	5	6	7	8	9
0	--	0.00	0.30	0.48	0.60	0.70	0.78	0.85	0.90	0.95
10	1.00	1.04	1.08	1.11	1.15	1.18	1.20	1.23	1.26	1.29
20	1.30	1.32	1.34	1.36	1.38	1.40	1.42	1.43	1.45	1.46
30	1.48	1.49	1.51	1.52	1.53	1.54	1.56	1.57	1.58	1.59
40	1.60	1.61	1.62	1.63	1.64	1.65	1.67	1.67	1.68	1.69
50	1.70	1.71	1.72	1.72	1.73	1.74	1.75	1.76	1.76	1.77
60	1.78	1.79	1.80	1.81	1.81	1.82	1.83	1.83	1.83	1.84
70	1.85	1.85	1.86	1.86	1.87	1.88	1.88	1.89	1.89	1.90
80	1.90	1.91	1.91	1.92	1.92	1.93	1.93	1.94	1.94	1.95
90	1.95	1.96	1.96	1.97	1.97	1.98	1.98	1.99	1.99	2.00
100	2.00	2.00	2.01	2.01	2.02	2.02	2.03	2.03	2.03	2.04
110	2.04	2.05	2.05	2.05	2.05	2.06	2.06	2.07	2.07	2.08
120	2.08	2.08	2.09	2.09	2.09	2.10	2.10	2.10	2.11	2.11
130	2.11	2.12	2.12	2.12	2.13	2.13	2.13	2.14	2.14	2.14
140	2.14	2.15	2.15	2.16	2.16	2.16	2.16	2.17	2.17	2.17
150	2.18	2.18	2.18	2.18	2.19	2.19	2.19	2.20	2.20	2.20
160	2.20	2.21	2.21	2.21	2.21	2.22	2.22	2.23	2.23	2.23
170	2.23	2.23	2.23	2.24	2.24	2.24	2.24	2.25	2.25	2.26
180	2.26	2.26	2.26	2.26	2.26	2.27	2.27	2.27	2.27	2.28
190	2.28	2.28	2.28	2.29	2.29	2.29	2.29	2.29	2.30	2.30
200	2.30	2.30	2.30	2.31	2.31	2.31	2.31	2.32	2.32	2.32

TABLE B-4 continued

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**FACTOR "D" FOR ALKALINITY (as ppm CaCO₃)*
200 to 890 ppm**

ppm	ppm, tens									
100's	0	10	20	30	40	50	60	70	80	90
200	--	2.32	2.34	2.36	2.38	2.40	2.42	2.43	2.45	2.45
300	2.48	2.49	2.51	2.52	2.53	2.54	2.56	2.57	2.58	2.59
400	2.60	2.61	2.62	2.63	2.64	2.65	2.66	2.67	2.68	2.69
500	2.70	2.71	2.72	2.72	2.73	2.74	2.75	2.76	2.76	2.77
600	2.78	2.79	2.80	2.81	2.81	2.81	2.82	2.83	2.83	2.84
700	2.85	2.85	2.86	2.86	2.87	2.88	2.88	2.89	2.89	2.90
800	2.90	2.91	2.91	2.92	2.92	2.93	2.93	2.94	2.94	2.95

* Use upper portion for values of "D" for 1-209 ppm, lower portion for 210-990 ppm.

TABLE B-5
EQUILIBRIUM pH VALUE (pH_{eq}) DETERMINED FROM TOTAL ALKALINITY

Alkalinity ppm	Alkalinity, ppm CaCO ₃ , tens									
hundreds	0	10	20	30	40	50	60	70	80	90
0	--	6.00	6.45	6.70	6.89	7.03	7.14	7.24	7.33	7.40
100	7.47	7.53	7.59	7.64	7.68	7.73	7.77	7.81	7.84	7.88
200	7.91	7.94	7.97	8.00	8.03	8.05	8.08	8.10	8.15	8.15
300	8.17	8.19	8.21	8.23	8.25	8.27	8.29	8.30	8.32	8.34
400	8.35	8.37	8.38	8.40	8.41	8.43	8.44	8.46	8.47	8.48
500	8.49	8.51	8.52	8.53	8.54	8.56	8.57	8.58	8.59	8.60
600	8.61	8.62	8.63	8.64	8.65	8.66	8.67	8.67	8.68	8.70
700	8.71	8.72	8.73	8.74	8.74	8.75	8.76	8.77	8.78	8.79
800	8.79	8.80	8.81	8.82	8.82	8.83	8.84	8.85	8.85	8.86
900	8.87	8.88	8.88	8.89	8.90	8.90	8.91	8.92	8.92	8.93

b. Example B-2: Water from a cooling tower has a total alkalinity of 100 ppm (as CaCO₃) and a measured pH of 8.2 (same as example B-1). From table B-5, the pH_{eq} is 7.47.

$$\text{PSI} = (2\text{pH}_s) - (\text{pH}_{\text{eq}}) = 2(6.77) - 7.47 \\ = 13.54 - 7.47 = 6.07$$

$$\text{RSI} = (2\text{pH}_s) - (\text{measured pH}) = 13.54 - 8.2 = 5.34$$

$$\text{LSI} = (\text{measured pH}) - (\text{pH}_s) = 8.2 - 6.77 = +1.43$$

c. The pH_{eq} may also be calculated as follows:

$$\text{pH}_{\text{eq}} = 1.485 \log \text{TA} + 4.54$$

where TA denotes total alkalinity.

B-4. Scaling severity keyed to indices.

a. Commonly accepted interpretation of the previously discussed indices is shown in table B-6.

b. In example B-2, the LSI predicted that the water would exhibit a severe to very severe scaling tendency. The RSI predicted that the water would exhibit a moderate to severe scaling tendency. The PSI predicted that the water is stable with no tendency to form or dissolve scale.

TABLE B-6
SCALING INDICES VERSUS CONDITION

LSI	PSI/RSI	Condition
3.0	3.0	Extremely severe scaling
2.0	4.0	Very severe scaling
1.0	5.0	Severe scaling
0.5	5.5	Moderate scaling
0.2	5.8	Slight scaling
0.0	6.0	Stable water, no scaling, no tendency to dissolve scale
-0.2	6.5	No scaling, very slight tendency to dissolve scale
-0.5	7.0	No scaling, slight tendency to dissolve scale
-1.0	8.0	No scaling, moderate tendency to dissolve scale
-2.0	9.0	No scaling, strong tendency to dissolve scale
-3.0	10.0	No scaling, very strong tendency to dissolve scale

Appendix C

Corrosion Testing With Coupon Type Test Specimens

C-1. Purpose. Corrosion tests with metal coupon test specimens are used to determine how corrosive a water is towards a specific metal. Coupon test specimens are particularly useful in monitoring the effectiveness of chemical corrosion control programs. The extent of both general and localized corrosion can be determined. Also, examination of the specimens as they are removed from the system can provide information regarding deposit accumulation or microbiological slime growth.

C-2. Application.

a. The coupons are metal tags of various sizes. Generally, low carbon steel specimens are used as the most susceptible metal to corrosion; however, copper, stainless steel, brass and other metals are available for special studies. The specimens are prepared and cleaned to ensure uniformity and then weighed. The general corrosion rate is determined after exposure. Coupons are cleaned and reweighed. Corrosion rates are calculated based on the weight loss, time of exposure and the area and specific gravity of the coupon, and are expressed in mils per year (mpy).

b. Since the goal of the corrosion testing program is to provide information regarding conditions within the system, the corrosion coupons should be exposed to conditions that reflect those in the system as a whole. Water velocity and temperature will significantly affect the corrosion rate. Corrosion rates can be significantly increased when velocity is either too low or too high. For best results, water velocity flowing by the test specimen should be 3 to 5 ft/sec and both adjustable and measurable. Temperature also affects the rate

of corrosion with higher temperatures usually increasing corrosion. Therefore, in cooling water systems both the cold supply water and the hot return water should be evaluated with corrosion coupons. When only one test rack can be installed, the warm water return at the tower should be used which provides an average hot water temperature.

c. Expose corrosion coupons for a minimum of 30 calendar days and a maximum of 90 calendar days except for special tests. Although spot checks are useful, a regular schedule will determine trends and recognize changes within the system. When corrosion test specimens of different metals are installed in the same corrosion test rack, the more noble or resistant metal should be downstream of less resistant metals.

d. Specimens are shipped in vapor-inhibited bags. Do not remove them from the bags until the specimen is to be installed. The vapor-inhibited bags should be saved for returning exposed specimens. Do not handle specimens directly with fingers since finger prints can initiate corrosion sites. Record on the appropriate form the exact location and date of installation.

e. After the specimens have been exposed for the desired time, (30, 60, or 90 calendar days), carefully remove, air dry without disturbing any deposits, and return them to the original vapor-inhibited bag. Record date of removal on the appropriate form. Then send the exposed specimens and completed forms to the supplier for evaluation. After evaluation, the results are presented and interpreted in a written report.

C-3. Installation of coupon type test specimens.

a. Coupons are usually installed in pipe "tees" by means of corrosion test racks which include a 1 inch pipe plug, drilled and tapped to accept a plastic or phenolic rod with a nylon nut and bolt for attaching the coupon to the rod. A bypass arrangement with 1 inch piping as shown in figure C-1 will facilitate installation and removal as well as allow the use of multiple specimens. Polyvinyl chloride (PVC) will eliminate electrical effects but cannot be used for hot condensate. A corrosion test rack may be purchased or constructed on site.

b. For steam and condensate return lines, install coupons in any convenient location where there are "tees". When using a bypass arrangement, condensate from the outlet is piped back into the system. Bypasses should be constructed of iron pipe and fittings and installed only where there is sufficient pressure differential to ensure a continuous flow through the bypass.

c. To ensure proper results, the following points should be checked:

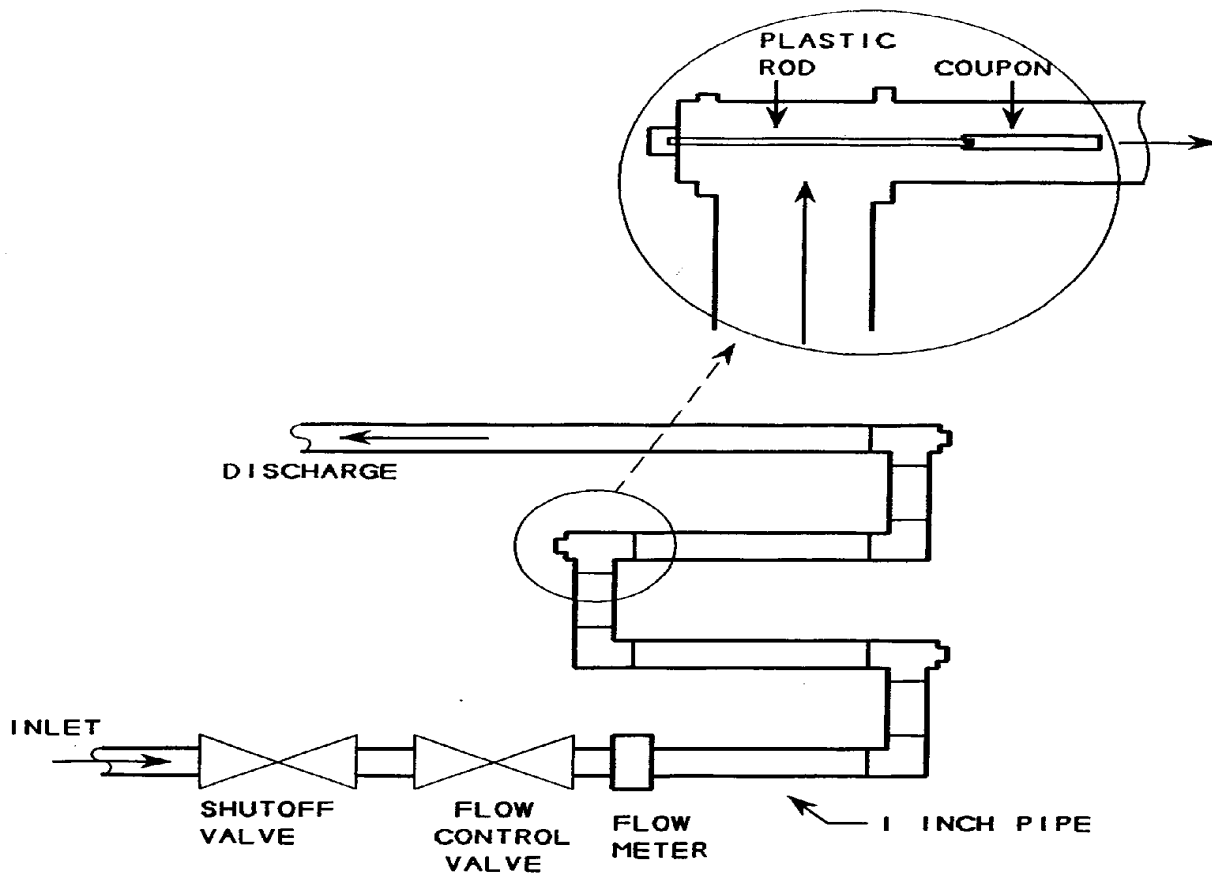
(1) Flow through the corrosion test rack must be continuous and measurable. Use flow meters for all installations. When a flow meter does not exist, flow must be measured by timing how long it takes to fill a container of known volume such as a five gallon pail.

(2) Normally, water velocity through the corrosion test rack should be 3 to 5 ft/sec. The velocities in ft/sec for given gpm flows for various pipe sizes are shown below:

Velocity	Flow Rate in gpm		
	1" line	1-1/4" line	1-1/2" line
3	8	14	19
5	13	23	30

d. Direction of flow should be as shown in figure C-1 to minimize turbulence around the corrosion test specimen and ensure that the test rack remains full of water.

FIGURE C-1
BYPASS PIPING FOR CORROSION TESTING
COOLING WATER AND CONDENSATE SYSTEMS



Appendix D

Corrosion Testing With Test Nipple Assembly

D-1. PURPOSE. Corrosion tests with metal test specimens are used to determine how corrosive a water is toward a specific metal. Although test nipple assemblies (referred to as "tester") can be used in many applications; they are used on Army installations to evaluate corrosion problems in steam condensate return systems.

D-2. APPLICATION.

a. The tester consists of three 3 inch by 3/4 inch NPT nipples, connected by two couplings (see figure D-1). The center nipple contains short inserts machined from steel tubing similar to the steel pipe in the condensate system. The outside diameter of the inserts is approximately the same as the inside diameter of the center 3/4 inch machined coupling. The two end nipples of the tester are to be installed between two unions in such a manner that condensate will constantly flow through the tester. See paragraph D-3 for detailed installation instructions.

b. Serious corrosion is more likely in large area heating systems which have long return lines. More concentrated systems, such as laundries, and low-pressure closed systems, in which there is very little feedwater makeup, generally experience much less condensate return line corrosion.

c. Information obtained from one or two condensate return systems on an Army installation is generally sufficient to serve as a survey of the entire facility, if the test points are well chosen. One or more testers would be installed in the largest area heating system and another in a smaller system. The testers should be installed at points where

maintenance work has been required due to corrosion.

d. The tester is provided by the supplier complete and ready for installation. An appropriate data form is also provided with the tester. This form must be completed by the user for correct interpretation of corrosion that may occur on the tester inserts. The user is required to draw a picture to show how and where the tester was installed.

e. At the end of the test period, the tester is removed. The tester is rinsed internally for several seconds with very hot water, drained, and immediately capped on both ends with the plastic caps which had been supplied with the tester.

f. A condensate sample is collected from the area where the tester was installed and returned to the supplier at the same time as the tester.

g. The tester is packed in any convenient package, enclosing the completed data sheet, and returned to the supplier.

D-3. INSTALLATION OF TESTER.

a. Install the tester in a horizontal return line. If morpholine treatment is being used, install the tester in a building near the end of the steam main where the treatment would be expected to be least effective. If a mixture of morpholine and cyclohexylamine is used, install a tester at each end of the system.

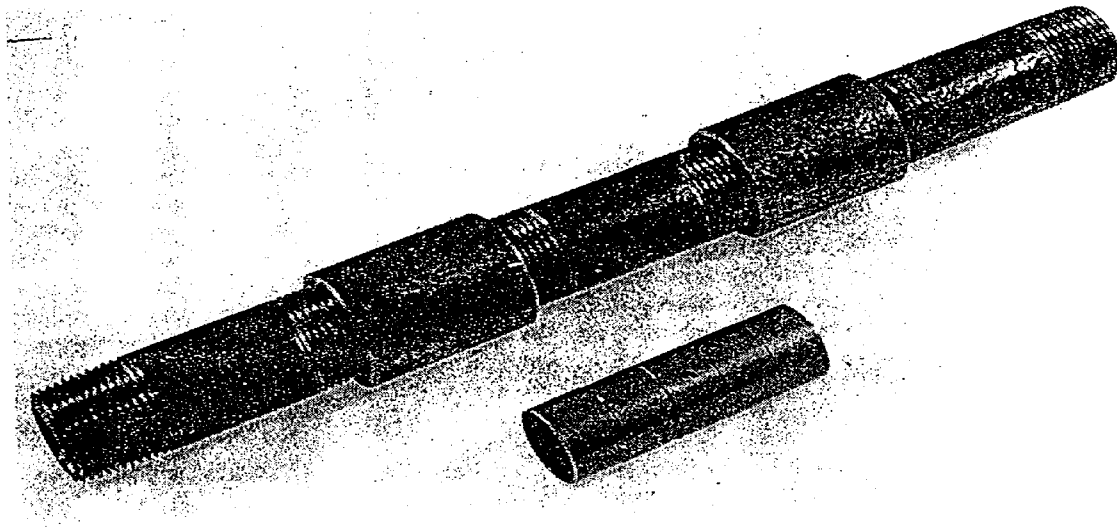
b. Insure representative sampling of the condensate by the tester. Do not install the tester to receive drips from steam mains. Drips may be less corrosive (less acidic) than the average condensate.

c. Place the tester horizontally to receive the condensate from a hot water generator or space heater that is drained by a 3/4 inch trap. Do not install the tester downstream from a pump in the condensate line. Avoid bypasses and do not overload the tester with condensate from several traps. Enough condensate should flow the tester to fill it at least halfway.

d. To install the tester, remove a section of the pipe from the condensate return system. Replace the section of pipe removed with the tester, unions, and any additional pipe needed to complete the installations.

e. Leave the tester in place for about 90 days. Record the dates the tester is installed and removed.

FIGURE D-1
CONDENSATE CORROSION TESTER
Appendix E



Testing Of Samples From Industrial Water Systems

E-1. Purpose of testing. Testing of industrial water is done to determine the amount of treatment chemicals in the water so that dosage levels can be properly regulated. These tests are the only known means of having reliable operations, as far as the water is concerned. Testing may be conducted in a permanent field laboratory or at the plant or site location using portable test kits.

E-2. Use of portable test kits.

Portable test kits are primarily for use at the site location where the sample is taken. They also can be used in the permanent field laboratory. Test procedures are provided with the test kit. For tests that can be conducted in the field laboratory or with a portable test kit, use of field laboratory test procedures is recommended for best results. The water analyst should periodically check the results of the portable test kit against the field laboratory test on the same water sample. Portable test kits are available from a number of commercial sources.

E-3. Testing techniques. Accurate test results depend on using the proper reagents and following good, basic laboratory procedures and techniques.

a. The chemical reagents kept at each field laboratory should be specific for the tests that are performed. The amount on hand should be adjusted to ensure the supply is fresh. Reagent containers must be tightly closed when not in use and stored in a cool place. Except for reagents with a shorter shelf life specified, the liquid reagents should be consumed within 1 year and the dry reagents consumed within 2 years. All reagents should be properly marked with

appropriate warning labels, batch control numbers, and date packaged or discard date clearly marked.

b. Water analyses require certain chemical apparatus. These are scientific instruments and are to be treated as such. The apparatus should be HANDLED WITH CARE! All of the apparatus will last indefinitely if given proper care.

c. It is necessary to keep everything in GOOD ORDER at all times. Have a place for everything and keep everything in its place! Be sure all bottles are properly labeled and avoid mixing bottles! All bottles should be tightly closed. Keep any reserve stock of solutions and reagents in a cool, dark place.

d. All equipment and apparatus, especially glassware, should be kept CLEAN! Unless this is done, the tests will not be reliable and errors will be introduced. Thoroughly rinse and air dry all glassware immediately after use. If color apparatus is employed, do not expose to heat or direct sunlight. If any liquid is spilled on any of the equipment or apparatus, wipe off at once and dry.

e. MEASURE CAREFULLY! The apparatus are precision instruments that are capable of very fine measurements. The results will be "off" if: improper amounts of samples are taken, incorrect volumes of solution are added, the burette is not read correctly, or if the methods prescribed are not performed exactly as written.

f. THE SUSPENDED MATTER OR SLUDGE will generally settle to the bottom if the sample is allowed to stand before testing. The clear water can then be used for the tests, making it unnecessary to filter

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(except for specific tests). Theoretically, all water analyses should be made at 77°F (25°C); however, no appreciable error will be introduced if the test is made between 68 and 86°F (20 to 30°C). In general, the shorter the time between the collection and the analysis of the sample, the more reliable will be the results.

g. When the water sample color interferes with the analysis it may be necessary to filter the sample through activated charcoal, except for the sulfite and nitrite tests.

Appendix F

Industrial Water Treatment Chemicals

1. ANTIFOAM, Polyamide or polyhydric alcohol
Use: Prevent foaming carryover in steam boilers
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6850-01-181-0160
2. ANTIFREEZE, inhibited, 87.6 percent ethylene glycol, 300°F minimum boiling point, nonflammable, protection to -60°F
Use: Closed hot and chilled water systems
Federal Specification: MIL-A-46153
Package/NSN: 1 gallon can, NSN: 6850-00-181-7929
5 gallon can, NSN: 6850-00-181-7933
55 gallon drum, NSN: 6850-00-181-7940
3. BIOCIDES, active ingredient, methylenebis(thiocyanate), 10 percent in water solution.
Use: Cooling towers with pH less than 7.5
Federal Specification: None
Package/NSN: 5 gallon, NSN: 6850-01-191-5033
4. BIOCIDES, active ingredient 20 percent 2,2-Dibromo-3-nitrilopropionamide, 80 percent inert ingredients
Use: Cooling towers with pH less than 7.5
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6850-01-191-5034
5. BIOCIDES, active ingredients 10 percent dodecylguanidine hydrochloride, 4 percent Bis(tri-n-butyltin)oxide
Use: Cooling towers with and pH less than 7.5
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6850-01-194-8306
6. BIOCIDES, active ingredients 20 percent n-Alkyldimethylbenzylammonium chloride and 3 to 4 percent Bis(tri-n-butyltin)oxide, pH greater than 10.5
Use: Cooling towers with pH greater than 7.5
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6840-01-189-8139
7. BIOCIDES, active ingredient 60 percent poly[oxyethylene(dimethyliminio)ethylene-(dimethyliminio)ethylene dichloride]
Use: Cooling towers with pH greater than 7.5
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6840-01-190-2551

8. BIOCIDE, active ingredients 60 percent consisting of 14 to 15 percent disodium cyanodithioimidocarbonate and 20 to 21 percent potassium n-methyldithiocarbamate
Use: Cooling towers with pH greater than 7.5
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6840-01-198-7945
9. BIOCIDE, active ingredient 96 to 98 percent 1-Bromo-3-chloro-5,5-dimethylhydantoin, granular
Use: Remote cooling towers with any pH
Federal Specification: None
Package/NSN: 35 pound can, NSN: 6840-01-185-7455
BORAX (see sodium nitrite-borax blend, item 40)
10. CALCIUM HYDROXIDE (slaked lime) ($\text{Ca}(\text{OH})_2$) technical, powder, 90 percent minimum by weight
Use: Lime-soda ash water softening
Federal Specification: O-C-110
Package/NSN: 50 pound bag, NSN: 6810-00-656-1091
11. CALCIUM HYPOCHLORITE, ($\text{Ca}(\text{OCl})_2$) technical, granular, 65 percent chlorine by weight
Use: Algae control in cooling towers and disinfectant in treatment for Legionnaire's Disease
Federal Specification: O-C-114
Package/NSN: 5 pound can, NSN: 6810-00-238-8115
100 pound drum, NSN: 6810-00-255-0472
CAUSTIC SODA (see sodium hydroxide, item 35)
12. CYCLOHEXYLAMINE, boiler feedwater compound, neutralizing amine, all drums to bear adequate caution labels to protect against fire, poison and caustic burn hazards
Use: Control corrosion by CO_2 in steam condensate lines
Federal Specification: O-C-940
Package/NSN: 60 percent, 400 pound drum, NSN: 6810-01-074-5201
60 percent, 15 gallon drum, NSN: 6810-00-515-2235
98 percent, 15 gallon drum, NSN: 6810-00-530-4695
98 percent, 55 gallon drum, NSN: 6810-00-805-9798
13. DIETHYLAMINOETHANOL (DEAE), 100 percent solution
Use: Control corrosion by CO_2 in steam condensate lines
Federal Specification:
Package/NSN: 55 gallon drum, NSN: 6810-949-8331
14. DIPHOSPHONIC ACID (HEDP), 1-hydroxyethylidene 1,1-diphosphonic acid, active ingredient 58 to 62 percent, specific gravity 1.45 at $20^\circ\text{C}/15^\circ\text{C}$, pH of 1 percent solution less than 2.0
Use: Inhibitor to prevent formation of calcium and magnesium scale in cooling water applications
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6850-01-190-5509
55 gallon drum, NSN: 6850-01-206-4601

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- ETHYLENE GLYCOL (see antifreeze, item 2)
HEDP (see diphosphonic acid, item 14)
15. HYDROCHLORIC ACID (muriatic), (HCl), technical, 31.45 percent minimum by weight, 20° Baumé (Bé)
Use: Iron fouled ion exchange material regeneration applications
Federal Specification: O-H-765
Package/NSN: 96 oz., NSN: 6810-00-222-9641
5 gallon can, NSN: 6810-00-236-5665
15 gallon carboy, NSN: 6810-00-823-8010
 16. MORPHOLINE, boiler feedwater compound, all drums to bear adequate caution labels to protect against fire, poison and caustic burn hazards
Use: Control corrosion by CO₂ in steam condensate lines
Federal Specification: O-M-575
Package/NSN: 40 percent 5 gallon can, NSN: 6810-00-419-4298
40 percent 55 gallon drum, NSN: 6810-00-559-9889
91 percent 55 gallon drum, NSN: 6810-00-616-9437
98 percent 55 gallon drum, NSN: 6810-00-559-9888
 17. OCTADECYLAMINE, nontoxic, creamy, white dispersion of octadecylamine, chemical formula C₁₈H₃₇NH₂, melting point of 114°F, boiling point of 697°F, filming amine
Use: Control corrosion by CO₂ in steam condensate lines
Federal Specification: None
Package/NSN: 55 gallon drum, NSN: None
- PHOSPHATE COMPOUNDS (see items 18-27)
18. DISODIUM PHOSPHATE, anhydrous (Na₂HPO₄), 49 percent P₂O₅ minimum
Use: Remove hardness in boiler water
Federal Specification: O-S-639
Package/NSN: 100 pound bag, NSN: 6810-00-264-6630
 19. DISODIUM PHOSPHATE, dodecahydrate (Na₂HPO₄ · 12H₂O), 19 percent P₂O₅ minimum
Use: Remove hardness in boiler water
Federal Specification: None
Package/NSN: 100 pound bag, NSN: None
 20. POLYPHOSPHATE GLASS, SLOWLY SOLUBLE, Minimum P₂O₅ content 67 percent, Solubility: 10 to 20 percent per month
Use: Treatment of cooling water in smaller cooling towers
Federal Specification: None
Package/NSN: 100 pound drum, NSN: 6850-00-014-3442
 21. SODIUM HEXAMETAPHOSPHATE (NaPO₃)₆ technical, type II, 66.5 percent P₂O₅, glassy form, beads or plates.
Use: A cathodic corrosion inhibitor in cooling towers and to remove hardness in boiler water
Federal Specification: O-S-635, Type II
Package/NSN: 100 pound bag, NSN: 6810-00-531-7805
 22. SODIUM TRIPOLYPHOSPHATE, anhydrous (Na₅P₃O₁₀), white granular, 56 percent

- P_2O_5
Use: Remove hardness in boiler water
Federal Specification: O-S-635, Type III
Package/NSN: 100 pound bag, NSN: 6810-00-753-5053
100 pound bag, NSN: 6810-00-926-4836
23. SODIUM TRIPOLYPHOSPHATE, Hexahydrate, ($Na_5P_3O_{10} \cdot 6H_2O$), granular or powder, 43 percent P_2O_5 minimum
Use: Remove hardness in boiler water
Federal Specification: None
Package/NSN: 100 pound bag, NSN: None
24. TETRASODIUM PYROPHOSPHATE, anhydrous, ($Na_4P_2O_7$), granular, 53 percent P_2O_5 , minimum
Use: Corrosion inhibitor in cooling towers and to remove hardness in boiler water
Federal Specification: O-S-377
Package/NSN: 100 pound bag, NSN: 6810-00-249-8038
25. TETRASODIUM PYROPHOSPHATE, decahydrate, ($Na_4P_2O_7 \cdot 10H_2O$), 31 percent P_2O_5 minimum
Use: Corrosion inhibitor in cooling towers and to remove hardness in boiler water
Federal Specification: None
Package/NSN: 100 pound bag, NSN: None
26. TRISODIUM PHOSPHATE (TSP), monohydrate ($Na_3PO_4 \cdot H_2O$) technical, powder or granular, 36 percent P_2O_5 minimum
Use: Remove hardness in boiler water
Federal Specification: O-S-642, Type III
Package/NSN: 100 pound bag, NSN: None
27. TRISODIUM PHOSPHATE (TSP), dodecahydrate ($Na_3PO_4 \cdot 12H_2O$) granular flake or crystalline, 16 percent P_2O_5 minimum
Use: Remove hardness in boiler water
Federal Specification: O-S-642, Type II
Package/NSN: 100 pound drum, NSN: None
28. POLYACRYLATE, low molecular weight, water white to light amber color, total solids 45 to 65 percent, pH of 2.2 to 7.5, approximate molecular weight 2000 to 5000, specific gravity 1.1 to 1.23 at 25°C, viscosity 400 to 1400 at 25°C
Use: Sludge dispersant in boilers
Federal Specification: None
Package/NSN:
29. POLYACRYLIC ACID, low molecular weight, water white to light amber color, total solids 45 to 65 $\pm$ 2 percent, approximate molecular weight 1000 to 4000, specific gravity 1.1 to 1.3 at 25°C, viscosity 200-1000 cps at 25°C
Use: Dispersant in cooling towers to prevent fouling by nonliving matter
Federal Specification: None
Package/NSN: 55 gallon drum, NSN: 6850-01-194-6613
30. POLYMETHACRYLATE, low molecular weight, clear amber liquid, total solids 29 to 41 percent, pH of 6.0 to 10.5, approximate molecular weight 3800 to 10000, specific gravity

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- 1.18 to 1.27 at 25°C, viscosity 50 to 700 at 25°C
Use: Sludge dispersant in boilers
Federal Specification: None
Package/NSN:
31. QUEBRACHO TANNIN EXTRACT, Type I, powder
Use: Sludge dispersant in boilers
Federal Specification:
Package/NSN: 50 pound bag, NSN: 6810-00-891-5741
SALT (see sodium chloride, item 33)
SLAKED LIME (see calcium hydroxide, item 10)
SODA ASH (see sodium carbonate, item 32)
32. SODIUM CARBONATE (soda ash) (Na_2CO_3), anhydrous technical, granular or powder form, 99.2 percent minimum by weight
Use: Remove calcium sulfate from water, increase alkalinity in boilers
Federal Specification: O-S-571
Package/NSN: 25 pound bag, NSN: 6810-00-262-0951
100 pound drum, NSN: 6810-00-233-1715
33. SODIUM CHLORIDE (salt) (NaCl), technical mineral type, crude-sized form, type I, water soluble salt, 98.5 percent NaCl by weight
Use: Regenerate ion exchange resins
Federal Specification: A-A-694
Package/NSN: 50 pound bag, NSN: 6810-01-026-0951
80 pound bag, NSN: 6810-00-227-0437
34. SODIUM HYDROSULFIDE ($\text{NaSH} \cdot 2\text{H}_2\text{O}$), technical grade, flake, 70 to 72 percent NaSH by weight
Use: Regenerate iron fouled ion exchange materials
Federal Specification: None
Package/NSN: 50 pound bag, NSN: None
35. SODIUM HYDROXIDE (caustic soda) (NaOH), technical, type I, flake form particle size gradation A/A, 96 percent minimum assay as NaOH
Use: Regenerate ion exchange material, increase alkalinity in boilers and adjust pH in water
Federal Specification: None
Package/NSN: 100 pound drum, NSN: 6810-00-174-6581
36. SODIUM HYPOCHLORITE SOLUTION (NaOCl), clear, light yellow liquid containing not less than 10 percent available chlorine by volume
Use: Disinfectant and treatment of Legionnaires' Disease in cooling towers
Federal Specification: O-S-602
Package/NSN: 5 gallon can, NSN: 6810-00-169-5163
55 gallon drum, NSN: 6810-00-214-8743
37. SODIUM MOLYBDATE, Dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), white, free flowing odorless powder, soluble in water, commercial grade

- Use: Corrosion inhibitor for open cooling systems
Federal Specification: None
Package/NSN: 200 pound lined fiber drum, NSN: None
38. SODIUM MOLYBDATE, solution, 35% as Na_2MoO_4 , clear liquid, soluble in water
Use: Corrosion inhibitor for open cooling systems
Federal Specification:
Package/NSN: 55 gallon drum, NSN:
39. SODIUM MOLYBDATE BLEND, Liquid, mixture of 10 to 12 percent sodium molybdate (Na_2MoO_4), 3 to 5 percent sodium hydroxide (NaOH), and 3 to 4 percent copper corrosion inhibitor
Use: Corrosion control in hot water systems, chilled and brine systems, combined hot and chilled water systems, and diesel engine jacket cooling systems. Compatible with ethylene glycol antifreeze.
Federal Specification: None
Package/NSN: 55 gallon drum, NSN: 6850-01-185-1188
40. SODIUM NITRITE (NaNO_2), granular, 97 percent NO_2 by weight, technical grade
Use: Corrosion control in hot water systems
Federal Specification: O-S-634
Package/NSN: 100 pound drum, NSN: None
41. SODIUM NITRITE-BORAX BLEND, powdered or granular, a mixture of 65 to 70 percent sodium nitrite, 8 to 12 percent borax (sodium tetraborate), 4 to 5 percent copper corrosion inhibitor, and 15 to 20 percent sodium carbonate, free of excess foreign matter
Use: Corrosion control in closed hot water systems. Compatible with ethylene glycol antifreeze.
Federal Specification: None
Package/NSN: 30 gallon can, NSN: 6850-01-185-1187
42. SODIUM SILICATE, relatively low alkalinity, 41° Baumé, approximately 28.8 percent SiO_2 , 6 to 7 percent Na_2O , not more than 0.5 percent suspended matter
Use: Cathodic corrosion inhibitor in cooling towers
Federal Specification: O-S-605
Package/NSN: 5 gallon can, NSN: 6810-00-247-0607
55 gallon drum, NSN: 6810-00-247-0609
43. SODIUM SULFITE, (Na_2SO_3), anhydrous, granular, 96 percent by weight minimum
Use: Remove oxygen from boiler feedwater and closed hot water systems (oxygen scavenger)
Federal Specification: O-S-650
Package/NSN: 100 pound bag, NSN: 6810-00-782-2677
44. SODIUM SULFITE, catalyzed with cobalt, granular, 95 percent by weight minimum
Use: Remove oxygen from boiler feedwater (oxygen scavenger)
Federal Specification: None
Package/NSN: 50 pound bag, NSN: 6850-01-109-5604
45. SULFONATED STYRENE COPOLYMER, low molecular weight, clear amber color, total solids, 23 to 27 percent, pH of 6.8, molecular weight 5000 to 10000, specific gravity

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- 1.2 at 25°C, viscosity 10 to 40 at 25°C
Use: Sludge dispersant in boilers
Federal Specification: None
Package/NSN:
46. SULFURIC ACID (H_2SO_4), technical, class A, grade 2, 93 percent sulfuric acid concentration, 66° Baumé
Use: Regenerate ion exchange resins, adjust pH in cooling towers
Federal Specification: O-S-809
Package/NSN: 13 gallon carboy, NSN: 6810-00-975-0707
Bulk, NSN: 6810-00-251-8007
47. TOLYLTRIAZOLE (TT), active ingredient 50 percent sodium tolyltriazole (43% TT)
Use: Corrosion inhibitor for copper alloys in cooling water systems
Federal Specification: None
Package/NSN: 5 gallon can, NSN: 6850-01-189-9949
48. ZINC SULFATE, monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$), white, free flowing powder, soluble in water
Use: Cathodic corrosion inhibitor in cooling towers
Federal Specification: None
Package/NSN: 50 pound bag, NSN: 6810-01-198-3832

GLOSSARY

ACID: A compound, usually having a sour taste, which is able to neutralize an alkali or base; a substance that dissolves in water with a formation of hydrogen ions.

AERATION: The bringing about of intimate contact between air and liquid by one of the following methods: spraying the liquid in the air; bubbling air through the liquid; or by agitation of the liquid to promote surface absorption of air.

ALGAE: Tiny plant life, usually microscopic, existing in water. They are mostly green, blue-green, or yellow-green, and are the cause of most tastes and odors in water. They create suspended solids when they grow in an industrial water system.

ALKALINITY: (a) A term used to represent the content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates in water. (b) The capacity of water to react with hydrogen ions.

ALKALINITY, TOTAL OR MIXED INDICATOR (M): A measure of the total alkalinity of water. Measured by the quantity of 0.02 N sulfuric acid required to bring water to pH of 4.4, as indicated by the change in color of methyl orange or a mixed indicator. Results are expressed in parts per million (ppm) as calcium carbonate.

ALKALINITY, PHENOLPHTHALEIN (P): A measure of hydroxide ions (OH⁻) plus one-half of the normal carbonates in water. Measured by the quantity of 0.02 N sulfuric acid required to bring the water to pH 8.2, as indicated by the decolorization of

phenolphthalein indicator. Results are expressed in parts per million (ppm) as calcium carbonate.

ALKALINITY, HYDROXYL: A measure of hydroxyl ion (OH⁻) contribution to the alkalinity. This is related to the system pH and also may be referred to as causticity.

BACKWASH: The reversal of flow through a filter or an ion exchanger to wash clogging material out of the filtering medium and reduce conditions causing loss of head.

BACKFLOW PREVENTOR: A device for a water supply pipe to prevent the backflow of water into the water supply system from the system which it supplies.

BACTERIA: Simple single-cell microscopic organisms generally free of pigment. They do not require light for their life processes.

BASE: An alkali or hydroxide of the alkali metals and of ammonia. They can neutralize acids to form salts and water. A base will ionize to form hydroxyl ions (OH⁻).

BIOCIDES: Material typically used to destroy microorganisms (also called microbiocides).

BIOLOGICAL DEPOSITS: Water-formed deposits of organisms or the products of their life processes. Biological deposits may be composed of microscopic organisms, as in slimes, or of macroscopic organisms such as barnacles or mussels.

BLOWDOWN: The action of draining a portion of water from a system to reduce the

concentration of dissolved solids or to discharge accumulations of materials carried by the water.

BRITISH THERMAL UNIT (BTU): The amount of heat necessary to raise the temperature of one pound of water one degree Fahrenheit (°F).

BRINE: A saturated solution for ion exchange regeneration, refrigeration, or cooling processes. It is usually a sodium chloride solution for ion exchange regeneration. It may be sodium chloride or calcium chloride for refrigeration.

CAUSTICITY: A common term that describes hydroxyl alkalinity or the alkalinity resulting from presence of the hydroxyl ion (OH⁻).

CONCENTRATION: A measure of the amount of dissolved substances contained per unit volume of solution. May be expressed as grains per gallon (gpg), pounds per million gallons (lb/mil gal), milligrams per liter (mg/l), parts per million (ppm) or percent.

CONDENSATE: The material formed when vapor returns to the liquid state. In steam heating systems, the water condensed from steam. In air conditioning, water extracted from air as by condensation on the cooling coil of a refrigeration machine.

CONDUCTIVITY, SPECIFIC

CONDUCTANCE: The reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature. Electrical conductivity is expressed in micromhos (μmhos), the reciprocal of

megohms. This is used as a measure of total dissolved solids.

CORROSION: The destruction of a substance, usually a metal, or its properties because of a reaction with its (environmental) surroundings.

CYCLES OF CONCENTRATION

(COC): In a system in which water lost through evaporation and blowdown is replaced with makeup water, COC is the ratio of the makeup quantity to the blowdown quantity, i.e., $COC = M/B$. It is the number of times the makeup water is concentrated in the system. The COC can also be calculated by dividing either the conductivity or the chloride content of the blowdown by the conductivity or chloride content of the makeup: $COC = \text{Cond}_{bd} / \text{Cond}_{mw}$.

DEAERATOR: Device for removing noncondensable gases from the boiler. They may operate on the principle of either heat or vacuum.

DEALKALIZATION: Exchange of bicarbonate for chlorides in an ion exchange process.

DEIONIZATION: Complete removal of ions from water.

DEMINERALIZATION: Reduction of the mineral content of water by a physical or chemical process; removal of salts.

DISINFECTION: The process of killing most (but not necessarily all) of the harmful and objectionable microorganisms in a fluid by various agents such as chemicals, heat, ultraviolet light, ultrasonic waves, or

radiation.

DISSOLVED SOLIDS: (a) Solids, usually minerals, that are present in solution. (b) The dried residue from evaporation of the filtrate after separation of suspended solids.

DISTRIBUTION RATIO (D.R.): This is a measure of the vapor/liquid ratio for a given material. Extremely high and low values are generally undesirable. A high D.R. results in high amine losses at any vents and/or little availability of amine at points of initial condensation. A low D.R. results in high amine losses in the blowdown.

EVAPORATION: The process by which water passes from a liquid state to a vapor. It is the main process by which heat is removed from a cooling tower and steam produced in a boiler.

FEEDWATER: Water being applied to the feedwater heater or to the boiler. This consists of both makeup and condensate return.

FILMING AMINES: Chemicals that form an impervious barrier between metal and the steam condensate to prevent corrosion.

FOULANTS: Deposition of materials normally in suspension. This includes such things as silt, air scrubbed dust, microbiological residuals, reaction products from treatment, and corrosion products.

GENERIC CHEMICALS: A chemical identified and purchased by the recognized chemical name such as the International Union of Pure and Applied Chemistry (IUPAC) designation. These generic chemicals may be blended or used separately.

They are usually much less expensive than special chemical blends developed by manufacturers under a trade name.

HARDNESS: (a) A characteristic of water, chiefly due to the existence of carbonate and sulfate (and occasionally the nitrite and chloride) salts of calcium, iron, and magnesium. (b) Commonly computed from the amount of calcium and magnesium in the water and expressed as equivalent calcium carbonate. (c) Causes "curding" of water when soap is used, increased consumption of soap, deposition of scale in boilers, injurious effects in some industrial processes, and sometimes objectionable taste in the water.

HARDNESS, CARBONATE: Hardness caused by the presence of carbonates and bicarbonates of calcium and magnesium in water. Such hardness may be removed to the limit of solubility by boiling the water. This is also called temporary hardness.

HARDNESS, NONCARBONATE: Hardness caused by calcium and magnesium sulfates and chlorides and compounds other than carbonates which cannot be reduced materially by boiling the water. (Also called "permanent hardness".)

HARDNESS, TOTAL: The sum of carbonate and noncarbonate hardness.

HYDROGEN ION CONCENTRATION: Commonly expressed as the pH value that represents the logarithm of the reciprocal of the hydrogen ion concentration.

INHIBITOR (APPLIED TO CORROSION): A chemical substance or mixture which effectively decreases corrosion when added to a liquid (usually in

small concentrations).

ION: A particle, atom or group of atoms, carrying either a positive or negative electrical charge which is formed when an electrolyte is dissolved in water.

ION EXCHANGE: A process where water is passed through a granular material and ions on the granular material are replaced by ions contained in the water. For example, in the zeolite softening process, the sodium ions (Na^+) of the granular zeolite are replaced by the calcium ions (Ca^{++}) in the water to leave the water free of calcium (the cause of hardness), but with an increased amount of sodium.

LANGELIER INDEX (SATURATION INDEX): An index based on the calcium hardness, total alkalinity, total dissolved solids, temperature, and pH. It classifies waters as to their ability to dissolve or deposit calcium carbonate. It is the algebraic difference between the actual pH and the calculated pH of saturation (pH_s). $\text{LI} = \text{pH} - \text{pH}_s$. A positive value indicates a scale forming tendency, a negative value indicates a scale dissolving tendency. It was one of the first indices developed for this purpose and was designed specifically for municipal water flowing in distribution lines.

MAKEUP WATER: Water supplied to replace the loss in a system by leaks, evaporation, wind drift, bleedoff, blowdown, or withdrawal.

MICROBIOCIDES: A material added to cooling tower water and to chilled water to control the growths of microorganisms such as algae, bacteria, and fungi.

MICROMHO: An electrical unit of conductance (one millionth of a mho) which is the reciprocal of electrical resistance.

MICROORGANISM: A minute plant or animal in water or earth that is visible only through a microscope.

MILLIGRAMS PER LITER (mg/l): A unit of the concentration of water or wastewater constituent. It is 0.001 gram of the constituent in 1,000 milliliters of water. It has replaced the parts per million (ppm) unit, to which it is approximately equivalent, in reporting the results of water and wastewater analyses.

NEUTRALIZING AMINES: Chemicals used to neutralize carbon dioxide in steam condensate to prevent corrosion.

NORMALITY: The concentration of a solution in relation to a normal solution. The normal solution contains a specific weight of a substance per liter based on the characteristics of the substance. Thus, a half-normal solution would be expressed as 0.5 N or N/2.

OXYGEN SCAVENGER: A chemical used to remove final traces of oxygen from a boiler feedwater.

pH: Measure of hydrogen ion concentration indicating degrees of acidity or alkalinity of a solution. The range pH varies from 1 to 14. Values below 7.0 indicate acidity and above 7.0, alkalinity.

pH_{eq} : The pH of equilibrium. The adjusted pH of a water based on the empirical relationship between total alkalinity and pH developed from studies of hundreds of

cooling systems. This is necessary because pH in cooling waters is often buffered, which affects the relationship between pH and bicarbonate alkalinity.

pH_s: The pH of saturation. It is the pH below which a material will go into solution and above which it will precipitate. It is used for calcium carbonate in the Langelier, Ryznar, and Practical Scaling Indices. It is a function of the calcium hardness, the total alkalinity, the total dissolved solids and the temperature. It is determined with graphs, tables, or special slide rules. This equation is useful:

$$\text{pH}_s = 12.27 - 0.00915T - \log \text{CaH} - \log \text{TA} + (\log \text{TDS})/10$$

PHOSPHATES: Chemicals used for corrosion control in cooling towers and for deposit control in boilers. Commonly these occur as orthophosphates or polyphosphates. The level of the active phosphate chemical is reported either as percent P₂O₅ (phosphorus pentoxide) or as PO₄ (phosphate) with these related by factor as follows: PO₄ = 1.34 x P₂O₅.

ppm: Parts per million; one pound of material dissolved in one million pounds of water.

PRECIPITATE: (a) To separate a substance in the solid form from a solution. (b) The substance in solid form which has been separated from solution.

PRACTICAL SCALING INDEX (PSI): A modified scaling index developed by P.R. Puckorius and J.M. Brooke to provide a better and more consistent indication of scaling conditions of cooling water. It is based on using the pH of equilibrium (pH_{eq})

rather than the actual pH, and is calculated as follows: $\text{PSI} = 2 \text{pH}_s - \text{pH}_{\text{eq}}$. As with the RSI, a value less than 6.0 in natural water indicates a scale forming tendency. A value greater than 6.0 in natural water indicates a scale dissolving tendency.

REGENERATION: That part of the operating cycle of an ion exchange process in which a specific chemical solution is passed through the ion exchange bed to prepare it for a service run.

RYZNAR INDEX (STABILITY INDEX): An index classifying waters as to their ability to dissolve or deposit calcium carbonate scale. It is twice the pH of saturation minus the actual pH ($\text{RI} = 2 \text{pH}_s - \text{pH}$). Although in theory an RI of 7.0 should be neutral, experiments indicate that 6.0 is a better value. A value less than 6.0 in natural water indicates a scale forming tendency. A value greater than 6.0 in natural water indicates a scale dissolving tendency.

SCALE: Deposition on a heat transfer surface of normally soluble salts. Scale is usually crystalline and dense, frequently laminated, and occasionally columnar in structure.

SLIME: Biological growths that may accumulate to the extent that they foul equipment.

SLUDGE: A water-formed deposit that will settle and may include all suspended solids carried by water. Sludge is commonly formed in boilers where it may be baked into place and become hard and adherent.

SOFTENING WATER: The process of removing from water certain mineral

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substances which produce a condition called hardness. There are two softening processes in general use: chemical precipitation (lime and lime/soda softening) and the zeolite ion exchange process.

SOLIDS, SUSPENDED: All matter in water which is not dissolved and which can be removed with filtration.

SOLIDS, DISSOLVED: The total concentration of all substances in a filtered solution which exist as solids after the liquid is completely evaporated from the solution.

SOLIDS, TOTAL: The sum of the suspended and dissolved matter (solids).

ZEOLITE: Natural minerals as well as synthetic resins used for ion exchange.