Produced Water Treatment technologies

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About the presenter

- Member of the Board scientists Egypt.
- Member of Scientific Professions Syndicate.
- Member of the Arab Society for experts and Safety Professionals.
- Member of the International Association of Engineers.
- Expert in water and waste water treatment technologies.
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Introduction

- Produced waters contain both soluble and insoluble petroleum fractions of complex mixtures of organic compounds similar to those found in crude oils and natural gases.
- The individual constituents cover a broad range of boiling points, carbon numbers, chemical families, and structural isomers.
- The hydrocarbon fractional groups commonly found in produced water include: alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and complex hydrocarbon compounds containing oxygen, nitrogen, and sulfur.

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- The International Energy Agency predicts that global oil production will increase to almost 100 million barrels per day by 2035. And as the oil industry grows, so does the amount of produced water that must be treated.
- Produced water quality Overall reported or estimated rejection in terms of TDS, sodium, organic constituents, heavy metals, ammonia, and others

Produced water composition

Table 3. Main organic constituents of produced water

Organic constituents (mg/l)	Magnus I + II [3]	Forties Delta	Ula	Cleeton	Clyde	Forties Charlie	N. Sea Platforms
Volatile fatty acids	220-240	380	13	52	25	300	80-930 [1]
Aliphatics	2.2-87	20	14	27	n/a	2.2	n/a
Phenols	7.5-15	10.2	0.09	29.5	8.8	5.5	2-23 [2]
MAH	23.1-29.8	9.9	12.4	40.7	4.8	19.6	0.5-670 [1]
Total bases	0.26-0.47	0.06	0.09	0.29	n/a	0.005	n/a
PAH	1.4-6.9	3.0	3.0	0.5	1.5	0.66	0.0005-3.0 [3]

na = not available

MAH = Monocyclic aromatic hydrocarbons (BTEX + C_3, C_4 benzenes)

PAH = Polycyclic aromatic hydrocarbons

[1] E&P Forum Report (1994)

[2] Tibbetts. PJC, et al, (1992)

[3] M-Scan Ltd data

[4] Denotes the range of Magnus data

Produced water fate

- Once water has been discharged, dilution will have the most immediate effect in mitigating potential environmental impacts of produced water.
- Volatilization and biodegradation are also important mechanisms in mitigating the environmental impacts of organic constituents.

Effect of bioremediation

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Table 5. Effect of biodegradation on selected organics

Time (Days)	TOC (mg/l)	VFA's (mg/l)	Phenols (μg/l)	BTEX (μg/l)	Total B/N (μg/l)*	PAH (μg/l)
0	45	25	8810	4800	9210	1460
8 days	1.42	6	4.7	<0.5	610	99
28 days	0.52	4	na	<0.5	630	4.6

na = not available

* Total Bases/Neutral Fraction, BTEX + non-volatile base neutrals

Effect of volatilization

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Table 6. Effect of volatilisation on selected organics

Sparging Time	VFA's (mg/l)	Phenols (µg/l)	BTEX (µg/l)	Total B/N (µg/l)*	PAH (µg/l)
0 hours	25	8810	4800	9210	1460
7 hours @ 10° C	28	5030	17	1820	28
7 hours @ 20° C	26	5190	5	680	2.9
7 hours @ 20° C+ 28 days Biodegradation	1.9	1.8	<0.5	420	5.4

* Total Base/Neutral Fraction, BTEX + non-volatile base neutrals

- Dispersion modelling of produced water discharges has indicated that the minimum dilution of the plume is likely to exceed 700 fold within 500 m of the platform. A minimum dilution of over 10,000 times was predicted by the time the plume has travelled about 20 km. A high proportion of the organic material in produced water samples has been observed to be highly biodegradable.

Dissolved component removal from oilfield waters

Table 1. Dissolved components in produced water

Components	Concentration - Oil Field		Concentration - Gas Field	
	Typical - mg/l	Range - mg/l	Typical - mgl	Range - mg/l
Aliphatics <C5	1	0-6	1	0-6
Aliphatics >C5	5	0-30	10	0-60
Aromatics				
BTX	8	0-20	25	0 - >50
Naphthalenes	1.5	0-4	1.5	0-4
Polar Compounds				
Phenols	5	1-11	5	0-22
Fatty Acids	300	30-800	150	0-500

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Methods for the removal of dissolved organics

- Different methods for the removal of dissolved organics will remove different components, such as BTX's, naphthalene's and phenols, with different efficiencies, resulting in discharged effluents with a potentially wide range of compositions.
- The potential environmental effects of different compositions is often difficult to predict with confidence, since the cumulative toxicity of the residual oil components will depend on knowledge of the concentrations of these components and on literature values for their toxicity.

Adsorption/absorption (solvent extraction) system

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- Adsorption of dissolved organic components using activated carbon is a physical process in which the compounds adhere to a porous carbon particle's surface or are trapped within its pores.
- Such a system for removing dissolved organics from produced water would typically have a moving bed of granular activated carbon which could be continuously removed from the bed for regeneration by wet air oxidation or other means

Table 3. Typical removal capability and ultimate fate for dissolved components

Technology	Components Removed	Ultimate Fate
Absorption/Adsorption Systems	Variable depending on medium	Disposal or Recovery
Wet Air Oxidation	All organic components destroyed	H_20 and $C0_2$
UV/Ozone/Peroxide Oxidation	All organic components destroyed	H_20 and $C0_2$
Pervaporation Systems	Variable depending on membrane	Disposal or Recovery

Table 4. Brief technical information on dissolved component removal systems

Technology	Advantages	Disadvantages	Removal Efficiency
Absorption/Adsorption Systems	Easily understood	Regeneration or disposal of materials	Up to 100% for specific components
Wet Air Oxidation	Potential for high efficiency	Energy requirements Initiation Concentrations	Theoretically 100%
UV/Ozone/Peroxide/ Oxidation	Potential for high efficiency	Reactive chemicals Controllability	Theoretically 100%
Pervaporation Systems	Selective removal	Selective removal Membrane damage	Up to 100% for specific components

Oxidation systems

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Wet Air

- In a wet air oxidation system, organic and inorganic contaminants are oxidized whilst remaining in the aqueous phase at elevated temperatures (typically 1 50-300°C and 15-150 bar).
- The presence of the liquid modifies the oxidation reactions, enabling them to occur at considerably lower temperatures than during open flame combustion.
- Where a high degree of oxidation occurs (at higher temperatures and pressures), hydrocarbons are broken down to carbon dioxide and water.
- At lower degrees of oxidation easily degraded low molecular weight organics such as acetic acid are formed.

UV/Peroxide/Ozone Oxidation Systems

- The systems offer a similar end result to wet air oxidation in that they are designed to break down the contaminants into carbon dioxide and water, the difference being that a catalyst is used to promote the reaction rather than high temperature and pressures.
- As with the wet air oxidation systems catalytic oxidation systems potentially offer single stage treatment through removal of both dispersed and dissolved hydrocarbons.
- Catalytic systems can also operate with much lower levels of hydrocarbon present in effluent, whereas wet air systems tend to require a high organic loading in the effluent to promote the reaction.

Pervaporation system

- Pervaporation is a membrane process in which a phase change takes place across the membrane.
- the difference between feed side vapor pressure and permeate side partial pressure is what drives the separation.
- The selective polymer absorbs the desired species, which is then desorbed by evaporation on the permeate side of the membrane.
- An elegant feature of the system is that the trace contaminant (oil) passes through the membrane whilst most of the water does not.
- Systems
- are now commercially available for the removal of VOC's and other organics from waste water streams.

Produced water reinjection (PWRI)

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- Produced water handling represents one of the more significant environmental challenges to the oil industry, not only from an environmental point of view, but also from a technical and cost view.
- Corrosion, erosion and scaling mechanisms may lead to high maintenance costs for produced water treatment equipment and extensive use of harmful chemicals.

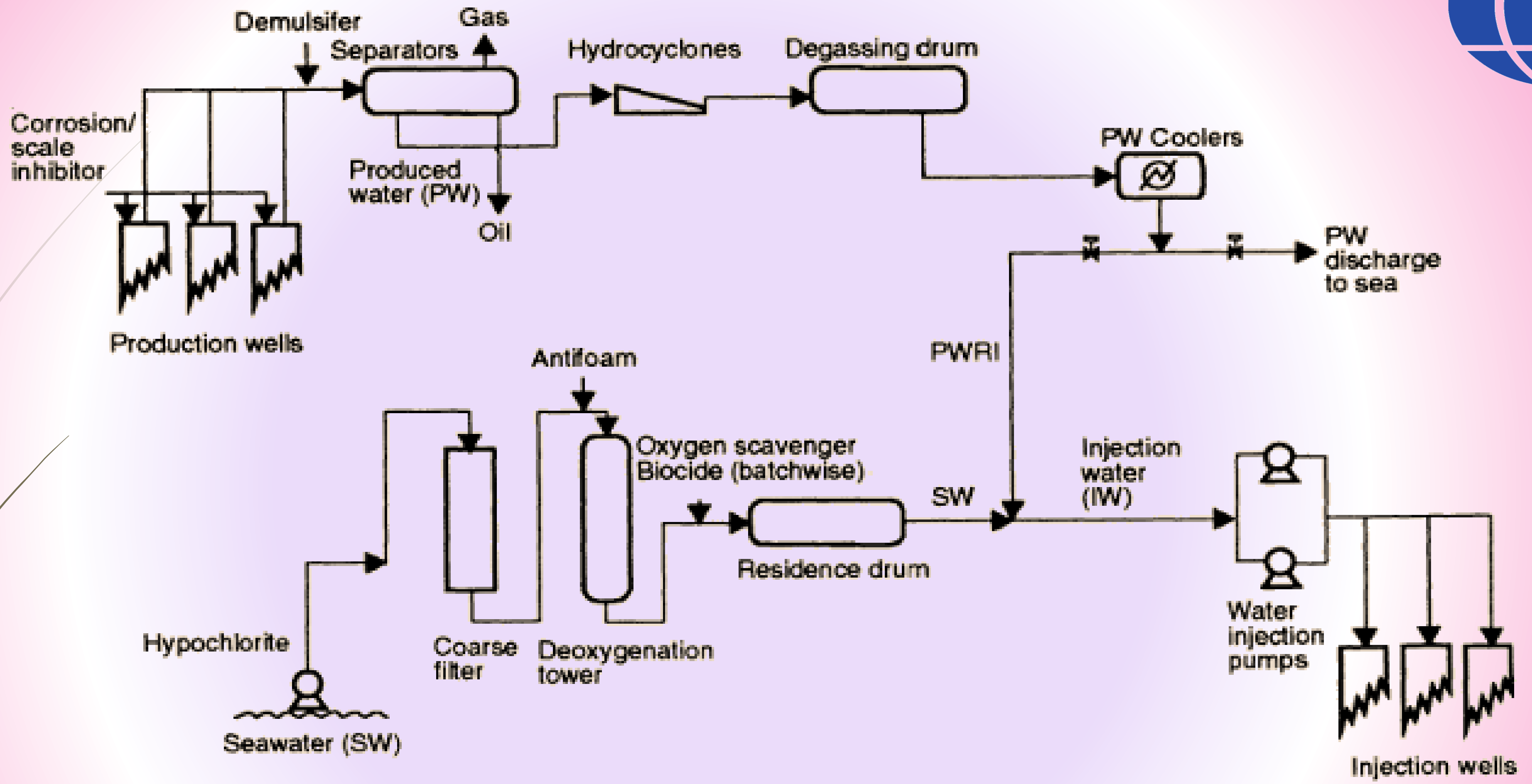


Figure 3. Schematic diagram of the process facilities used for the full scale PWRI trial on Ula.

Produced water reinjection (PWRI)

- The produced water is handled in the separators, treated in the hydrocyclones and the degassing drum before it is cooled down to approximately 50°C.
- Downstream the coolers, the produced water (PW) is either mixed with seawater (SW) and reinjected (PWRI) or discharged. PWRI is, however, the normal mode of operation and discharge is only occurring if the water injection system is closed down, or the temperature of the PW exceeds 55°C. This temperature limit was set to avoid cavitation of the injection pumps.
- The SW is treated in the coarse filters, the deoxygenation tower and the residence drum before being mixed with PW prior to water injection.

Scaling potential

- Scale predictions of the produced water (PW) have shown that scale formation is likely to be a minor problem at temperatures of 60°C and less. Any significant quantities of scale would only be formed in the reservoir, well away from the injection wells.
- At high temperatures such as those in the reservoir, there would be a strong tendency to form calcium sulphate ($CaSO_4$) and some calcium carbonate($CaCO_3$).
- Ula, the PW contains approximately 85% SW and 15% formation water.
- Increasing the proportion of SW will reduce the potential to form both barium sulphate ($BaSO_4$), strontium Sulphate ($SrSO_4$) and $CaCO_3$ while the tendency to deposit CaS04will be slightly increased

Corrosion Potential

- The water quality parameters that could influence the corrosion rates of carbon steel in the injection system are free carbon dioxide, oxygen, free chlorine, pH and SRB, as well as residual oxygen scavenger. Some changes in the water quality are occurring when produced water is reinjected on Ula, but since the PW already contains 85% seawater, no dramatic changes have been seen.

- The fact that PW also contains some oil could influence the formation of a protective surface film on the pipe walls. The variation in water quality occurring when PW is not reinjected could negatively influence the protective surface film.

Down Hole Separation (DHS) Technology

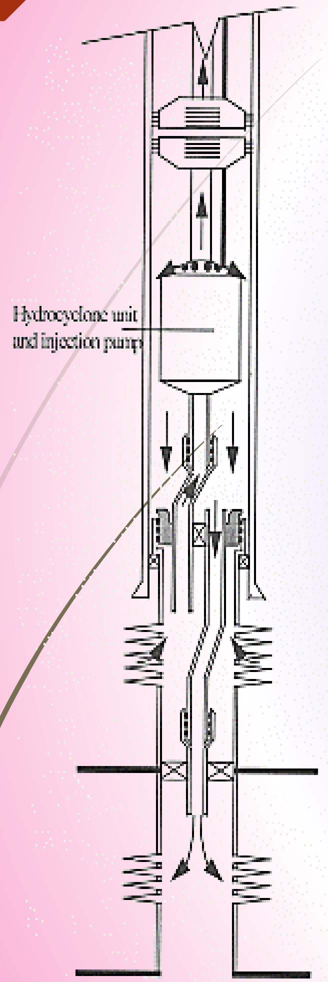
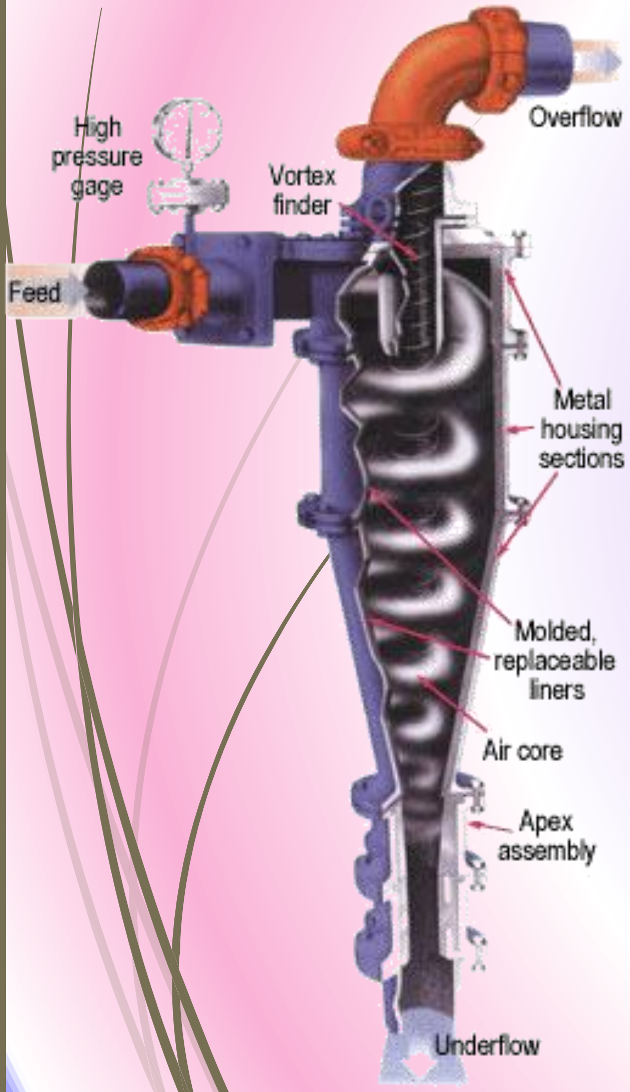


Figure 1. Separation unit and re-injection of water below the production zone.

- Liquid separation is one of the heavy processes on an oil production facility
- The Down Hole Separation (DHS) technology provides an efficient method to reduce the space occupied by process equipment on an oil rig.
- a new separation process (DHS) designed to fit inside the casing at the bottom of the well.
- The DHS is designed to remove a large portion of the produced water from the oil.

Hydrocyclone separation



- Hydrocyclones are a conical device that make use of centrifugal force to separate the light phase from the heavier phase.
- This core is drawn off through a vortex finder into the overflow. The heavy phase accumulates on the cone wall and is rejected via the underflow. In the case of liquid separation oil is removed in the overflow and water goes to the underflow.

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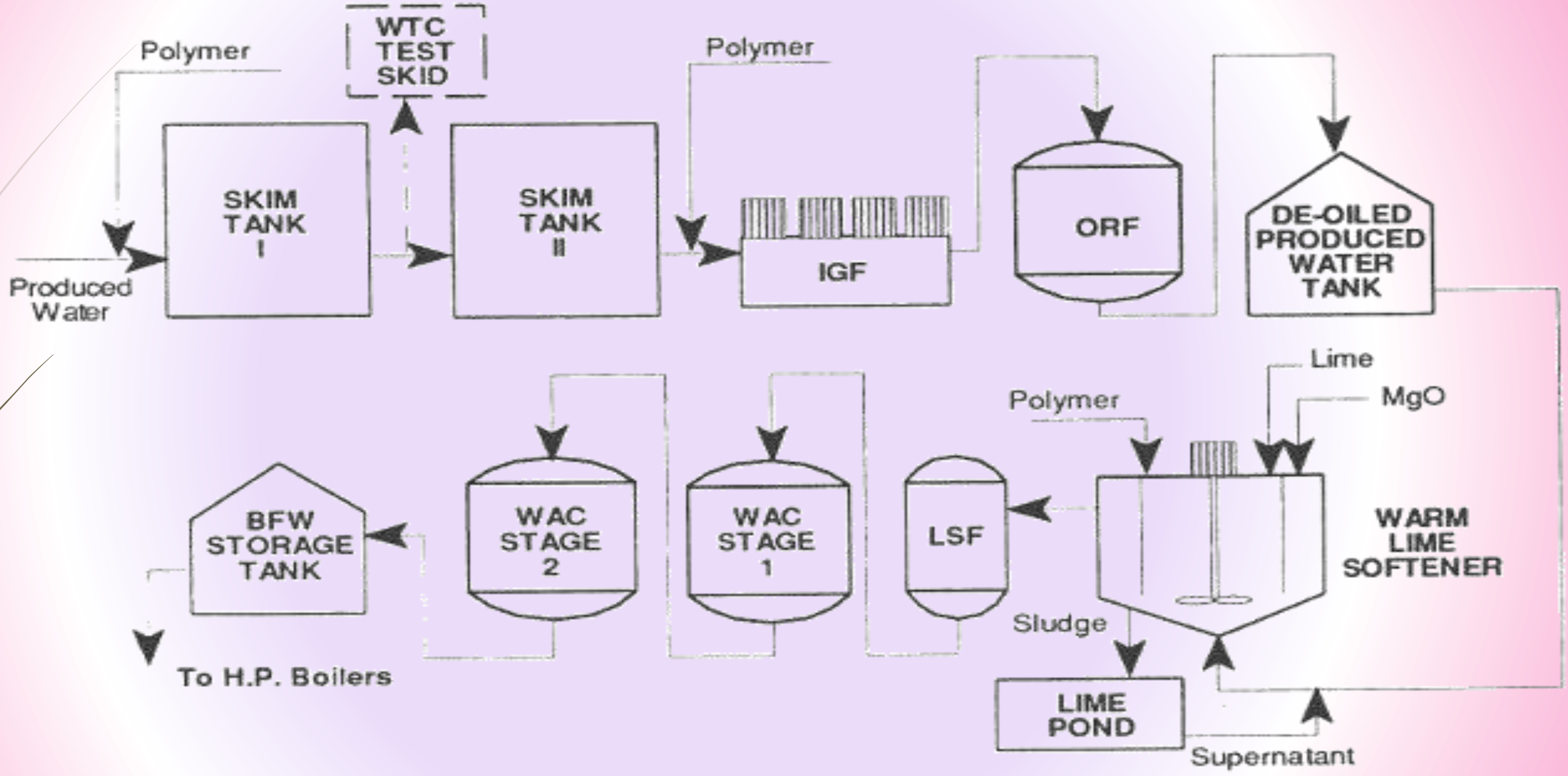

AMOCO produced water treatment train.

- The result of the Nano filtration flat sheet screening demonstrated the difficulties in applying these types of materials to the relatively high temperatures of produced water feed streams.

Biological treatment process for removing petroleum hydrocarbons

- "Produced water" is the single largest volume of waste generated by the oil and gas industry.
- The amount of produced water generated is dependent upon the method of recovery and the nature of formation.
- The reactor configuration consisted of a 4 x l0 x 4 ft. 12 gauge steel tank with three compartments in series, followed by two 4 x 4 x 4 ft. slow sand filters in parallel.
- The first compartment (945-L ; 250 gal) served as a completely-mixed (no cell recycle) pre-aeration tank designed to increase the dissolved oxygen content of the produced water to an operating concentration of approximately 3 to 4 mg/L. This would allow for stimulation of any naturally existing aerobic microbial cultures.
- An air flow rate of 0.345 m /min. (12 cfm, equivalent to 305 lbs/day of oxygen) was provided using a Fuji ring compressor to ensure complete mixing and adequate oxygen transfer.

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- Clean-up and backwashing of the filter media. The second compartment (945-L; 250 gal), designated as the aeration tank, received the effiuent from the pre-aeration tank. This tank was initially bioaugmented with a commercial culture (Petrobac-S®). Complete mix of the cells was provided by delivering 0.431 m /min. (15 cfm) of air (equivalent to 382 lbs/day of oxygen) which maintained the bacterial cells in total suspension while providing an operating dissolved oxygen concentration in the range of 3 to 4 mg/L.

- The effluent from the aeration tank then entered the third compartment (1 ,050-L; 278 gal) which served as a clarifier. A biomass recycle system was installed between the clarifier and the aeration tank to maintain the desired MLSS concentration in the aeration tank. The clarified effiuent was discharged into one of the two parallel slow sand filters to remove any carryover of bacterial cells. The two filters were operated on an alternating basis, allowing for continuous flow of the waste stream during clean-up and backwashing of the filter media.

Results of water quality analysis across the treatment systems

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		Produced water source	
		Open tank	Closed tank
Raw water characteristics			
Dissolved oxygen	[mg/L]	< 1.0	< 1.0
Total dissolved solids	[mg/L]	52,164	55,023
Total n-alkanes	[mg/L]	126	115
Total aromatics	[mg/L]	3.1	7.7
Total petroleum hydrocarbons	[mg/L]	135	126
Effluent from pre-aeration tank			
Dissolved oxygen	[mg/L]	3.1	2.6
Total dissolved solids	[mg/L]	54,256	57,329
Total n-alkanes	[mg/L]	51.1	56.5
Total aromatics	[mg/L]	ND	ND
Total petroleum hydrocarbons	[mg/L]	58.3	61.1
Effluent from aeration tank			
Dissolved oxygen	[mg/L]	3.9	3.8
Total dissolved solids	[mg/L]	54,229	57,128
Total n-alkanes	[mg/L]	0.04	0.16
Total aromatics	[mg/L]	ND	ND
Total petroleum hydrocarbons	[mg/L]	0.27	0.44
Effluent from settling tank			
Dissolved oxygen	[mg/L]	2.3	2.9
Total dissolved solids	[mg/L]	51,637	54,647
Total n-alkanes	[mg/L]	0.01	0.02
Total aromatics	[mg/L]	ND	ND
Total petroleum hydrocarbons	[mg/L]	ND	ND
Effluent from sand filters			
Dissolved oxygen	(mg/L)	2.7	2.8
Total dissolved solids	(mg/L)	51,234	54,196
Total n-alkanes	(mg/L)	0.01	0.03
Total aromatics	(mg/L)	ND	ND
Total petroleum hydrocarbons	[mg/L]	ND	ND

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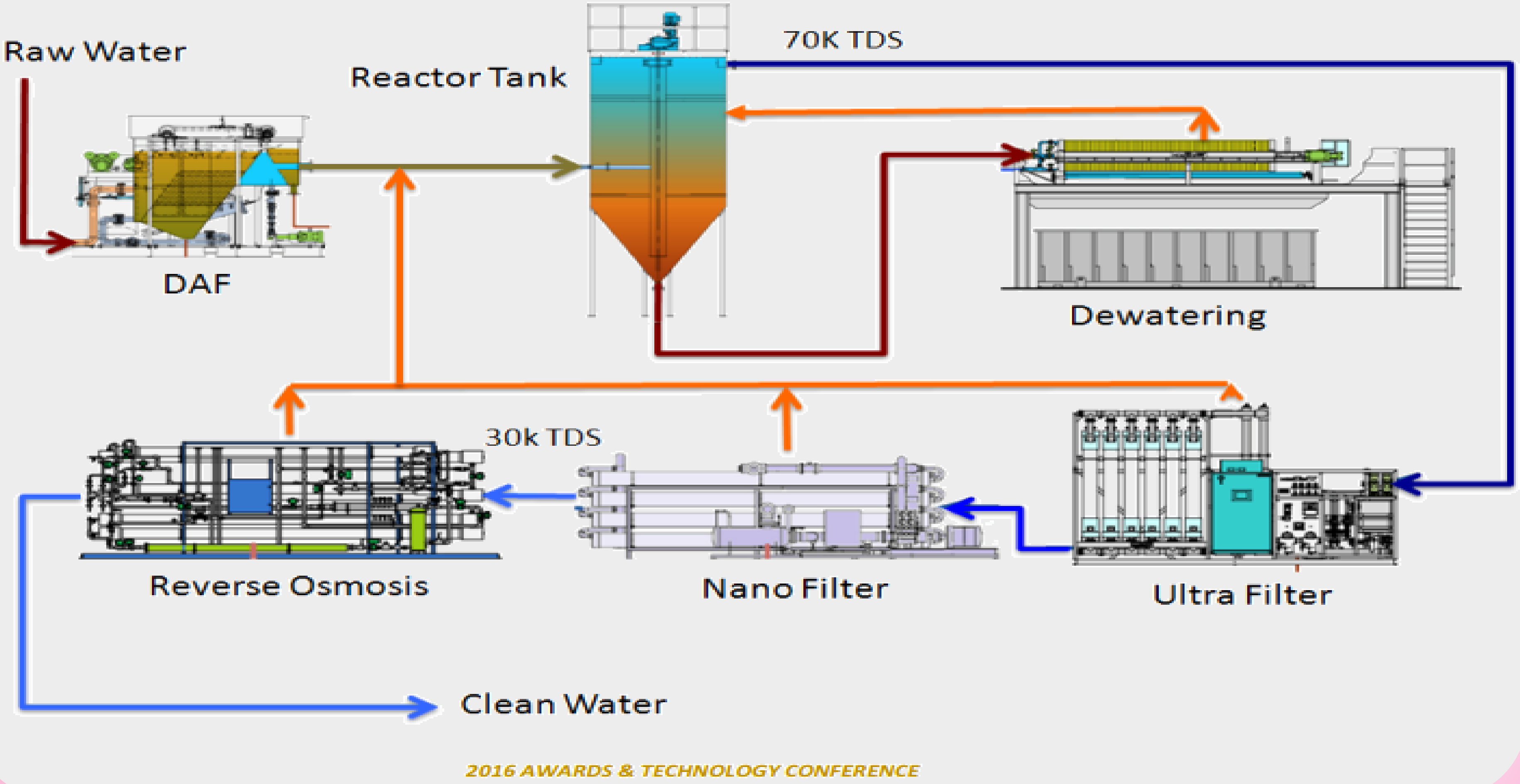
PRODUCED WATER TREATMENT



Pretreatment of oil field and mine waste waters for reverse osmosis

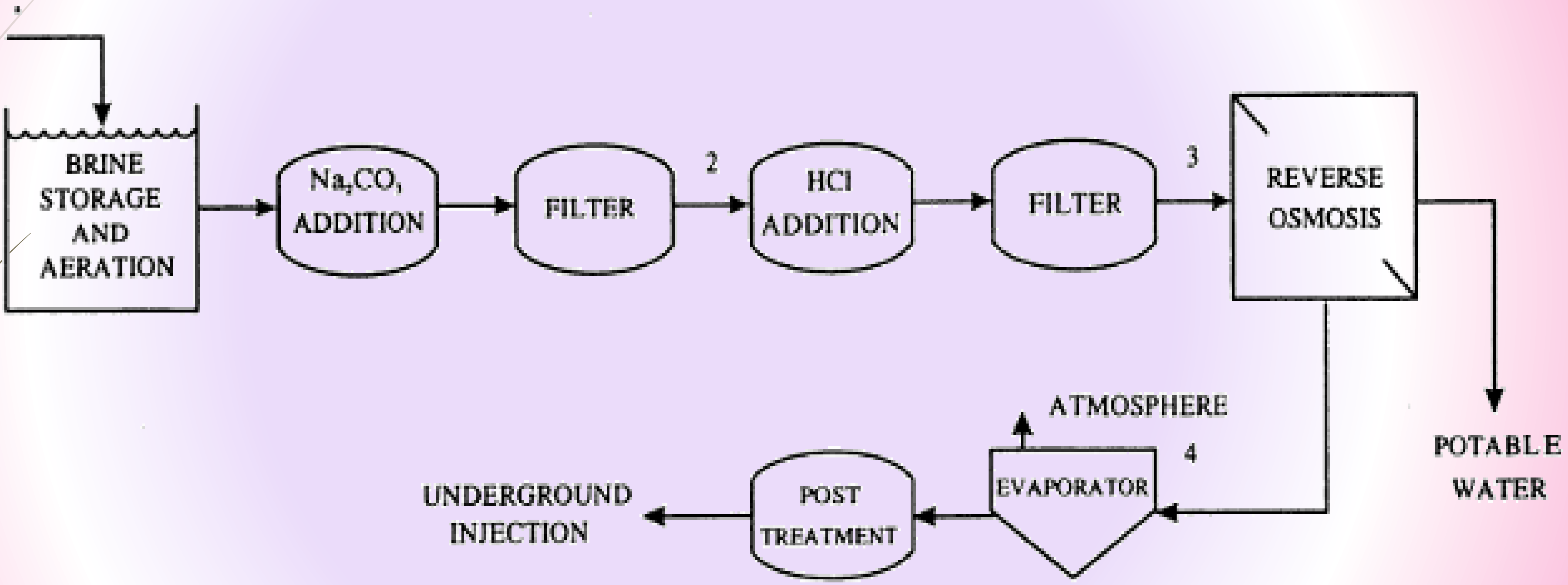


Figure 1. Schematic diagram of brine pretreatment process.

Pretreatment of oil field and mine waste waters for reverse osmosis

- oxidation by air which precipitates iron, manganese, and other metal oxides less soluble under oxidizing conditions.
- Sodium carbonate is then added to the brine. The pH rises and carbonate minerals precipitate.
- After a sufficient amount of carbonate is added, the precipitate phases are removed from the system, simulating the filtering of the precipitate sludge.
- HCl is then added to the brine to reduce the pH to 6.0
- Passage of the brine through the reverse osmosis unit.

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Post treatment of brine from reverse osmosis process

- Usually the most cost-effective post treatment is the dilution of the concentrated brine from the reverse osmosis process with a portion of the original brine feed stream.
- In most cases, filtration, followed by dilution and addition of a small amount of acid would prevent scale formation during injection of the brine into an underground formation.
- The optimum amounts of dilutant and acid can be determined by use of the EQ3/6 geochemical modeling codes. A minimum amount of dilutant clearly is desirable for economic reasons.

References

- Produced water 2 Environmental Issues and Mitigation Technologies handbook – Mark Reed and Stale Johnsen.

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Thank you