AD-A252 360

TECHNICAL LITERATURE REVIEW
AND TECHNOLOGIES EVALUATION

FOR

ASSESSMENT OF OIL PRETREATMENT TECHNOLOGIES
TO IMPROVE PERFORMANCE OF REVERSE OSMOSIS SYSTEMS

Contract No.: DAAK70-91-K-0004

Prepared for

U.S. Army Troop Support Command (TROSCOM)
Belvoir RD & E Center
Fort Belvoir, VA 22060-5606

Technical Supervisor: Robert Shalewitz, STRBE-FSE

Principal Investigators

Dr. Berrin Tansel
Dr. Jose Villate

Florida International University
Miami, Florida

June 1992

92-16926

92 6 2 1

Technical Literature Review and Technologies Evaluation

Assessment of Oil Pretreatment Technologies to Improve Performance of Reverse Osmosis Systems

Contract No.: DAAK70-91-K-0004

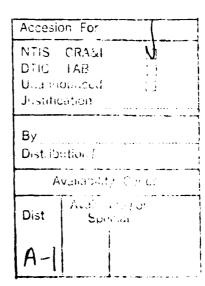|	
Title:	Assessment of Oil Pretreatment Technologies to Improve Performance of Reverse Osmosis Systems
Contract No.:	DAAK70-91-K-0004
Issuing Activity:	U.S. Army Troop Support Command (TROSCOM) Belvoir RD & E Center Fort Belvoir, VA 22060-5606
Procuring Contracting Officer:	Gregory C. Landon, STRBE-PRA
Technical Supervisor:	Bob Shalewitz, STRBE-FSE
Contract Specialist:	Angela Williams, STRBE-PRA
Principal Investigators:	Dr. Berrin Tansel and Dr. Jose Villate Florida International University
Title of Data Item:	Technical Literature Review
Subtitle:	---
Identification No.:	DI-S-30592
Data Item No.:	A004
Date:	June 19, 1992
Security Classification:	Unclassified

TECHNICAL LITERATURE REVIEW AND TECHNOLOGIES EVALUATION

FOR

ASSESSMENT OF OIL PRETREATMENT TECHNOLOGIES TO IMPROVE PERFORMANCE OF REVERSE OSMOSIS SYSTEMS

TABLE OF CONTENTS

EXECUTIVE SUMMARY

TECHNICAL LITERATURE REVIEW AND TECHNOLOGIES EVALUATION

ASSESSMENT OF OIL PRETREATMENT TECHNOLOGIES
TO IMPROVE PERFORMANCE OF REVERSE OSMOSIS SYSTEMS

The objective of this report is to identify the short list of technologies to be carried forward to the experimental phase of the program. This phase investigates the effectiveness and applicability of the technologies as a treatment process for removal of petroleum hydrocarbons from water.

In this report, the technologies identified during the literature review process were evaluated and compared. The candidate technologies considered were limited to physical and chemical processes; due to the long detention time needs and sensitivity of biological processes. The potential technologies to remove petroleum contamination were studied from both technical and economical perspectives. Table 1. presents the list of candidate technologies considered.

A two tiered approach was used to evaluate and select technologies most appropriate for removal of petroleum contamination in water supplies. The first tier evaluation and screening considered only technical criteria and eliminated those technologies with severe limitations for the desired performance requirements. The second tier screening considered both the technical and cost criteria to identify those technologies with the most potential to achieve the performance objectives most economically.

The following technologies are recommended to be carried forward to the experimental investigation phase.

Centrifugation
Coagulation/Filtration
Dissolved air flotation
Ultra/Nano Filtration

Although each of the four technologies identified are applicable to remove a variety of petroleum related contaminants within a wide range of concentration levels, each technology has optimum contaminant types and levels for effective removal.

The experimental phase should include considerations for a pretreatment scheme which could include combinations of these three technologies.

Table 1. Candidate technologies and the technologies remaining after preliminary and detailed evaluation and screening.

CANDIDATE TECHNOLOGIES (21)	TECHNOLOGIES REMAINING AFTER PRELIMINARY EVALUATION AND SCREENING (8)	TECHNOLOGIES REMAINING AFTER DETAILED EVALUATION AND SCREENING (4)
Air stripping	Carbon adsorption	Centrifugation
Carbon adsorption	Centrifugation	Coagulation/Filtration
Centrifugation	Coagulation/Filtration	Dissolved air flotation
Coagulation/Filtration	Chemical oxidation	Ultra/Nano filtration
Chemical oxidation	Dissolved air flotation	
Dissolved air flotation	Ozone/ultraviolet irradiation	
Electrocoagulation	Steam stripping	
Electrodialysis	Ultra/Nano filtration	
Electron beam irradiation		
Evaporation		
Freeze concentration		
Gravity oil/water separation		
Ion exchange		
Neutralization		
Ozone/ultraviolet irradiation		
Pervaporation		
Photolysis		
Sonic treatment		
Steam stripping		
Ultra/Nano filtration		
Wet air oxidation		

CHAPTER 1

INTRODUCTION

The services provided under this contract include both theoretical and experimental research for development of an appropriate technology for treatment of petroleum hydrocarbons in source water for reverse osmosis (RO) systems.

This report evaluates and screens the candidate technologies identified during the literature review in accordance with the approved Technology Evaluation Plan. A short-list of technologies that warrant further study is recommended to be carried forward to the experimental phase.

1.1. PROBLEMS ASSOCIATED WITH REMOVAL OF PETROLEUM CONTAMINANTS

The contamination problems due to petroleum hydrocarbons have been long recognized. However, the treatment technologies available for treatment of petroleum contaminated media are still very limited.

Major limitations relative to treatment of petroleum hydrocarbons include:

o   Exact chemical composition is not defined

o   Aerobic treatment processes are not effective for breaking down heavy petroleum hydrocarbons

o   Anaerobic treatment processes are slow

o   Physical/chemical treatment processes are expensive and there is usually additional waste produced during treatment of the contaminated media

1.2. PRETREATMENT NEEDS FOR REMOVAL OF PETROLEUM CONTAMINANTS FOR REVERSE OSMOSIS PROCESS

Treatment of organic contaminants in drinking water depends on the nature of the contaminants targeted for removal. Membrane processes, such as reverse osmosis, are used in water treatment primarily for removal of dissolved solids and for demineralization of water. However, when the source water (i.e., salt water, groundwater or brackish water) is contaminated with petroleum hydrocarbons, such as oil, the RO membrane cannot function

due to the surficial fouling by oil limiting the functional capability of the RO systems in obtaining drinking water (James M. Montgomery Consulting Engineers, Inc., 1985; U.S. EPA, 1989).

Agents such as precipitates, colloids, microorganisms, and particulates may damage the membrane or effect the efficiency of the membrane process. Therefore, pretreatment is often needed for RO systems.

Lack of pretreatment can cause rapid "fouling" of the membranes and reduce water productivity. In addition, both pressure drop and salt passage are significantly affected by fouling. Fouling involves the trapping of materials within the pores or on the surface of the membranes. Five types of fouling can be identified (E.I. Dupont De Nemours and Company, 1978):

1. Membrane scaling
2. Fouling by metal oxides
3. Plugging
4. Colloidal fouling
5. Biological fouling

Dispersed oil in water can cause membrane deterioration and fouling thereby decrease the effectiveness of the RO process.

1.3. CONTENTS OF THE REPORT

This report is divided into five chapters.

o   Chapter two discusses the characteristics of petroleum contamination in water media. The physical and chemical characteristics of contaminants associated with crude and fuel oil spills are discussed.

o   Chapter three presents discussions of each technology identified during the literature review phase. For each technology a brief process description, type of contaminants that can be removed, technology development status, key process considerations, process performance (removal efficiency), economics and related references are provided.

o   Chapter four provides the two tiered evaluation and screening results for the technologies discussed in Chapter three. For each technology preliminary and detailed evaluation considerations are provided.

o   Chapter five presents the conclusions and recommendations for the experimental phase.

References:

E.I. Dupont De Nemours & Company, 1978, Engineering Design Manual, Permase Permeator, Wilmington, DE.

United Stated Environmental Protection Agency, 1989, Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, Office of drinking Water, Cincinnati, Ohio, EPA/625/4-89/023.

James M. Montgomery Consulting Engineers, Inc., 1985, Water Treatment Principles and Design, John Wiley and Sons.

CHAPTER 2

CHARACTERISTICS OF CRUDE OIL AND FUEL OIL CONTAMINATION

Petroleum and fuel oils are complex mixtures of hydrocarbons comprised primarily of alkane, alkene, and aromatic hydrocarbons. Gasoline spilled or leaked can form a liquid phase called free product and also can dissolve in water. Selection of an appropriate technology for treatment of crude oil or fuel oil contaminated water depends on the type of contaminant, concentration levels and state of the contaminants (dissolved only or immiscible and dissolved phases).

The two most important characteristics that determine the selection of an appropriate treatment process and its effectiveness are:

o   Contaminant composition, and

o   Solubility of contaminants.

This chapter presents an overview of the composition and solubility characteristics of crude and fuel oil contamination in water.

2.1.   COMPOSITION OF CRUDE OILS AND FUEL OILS

The petroleum product is not a homogeneous compound but a mixture of hydrocarbons. The characteristics of petroleum related contamination is controlled not only by the characteristics of each hydrocarbon but by the properties of the mixture.

There are several hundred different types of petroleum hydrocarbons. The liquid petroleum hydrocarbons can be classified into four basic groups:

a) paraffins (alkanes);
b) olefins (alkenes);
c) napththenes; and
d) aromatics.

Figure 2.1. presents the chemical structures of some examples of different types of petroleum hydrocarbons.

PARAFFINS   Octane C_8H_{18}

C_nH_{2n+2}

$$H-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-H$$

OLEFINS   2 methene 4 pentene C_6H_{12}

C_nH_{2n}

$$C=C-C-C-H$$

NAPHTHENES   Cyclohexane C_6H_{12}

C_nH_{2n}

Benzene C_6H_6 Athyl benzene C_8H_{10}

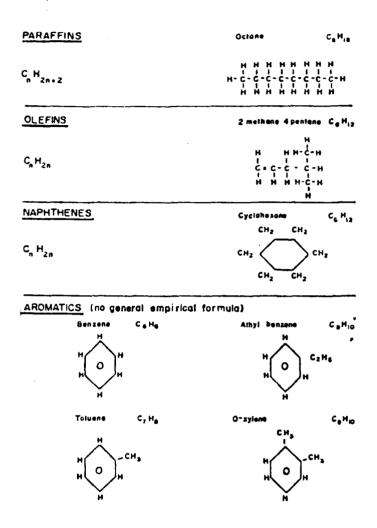Toluene C_7H_8 O-xylene C_8H_{10}

Figure 2.1. Examples of liquid hydrocarbons (Rubin and Mechrez, 1989).

Table 2.1. presents the distribution of hydrocarbon fractions in various crude oils. The hydrocarbon groups are themselves a mixture of components with different molecular structures (e.g., n-paraffins include C_{11} to C_{32}; iso-paraffins include 1-ring to 6-ring cycloparaffins, aromatics, benzene, toluene, C_8 to C_{11} aromatics) (Yaron, 1989). Table 2.2. shows the volume and weight fractions of different types of hydrocarbons in fuel oil No.6. The relative ratio between the hydrocarbon groups and the composition of each group is defined by both the origin of the crude oil and the distillation procedure (Lord and Perwak, 1988). Table 2.3. Shows partition coefficients of several types of crude oils with composition of No.2 and No.6 fuel oils.

2.2. CHARACTERIZATION OF FUEL OILS

The principal liquid fuels are made by fractiona! distillation of petroleum (crude oil), which is a mixture of hydrocarbons and hydrocarbon derivatives ranging from molecular weight from methane to heavy bitumen (Wittcoff and Reuben, 1980). Figure 2.2. presents the products of fractional distillation process. Petroleum fuels consist primarily of paraffins, isoparaffins, aromatics, and naphthenes, plus related hydrocarbon derivatives of sulfur, oxygen, and nitrogen that were not removed by refining. Olefins are absent or negligible except when created by cracking or other severe refining. The black, viscous distillation tower bottoms may be taken directly from the still and burned as industrial fuel without cooling below 450°F, or may be blended into the residual fuels of commerce. Diluted with 5 to 20 percent distillate this becomes No.6 fuel oil, or it may be cut back with 20 to 50 percent distillate to make No. 4 and 5 fuels for commercial use, as in schools and apartment houses. Distillate residual blends are also used as diesel fuel in large stationary and marine engines. Vanadium and nickel compounds are low in volatility and do not distill into the No. 1 and 2 fuel oil fractions. No. 6 fuel oil contains 10 to 500 ppm vanadium and nickel in complex organic molecules, principally porphyrins, which cannot be economically refined out of the oil. Salt, sand, rust, and dirt may also be present, giving No.6 a typical ash content of 0.01 to 0.5 percent by weight (Perry, 1982).

Desulfurization, hydrogenation, cracking (to lower molecular weight), and other refining processes may be performed on selected fractions before they are blended and marketed as fuels.

Figure 2.3. shows the viscosity-gravity-boiling point range relationships for common fuels. Table 2.4. shows the characteristics of the fuel oils as defined by ASTM Burner Fuel Specification D 396. One difficulty in the treatment of contaminated media (water and/or soil) is the fact that equipment manufacturers and large volume users (military services, government agencies, airlines, utility companies) often write their own fuel specifications to suit their particular equipment, operating conditions, and economics.

Table 2.1. Distribution of hydrocarbons in three types of crude oil (Yaron, 1989).

Hydrocarbons	Prudhoe	South Lousiana	Kuwait
Naphtha Fraction, wt%	23.2	18.6	22.7
Paraffins	12.5	8.8	16.2
Naphthenes	7.4	7.7	4.1
Aromatics	3.2	2.1	2.4
Benzenes	0.3	0.2	0.1
Toluene	0.6	0.4	0.4
C_8 Aromatics	0.5	0.7	0.8
C_9 Aromatics	0.06	0.5	0.6
C_{10} Aromatics		0.2	0.3
C_{11} Aromatics		0.1	0.1
Indans			0.1
High-Boiling Fraction wt%	76.8	81.4	77.3
Saturates	14.4	56.3	34.0
n-Paraffins	5.8	5.2	4.7
C_{11}	0.12	0.06	0.12
C_{12}	0.25	0.24	0.28
C_{13}	0.42	0.41	0.38
C_{14}	0.50	0.56	0.44
C_{15}	0.44	0.54	0.43
C_{16}	0.50	0.58	0.45
C_{17}	0.51	0.59	0.41
C_{18}	0.47	0.40	0.35
C_{19}	0.43	0.38	0.33
C_{20}	0.37	0.28	0.25
C_{21}	0.32	0.20	0.20
C_{22}	0.24	0.15	0.17
C_{23}	0.21	0.16	0.15
C_{24}	0.20	0.13	0.12
C_{25}	0.17	0.12	0.10
C_{26}	0.15	0.09	0.09
C_{27}	0.10	0.06	0.06
C_{28}	0.09	0.05	0.06
C_{29}	0.08	0.05	0.06
C_{30}	0.08	0.04	0.07
C_{31}	0.08	0.04	0.06
C_{32} plus	0.07	0	0.06
iso-Paraffins		14.0	13.2
1-ring cycloparaffins	9.9	12.4	6.2
2-ring cycloparaffins	7.7	9.4	4.5
3-ring cycloparaffins	5.5	6.8	3.3
4-ring cycloparaffins	5.4	4.8	1.6
5-ring cycloparaffins		3.2	0.4
6-ring cycloparaffins		1.1	
Aromatics, wt%	25.0	16.5	21.9
Benzenes	7.0	3.9	4.8
Indans and tetralins		2.4	2.2
Dinaphtheno benzenes		2.9	2.0
Naphthalenes	9.9	1.3	0.7
Acenaphthenes		1.4	0.9
Phenanthrenes	3.1	0.9	0.3
Acenaphthalenes		2.8	1.5
Pyrenes	1.5		
Chrysenes			0.2
Benzothiophenes	1.7	0.5	5.4
Dibenzothiophenes	1.3	0.4	3.3
Indanothiophenes			0.6
Polar materials, wt%	2.9	8.4	17.9
Insolubles, wt%	1.2	0.2	3.5

2 - 4

Table 2.2. Relative percent contribution of hydrocarbons in fuel oil No. 6 (Domask, 1984)

Hydrocarbon Type	Volume Percentage in Fuel	Percentage Accounted for by Major Contributors	Major Contributors
n-Paraffins C_3 C_{10}	11.40	10.19	C_4 n-butane
			C_5 n-pentane
		+	C_6 n-hexane
		10.19 (90% of n-paraffins)	
Isoparaffins C_4-C_{13}	46.55	1.14	C_4 isobutane
		10.26	C_5 isopentane
		8.81	C_6 2-methylpentane
			3-methylpentane
			2,3-dimethylbutane
		4.54	C_7 2-methylhexane
			3-methylhexane
			2,3-dimethylpentane
			2,4-dimethylpentane
		11.75	C_8 2,2,4-trimethylpentane
			2,3,4-trimethylpentane
			2,3,3-trimethylpentane
			2,2,3-trimethylpentane
			2,2,5-trimethylpentane
		1.51	C_9 2-methyloctane
			3-methyloctane
		+	4-methyloctane
		38.01 (80% of isoparaffins)	
Cycloparaffins (naphthenes) C_5 C_{11}	4.68	0.15	
		0.97	C_5 cyclopentane
		0.77	C_6 methylcyclopentane
			C_7 methylcyclohexane
		+	1-cis-3-dimethylcyclopentane
			1-trans-3-dimethylcyclopentane
		1.89 (40% of cycloparaffins)	
Mono-olefins C_2 C_{12}	8.96	0.03	
		0.75	C_3 propylene
			C_4 trans-butene-2
		1.22	cis-butene-2
			C_5 pentene-1
			trans-pentene-2
		1.26	cis-pentene-1
		+	C_6 2-methylpentene-1
			2-methylpentene-2
		3.26 (36% of mono-olefins)	
Aromatics (alkylbenzenes) C_6 C_{12}	26.08	1.69	
		3.99	C_6 benzene
		9.83	C_7 toluene
			C_8 ethylbenzene
			o-xylene
			m-xylene
		5.33	p-xylene
			C_9 1-methyl, 3-ethylbenzene
		+	1-methyl, 4-ethylbenzene
			1,2,4-trimethylbenzene
		20.84 (80% of alkylbenzenes, 73% of aromatics)	
Indans tetralins C_9 C_{11}	1.54		
Naphthalenes C_{10} C_{12}	0.74	+	
	28.36	74.2	
Total	100.00		

Additives 5 lb/1000 bbl ethyl 733 antioxidant
          5 lb 1000 bbl Du Pont DMD-2 metal deactivator

Table 2.3. Partition coefficients of several types of crude oils with composition of No.2 and No.6 fuel oils (Shiu et al., 1990).

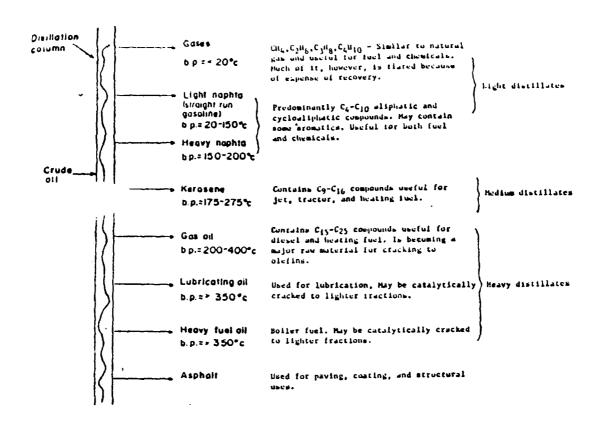| Component	Western Sweet Blend crude	South Louisiana crude	Prudhoe Bay crude	Gasoline	Fuel oil no. 6	Fuel oil no. 2
Pentane & lighter	1 883	1 556	1 043	2 420	40	11
Benzene	121	106	75	228	72	80
Toluene	386	382	249	934	207	161
Ethylbenzene & xylenes	1 105	1 248	895	4 758	568	524
Naphthalene	2 126	1 975	1 947	5 986	1 178	2 319
Methyl naphthalene	—	—	—	—	3 930	5 160
Dimethyl naphthalene	—	—	—	—	7 716	42 351

Figure 2.2. Crude oil distillation (Rubin and Mechrez, 1989).
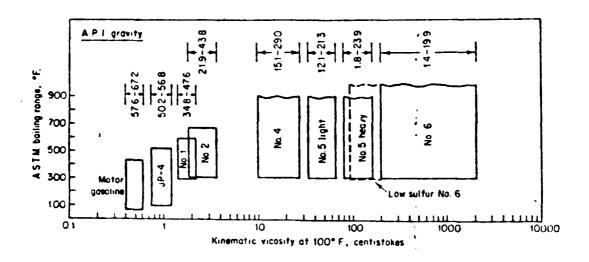
Figure 2.3.   Viscosity, gravity, boiling point range relationships
               for common fuels (Perry, 1982).

Table 2.4.   Characteristics of fuel oils as defined by ASTM Burner Fuel Specification D 396 (Perry, 1982).

Fuel oil grade	Description and requirements for use	Flash point, °F (°C), Min	Pour point, °F (°C), Max	Water and sediment, vol %, Max	Carbon residue on 10% bottoms, %, Max	Ash, wt %, Max	Distillation temperature, °F (°C)			Saybolt viscosity, sec				Kinematic viscosity, centistokes				Grav ity, °API, Min	Copper strip corrosion, Max
							10% point Max	90% point Min	90% point Max	Universal at 100°F (38°C) Min	Max	Furol at 122°F (50°C) Min	Max	At 100°F (38°C) Min	Max	At 122°F (50°C) Min	Max		
No. 1	A distillate oil intended for vaporizing pot-type burners and other burners requiring this grade of fuel	100 or legal (38)	0	Trace	0.15	...	420 (215)	...	550 (288)	...	...	...	...	1.4	2.2	...	...	35	No. 3
No. 2	A distillate oil for general-purpose domestic heating for use in burners not requiring No. 1 fuel oil	100 or legal (38)	20 (−7)	0.10	0.35	...	...	540 (282)	640 (338)	(32.6)	(37.93)	...	...	2.0	3.6	...	...	30	...
No. 4	Preheating not usually required for handling or burning	130 or legal (55)	20 (−7)	0.50	...	0.10	...	...	...	45	125	...	...	(5.8)	(26.4)	...	...		
No. 5 (light)	Preheating may be required depending on climate and equipment	130 or legal (55)	...	1.00	...	0.10	...	...	...	150	300	...	...	(32)	(65)	...	...		
No. 5 (heavy)	Preheating may be required for burning and, in cold climates, may be required for handling	130 or legal (55)	...	1.00	...	0.10	...	...	...	350	750	(23)	(40)	(75)	(162)	(42)	(81)		
No. 6	Preheating required for burning and handling	150 (65)	...	2.00	...	...	...	...	...	(900)	(9000)	45	300	...	...	(92)	(633)		

*ASTM Burner Fuel Specification D 396

2.3. DISSOLUTION OF CRUDE OILS AND FUEL OILS IN WATER

The partitioning of petroleum hydrocarbons, both immiscible with water and miscible with water, is of major importance in selecting an appropriate process to remove the contaminants. The rate of dissolution for the various components of a petroleum spill depends on the complex interactions dependent on properties inherent to the oil (i.e., molecular structure of compounds and relative abundance of these components) and the physico-chemical properties of the immediate environment (i.e., salinity, temperature).

Solubility is the partitioning of a chemical between the nonaqueous (free product layer) and water phase. Dissolution occurs as soluble petroleum components come into contact with water. Potential for dissolution of petroleum components is a function of each compound's solubility.

Table 2.5. presents the solubility of selected petroleum hydrocarbons in distilled and salt water as affected by the carbon number. The solubility in water, in general, decreases as the carbon number increases. The solubility of both chain and ring structures is inversely proportional to the degree of saturation of petroleum hydrocarbons (Jordan and Payne 1980). The addition of a second or third double bond increases solubility proportionally and the presence of a triple bond increases solubility more significantly than the presence of two double bonds (McAuliffe 1966). Therefore, in general, the most water soluble petroleum hydrocarbons are those with the lowest molar volume and greatest aromatic/olefinic character. The salinity level of water reduces the solubility of hydrocarbons. The solubility in sea water is approximately 30-40% less than that in distilled water (Jordan and Payne, 1980)

Figure 2.4. shows the change in water soluble fraction concentration as a function of water-to-oil ratio for three different crude oils. Each figure shows that water soluble fraction (WSF) concentration and the concentrations of some major components that constitute the WSF. The general dependence of the WSFs on the water-to-oil ratio are very similar for the three crude oils with only minor differences in the relative abundance of some compounds. As the figures illustrate, the concentration of the WSF decreases as the water-to-oil ratio increases and the composition of the WSF changes as the ratio changes. At low water-to-oil ratios, the WSF is mainly (80% of the total) composed of benzene, toluene, ethylbenzene and xylenes. As the water-to-oil ratio increases, these compounds become less important and account for a smaller portion of the dissolved compounds. At a ratio of 10,000, these compounds account only for only 15-30% of the total WSF. There is thus a change in he dominant characteristic hydrocarbons found in the soluble fraction. At low water-to-oil ratio (<100), benzene is the predominant hydrocarbon species in the WSF, but at higher ratios (100-1,000) toluene becomes the predominant component.

As the ratio is increased further (e.g., 10,000), no single compound accounts for a significant portion and the WSF composed of many compounds, each accounting for only a small fraction of the WSF composition.

The concentration of the less soluble compounds, such as highly alkylated benzenes and napthalenes, is far less dependent upon the water-to-oil ratio than the more soluble compounds. Their concentration remains relatively constant over the range of water-to-oil ratios tested while the concentration of the more soluble compounds shows a dramatic decrease as the ratio increases. Therefore, the presence of these less soluble compounds becomes more important as the ratio is increased.

Figure 2.5. shows the composition and concentration of WSFs prepared from gasoline. The general form of the curves is similar to those of the crude oils except that the concentrations of the volatile aromatics are significantly higher and less volatile materials (above naphthalene) are absent.
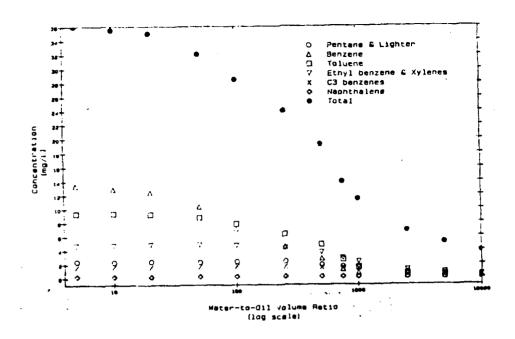
Figure 2.6. shows the dissolution characteristics of No. 6 (Bunker C) fuel oil. The WSFs of No. 6 fuel oil lack the volatile aromatics which were predominant in the WSFs of the crude oils and gasoline. These WSFs contain a larger number of compounds and a large portion of less soluble, non-volatile compounds.

The solubility behavior of fuel oil no.2 is shown in Figure 2.7. The total concentration for No.2 oil changes significantly as the water-to-oil ratio is increased, especially at ratios less than 100. This dependence is primarily due to the large concentration of pentene and compounds of lower molecular weight present in the WSF at these low water-to-oil ratios. The WSFs of the fuel oil contains significantly more compounds than those of crude oils and gasoline, and they have a relatively higher portion of nonvolatile compounds.
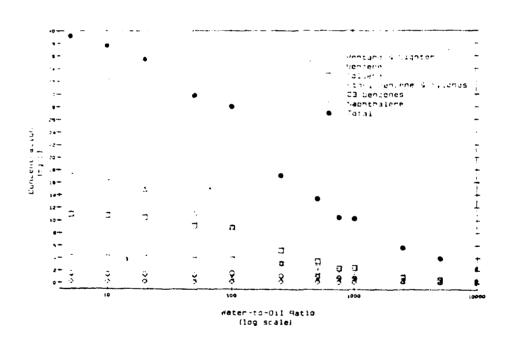
The water-to-oil volume used in oil and water equilibrium can significantly influence the concentration and composition of the WSF. In general, at low water-to-oil ratios, the more soluble compounds present in the oil are the dominant WSF components, and total WSF concentration is fairly high. As the water-to-oil ratio increases, the concentration of these compounds and the total WSF concentration decreases, and the less soluble compounds in the oil make up a larger portio of the WSF. Maijenen et al. (1984) described this behavior as a "depletion effect" such that the oil becomes depleted of water as the water-to-oil ratio is increased, thus causing the apparent solubility to decrease.

Table 2.5.   Solubilities of selected petroleum hydrocarbons in distilled and salt water as affected by the carbon number.

| Compound	Solubility in Distilled Water	Solubility in Seawater
Dodecane (C₁₂)	3.7 (ppb)	2.9 (ppm)
Tetradecane (C₁₄)	2.2	1.7
Hexadecane (C₁₆)	0.9	0.4
Octadecane (C₁₈)	2.1	0.8
Eicosane (C₂₀)	1.9	0.1
Hexacosane (C₂₆)	1.7	0.1
Toluene	534.8±4.9 (ppm ±S.E.)	379.3±2.8 (ppm ±S.E.)
Ethylbenzene	161.2±0.9	111.0±1.3
o-Xylene	170.5±2.5	129.6±1.8
m-Xylene	146.0±1.6	106.0±0.6
p-Xylene	156.0±1.6	110.9±0.9
Isopropylbenzene	65.3±0.8	42.5±0.2
1,2,4-Trimethylbenzene	59.0±0.8	39.6±0.5
1,2,3-Trimethylbenzene	75.2±0.6	48.6±0.5
1,3,5-Trimethylbenzene	48.2±0.3	31.3±0.2
n-Butylbenzene	11.8±0.1	7.09±0.07
s-Butylbenzene	17.6±0.2	11.9±0.2
t-Butylbenzene	29.5±0.3	21.2±0.3
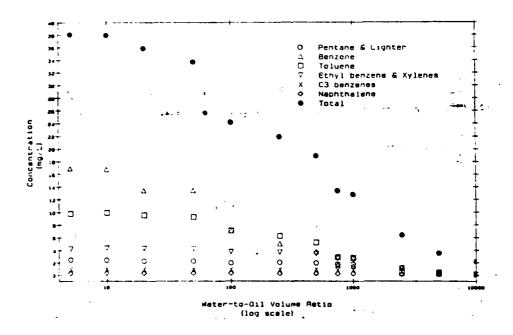
a. Western Sweet Mixed Blend crude oil

b. Prudhoe Bay crude oil

Figure 2.4.   Change in water soluble fraction concentration as a function of water-to-oil ratio for three different crude oils (Shiu et al., 1990).

c. Southern Louisiana

Figure 2.4. Contd.

Figure 2.5.   Change in water soluble fraction concentration as a function of water-to-oil ratio for regular unleaded gasoline (Shiu et al., 1990).

Wan Ying Shiu, et al.

Figure 2.6.   Change in water soluble fraction concentration as a function of water-to-oil ratio for No. 6 (Bunker C) fuel oil (Shiu et al., 1990).
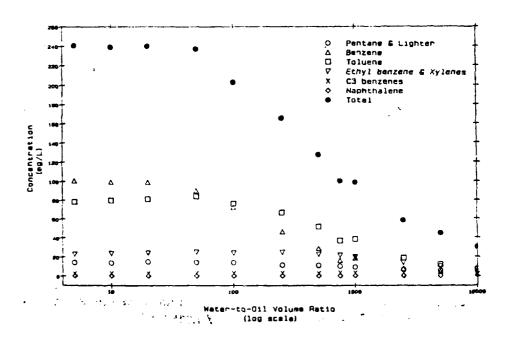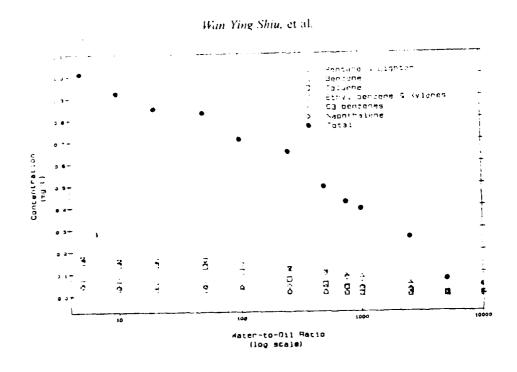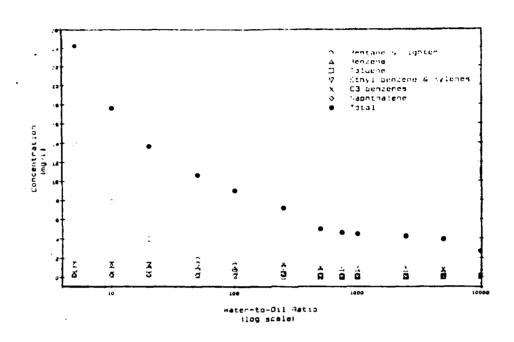
Figure 2.7.   Change in water soluble fraction concentration as a function of water-to-oil ratio for No. 2 fuel oil (Shiu et al., 1990).

References:

Domask, W.G., 1984, Introduction to Petroleum Hydrocarbons: Chemistry and composition in Relation to Petroleum Derived Fuels and Solvents, Renal Effects of Petroleum Hydrocarbons, Adv. Mod. Environ. Tox., Vol 8, p.1-26.

Jordan,E.R., and Payne, J.R., (1980) Fate and weathering of Petroleum spills inmarine environment. Ann Arbor Science Publ. Ann Arbor., Michigan.

Lord, H.J., and Perwak, J., 1988, "An Approach for Assessing Risks to Health and Environment at Petroleum Contaminated Sites", in Soils Contaminated by Petroleum : Environmental and Health Effects, Edited by E. Calabrese and P.T. Kostecki, John Wiley and Sons, 1988.

McAuliffe, C. (1966) Solubility in water of paraffin, olefin, acetylene, and aromatic hydrocarbons. J. Phys. Chem. 70:1267-1275.

Perry Chemical Engineers Handbook

Rubin, H., and Mechrez, E., 1989, Transport of Organic Pollutants in a Multiphase System, in Toxic Organic Chemicals in Porous Media, Edited by Z. Gerstl, Y. Chem, U. Mingelgrin and B. Yaron, Springer-Verlag, p. 231-250.

Shiu, W.Y., Bobra, M., Bobra, A.M., Maijanen, A., Suntino, L., Mackay, D., 1990, "The Water Solubility of Crude Oils and Petroleum Products", Oil and Chemical Pollution, Vol. 7, p.57-84.

Wittcoff, H.A., and Reuben, B.G., (1980) Industrial organic chemicals in perspective. Wiley. New York. p.41-45.

Yaron, B., 1989, On the Behavior of Petroleum Hydrocarbons in the Unsaturated Zone: Abiotic Aspects, in Toxic Organic Chemicals in Porous Media, Edited by Z. Gerstl, Y. Chem, U. Mingelgrin and B. Yaron, Springer-Verlag, p. 211-230.

CHAPTER 3

AVAILABLE TREATMENT TECHNOLOGIES

The development and evaluation of pretreatment technologies for removal of petroleum hydrocarbons requires identification of appropriate technologies. This chapter presents specific information about the available technologies for removal of contaminants. The technologies considered for potential pretreatment processes for removal of petroleum related contaminants are shown below. The biochemical processes are not considered due to their long detention time requirements and sensitivity to environmental conditions (temperature, pH).

Candidate Technologies Considered as a Pretreatment Process

Technology Type	Technology
Physical	Air stripping Centrifugation Coagulation/Filtration Dissolved air flotation Electrocoagulation Electrodialysis Evaporation Freeze crystallization Gravity oil/water separation Pervaporation Sonic treatment Steam stripping Ultra/Nano filtration
Chemical	Carbon adsorption Chemical oxidation Electron beam treatment Ion exchange Neutralization Ozone/ultraviolet irradiation Photolysis Wet air oxidation

3.1. AIR STRIPPING

Process description:

Air stripping technology involves the transfer of volatile compounds from the aqueous phase to the gas phase by passing an inert gas (air) through the liquid phase. The efficiency of separating volatile compounds is based on the equilibrium partitioning of the compound between water and air and mass transfer rates of the compound within the aqueous phase, across the gas-liquid interface and within the gas phase.

The Figure 3.1. presents a typical flow diagram of an air stripping process using a continuous countercurrent packed column. The process can be operated as cocurrent and countercurrent. The packed column is most commonly used for large volumes of water, difficult separations, and where high treatment efficiencies are required (Gas Research Institute, 1987).

Applicable chemicals:

Aromatics, naphthalene, ammonia and hydrogen sulfide.

Technology status:

Full scale.

Key process consideration:

The following table presents the important design and operating considerations (Wallman and Cummings, 1986; Hand et al, 1986).

Design variables	Operating variables
Contaminant concentration Flow rate Amount of air required	Quality of effluent Pretreatment (if required)

Performance:

Air stripping is theoretically applicable over the entire range of aqueous solubility of volatile organic compounds with Henry's law constants greater than 2.5×10^{-5} atm-cu m/g-mole at 20 to 25°C (Smith et al., 1981 and Stover, 1982). Based on Henry's law constant, aromatics and naphthalene can be removed by air stripping and phenols and most PAHs are not likely to be removed. Full scale experience has demonstrated that treated water quality of 1 ppb can be achieved for the aromatic compounds. Laboratory and full scale data show that the

3 - 2

performance of air stripping process is poor for phenols (Troung and Blackbrun, 1984).

Economics:

Capital cost is the primary concern that limits the use of air stripping process. The reported cost of treatment ranges from $0.04 to $0.85 per 1,000 gallons of water treated for the flow range of 30,000 to 4,300,000 gpd.

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Hand, D.W., J.C. Crittenden, J.L. Gehin, B.W. Lykins Jr., 1986, "Design and Evaluation of an Air Stripping Tower for Removing VOCs from Ground Water", J. of AWWA, Research & Technology, Vol. 78, No. 9, September, p. 87-97.

Smith, J.D., D.C. Bomberger, and D.L. Haynes, 1981, "Volatilization Rates of Intermediate and Low Volatility Chemicals from Water", Chemosphere, Vol. 10, No.3, p. 281-289.

Stover, E.L., 1982, "Removal of Volatile Organics from Contaminated Ground Water", presented at the Second National Symposium on Aquifer Restoration and Ground Water Monitoring, Columbus, Ohion, May 26-28.

Troung, K. and J.W. Blackbrun, 1984, "The Stripping of Organic Chemicals in Biological Processes", Environmental Progress, Vol. 3, No. 3, August, p. 143-152.

Wallman, H. and M.D. Cummings, 1986, Design Scale-Up Suitability for Air Stripping Columns, EPA/600/2-86-009.
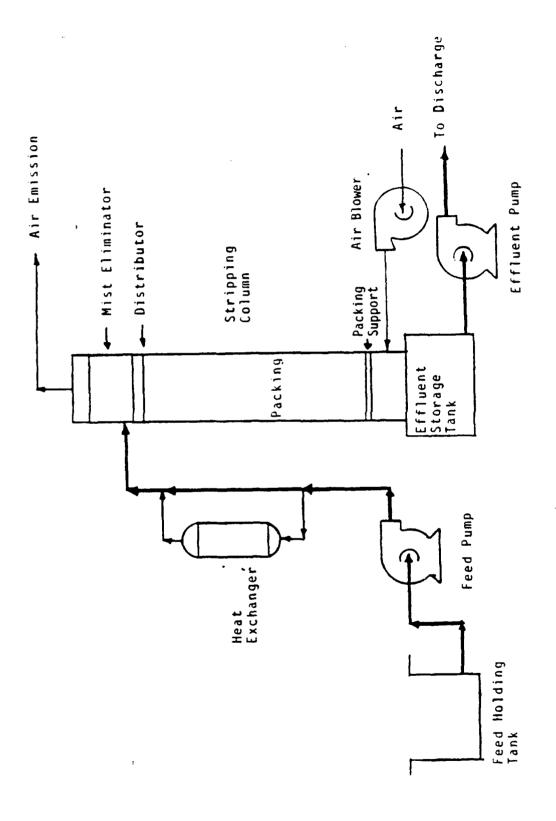
Figure 3.1. Schematic of a packed air stripping system (Gas Research Institute, 1987).

3.2. CARBON ADSORPTION

Process description:

Activated carbon, in granular form or as a powder, is an adsorbent that is generally effective in removing organic matter from water. Granular activated carbon (GAC) in a fixed bed provides for removal of petroleum hydrocarbons of approximately 50%, although removal of some species may exceed 90%. Powdered activated carbon is more efficient at organic removal, greater than 90%, due to its very large surface area and its dispersal when fluidized within water, but handling is difficult and a settling tank of sufficiently large surface area for removal of fine particles is required.

The carbon adsorption process is based on removal of dissolved contaminants by solids adsorbent as a result of weak chemical bond between the contaminants and the surface of adsorbent. Granular activated carbon columns can be operated in parallel, series, moving bed, or upflow configurations. Figure 3.2. presents a typical adsorption process. When the first column reaches its capacity, it is taken off line and the carbon is regenerated. The typical loading for a GAC system is 2-5 gpm/ft^2.

Applicable chemicals:

All soluble organic chemicals, potentially effective for certain metals and cyanide compounds.

Technology status

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Backwash requirements
Carbon loading	Pretreatment (if required)
Carbon type	
Column cross sectional area	
Column length	
Retention time	

Performance:

Activated carbon has been found to adsorb a wide variety of organic and some inorganic

chemicals. The organic compound that can be removed by activated carbon include aromatics (BTX), napthalenes, PAHs, and phenols.

Oil removal of 50% for GAC may be adequate to justify its use, the removal providing for lengthened membrane run times before fouling for the reverse osmosis process. The bed also provides filtration that will tend to reduce fouling. However, its performance is only marginal. Powdered activated carbon is very effective at petroleum hydrocarbon removal.

Activated carbon processes produce saturated carbon as their by-product. The by-product can be regenerated, probably not practical for a mobile system, or disposed of. The saturated carbon is reactivated by heating in an oxygen depleted atmosphere to remove the adsorbent from the surface pores. Disposal, due to the contaminant oil waste, may also present a problem.

The removal effectiveness of GAC suggests that a process including it may required additional treatment. Due to its filtering process it might best be used as a follow-on to another process (i.e., precipitation-sedimentation). There is little justification for using it as the first step in a pretreatment process. Powdered activated carbon should require no additional treatment (Martin and Johnson, 1987).

Economics:

Treatment costs range from $0.22 to $2.52 per 1,000 gallons of water treated for the flow range of 7,000 to 216,000 gpd (Clark et al., 1989).

References:

Clark, Robert M. and Benjamin W. Lykins, Jr. Granular Activated Carbon: Design, Operation and Cost. Chelsea, MI: Lewis. 1989.

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Martin, Edward J. and James H. Johnson, Jr., Ed. Hazardous Waste Management Engineering. New York: Van Nostrand Reinhold. 1987.

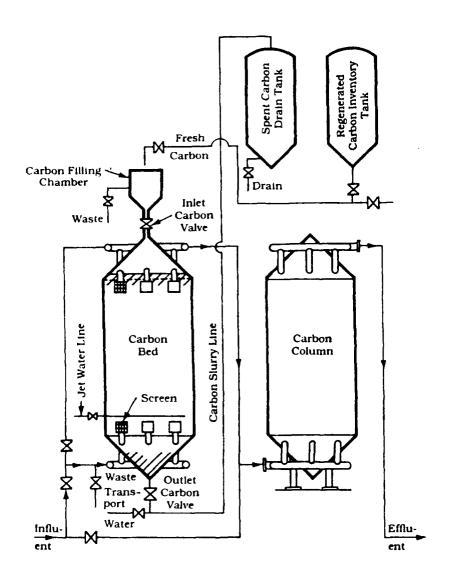Reynolds, T.D., 1982, Unit Operations and Processes in Environmental Engineering, PWS Kent Publishing Co.

Figure 3.2. Schematic of a carbon adsorption system (Reynolds, 1982).

3.3. CENTRIFUGATION

Process description:

Centrifugation is an effective unit operation for both thickening and dewatering sludges from physical-chemical and biologically treated wastewater. Centrifugal forces can be used to separate oils of varying densities from water. Centrifugation basically increases the settling rate of settling velocity of oils by increasing the gravitational forces. Oils settle on top of the water in the form of layers. The oily layers can be removed by skimmers, orifices in the bowl walls or over a weir at the top the unit.

Centrifuges are of various types i.e solid bowl conveyor centrifuge, disc-nozzle centrifuge and basket centrifuge. The disc-nozzle and tubular bowl centrifuges are generally used for oil-water separations. Table 3.1. shows the different types of centrifuges and their applications to various wastewaters. Fig 3.3. presents a typical schematic of a centrifuge.

Applicable chemicals:

All types of inorganic and organic sludges, oils and greases.

Technology status

Full scale

Key process consideration:

Design variables	Operating variables
Bowl design	Feed rate
Bowl speed	Influent solids concentration
Pool depth	Nature of solids
Conveyor speed	Polymer addition
	Temperature

Performance:

A counter current centrifuge with a sludge feed of 0.5% to 0.7% solids by weight and a feed rate of 0.038 m³/sec(600gal/min) showed a solids capture of 85% without the addition of any polymer.
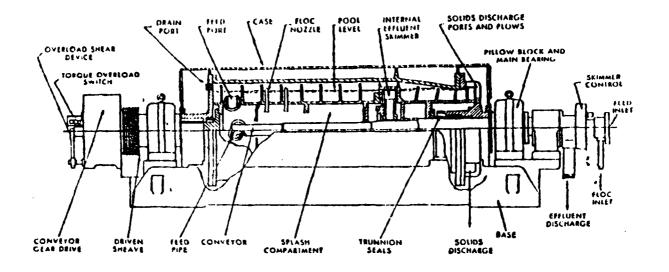
Economics:
Treatment costs range from $5.0 - $15.00 per 1000 gallons of water treated for a range upto 800,000 gpd (Gary S et al., 1991).

Table 3.1. Centrifuges and their applications to various wastewater systems (Adams, 1974).

| Application		Solids		Cake	Polymer added[*]
Effluent	Treatment	As fed	As discharged	(% solids)	(lb/ton)
SOLID BOWL SCROLL CENTRIFUGE					
Paper mill, paper	Primary; primary., secondary	Coarse, fibrous, claylike	Relatively dry	28-40	None
Municipal	Primary raw	Coarse, fibrous, claylike	Relatively dry	30-40	1.5-2.5
Municipal	Primary digested, mixed digested	Coarse, fibrous, slimy	Slimy to dry; depends on primary-secondary ratio	20-30	3-6
Municipal	Primary raw, secondary	Coarse, fibrous, slimy	Slimy to dry; depends on primary-secondary rate	18-22	4-6
Refinery	.	Gritty, coarse	Dry to pudding	20-25	None
Paper mill, municipal	.	Slimy, thickened	Thick pudding	18-22	10-20
Paper mill, water treatment	Lime sludge, water softening	Claylike	Dry	40-60 (depends on % hydroxide)	None
Steel mill	Pickle liquor, neutralized	Some floccy, some clay	Very thick pudding (can be shoveled)	20-30	1-2
DISC-TYPE CENTRIFUGE WITH NOZZLES					
Paper, municipal	Waste activated	Slimy	Thickened (for further dewatering or digestion)	6-7	None (or <1)
Refinery	Liquid-liquid solids	Oil-water emulsion; some fine claylike solids	Oil-water emulsion split; solids concentrated	Oil (<1%) water), solids (7-10%)	None
Water treatment plant	Alum floc	Slimu, floccy	Thin, floccy	5-7	<1
SOLID-BOWL BASKET (IMPERFORATE) CENTRIFUGE					
Municipal	To improve recovery[†]	Floccy, slimy	Thick pudding	10-14	None
Water treatment chemical waste	Alum floc, hydroxide sludges	Floccy	Very thick pudding	15-25	None (or <1)

* Recovery 85-90%
† Following solid-bowl scroll
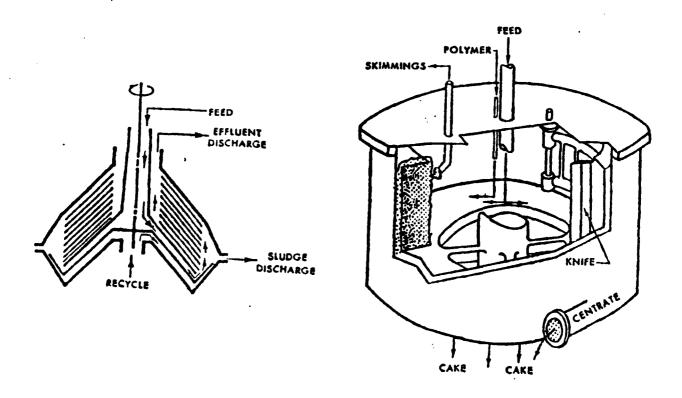
Figure 3.3. Schematic of centrifuge candidates (Research & Education Association, 1978).

3.4. CHEMICAL OXIDATION

Process description:

Chemical oxidation process converts undesirable chemicals to an acceptable form. Figure 3.4. presents two possible treatment schemes for chemical oxidation. The retention time in the reaction tanks and the dosages of oxidants vary with the composition of the water to be treated.

The three chemical oxidation processes widely used are:
i.   chlorination
ii.   chlorine dioxide
iii. hydrogen peroxide oxidation

Each of these processes require supply of chemicals. Chlorine dioxide in gaseous form is highly unstable and therefore aqueous solutions of gas are required. The solutions also decompose rapidly and should be synthesized at the site. Hydrogen peroxide is also utilized as an aqueous solution. Chlorine gas or a salt can be metered directly into the tank. Hydrogen peroxide can also be obtained in bulk and metered directly into the reaction tank.

Chemical dosage and contact times for each of these processes are presented below:

Chlorination: 7-100 mg/l   15-180 minutes
Chlorine dioxide: 3-75 mg/l   0.15-60 minutes
Hydrogen peroxide: 2-720 mg/l   15-210 minutes

The Figure 3.4. presents a typical flow diagram of a chemical oxidation process.

Applicable chemicals:

Ammonia, cyanide, sulfides, thiocyanates, metals, purgeable aromatics, phenolics, polynuclear aromatic hydrocarbons, napthalene, oil and grease, total organic carbon.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration Flow rate Amount of air required Particulate rise rate Solids loading rate Air-to-solids ratio Recycle ratio Operating pressure Retention time Flocculation Coagulation Range of agitation	Quality of effluent Concentration of skimmings Pressure on recycle Periodic cleaning requirements Pretreatment (if required)

Performance:

The removal efficiencies for the three oxidation processes are presented below (Gas Research Institute, 1987):

Chlorination:

Ammonia	96+%
Cyanide	99+%
Lead	29-36%
Purgeable aromatics	14-21%
Phenol	99+%
PAHs and napthalene	10-75%
Total organic carbon	45-50%

Chlorine dioxide:

Arsenic	20-25%
Zinc	75-85%
Oil and grease	99+%
Phenolics	95-99%
Sulfides	85-99+%
PAHs and napthalene	99+%
Purgeable aromatics	90-99+%

Hydrogen peroxide:

Cyanide	99+%
phenolics	50-99+%
PAHs	5-55%

Economics

For a chemical oxidation process with a five year design life, both the capital and O&M cost is estimated as $4.36 per 1000 water treated (EPA, 1981).

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

U.S. Environmental Protection Agency, 1981, "Cost Comparisons of Treatment and Disposal Alternatives for Hazardous Wastes: Volume I and Volume II", NTIS Publication Nos. PB 81-125514 and PB 12-128522, Springfield, Virginia.
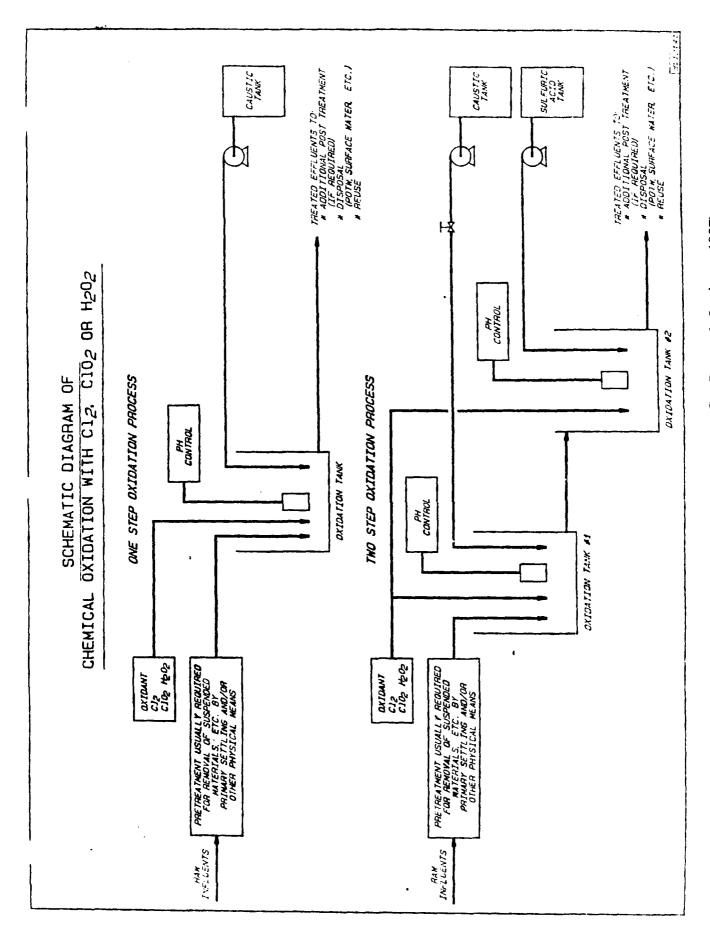
SCHEMATIC DIAGRAM OF
CHEMICAL OXIDATION WITH Cl₂, ClO₂ OR H₂O₂

Figure 3.3. Schematic of a chemical oxidation system (Gas Research Institute, 1987).

3.5. COAGULATION/FILTRATION

3.5.1. COAGULATION

Process description:

Coagulation is a process which generally occurs by the following mechanisms: ionic layer compression, adsorption and charge neutralization, chemical particle destabilization and physical inter particle bridging. The coagulation process can be accomplished with two tanks in series: rapid mixing tanks for coagulant addition, in situ coagulant formation, and particle destabilization; and flocculation tanks to enhance interparticle coalesce's. Coagulation can be used to remove color, turbidity and organic contaminants i.e natural organic matter, synthetic organic chemicals and chemical by products and additives in the water added during the experiment.

Polymeric inorganic or organic coagulants are added to enhance the formation of flocs. The flocs are removed by the filtration processes. The selection and optimum dosages of coagulants are determined experimentally by the jar tests. Fig 3.5.1. presents a schematic of a Coagulation and flocculation process.

Applicable chemicals:

All organic and inorganic contaminants including petroleum hydrocarbons.

Technology status:

Full scale

Key process consideration:

Design variables	Operating variables
Coagulant type	Quality of effluent
Coagulant dosage	Temperature
Mixing	pH
Contaminant concentration	Removal of coagulation sludge
Retention time	Pretreatment (if required)
Flow rate	

Performance:

Coagulation and flocculation of oils can be accomplished with the use of specific polymers designed to bond with petroleum hydrocarbons. A removal efficiency of 85% - 95% can be

achieved based on optimum dosage, retention time, contaminant type, and contaminant concentration.

Economics:

The cost is dependent on the type of polymer used and the dosage. The cost should be comparable to the current polymer used in ROWPU system.

References:

American Water Works Association (AWWA), 1990, Water Quality and Treatment, Mc Graw Hill, Inc., NY.

James Montgomery Consulting Engineers, Inc., 1985, Water Treatment Principles and Design, John Wiley and Sons.

Peavy S. Howard., Rowe R. Donald., Tchobanoglous George., 1985, Environmental Engineering, Mc Graw Hill, Inc., NY

3.5.2 GRANULAR MEDIA FILTRATION

Process description:

Filtration is the removal of suspended solids from water by passing it through a porous media. Granular media filtration is used to remove suspended solids and oils, this process usually precedes an alternative treatment. Filters can be enclosed in a container that is either closed or open to the atmosphere. Flow can be either pressure or gravity induced. The materials most commonly used as granular media are anthracite coal, granular activated carbon, sand, garnet, and ilmenite. Filter efficiency is dependent on the filtration rate. Single media filters usually operate at rates of approximately 2 gpm/sq ft. Greater depth removal is attained by using mixed media filters which operate at rates of approximately 5 gpm/sq ft.

Optimum water quality is obtained by effectively backwashing the media. In addition, backwashing promotes extended life for the media. In order for the filter to work effectively, appropriate methods of pretreatment are necessary. Disruptions in the operative practices in pretreatment will deteriorate the water quality. Filter performance is dependent on the properties of the granular media. The granular media properties of importance include density, porosity, size distribution and shape.

Granular media filtration is classified by several different methods. The filters can be classified according to:
1.   Direction of flow: Upflow, downflow or horizontal

2. Type(s) of media: Single medium, dual media or multi media; also by type of media, i.e., sand, coal, anthracite, etc.
3. Driving force: Gravity or pressure
4. Flow control: Constant rate or variable declining rate.

Figure 3.5-2. shows typical schematics granular media filtration processes.

Applicable chemicals:

Suspended solids, oil and grease, polynuclear aromatic hydrocarbons.

Technology status:

The technology of granular media filtration has been in use since the early 1800's. The mechanisms of granular filtration are understood and the process is well established and proven.

Key process consideration:

Design variables	Operating variables

Filter medium characteristics
  grain size
  grain size distribution
  grain shape
  grain density
  grain composition
Filter bed porosity
Filter bed depth
Filtration rate
Allowable head loss
Influent characteristics
  suspended solids
  particle size distribution
  floc strength
  floc charge
  fluid properties
	Head loss
	Periodic back washing

Performance:

Except for special cases, an influent suspended solids concentration of less than 200 mg/l will be suitable for granular media filtration and water containing greater than 200 mg/l will not be suitable. Filtration efficiency is dependent upon factors such as influent flow rate,

filter media type, media pore size and the characteristics of the water to be filtered.

Granular filtration process can remove some organics as shown below (Gas Research Institute, 1987):

Parameter	% removal
Suspended solids	> 80%
Oil and grease	> 50%
PAH	decreases as solubility of the constituent increases
Phenolics	minimal or no

Economics:

A 1981 EPA document estimates the average cost of DAF with a 10-year design life to be $2.31 per 1,000 gallons treated (EPA, 1981).

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

U.S. Environmental Protection Agency, 1981, "Cost Comparisons of Treatment and Disposal Alternatives for Hazardous Wastes: Volume I and Volume II", NTIS Publication Nos. PB 81-125514 and PB 12-128522, Springfield, Virginia.
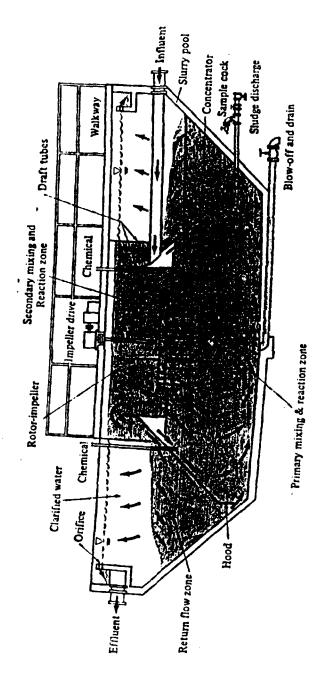
Figure 3.5.1. Schematic of a coagulation and flocculation process (Peavy, 1985).

TYPICAL FILTER CONFIGURATIONS

TYPICAL PRESSURE FILTER (DUAL MEDIA)

BACKWASH OUTLET
WASTE INLET
FILTER OUTLET
INLET DISTRIBUTOR AND BACKWASH COLLECTOR
COAL
SAND
GRAVEL
AIR INLET
EFFLUENT NOZZLES
BACKWASH INLET

TYPICAL UPFLOW FILTER

FILTER EFFLUENT
FLUSH TO WASTE
PRESSURE VESSEL
AIR INLET
SAND RETAINING GRID
GRADED BED OF FILTER MEDIA
NOZZLE PLATE DISTRIBUTOR
RAW WATER IN

TYPICAL GRAVITY FILTER

WATER IN
BACKWASH TO WASTE
WATER OUT
BACKWASH INLET
SAND
GRAVEL

Figure 3.10. Typical filter configurations (Gas Research Institute, 1987).

3 - 21

3.6. DISSOLVED AIR FLOTATION

Process description:

The two air flotation methods utilized in oil separation are dissolved air flotation and induced air flotation. The two methods differ primarily in the means by which air bubbles are introduced to the process stream. In dissolved air flotation (DAF) the stream is pressurized in the presence of an air-water interface, air entering the liquid stream, and then air bubbles are formed when the pressure is released. In induced a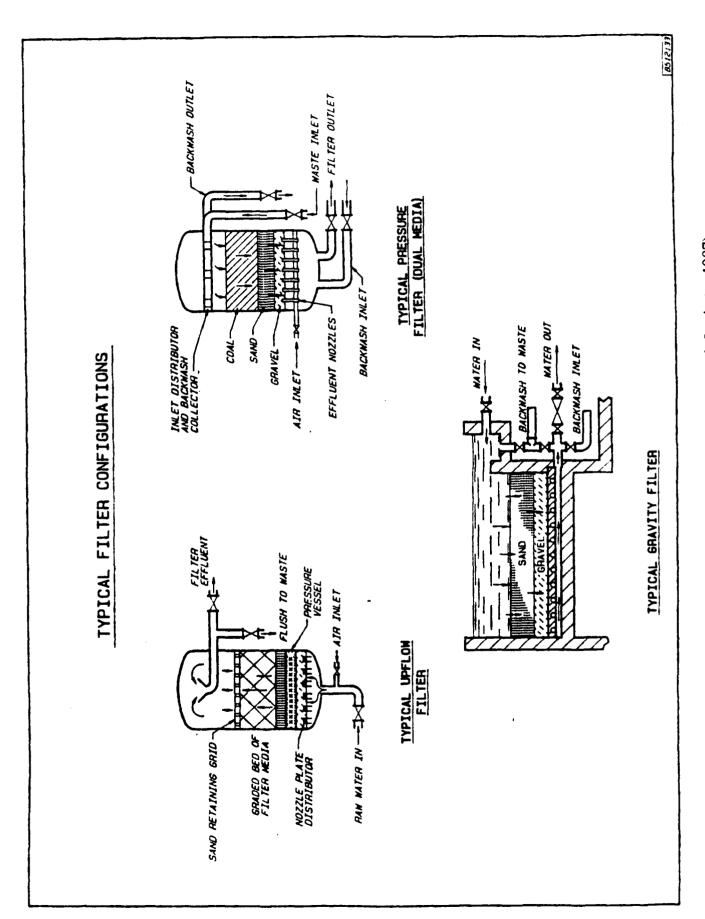ir flotation (also known as dispersed air flotation) air bubbles enter the stream by mechanical means. The air bubbles rise in the stream and bring oil and suspended solids to the surface, where they are removed by skimming. The process is only effective when coagulant aids are added to the stream to neutralize the electrical double layer of colloidal particles.

DAF can be considered as the reverse of gravity sedimentation process. The dissolved air flotation process produces bubbles through pressure reduction in a water overloaded with air. The bubbles which are produced attach to oils or suspended solids and later agglomerate and float on the surface. The floating matter is cleared by flooding or scraping. The remaining water on the bottom is transferred. The DAF process is generally used on waste streams where the specific gravity of the material to be separated is close to water.

The bubble floc forms by three mechanisms:

1. Bubbles join with floc in the course of collisions.
2. Bubble entrapment inside of a concentrated system of particle floc.
3. Bubble growth in the nuclei inside of the floc.

The basic principle in the DAF process is the fact that as the pressure increases on water, it is able to contain more dissolved air, nitrogen and other gas molecules. When the pressure is reduced, the gases are released as extremely fine bubbles.

There are three variations of pressure flotation process:

o   Direct: Pressurization of the entire waste stream
o   Partial: Partial pressurization of the waste stream
o   Recycle: Pressurization of recycled effluent

Figure 3.6. illustrates the effluent recycle DAF process.

Applicable chemicals:

Oil and grease, polynuclear aromatics.

Technology status:

Dissolved air flotation has been used in industry for several decades.

Key process variables:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Concentration of skimmings
Amount of air required	Pressure on recycle
Particulate rise rate	Periodic cleaning requirements
Solids loading rate	Pretreatment (if required)
Air-to-solids ratio	
Recycle ratio	
Operating pressure	
Retention time	
Flocculation	
Coagulation	
Range of agitation	

Performance:

The DAF process can effectively remove oil and grease, suspended solids, and any compound that can stay within the oil phase. The data available is sufficient to verify DAF for the removal of oil and grease and suspended solids. However, removal of any other constituents appears to be wastewater related. Therefore, more information is required on the effect of DAF on purgeable aromatics (benzene, toluene, xylene) to determine if they are possibly air stripped during the DAF process.

Data accumulated indicates that removal to oil levels of 20 mg/l can be accomplished when the correct coagulant aid is selected. Selection of the coagulant aid is critical in achieving the desired contaminant removal level of 5 mg/l.

The waste stream will contain the coagulant aid in addition to the oil and solids separated. The nature of the coagulant aid in terms of toxicity may generate some concern, however it is unlikely that the waste stream will present any significant concern.

The process does not achieve desired effluent standards, but addition of a follow-on treatment is not likely. Pretreatment with a coagulant prior to the process is required.

The air flotation processes can be sized adequately for the intended use and flow rate. The

time required is dependent upon the flotation velocity and reactor dimensions.

Economics:

A 1981 EPA document estimates the average cost of DAF with a 10-year design life to be $1.26 per 1,000 gallons treated (EPA, 1981).

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Szabo, A.J.; Larry F. LaFleur; Felon R. Wilson. Dissolved Air Flotation Treatment of Gulf Shrimp Cannery Wastewater. Cincinnati, OH: US Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, 1979. EPA-600/2-79-061.

U.S. Environmental Protection Agency, 1981, "Cost Comparisons of Treatment and Disposal Alternatives for Hazardous Wastes: Volume I and Volume II", NTIS Publication Nos. PB 81-125514 and PB 12-128522, Springfield, Virginia.

Webb, Chris. "Separating oil from water." The Chemical Engineer, n. 494, 11 April 1991, p. 19-24.
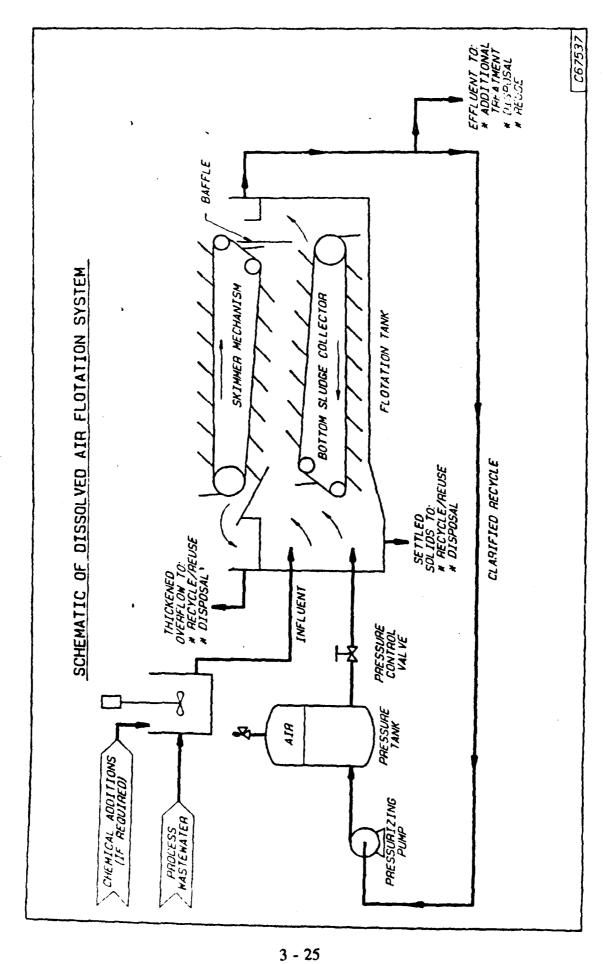
SCHEMATIC OF DISSOLVED AIR FLOTATION SYSTEM

C67537

Figure 3.4. Schematic of a dissolved air flotation system (Gas Research Institute, 1987).

3.7. ELECTROCOAGULATION

Process description:

The electrocoagulation process is a chemical coagulation process conducted in a reactor with an electric field applied. When a direct current field is applied, the overall efficiency improves and coagulant dosage requirements are reduced. The nature of the oil-in-water emulsion dictates the dosage and the mechanism. Generally, in a flocculent solution, a DC field applied with the stirrer as the positive electrode will cause the migration of negatively charged colloids (the preponderance of colloids) toward the stirrer, creating a elevated density gradient and therefore enhancing coagulation. If the reactor wall is the positive electrode, the migration is reversed and removal is not improved. In the study cited, the coagulant used was ferric sulfide.

Biswas (1991) used this technology with a current application time of 1 minute (only during rapid mixing) and 16 minutes (rapid mixing and flocculation) in a laboratory experiment. The results showed no effect of current application during rapid mixing, the removal cited above coming only after flocculation. Therefore removal efficiency is a function of detention time, with design requiring incorporation of adequate time for adequate flocculation. Figure 3.7. presents a schematic of the coagulation process.

Applicable chemicals:

Oils in emulsion form can be removed by electrocoagulation process. Petroleum hydrocarbons in emulsion such as purgeable aromatics, phenolics, polynuclear aromatic hydrocarbons, napthalene, oil and grease, total organic carbon can be removed.

Technology status:

The cited study was conducted using beakers in a laboratory. No scaling-up data was identified in the research.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Removal of coagulation sludge
Dosage of chemicals	Periodic cleaning requirements
Retention time	Pretreatment (if required)
Turbulence reduction in tank	

Performance:

Application of the results in the cited study, conducted on an emulsion of a synthetic oil-in-water, to the research objective may introduce error. In the study, the optimum configuration, a 200 mg/l ferric sulfate concentration (maximum studied) and a 100V applied field (maximum studied), produced removal of 98% of the oil emulsion, from 500 mg/l to 10 mg/l. The removal efficiency is high, but the effluent concentration exceeds the target of 5 mg/l with high initial concentrations.

The enhanced coagulation process, electro- coagulation generates a hazardous settled sludge, which may create a disposal problem. Settling of the floc following the coagulation and flocculation stage is required.

Economics:

No data was found on economics of this process. Based on the flow diagram of the process, the capital and operating costs should be relatively low.

References:

Biswas, N.; G. Lazarescu, 1991. "Removal of oil from emulsions using electrocoagulation." International Journal of Environmental Studies, v. 38, pp. 65-75.
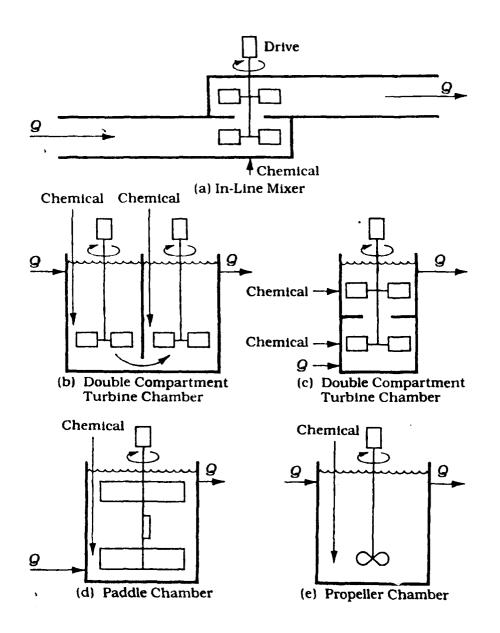
Figure 3.5. Schematic of coagulation processes (Reynolds, 1982).

3.8.   ELECTRODIALYSIS

Process description:

Electrodialysis is an electrochemical partitioning method where ions are transported via membranes that are anion and cation discriminating traps. Direct electric current flow, force ions to part from a solution of low concentration to one of higher concentration.

Electrodialysis reversal is a modified form of electrodialysis where the electrodes' polarity has been reversed. The resultant of the reversed polarities is to alter ion flow in a stacked membrane. In membrane stacks, polarity reversal is usually applied at intervals of approximately twenty minutes. Electrodialysis reversal must provide for automatic flushing to remove material that adhere to the surface of the membrane, particularly scale forming material.

Figure 3.8. presents a typical electrodialysis process. There are basically three elements to the system:

1.   Supply of pressurized water,
2.   Membrane stack, and
3.   DC power supply.

Applicable chemicals:

Cations and anions and organics with charges.

Technology status:

Pilot/full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration Flow rate Voltage applied Retention time Turbulence reduction in tank	Quality of effluent Periodic cleaning requirements Pretreatment (if required)

Performance:

Some pretreatment is often necessary for feed water. Normally acid addition to prevent precipitation of sparingly soluble salts and filtration for removal of suspended matter is used as pretreatment processes (James Montgomery Consulting Engineers, Inc., 1985).

Economics:

System maintenance is too complex. Operating costs are high.

References:

USAID, 1980, The USAID Desalinization Manual, International Desalinization and Environmental Association, August.

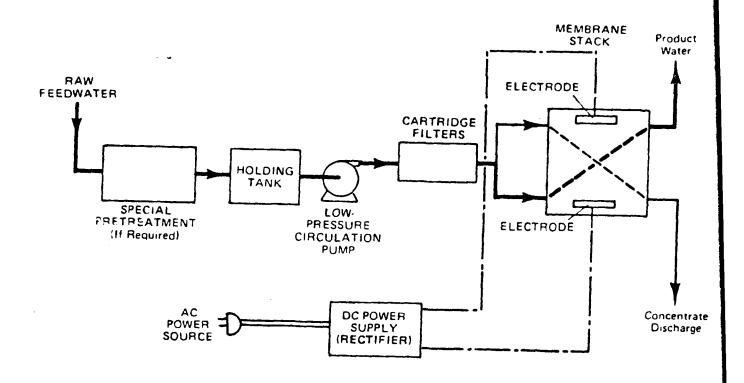James Montgomery Consulting Engineers, Inc., 1985, Water Treatment Principles and Design, John Wiley and Sons.

Figure 3.6. Schematic of the electrodialysis process (USAID, 1980).

3.9. ELECTRON BEAM TREATMENT

Process description:

Electron beam processing involves exposing the material to be irradiated to a stream of high energy (fast) electrons. These electrons interact with the material in less than 10^{-12} seconds to produce electrons of lower and lower energy. Eventually a large number of slow electrons with energies less than 50 eV is produced and these electrons interact with molecules to produce excited states of these molecules, positive ions and electrons. Eventually the electrons slow to thermal energies and get trapped. In materials of low dielectric constant most electrons do not escape the pull of the positive ions formed when they were produced. The electrons are attracted back to the positive ions causing a chemical reaction. This is termed direct radiolysis. In high dielectric materials such as water and aqueous solutions, most electrons escape the pull thus leaving both the positive ions and electrons free to react with the water or waste components in it. This is referred to as indirect radiolysis. The ratio of direct to indirect radiolysis in wastewater is approximately the weight fractions of waste to water (Singh et al., 1985).

Figure 3.9. presents a schematic of the pilot plant at the Virginia Key Wastewater Treatment Plant which is within 10 mile distance of the FIU. The capacity of the pilot plant is 610 liters per minute. The pilot plant is equipped with a horizontal accelerator with 1.5 MeV electron beam, rated at 50 Ma. The accelerator has capability to apply variable beam current within the 0 to 50 Ma range corresponding to doses within the 0 to 650 krads.

Because the system is being used for research, and water quality is one of the main experimental variables, three influent streams are directly connected to the facility. These three influent streams are potable water, chlorinated secondary wastewater and secondary anaerobically digested sludge that is 2-5% in solids. Batch experiments can be run at the facility utilizing a 6000 gallon tank truck connected to the influent pump. Experiments have been conducted using raw wastewater collected and transported in the tank trucks.

Applicable chemicals:

Purgeable aromatics, phenolics, polynuclear aromatic hydrocarbons, napthalene, oil and grease, total organic carbon.

Technology status:

Pilot scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration Flow rate Amount of irradiation required Duration of radiation	Quality of effluent Periodic cleaning requirements Pretreatment (if required)

Performance:

The electron beam irradiation is effective with PCBs and chlorinated organics. Some by products may be left in the treated solution.

Economics:

The plant was constructed as part of the Environmental Protection Agency's innovative technology program and became operational in 1984. The construction cost of the pilot plant was approximately 1.7 million dollars (1984).

References:

Singh, A., N.H. Sagert, J. Borsa, H. Singh and G.S. Bennett. The use of high-energy radiation for the treatment of wastewater: A review. Proceedings of the 8th Symposium on Wastewater Treatment, Montreal, 1985.

Cooper, W.J., M.G. Nickelsen, T.D. Waite, and C.N. Kurucz. High-energy electron beam irradiation: An advanced oxidation process for the treatment of aqueous based organic hazardous wastes. Symposium on Advanced Oxidation Processes for the Treatment of Contaminated Water and Air, Toronto, Canada, 1990.
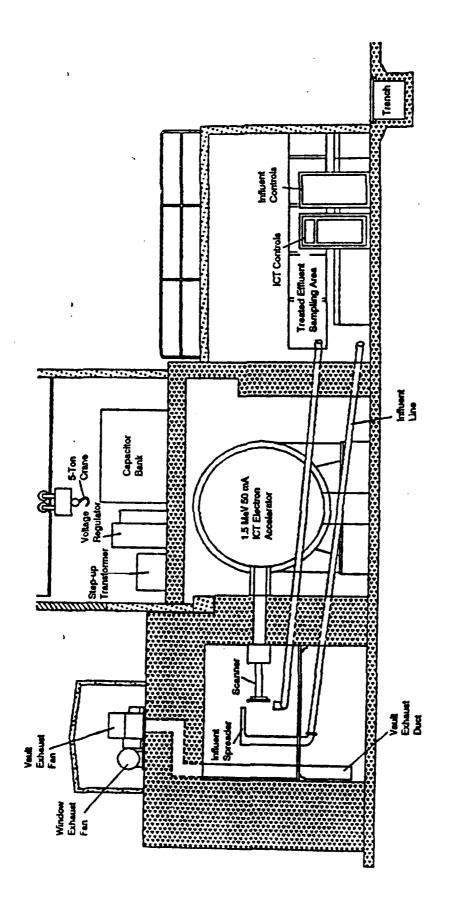
Figure 3.7. Schematic of the electron beam process.

3.10. EVAPORATION

Process description:

Evaporation is simply a process where solids and liquids vaporize into the atmosphere. The process of vaporization involves the following steps:

(a)   Departing from the surface - this step is dependent on the temperature and the accompanying vapor pressure of the contaminant.

(b)   Diffusion in the boundary layer (layer of air over the liquid or solid surface).

(c)   Advection and/or dispersion - the form of transport of the contaminant. In advection the contaminant travels at the same velocity as the groundwater. In dispersion the contaminant is diluted exhibiting either longitudinal dispersion or lateral dispersion. Longitudinal dispersion occurs when the contaminant and the fluid with which it flows mix along the streamline. Lateral dispersion is mixing that occurs normal to the path of flow.

There are several classifications of evaporators, including tubular or plate evaporators, wiped film evaporators, direct contact evaporators, and natural energy evaporators.

Figure 3.10. shows a typical schematic of an evaporator. The evaporators can be mounted on transportable units.

The multieffect distillation process was the first treatment process used to produce significant amounts of desalinated water from seawater. Today it is not used extensively due to high energy requirements for the process. Today mostly multistage flush distillation and solar distillation processes are used. Multistage flush distillation process utilizes 16 to 50 stages in series. In each stage, the operating pressure is less than the preceding one. Brine from a previous stage is input into the current stage and is recycled (Khan, 1986; Speigler and Laird, 1980).

Applicable chemicals:

For aqueous mixtures, evaporation is applicable to all chemicals of interest. However, the volatilization of strippable compounds (e.g., BTX, naphthalene, and most PAHs) may require treatment of the evaporated water prior to use.

Technology status

Full scale.

Key process consideration:

Design variables	Operating va . es
Flow rate Corrosion potential of feed Presence of solids Operating temperature Retention time	Quality of effluent Periodic cleaning requirements Pretreatment (if required)

Performance:

Information on applicability of evaporation to remove petroleum hydrocarbons is limited. Limited data exists relative to removal of phenol from tar residues (Gas Research Institute, 1987).

Economics:

Aqueous evaporation systems are energy intensive. Based on $0.10 kwh, the power cost would result in approximately $7-9/1000 gallons of treated water. Capital costs are significant and are very dependent on the characteristics of the water and its corrosivity (Gas Research Institute, 1987).

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Khan, A.H., 1986, Desalination Processes and Multistage Flash Distillation Practices, Elsevier Science Publishing Co., New York.

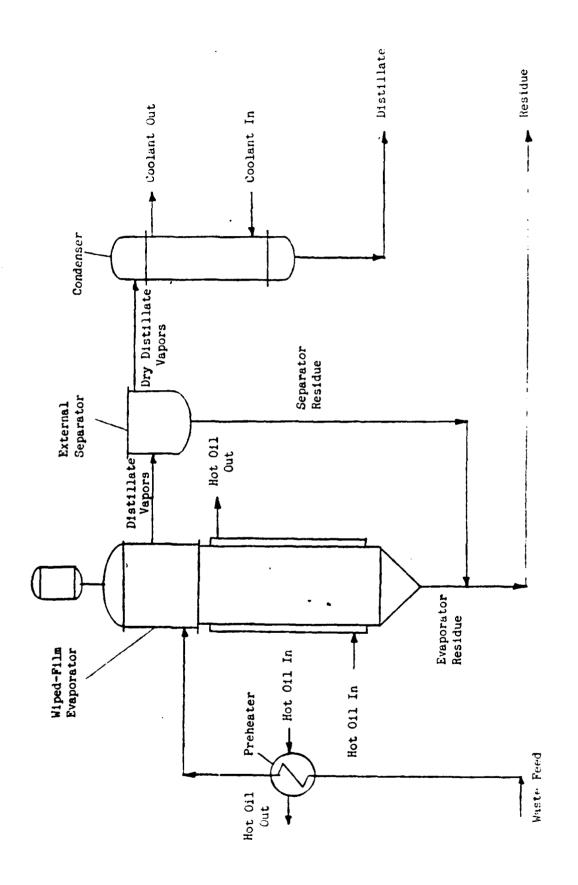Speigler, K.S., Laird, A.D.K., Principles of Desalination, Academic Press, New York.

Figure 3.8. Schematic of an evaporation system (Gas Research Institute, 1987).

3.11. FREEZE CRYSTALLIZATION

Process description:

Freeze crystallization operates on the principle that when water freezes, the ice crystal structure that forms naturally excludes the contaminants from the water molecule matrix. The ice crystals, when separated from the aqueous solution, washed and melted to produce clean water.

The process utilizes a vertical freeze exchanger. The solution moves downward as a falling film inside the exchanger tubes while refrigerant is outside the tubes. A flow schematic of freeze crystallization process is shown in Figure 3.11. (EPA, 1988).

There are some variations to the process such as vacuum freezing vapor compression, vapor absorption method, secondary refrigerant methods and vacuum freezing ejector absorption process. In vacuum freezing vapor compression, the cold incoming salt water is sprayed into the freezing chamber. The ice is transferred to a melting unit and the vapor originating in the freezing chamber is compressed and discharged to the melting unit. In the vapor absorption method, the vapor produced is absorbed rather than compressed. The secondary refrigerant method involves the direct evaporation of an immiscible refrigerant (e.g., isobutane) in contact with the saline water. It is very similar to the vacuum freezing vapor compression method. The vacuum freezing ejector absorption process is a combination of vacuum freezing vapor compression and vapor absorption method (Speigler, 1980).

Applicable chemicals:

Liquid waste containing ions, metals, organics compounds and pesticides are suitable for this technology.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Flow rate	Quality of effluent
Corrosion potential of feed	Periodic cleaning requirements
Concentration of contaminants	Pretreatment (if required)
Operating temperature	
Retention time	

3 - 38

Performance:

The freeze crystallization process is suitable for removal of both organics and inorganics at high concentrations where stripping, sorption and membrane processes would not be appropriate.

Economics:

No cost data was found on this process.

References:

Speigler, K.S., Laird, A.D.K., Principles of Desalination, Academic Press, New York.

U. S. EPA, 1988, The Superfund Innovative Technology Evaluation Program: Technology Profiles, EPA/540/5-88/003.
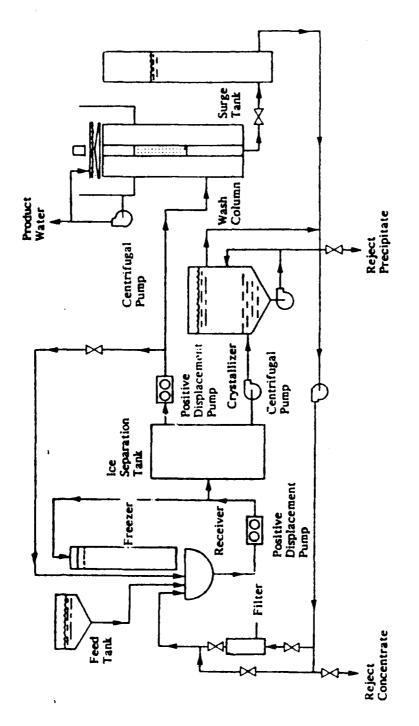
Figure 3.9. Schematic of a freeze crystallization system (Gas Research Institute, 1987).

3.12. GRAVITY OIL/WATER SEPARATION

Process description:

Gravitational forces can be used to separate oils that have varying densities. Oil and water can adopt the latter method so that separation occurs. Oil and water are partitioned by gravitational forces that leave oil floating on the surface and the remaining water on the bottom of the tank. The oil on the surface is removed by skimmers, while the remaining separated water departs through the lower portion of the tank.

A rectangular multichanneled unit is the most common configuration of gravity separators. However, higher performance design such as inclined plate coalesce are becoming more common. Figure 3.12. shows a typical schematic of gravity oil/water separation process.

Applicable chemicals:

Oil and grease, suspended solids, PAHs, napthalene.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Amount of free oil in the waste stream	Temperature
Flow rate	Flow rate
Space available for installation	Ph
Specific gravities of contaminants	Periodic cleaning requirements
Viscosity of water	
Retention time	
Turbulence reduction in tank	

Performance:

Reduction in oil and grease, suspended solids, turbidity, and PAHs was observed. Phenol removal is minimal. General performance of oil water separators can be summarized as follows (Oil and Gas Research, 1987):

o   Oil and grease and suspended solids removal may exceed 90%

o   Total PAH reduction may be as high as 80%

o   Percent napthalene reduction is usually less than the percent PAH reduction.

The water requires additional treatment since the contaminants dissolved in water will not be removed.

Economics:

A 1981 EPA document estimates the average cost of an oil/water separation process with a 10-year design life to be $0.48 per 1000 gallons of water treated (EPA, 1981).

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

U.S. Environmental Protection Agency, 1981, "Cost Comparisons of Treatment and Disposal Alternatives for Hazardous Wastes: Volume I and Volume II", NTIS Publication Nos. PB 81-125514 and PB 12-128522, Springfield, Virginia.
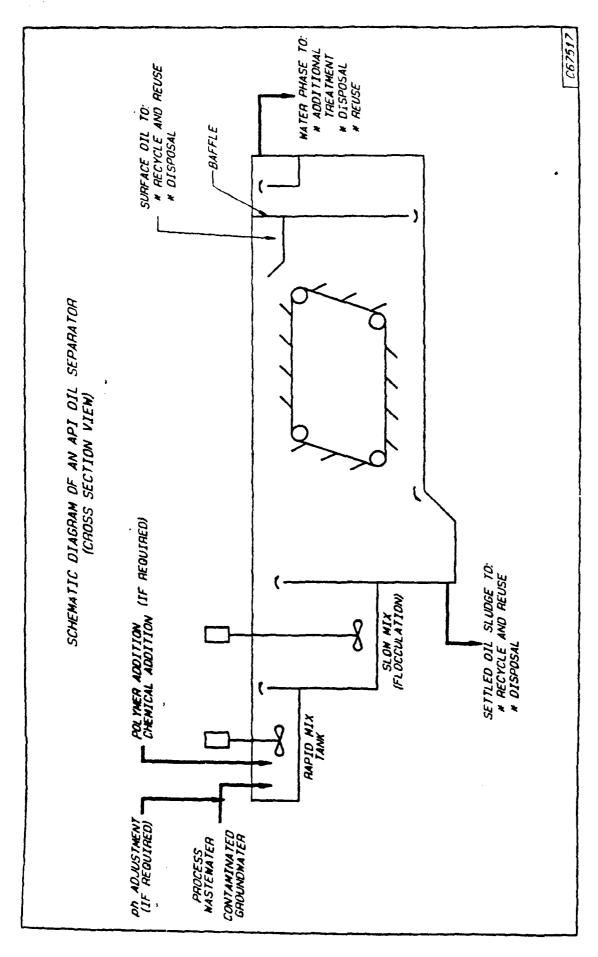
Figure 3.11. Schematic of an API oil separator (Gas Research Institute, 1987).

3.13. ION EXCHANGE

Process description:

Ion exchange is a process in which selected pollutant ions in an aqueous solution are removed by the ion exchange media. Although natural ion exchange materials exist (e.g., zeolites), most industrial applications use synthetic resins. Synthetic resins are normally high molecular weight organic polymers onto which chemical functional groups (e.g., sulfonic, carboxylic, phenolic, aminos) are added by reaction.

Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers. Commercially available ion exchange resins employ $H+$ and $Na+$ as the predominant exchangeable cations while Cl- and OH- appear as the predominant exchangeable anions.

Figure 3.13. presents a typical flow diagram for an ion exchange process. A storage tank is normally needed to provide a surge volume in the system, to allow the exchangers to be operated at a constant rate, and to be used to settle coarse solids in the feed water.

Applicable chemicals:

All inorganic cations, such as heavy metals and ammonia, and anions such as sulfate. Also potentially applicable to ionic organic compounds such as phenolics and pyridine.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Temperature
Retention time	Ph
Resins type	Pretreatment (if required)
Column area	
Column height	
Resin regeneration	

Performance:

Ion exchange can theoretically remove all of selected ionic constituents if adequate resin contact time and proper resin is used. Industrial experience has shown 50-100 ppb level of various metals concentration in the effluent.

Economics:

Estimated ion exchange equipment costs range from $55,000 to $45,000 for a single (cation or anion) unit of 20 to 600 cubic feet of resin with corresponding flow rates ranging from 10 to 500 gpm (DOW, 1985). The chemical costs for demineralizing water ranged from $0.02 to $0.05 per 1000 gallons of water treated (DOW, 1985). Estimated total treatment costs ranged from $0.60 to over $1.00 per 1000 gallons of water treated.

References:

DOW, 1985, "Water Conditioning Manual", DOWEX Ion Exchange Resin, The Dow Chemical Company.
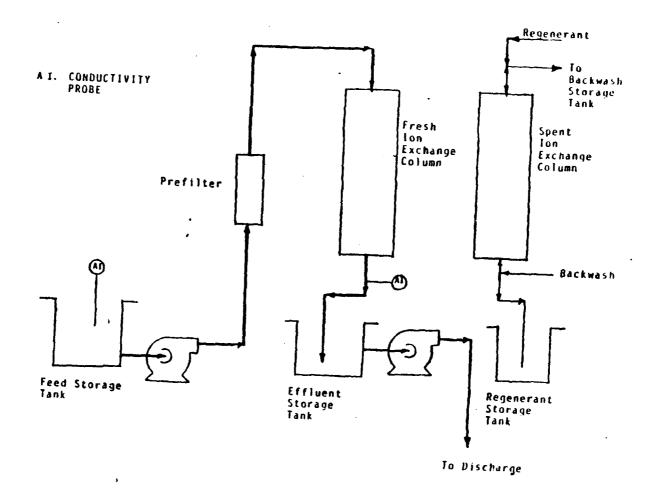
Figure 3.12. Schematic of an ion exchange system (Gas Research Institute, 1987).

3.14. NEUTRALIZATION

Process description:

Neutralization is essentially mixing of an aid and a base. The addition rate of a given neutralizing agent is controlled by pH. This can be either continuous or batch. Neutralization of an acid stream is generally achieved using reagent containing sodium, calcium or magnesium (Davidson, 1978). Lime, caustic soda or magnesium in the oxide or carbonate form are usually used.

Figure 3.14. presents a typical flow diagram for a neutralization process.

Applicable chemicals:

Metals and inorganics.

Technology status

Laboratory bench scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration Flow rate pH of influent Neutralizing agent Production of any toxic vapors Flexibility of required Ph Area available for installation of process	Quality of effluent Ventilation Maintenance of pH probes and chemical feed equipment

Performance:

Data from wastewater studies indicate that the total metals concentration can be decreased by pH adjustment and precipitation with lime by approximately 48%. Total soluble metals can be decreased by 80% (Edison Electric Institute, 1984; EPA, 1973).

Economics:

Equipment for neutralization includes tanks, mixers, pumps, chemical storage, and pH meters. Due to simple configuration of the process the cost of treatment is not high.

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Davidson, L.N., 1978, Neutralization: Unit Operations for Treatment of Hazardous Industrial Waste, Edited by D.J. De Renzo, Park Ridge, NJ, Noyes Data Corp.

Edison Electric Institute, 1984, Handbook of manufactured Gas Plant Sites, Prepared by Environmental Resources, Inc., and Koppers Company, Inc.

U.S. Environmental Protection Agency, 1973, Waste treatment: Upgrading Metal Finishing Facilities to Reduce Pollution, Technology Transfer, July, Document No. 625/3-73-002.
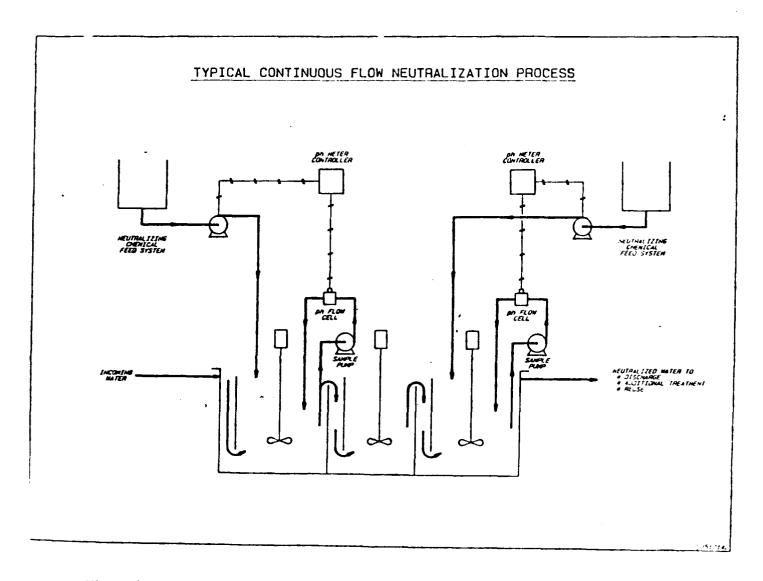
Figure 3.13. Typical continuous flow neutralization process (Gas Research Institute, 1987).

3.15. OZONE/ULTRAVIOLET IRRADIATION

Process description:

The ozone/ultraviolet irradiation process can be used for destroying especially chlorinated hydrocarbons, in dilute concentrations in water. The process oxidizes toxic and refractory compounds in concentrations measured in the ranges of ppm or ppb. No residues, sludges or spent adsorbents are generated.

The ozonation process components include air/oxygen supply system, the ozone generator, and the reaction vessel. Figure 3.15. presents a typical flow diagram for a ozone/UV irradiation process. For the ozone/UV process the reaction vessel design is altered to accommodate ultraviolet lights.

The ozone reactor is designed to provide contact between the ozone enriched gas and the water to be treated. Several reactor configurations are available. Reactors for the ozonation are typically a minimum of 15 feet tall to ensure adequate contact time. The units are generally designed to operate as countercurrent to enhance mass transfer.

Ozone can undergo two different types of reaction, direct and indirect. In the direct reaction, ozone reacts directly with substrates. The indirect reaction introduces the creation of the hydroxyl radical which is a highly reactive species. The hydroxyl radical is produced as the ozone decomposes.

The ozone dosage and reaction efficiency is associated with a reaction time needed for a required removal rate. The rate constant for the reaction to occur is proportional to its related reaction time (EPA, 1988).

Applicable chemicals:

Cyanide, sulfide, purgeable organics, phenolics, PAHs and napthalene.

Technology status

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration Flow rate Ozone dosage Reactor contact time System Ph Materials of construction Cooling water requirements Flow equalization By-product generation	Quality of effluent Pretreatment (if required)

Performance

Direct ozonation is not appropriate for reducing concentrations of benzene, some aldehydes, chlorinated alkenes, alkenes, and saturated compounds. The time required for contaminant removal of common pollutants is lengthy. Ozone is unstable and therefore must be made at the place of use. In addition, ozonation is a costly process.

Ozone/UV has been shown to achieve the following removal efficiencies:

Cyanide	20-90%
Sulfide	25-99%
Phenolics	10-99+%
PAHs	50-99+%
Napthalene	37-99+%

Economics:

The process requires an ozone generator, reaction vessels, equalization tanks and ozone monitors. The capital costs are high. The UV unit requires frequent cleaning and maintenance. The process costs are high in comparison to other oxygenation processes.

References:

U. S. EPA, 1988, The Superfund Innovative Technology Evaluation Program: Technology Profiles, EPA/540/5-88/003.

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.
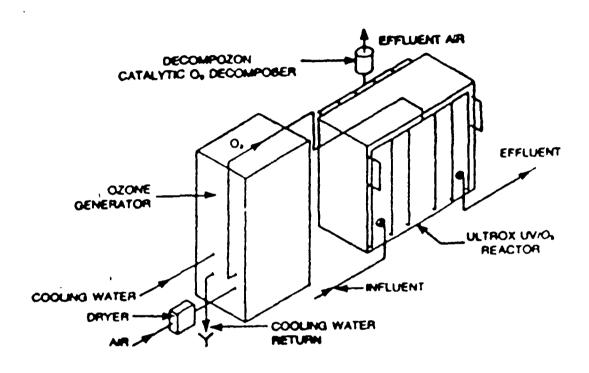
Figure 3.14. Schematic of the ozone/UV process (EPA, 1988).

3.16. PERVAPORATION

Process description:

This technology is a membrane process that utilizes the laws of vapor pressure to separate solvent from water. During the pervaporation process, liquid contacts one side of the membrane and removed as a vapor from the other side. By using a condenser on the permeate side, the feed side will have a higher vapor pressure and therefore create movement through the membrane. Depending on the type of membrane and the pressure used, different compounds can be rejected by the membrane. Figure 3.16. represents a typical flow diagram of the pervaporation process.

Unlike other membrane processes, pervaporation does not depend on the molecular cutoff weight of the compound to obtain effective removal. The controlling factor is the vapor pressure of these compounds. Therefore, the typical problems associated with other membrane processes (ie. fouling) are significantly reduced. Pretreatment is limited to filtration of particle sizes greater than 20 micrometers and removal oil emulsions.

Applicable chemicals:

Organic solvents; hydrophobic solvents (benzene), process waste waters (ethyl acetate), hazardous waste streams (dioxane, acetone, methanol).

Technology status:

Full scale

Key process consideration:

Design variables	Operating variables
Contaminant type	Periodic cleaning requirements
Contaminant concentration	Periodic replacement of membranes
Flow rate	Pretreatment (if required)
Operating pressure	
Retention time	

Performance:

The pervaporation system consists of several modules in series. The performance of the system is a function of the membrane surface area and the flux. The choice of the membrane is a critical factor in the overall performance of the system. Therefore, approximate contents

3 - 53

of the feed water must be known to effectively determine the type of membrane used and the ideal vapor pressure to be used.

The use of pervaporation has been proven effective to remove organic solvents in aqueous streams. Such removal can be divided into three main categories; pollution control of dilute solutions of hydrophobic solvents, solvent recovery from process waste waters, and volume reduction of mixed-solvent hazardous waste. The use pervaporation in the removal of hydrophobic solvents such as benzene, can obtain a removal rate of 99%. For example, a high concentration of 1000 ppm can be reduced to a concentration of 10 ppm or less. Using pervaporation to recover such solvents as ethyl acetate has achieved 90% separation. Pervaporation has also been used in the past as a volume reduction technique for removing hazardous waste streams by reducing such toxins as dioxane (6.0 % to <0.1%), acetone (0.6% to <0.05%), and methanol (0.1% to <0.01%).

Economics:

The cost for pervaporation is very high, approximately $14 per 1000 gallons of treated water.

References:

Wijmans, J.G.; Kaschemekat, J.; Davidson, J.E.; and Baker, R.W.; "Treatment of Organic-Contaminated Wastewater Streams by Pervaporation"; Environmental Progress, Vol. 9, No. 4; November 1990.

Lipski,C. and Cote, P.; "The Use of Pervaporation for the Removal of Organic Contaminants From Water"; Environmental Progress, Vol.9,No.4; November 1990.

Train of pervaporation modules in series / parallel

Influent

Feed pump

Treated Effluent

Condenser

Vacuum pump

Condensate
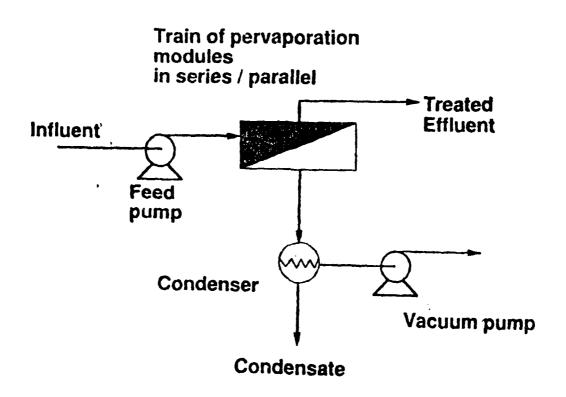
Figure 3.16. Schematic of the pervaporation process (Lipski and Cote, 1990)

3.17 PHOTOLYSIS

Process description:

This technology is designed to photochemically oxidize organic compounds through the application of ultraviolet radiation. The reactor is capable of destroying very low concentrations of organic compounds. Air is sprayed through the solution to maintain the dissolved oxygen required for oxidation of organic compounds formed by photolysis. The detoxified water is sent for degassing where volatile compounds are released to the atmosphere (EPA, 1988). Figure 3.17. presents a typical flow diagram for the photolysis process.

Applicable chemicals:

PCBs, dioxins and other toxic dichlorinated compounds. Potential removal for most organic compounds.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration Flow rate Amount of irradiation required Retention time	Quality of effluent Periodic cleaning requirements Pretreatment (if required)

Performance:

UV photolysis can be used to catalyze or initiate the dechlorination of organic chemicals in either aqueous or solvent systems. Degradation products of these reactions include polymeric tars and oxygenated compounds. Treatment of chlorophenols to below 1 ppm and chlorinated dioxins to 1 ppb in a solvent system has been demonstrated.

Economics:

No cost data was found for this technology.

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

U. S. EPA, 1988, The Superfund Innovative Technology Evaluation Program: Technology Profiles, EPA/540/5-88/003.
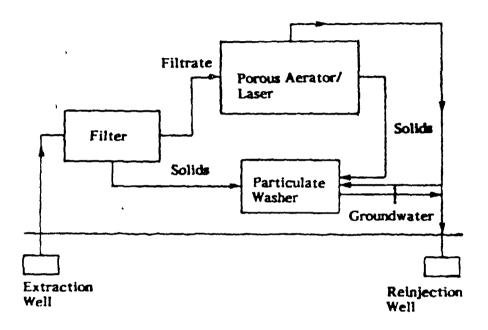
Figure 3.15. Schematic of the photolysis system (EPA, 1988).

3.18. SONIC TREATMENT

Process description:

A conceptual schematic for a sonic treatment process is shown in Figure 3.18. Emulsions and sludges can be pumped to a heated storage tank to provide uniform flow and composition to the sonic treatment unit. Emulsions from the tank is pumped to the treatment units where it is subjected to sonic vibration at 18 to 27 kilohertz. The detention time at the chamber is approximately 5 to 10 minutes.

In the sonic treatment unit, the droplets of the emulsion coalesces into much larger drops. The solids in the emulsion is freed from the surface of the droplets. The water is then sent to a gravity settler where the treated emulsion separates into hydrocarbon, water and solids phases.

Applicable chemicals:

Insoluble portion of all the organic chemicals of interest. Sonic treatment when combined with conventional settling or centrifugation techniques may separate a low solids emulsion into its hydrocarbon, water and solids components.

Technology status:

Pilot/full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Temperature
Frequency of sonic waves	Periodic cleaning requirements
Retention time	Not enough information available to make
Turbulence reduction in tank	generalizations.

Performance:

Limited data are available on applications to treat mixed oil/water emulsions. The hydrocarbon phase recovered from one full scale application was suitable for use as No.6 fuel oil. No data have been found on dissolved or entrained organics in the aqueous phase.

Economics:

Operating costs has been reported as $0.06/gallon (Weil and Jubenville, 1985). This cost does not include any cost elements except for labor and power. Capital and preoperational costs would need to be considered.

References:

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Weil and Jubenville, 1985, Recovery of Hydrocarbon Wastes Using Sonic Energy Technology, National Petroleum Refiners Association Annual Meeting, March.
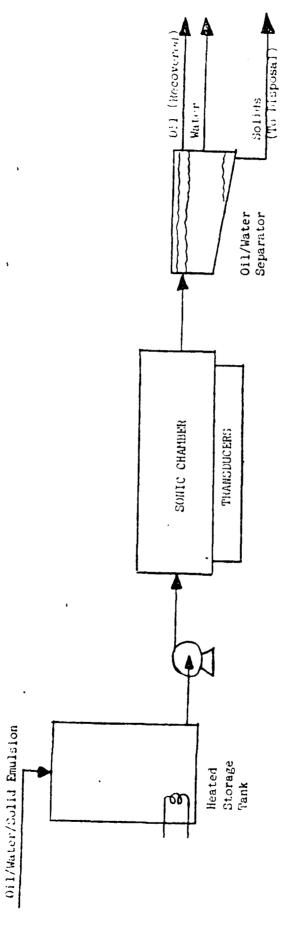
Figure 3.16. Schematic of the sonic treatment process (Gas Research Institute, 1987).

3.19. STEAM STRIPPING

Process description:

Steam stripping is a distillation separation techniques applicable to removing certain organic compounds or dissolved gases from dilute aqueous solutions. This techniques depends on the relative volatilities of compounds being stripped to the volatility of water.

Figure 3.19. presents a typical flow diagram for a steam stripping process. The vapor and liquids phases in contact in a steam stripper column are at essentially the same temperature (e.g., 100°C) and pressure (e.g., near atmospheric). Steam stripping is usually carried out continuously in a countercurrent flow column to provide adequate contact between the liquid and vapor phases. Feed materials is introduces at the top or part way down the column, with treated water exiting the bottom and the volatile components and some water vapor condensing at the top.

Applicable chemicals:

Aromatics, napthalene, most PAHs, phenolics, free ammonia and hydrogen sulfide.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Volatility of contaminants Concentration Flow rate Number of equilibrium stages Steam to feed ratio Material of construction Retention time	Quality of effluent Ph control Vent control

Performance:

Steam stripping is theoretically applicable over the entire range of aqueous solubility of all strippable and potentially strippable organic compounds in water. When the relative volatility of the contaminants to water is greater than 4, steam stripping may be an economically viable alternative. The range of aqueous solubilities and relative volatilities of some organic compounds of interest are presented below:

Compound	Solubility (mg/l at 25°C)	Relative Volatility
Aromatics (BTX)	130-1,800	254-5,589
Napthalene	31.7	368
Phenol	82,000	2.26
Other PAH	0.0002-3.9	0.104-6,304,000

Steam stripping can be used in combination with chemical oxidation if phenols and cyanides are present. Pretreatment would be required to remove insoluble organics or suspended solids.

Economics:

Steam stripping is an energy intensive process. The limitation imposed by energy requirements and maintenance cost are the primary factors limiting the use of this technology. Capital cost is relatively high. Although the labor requirements are low, the process requires continuous operator monitoring. Operating costs (not including capital cost) have been estimated to be within the range from $0.44-8.46 per 1000 gallons of water treated for a flow range of 100 to 1000 gpm (Resource Conservation Co., 1986). Capital cost for a 17 gpm packed column stripper was approximately $300,000 (Chementator, 1984).

References:

"Chementator", 1984, Chemical Engineering, p.17.

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV: Site Restoration, October.

Resource Conservation Co., 1986, "AquaDetox - A Superior Stripping Technology which Removes Toxic Organic Pollutants from Water Streams", technical literature published by Resource Conservation Co., Belleuve, WA.
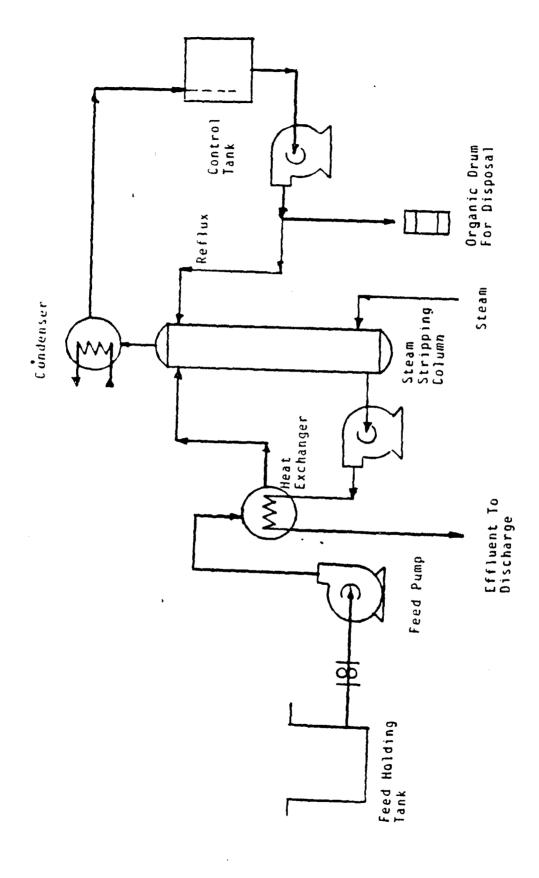
Figure 3.17. Schematic of the steam stripping process (Gas Research Institute, 1987).

3.20. ULTRA/NANO FILTRATION

Process description:

Ultrafiltration employs semipermeable membranes to partition macromolecules from a solution. Figure 3.20. presents a typical flow diagram for the ultrafiltration process. Retention factors of importance are the solutes shape and size. The rate of solute denial is based upon the molecular weight cutoff factor that is particular to the membrane and the solutes molecular weight. Commercially available ultrafiltration membranes have MWC ranges between 1000-50,000. In contrast, reverse osmosis (RO) membranes have MWC ratings of approximately 100. Furthermore, pumping equipment used in the ultrafiltration system cost less and is more accessible than what is used in RO.

Ceramic membranes function as an ultrafiltration media. Pore sizes vary from micron range to 40 Angstroms. Research by the Aluminum Company of America (ALCOA) conducted upon alumina membranes has shown them to be effective in separation of oil emulsions from water. The process used by ALCOA involved the following operational cycle: 120 second crossflow (0.9-4.5 m/s loading, 0.35-2.76 atm pressure differential); 0.5 second backflush (5.4 atm); and 4-5 second fast flushing (6 m/s). Initial oil and grease concentrations of 165-580 mg/l were reduced to less than 9 mg/l and of 25-110 mg/l to less than 5 mg/l.

Nanofiltration employs semipermeable membranes to partition macromolecules from solution. Similar to the ultrafiltration process, nanofiltration discriminates according to the molecular cutoff weight. The range for nanofiltration bridges the gap between ultrafiltration and reverse osmosis from MW 100 to 10,000. Unlike ultrafiltration, nanofiltration operates under similar pressures as reverse osmosis.

Today, ultrafiltration and nanofiltration are offering an alternate form of organic removal and is being rapidly considered a viable substitute for RO processes.

Applicable chemicals:

Purgeable aromatics, phenolics, polynuclear aromatic hydrocarbons, napthalene, oil and grease, total organic carbon.

Technology status:

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Periodic cleaning requirements
Operating pressure	Periodic replacement of membranes
Retention time	Pretreatment (if required)

Performance:

Ultrafiltration systems are much easier to maintain than RO systems because ultrafiltration requires operations at low pressures and also ultrafiltration does not require a specific water quality for treatment. Even though these advantages exist, system components for both technologies are similar and therefore maintenance complexity equally applies to both technologies.

Results presented above may not be applicable to removal of weathered crudes from water, due to the low molecular weight of the hydrocarbons of concern (~ 100). The ALCOA results involved the use of 0.2-0.8 um membranes on high molecular weight compounds (unspecified MW, but data for a 5nm membrane shows removal in the 10,000 to 100,000 MW range). Use of a smaller pore size would reduce flow rate considerably. Very fine ceramic membranes have been shown to be effective for desalinization of water, much as reverse osmosis, so their application to oily water would seem to only move the entire purification process upstream. However, application of coagulants to the influent stream may allow operation with larger pore membranes.

Without any coagulant addition to the influent stream, there is no byproduct generation associated with this process. The waste discharge stream from the process will be a more concentrated oil solution, and should be discharged away from the plant intake, just as the brine discharge, so it should present no problem when integrated into the system. The waste discharge stream from a process using a coagulant may present a by-product dependent upon the nature of the coagulant.

No treatment after the process should be necessary. Pretreatment with a coagulant prior to the process is likely to be required. Loading for the ALCOA testing, as cited above, was 0.9 to 4.5 m/s. The applicability of these numbers to the likely influent is unknown, and may be considered questionable. As a filtration process, the time required is dependent upon the membrane area.

Economics:

The cost for ultrafiltration process is similar to or may be cheaper than that of reverse osmosis process. No cost information is available for the nanofiltration process.

References:

Hsieh, H.P., P.K.T Liu, T.R. Dillman. "Microporous ceramic Membranes." Polymer Journal, v. 23, n. 5, pp. 407-415 (1991).

Personal communication with Dr. Hsieh and Dr. Liu.
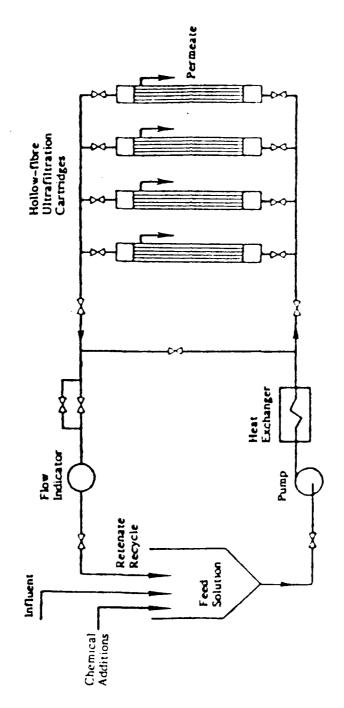
Figure 3.18. Schematic of the ultrafiltration process (Gas Research Institute, 1987).

3.21. WET AIR OXIDATION

Process description:

Wet air oxidation (WAO) also known as Zimpro process is the oxidative biodegradation of organics in aqueous streams using air as the oxygen source. In a typical WAO system, contaminated water and air are continuously injected into a high pressure reactor. Destruction of most organics requires temperatures between 350 and 650°F and pressures of 1,000 to 3,000 psig. WAO may be appropriate for aqueous solutions that are too toxic for biotreatment and too dilute for economical incineration.

Figure 3.21. presents a typical flow diagram for the wet air oxidation process. The WAO reactor is a vertical bubble column which provides gas-liquid contacting and residence time for the oxidation reactions. A one-hour residence time is sufficient for treatment of most organics. Preheating of the feed may be necessary to maintain the reactor operating temperature for waste streams that do not contain enough oxidizable organic to supply adequate heat.

Applicable chemicals:

All organic chemicals, cyanides, sulfides.

Technology status

Full scale.

Key process consideration:

Design variables	Operating variables
Contaminant concentration	Quality of effluent
Flow rate	Pretreatment for solids separations and
Amount of air required	oil/water separation (if required)
Operating pressure	
Retention time	

Performance:

Full scale experience indicates tat the toxicity of wastewaters with high levels of organics can be significantly reduced by WAO treatment. Typical WAO treatment can destroy 99 percent or more of phenols, cyanides, aromatics and PAH in wastewater. Effluent concentrations of 1 ppm or lower have been achieved in laboratory or pilot scale studies. WAO treated wastewater usually requires further treatment (e.g., biological) to remove intermediate

3 - 69

oxidation products (Gas Research Institute, 1987; Harris et al., 1983).

Economics:

The operating costs reported for WAO are in the range of $0.03 to $0.09 per gallon. The capital cost of a 10 gpm transportable unit was reported as $1.25 million in (Baillod and Faith, 1988).

References:

Baillod, C.R., and Faith, B.M., 1988, Wet Air Oxidation of Specific Organic Pollutants, EPA 600/s2-83-060, October.

Gas Research Institute, 1987, Management of Manufactured Gas Plant sites, Volume IV: Site Restoration, October.

Harris, M.T., Oswald, G.E., Jolley, R.C., 1983, Oak Ridge National Laboratory, Wet Oxidation of Phenol and Napthalene in Aqueous and Sludge Solutions", Triangle Conference on Environmental Technology, Chapel Hill, NC, April.
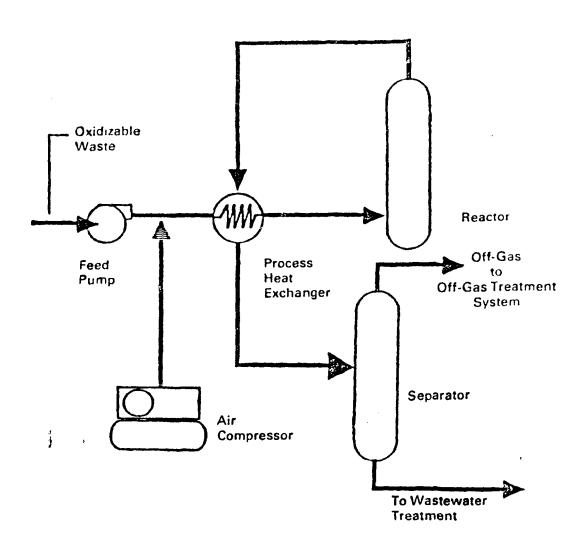
Figure 3.21. Schematic of the wet air oxidation system (Baillod, 1988).

CHAPTER 4

EVALUATION OF TECHNOLOGIES

A two-tiered approach was used to evaluate candidate technologies and select those technologies most appropriate for removal of petroleum hydrocarbons as a pretreatment process for reverse osmosis systems. The first tier technologies evaluation and screening eliminated the technologies with severe limitations for the desired performance requirements. The second tier screening identified the technologies with the highest potential to achieve the performance objectives at minimum cost.

This chapter presents:

o   Technologies evaluation plan;

o   Preliminary evaluation criteria and weighing factors;

o   Preliminary screening of technologies;

o   Detailed evaluation criteria and weighing factors;

o   Detailed screening of technologies.

The following criteria was used for the preliminary evaluation of technologies.

Preliminary Evaluation Criteria	Points
a) Removal effectiveness	30
b) Capacity	30
e) Time required for treatment	20
d) Technology status	20
TOTAL ·	100

The detailed evaluation and screening included both technical and cost criteria as shown below:

Detailed Evaluation Criteria	Points
I. Technical Criteria	
a) Size and weight	15
b) Supportability	15
c) Operability/simplicity	10
d) Removal effectiveness	10
e) Maintainability	10
f) Capacity	5
g) Time required for treatment	5
h) Technology status	5
i) Flexibility	5
II. Cost	
a) Capital cost	5
b) O&M Cost	5
c) Present worth	10
TOTAL	**100**

The following presents the list of candidate technologies and the technologies remaining after preliminary and detailed screening.

List of candidate technologies and the technologies remaining after preliminary and detailed screening

CANDIDATE TECHNOLOGIES (21)	TECHNOLOGIES REMAINING AFTER PRELIMINARY EVALUATION AND SCREENING (8)	TECHNOLOGIES REMAINING AFTER DETAILED EVALUATION AND SCREENING (4)
Air stripping	Air stripping	Centrifugation
Carbon adsorption	Carbon adsorption	Coagulation/Filtration
Centrifugation	Centrifugation	Dissolved air flotation
Coagulation/Filtration	Coagulation/Filtration	Ultra/Nano filtration
Chemical oxidation	Dissolved air flotation	
Dissolved air flotation	Ozone/ultraviolet irradiation	
Electrocoagulation	Steam stripping	
Electrodialysis	Ultra/Nano filtration	
Electron beam irradiation		
Evaporation		
Freeze concentration		
Gravity oil/water separation		
Ion exchange		
Neutralization		
Ozone/ultraviolet irradiation		
Pervaporation		
Photolysis		
Sonic treatment		
Steam stripping		
Ultra/Nano filtration		
Wet air oxidation		

4.1. TECHNOLOGIES EVALUATION PLAN

A two tiered approach was used to evaluate the candidate technologies and select those technologies most appropriate for removal of petroleum hydrocarbons as a pretreatment process for reverse osmosis systems. The first tier technologies evaluation and screening process was based on technical considerations only to eliminate those technologies with severe limitations for the desired performance requirements. The second tier screening was based on both technical and cost criteria to identify the technologies with the most potential to achieve the performance objectives at minimum cost.

4.2. PRELIMINARY EVALUATION

The preliminary evaluation was based on technical criteria only in an attempt to eliminate those technologies which are not appropriate for the removal of organics from water. The technologies with capability to remove organics were carried forward for the detailed evaluation.

4.2.1 Preliminary Evaluation Criteria and Weighing Factors

A preliminary evaluation was used to eliminate those technologies which do not show adequate removal potential for organics from water. Therefore, only technical criteria was considered in the preliminary screening stage.

- a) Removal effectiveness
- b) Capacity
- c) Time required for treatment
- d) Technology status

The preliminary criteria is ranked in relation to the relative importance of each criterion for use as pretreatment process for an RO system. The preliminary weighing factors were assigned as shown below:

Preliminary Evaluation Criteria	Points
a) Removal effectiveness	30
b) Capacity	30
c) Time required for treatment	20
d) Technology status	20
TOTAL	100

Removal effectiveness was judged based on:

o   Effectiveness of the process to remove organics (straight chain and aromatic) and
     other petroleum hydrocarbons and chemicals (e.g., pesticides).

o   By-product formation during the process was also considered in assigning scores for
     the removal effectiveness. A high level by-product formation as well as toxicity was
     considered undesirable.

o   Need for additional treatment will be considered to evaluate the process waste
     products (liquid, solid and gas) and whether adequate treatment could be achieved in
     one step treatment.

Capacity was judged based on the size and capacity of process units currently in use.

Time required was evaluated based on the detention time of the process.

Technology status criteria considered whether the process has been used in full scale
application or at the pilot scale or laboratory scale.

4.2.2. Scoring System

Scores were assigned to each technology based on the findings from the literature review.
Those processes with significantly higher scores and overall potential for use as a
pretreatment process based on the literature review were carried forward for detailed
evaluation. The cut-off score was selected as 85 for the preliminary evaluation.

4.3. DETAILED EVALUATION

The detailed evaluation included both technical and cost criteria to eliminate those
technologies which are not applicable for the removal of organics from water. The technical
criteria will be more extensive and would include both design and operational considerations.

After the detailed evaluation, a short list of technologies (maximum of four) were identified
to be carried forward to the experimental phase.

4.3.1   Detailed Evaluation Criteria and Weighing Factors

The detailed evaluation criteria includes both technical and cost criteria as shown below:

I. Technical Criteria
     a) Size and weight
     b) Supportability

c) Operability/simplicity
d) Removal effectiveness
e) Maintainability
f) Capacity
g) Time required for treatment
h) Technology status
i) Flexibility

II. Cost
    a) Capital cost
    b) O&M Cost
    c) Present worth

The detailed evaluation criteria was ranked in relation to the relative importance of each criterion and the appropriate weighing factors were assigned to each criterion as shown below:

Detailed Evaluation Criteria	Points
I. Technical Criteria	
a) Size and weight	15
b) Supportability	15
c) Operability/simplicity	10
d) Removal effectiveness	10
e) Maintainability	10
f) Capacity	5
g) Time required for treatment	5
h) Technology status	5
i) Flexibility	5
II. Cost	
a) Capital cost	5
b) O&M Cost	5
c) Present worth	10
TOTAL	100

Size and weight criterion was judged based on the transportability and the typical dimensions of the units currently available.

Supportability was judged based on the process needs for chemical, special equipment and supplies.

Operability/simplicity was judged based on the number of process steps each technology required for full implementation, and difficulty of operational procedures for each step.

Removal effectiveness was judged based on:

o   Effectiveness of the process to remove organics (straight chain and aromatic) and other petroleum hydrocarbons and chemicals (e.g., pesticides).

o   By-product formation during the process was also considered in assigning scores for the removal effectiveness. A high level of by-product formation as well as toxicity was considered undesirable.

o   Need for additional treatment will be considered to evaluate the process waste products (liquid, solid and gas) and whether adequate treatment could be achieved in one step treatment.

Maintainability of the process was judged based on the maintenance and periodic clean up requirements of the process.

Capacity was judged based on the size and capacity of process units currently in use.

Time required was be evaluated based on the detention time of the process.

Technology status criteria considered whether the process has been used in full scale application of at the pilot scale of laboratory scale.

Flexibility was judged based on the tolerance of the process to changes in flow rate, contaminant concentration, pH and temperature.

Cost was judged based on the reported costs for capital cost, O&M cost and present worth for the processes in the literature. Most often a cost value per gallon of treated water was found and used in comparing different technologies.

4.3.2. Scoring System

A matrix of technologies versus criteria was developed. For each technology, the assigned criteria points were added. The technologies with the highest scores were identified to be carried forward to the experimental phase.

4.4. PRELIMINARY EVALUATION OF TECHNOLOGIES

For each candidate technology, the assigned scores and justifications for each sub-criterion are provided below:

AIR STRIPPING

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Full scale experience shows 0.9 ppb aromatics removal. No data has been found for other organic chemicals. Theoretical studies indicate naphthalene should be effectively removed, however, very low or no removal of PAHs and phenolics. Presence of surfactants, oils, salts and biomass will affect removal rate.	18
Capacity	Units up to 1,600 gpm.	30
Treatment time	Liquid flow rate should be 1-3 gpm per square foot.	10
Technology status	Full scale.	20
TOTAL SCORE		78

CARBON ADSORPTION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Full scale experience indicates removals of aromatics, phenol and PAH to 1 ppb or less.	30
Capacity	Full scale units in the range of 5-400 gpm.	30
Treatment time	Hydraulic loading in the range of 0.4-22 gpm/sq ft. Typical loading range is 0.4-2.5 gpm/sq ft.	10
Technology status	Full scale.	20
TOTAL SCORE		90

CENTRIFUGATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Based on coagulant used. Removal of oil is around 85% +.	25
Capacity	Can be designed to any capacity.	30
Treatment time	Retention time dependent on design criteria and operation.	20
Technology status	Full scale.	20
TOTAL SCORE		95

CHEMICAL OXIDATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Based on type of oxidant used, greater than 99% removal of PAHs, phenolics, oil and grease can be accomplished. However, some oxidants can react adversely with RO membranes.	10
Capacity	Can be designed to any capacity.	30
Treatment time	Reaction time: Hydrogen peroxide: 15-210 minutes Chlorination: 15-180 minutes Chlorine dioxide: 0.15-60 minutes	20
Technology status	Full scale.	20
TOTAL SCORE		80

COAGULATION/FILTRATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Removal based on type of coagulant, dosage, Ph, mixing, and the order of chemical addition. Filtration effectiveness is based on type of media, depth, flow rate, and size of floc.	20
Capacity	Can be designed to any capacity.	30
Treatment time	Hydraulic loading is typically between 1-5 gpm/sq ft for filtration.	15
Technology status	Full scale.	20
TOTAL SCORE		85

DISSOLVED AIR FLOTATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Greater than 90% removal of oil and grease, near 90% removal of PAH, near 50% removal of naphthalene.	25
Capacity	Can be designed to accommodate any flow rate.	30
Treatment time	Retention time is usually 30-60 minutes.	20
Technology status	Full scale.	20
TOTAL SCORE		95

ELECTROCOAGULATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	The optimum configuration, a 200 mg/l ferric sulfate concentration (maximum studied) and a 100V applied field (maximum studied), produced removal of 98% of the oil emulsion, from 500 mg/l to 10 mg/l. The removal efficiency is high, but the effluent concentration exceeds the target of 5 mg/l.	28
Capacity	Laboratory scale.	2
Treatment time	Current application time: 1 minute (only during rapid mixing) Rapid mixing and flocculation time: 16 minutes The results showed no effect of current application during rapid mixing, the removal cited above coming only after flocculation. Therefore removal efficiency is a function of detention time, with design requiring incorporation of adequate time for adequate flocculation.	20
Technology status	Bench scale.	2
TOTAL SCORE		52

ELECTRODIALYSIS

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Cations and anions and organics with charges can be removed. Some pretreatment is often necessary for feed water.	15
Capacity	Limited experience with a full scale unit.	15
Treatment time	1-3 hours retention time.	15
Technology status	Pilot/full scale.	15
TOTAL SCORE		60

ELECTRON BEAM IRRADIATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	The electron beam irradiation is effective with PCBs and chlorinated organics. Some by products may be left in the treated solution.	20
Capacity	The capacity of a pilot plant is 610 liters per minute.	15
Treatment time	5-10 minutes.	5
Technology status	Pilot scale.	5
TOTAL SCORE		45

EVAPORATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	For aqueous mixtures, evaporation is applicable to all chemicals of interests. However, the volatilization of strippable compounds (e.g., BTX, naphthalene and most PAHs) may require treatment of the evaporated water. Data on capability of removing phenolics and BTX from hydrocarbon tars is not available. Presence of inorganic ions can result in scale formation and increase heat transfer coefficient.	10
Capacity	Typical units are 330 gpm.	30
Treatment time	30 minutes to 2 hrs.	5
Technology status	Full scale.	20
TOTAL SCORE		65

FREEZE CRYSTALLIZATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Suitable for removal of both organics and inorganics at high concentrations where stripping, sorption and membrane processes would not be appropriate.	30
Capacity	Can be constructed to accommodate needs. Energy costs will limit for treatment of large quantities.	15
Treatment time	30 minutes to 2 hours.	10
Technology status	Full scale.	20
TOTAL SCORE		75

GRAVITY OIL/WATER SEPARATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Effective for oil and grease and suspended solids removal. PAH reduction is achieved by removing the portion that stays within the oil phase. Total organic carbon is decreased by the amount that oil and grease constitute. Oil and grease and suspended solids reduction near 90%, total PAH reduction near 80% and significant phenolics reduction can be achieved.	8
Capacity	Filter efficiency is dependent on the filtration rate. Single media filters usually operate at rates of approximately 2 gpm/sq ft. Greater depth removal is attained by using mixed media filters which operate at rates of approximately 5 gpm/sq ft.	30
Treatment time	Settling time is approximately 30 mins.	15
Technology status	Full scale.	20
TOTAL SCORE		73

ION EXCHANGE

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Effective for removal of inorganic cations, such as heavy metals and ammonia, and anions, such as sulfate. Also potentially can remove ionic organic compounds such as phenolics and pyridine.	5
Capacity	Typical flow rates range from 10 to 500 gpm.	20
Treatment time	30 minutes to 1 hour.	2
Technology status	Full scale.	20
TOTAL SCORE		47

NEUTRALIZATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Metals and inorganics.	3
Capacity	Can be designed to accommodate any size.	20
Treatment time	Variable.	3
Technology status	Full scale.	20
TOTAL SCORE		46

OZONE/ULTRAVIOLET IRRADIATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	The use of ozone in combination of ultraviolet light has been shown to enhance the reactivity of certain chemicals. Ozone/UV has been shown to achieve 20-90% removal of cyanide, 25-99% removal of sulfide, 10-99+% removal of phenolics, 50-99+% removal of PAHs, 37-99+% removal of naphthalene.	29
Capacity	Can be designed to any capacity.	20
Treatment time	Contact time is between 1-100 mins. Typical contact time is 15 mins.	20
Technology status	Full scale.	20
TOTAL SCORE		89

PERVAPORATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Benzene and other highly toxic waste have 99% removal.	30
Capacity	Can be designed for any capacity.	30
Treatment time	Flow rate at approximately 2000 gpd.	15
Technology status	Full scale.	15
TOTAL SCORE		90

PHOTOLYSIS

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Capable of removing very low concentrations of organics. Limited data are available.	10
Capacity	Pilot scale unit of 10 gpm.	15
Treatment time	Limited data are available. Based on intensity of radiation, the required detention time could be relatively short.	15
Technology status	Pilot scale with full scale applications in planning state.	15
TOTAL SCORE		55

SONIC TREATMENT

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Limited data are available on applications to treat mixed oil/water emulsions. Experience indicae that insoluble portion of all the organic chemicals can be removed.	3
Capacity	Pilot scale experience with a 12 gpm system.	5
Treatment time	Residence time is 5-10 mins. Based on 12 gpm rate used in pilot scale testing, treatment of 100,000 gallons would take one week.	20
Technology status	Pilot scale (limited full scale experience).	8
TOTAL SCORE		36

STEAM STRIPPING

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Based on theoretical estimates, levels of 1-10 ppb should be achieved for strippable organics. Pilot scale data for BTX show levels of 0.5 ppb can be achieved. Aromatics, naphthalene, most PAHs and phenolics, free ammonia, cyanide and hydrogen sulfide can be removed.	27
Capacity	Full scale experience with 17 gpm packed column. Units with 100 to 1000 gpm capacity can be designed.	30
Treatment time	Varies based on the operation. Typical detention time is 10-30 minutes.	18
Technology status	Full scale.	20
TOTAL SCORE		95

ULTRA/NANO FILTRATION MEMBRANES

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Removal of organics is based on the molecular cut-off weight of the contaminant. Ultrafiltration removes MW of 1,000 - 50,000 and nanofiltration removes MW of 100 - 10,000.	25
Capacity	Can be used for any capacity.	30
Treatment time	120 second crossflow (0.9-4.5 m/s loading, 0.35-2.76 atm pressure differential); 0.5 second back flush (5.4 atm); and 4-5 second fast flushing (6 m/s).	15
Technology status	Full scale.	20
TOTAL SCORE		90

WET AIR OXIDATION

CRITERIA	COMMENTS	SCORE
Removal effectiveness	Typically 99+% removal of phenols, cyanides, aromatics and PAH in wastewater. Effluent concentrations of 1 ppm or lower have been achieved in laboratory and pilot studies. Usually further treatment is required to remove intermediate oxidation products.	20
Capacity	Can be designed to any size.	25
Treatment time	A one-hour residence time is sufficient for treatment of most organics.	18
Technology status	Full scale.	20
TOTAL SCORE		83

4.5. PRELIMINARY EVALUATION SUMMARY

The final scores assigned to each technology after the preliminary evaluation are summarized below:

TECHNOLOGY	SCORE	RANK
Air stripping	78	11
Carbon adsorption	90	4
Centrifugation	95	1
Chemical oxidation	80	10
Coagulation/Filtration	85	8
Dissolved air flotation	95	2
Electrocoagulation	52	17
Electrodialysis	60	15
Electron beam irradiation	45	20
Evaporation	65	14
Freeze crystallization	75	12
Gravity oil/water separation	73	13
Ion exchange	47	18
Neutralization	46	19
Ozone/ultraviolet irradiation	89	7
Pervaporation	90	5
Photolysis	55	16
Sonic treatment	36	21
Steam stripping	95	3
Ultra/Nano filtration membranes	90	6
Wet air oxidation	83	9

The following technologies with a score of 85 or higher are carried forward for detailed evaluation.

Carbon adsorption
Centrifugation
Coagulation/Filtration
Dissolved air flotation
Ozone/Ultraviolet irradiation
Pervaporation
Steam stripping
Ultra/Nano filtration

4.6. DETAILED EVALUATION OF TECHNOLOGIES

The assigned scores and justifications for each technology identified for the detailed evaluation are provided below:

CARBON ADSORPTION

CRITERIA	COMMENTS	SCORE
Size and weight	Typical full scale unit for gasoline products (influent 450 ppm BTX) is 5.5 ft wide, 7 ft high, 16 ft long with 800 pounds of carbon. Carbon depths within the range of 10-30 ft are common.	4
Supportability	Carbon should be added to make for the lost carbon during regeneration. When the carbon is contaminated by high levels of organics, high quality "virgin" carbon may be necessary to meet the drinking water criteria. Typical carbon usage ranges from 0.05-1 lb/1,000 gals.	5
Operability/ simplicity	System temperature, pH, and feed concentrations should be monitored. Periodic carbon regeneration is necessary.	6
Removal Effectiveness	Full scale experience indicates removals of aromatics, phenol and PAH to 1 ppb or less. Due to its filtering process it might best be used as a follow-on to another process (i.e., precipitation-sedimentation). There is little justification for using it as the first step in a pretreatment process. Powdered activated carbon should require no additional treatment.	10
Maintainability	Activated carbon process produces saturated carbon as by-product. The by-product can be regenerated, probably not practical for a mobile system, or disposed of. The saturated carbon is reactivated by heating in an oxygen depleted atmosphere to remove the adsorbent from the surface pores. Disposal, due to the contaminated waste, may be a problem.	2
Capacity	Full scale units in the range of 5-400 gpm.	4
Time required for treatment	Hydraulic loading in the range of 0.4-22 gpm/sq ft. Typical loading range is 0.4-2.5 gpm/sq ft.	2
Technology status	Full scale.	5
Flexibility	Insoluble liquid\solid chemicals should be removed from the feed.	2
Cost	$0.22 to $2.52 per 1,000 gallons of treated water.	15
TOTAL SCORE		55

CENTRIFUGATION

CRITERIA	COMMENTS	SCORE
Size and weight	Typical liquid-liquid disc-nozzle type has bowl diameter between 12-30 inches.	12
Supportability	Coagulant and flocculants may be used to improve process performance.	12
Operability and simplicity	Speed of rotation and the time of operation to be monitored. Easy to handle.	10
Removal effectiveness	Depending on the coagulant used, removal of oils is 85% +.	8
Maintainability	Periodic cleaning is required.	10
Capacity	Full scale units run up to 24,000 gal/hr capacity.	5
Time required for treatment	The time required is dependent on design criteria and operation.	4
Technology status	Full scale.	5
Flexibility	Pretreatment may be necessary.	4
Cost	No recent cost data is available on specific removal of oils. However, cost for treating waste water is $10.0 per 1000 gallons.	15
TOTAL SCORE		85

COAGULATION/FILTRATION

CRITERIA	COMMENTS	SCORE
Size and weight	This process requires feed pump for polymer along with filter media chamber comparable to existing ROWPU unit.	15
Supportability	Coagulant and flocculants require a feed pump. Also, to regenerate filter media, backwashing is recommended for better performance.	13
Operability/ simplicity	Flow rate and polymer mixing should be monitored.	13
Removal Effectiveness	Based on type of coagulant and filter media used.	5
Maintainability	Periodic backwashing is required to improve filter performance.	6
Capacity	Can be designed to any capacity	5
Time required for treatment	Hydraulic loading is typically between 1-5 gpm/sq ft for filtration.	4
Technology status	Full scale.	5
Flexibility	Preliminary screening for large particles as currently used in ROWPU system.	5
Cost	No specific cost analysis is available at this time, but is comparably less than the other processes.	17
TOTAL SCORE		88

DISSOLVED AIR FLOTATION

CRITERIA	COMMENTS	SCORE
Size and weight	The process requires pressurizing pump, tank and chemicals if pretreatment is required. Space requirements may be significant.	12
Supportability	Coagulant and flocculants may be used to improve process performance.	13
Operability/ simplicity	Pressure and recycle ratio should be monitored.	13
Removal Effectiveness	Greater than 90% removal of oil and grease, near 90% removal of PAH, near 50% removal of naphthalene.	5
Maintainability	Periodic cleaning is required.	10
Capacity	The air flotation processes can be sized adequately for the intended use and flow rate.	5
Time required for treatment	The time required is dependent upon the flotation velocity and reactor dimensions. Retention time is usually 30-60 minutes.	5
Technology status	Full scale.	5
Flexibility	Pretreatment may be necessary.	4
Cost	$1.26 per 1000 gallons of treated water.	15
TOTAL SCORE		87

OZONE/ULTRAVIOLET IRRADIATION

CRITERIA	COMMENTS	SCORE
Size and weight	Reactors for the ozonation are typically a minimum of 15 feet tall to ensure adequate contact time.	3
Supportability	Ozone is unstable and therefore must be made at the place of use.	3
Operability/ simplicity	The ozone dosage and reaction efficiency is dependent on the reaction time needed for a required removal.	4
Removal Effectiveness	Direct ozonation is not appropriate for reducing concentrations of benzene, some aldehydes, chlorinated alkanes, alkenes, and saturated compounds. Ozone/UV has been shown to achieve the following removal efficiencies: Cyanide 20-90% Sulfide 25-99% Phenolics 10-99+% PAHs 50-99+% Naphthalene 37-99+%	9
Maintainability	UV unit should be periodically cleaned. Accumulated deposits can reduce penetration of UV light into the ozone/water system.	3
Capacity	Reactor volume can be between 3 liters to 600 gallons.	2
Time required for treatment	Contact time is between 1-100 mins. Typical contact time is 15 mins.	4
Technology status	Full scale.	5
Flexibility	Suspended material and free and emulsified oils should be removed before the ozone/UV process to prevent accumulation in the reactor and prevent fouling of the ultraviolet lamps. Shock loadings both in terms of flow and concentration should be avoided.	1
Cost	No cost data was found for ozone/UV system. Ozone treatment only is $4.36 per 1000 gallons of water treated.	10
TOTAL SCORE		44

PERVAPORATION

CRITERIA	COMMENTS	SCORE
Size and weight	Typical industrial-sized pervaporation module 4-5 m^2 of membrane. Comparable to current RO unit size.	15
Supportability	Possible pretreatment with coagulation. Also cleaning requirements with solvent.	12
Operability and simplicity	Flow rate should be monitored.	8
Removal effectiveness	Removal of benzene and other hazardous compounds up to 99% depending on initial contaminant concentration.	10
Maintainability	Membranes should be cleaned when flow rate falls below normal.	4
Capacity	Can be designed for any capacity.	5
Time required for treatment	2000 -12,000 gpd.	5
Technology status	Full scale.	5
Flexibility	No particles greater than 20 μm or oil emulsions.	2
Cost	$14.00/ 1000 gallons of treated water.	0
TOTAL SCORE		66

STEAM STRIPPING

CRITERIA	COMMENTS	SCORE
Size and weight	Typical height is 6 ft. For mobile stripping columns, the trailer should be equipped with hydraulic stabilizer feet to provide support for the column. The column should also be secured for wind stability.	15
Supportability	Steam stripping is an energy intensive process. The limitation imposed by energy requirements and maintenance cost are the primary factors limiting the use of this technology. If steam is not available on site, a portable fired boiler or electric steam generator should be provided.	5
Operability/ simplicity	System temperature and emissions quality should be monitored. Cooling water and reflux ratio (for systems with rectification) should be monitored.	8
Removal Effectiveness	Based on theoretical estimates, levels of 1-10 ppb should be achieved for strippable organics. Pilot scale data for BTX show levels of 0.5 ppb can be achieved. Aromatics, naphthalene, most PAHs and phenolics, free ammonia, cyanide and hydrogen sulfide can be removed.	10
Maintainability	Periodic clean up requirements.	7
Capacity	Full scale experience with 17 gpm packed column.	3
Time required for treatment	The time required for contaminant removal of common pollutants is lengthy.	1
Technology status	Full scale.	5
Flexibility	Pretreatment would be required to remove insoluble organics or suspended solids. The steam to feed ratio can be raised and lowered in a particular size column within certain limitations.	1
Cost	Capital cost is relatively high. Although the labor requirements are low, the process requires continuous operator monitoring. Operating costs (not including capital cost) have been estimated to be within the range from $0.44-8.46 per 1000 gallons of water treated for a flow range of 100 to 1000 gpm. Capital cost for a 17 gpm packed column stripper was approximately $300,000.	0
TOTAL SCORE		55

ULTRA/NANO FILTRATION

CRITERIA	COMMENTS	SCORE
Size and weight	Typical size comparable with RO membrane size.	15
Supportability	Pretreatment with coagulant may be required. Also, cleaning with solvent is required.	12
Operability and simplicity	Flow rate should be monitored.	12
Removal Effectiveness	Removal of organics is based on the molecular cut-off weight of the contaminant. Ultrafiltration removes MW of 1,000 - 50,000 and nanofiltration removes MW of 100 - 10,000.	9
Maintainability	Membranes should be cleaned regularly to prevent permanent fouling.	7
Capacity	Can be designed for any capacity.	5
Time required for treatment	120 second crossflow (0.9-4.5 m/s loading, 0.35-2.76 atm pressure differential); 0.5 second back flush (5.4 atm); and 4-5 second fast flushing (6 m/s).	5
Technology status	Full scale.	5
Flexibility	Pretreatment may be required to improve performance.	4
Cost	Cost information is not available on the specific removal of oils. However, cost is medium, as compared to the other technologies.	12
TOTAL SCORE		86

4.7. DETAILED EVALUATION SUMMARY

The final scores assigned to each technology after the detailed evaluation are summarized below:

TECHNOLOGY	SCORE	RANK
Carbon adsorption	55	6
Centrifugation	85	4
Coagulation/Filtration	88	1
Dissolved air flotation	87	2
Ozone/ultraviolet irradiation	44	8
Pervaporation	66	5
Steam stripping	55	7
Ultra/Nano filtration	86	3

The following technologies with a score of 85 or higher will be carried forward to the experimental phase.

> Centrifugation
>
> Coagulation/Filtration
>
> Dissolved air flotation
>
> Ultra/Nano filtration

5. BIBLIOGRAPHY

Eckenfelder, W.W., 1979, Principles of Water Management Control, CBI Publishing Company.

E.I. Dupont De Nemours & Company, 1978, Engineering Design Manual, Permasap Permeator, Wilmington, DE.

Gas Research Institute, 1987, Management of Manufactured Gas Plant Sites, Volume IV, Site Restoration.

United Stated Environmental Protection Agency, 1989, Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, Office of drinking Water, Cincinnati, Ohio, EPA/625/4-89/023.

Weber, W.J., 1972, Physicochemical Processes for Water Quality Control, John Wiley and Sons.

James M. Montgomery Consulting Engineers, Inc., 1985, Water Treatment Principles and Design, John Wiley and Sons.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Technologies identified during the literature review were compared in accordance with the Technology Evaluation Plan. The following technologies are recommended to be carried forward to the experimental investigation phase.

Centrifugation
Coagulation/Filtration
Dissolved air flotation
Ultra/Nano filtration

Although each of the four technologies identified are applicable to remove a variety of petroleum related contaminants within a wide range of concentration level, each technology has limitations for optimum performance.

The centrifugation process is effective in removing the oil-water emulsions. Pretreatment and/or addition of polymers is required for better performances. However, it may not be solely able to remove the oily contaminants.

The coagulation/filtration process is currently used in the ROWPU system now. The possibility exists that for effective oil removal the current system can be modified by the addition of another filtration media or by changing the polymer feed solution.

The dissolved air flotation process is very effective to remove solids as well as oil contamination.

The ultra/nano filtration process is effective in removing particles based on the molecular weight of the contaminant. However, this membrane process may incur similar fouling problems as seen in the RO membranes.

The experimental phase should include considerations for a pretreatment scheme which could include combinations of these four technologies.