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Fox, J.P.

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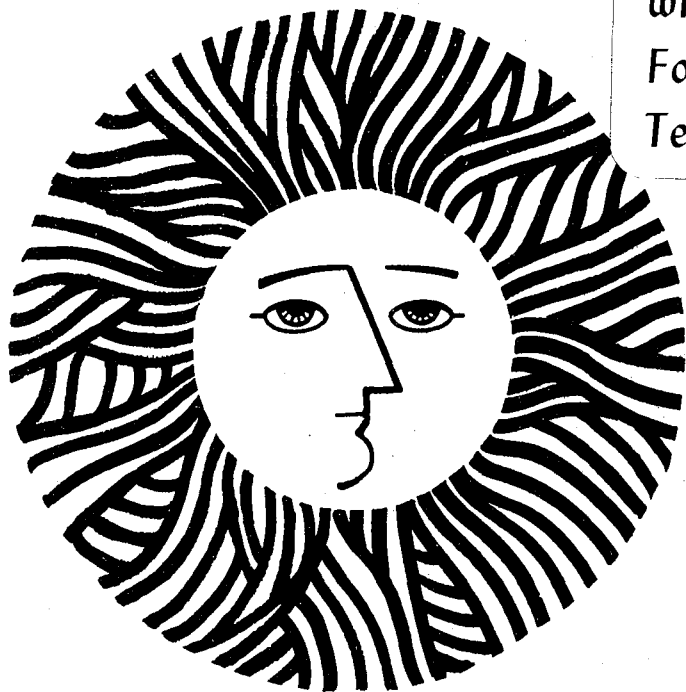
WASTEWATER TREATMENT IN THE OIL SHALE INDUSTRY

J.P. Fox and T.E. Phillips

August 1980

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J. P. Fox

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

T. E. Phillips

Division of Environmental Science
Laramie Energy Technology Center
Laramie, Wyoming 82071

presented at

Oil Shale, The Environmental Challenges

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J. P. Fox

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

T. E. Phillips
Laramie Energy Technology Center
Laramie, Wyoming 80270

INTRODUCTION

The Green River oil shale deposits are located in the Upper Colorado River Basin where water supply and water quality have long been issues of national and international importance. A large-scale oil shale industry may consume from 71 to 278 gallons of water per barrel of oil produced and may generate even larger volumes of aqueous wastes that must be disposed of (Fox, 1980b). Because of the stringent state and federal standards governing the discharge of wastes into local waters and the limited water supplies in this area, an oil shale industry will probably reuse process effluents to the maximum extent possible and evaporate the residuals. Therefore, discharge of effluents into surface and ground waters may not be necessary.

This paper reviews the subject of wastewater treatment for an oil shale industry and identifies key issues and research priorities that must be resolved before a large-scale commercial industry can be developed. It focuses on treatment of the waters unique to an oil shale industry: retort water, gas condensate, and mine water.

BACKGROUND

Water may be used at an oil shale plant for mining operations, dust control, steam and power generation, transport, compaction and revegetation of processed shale, potable water supply, pre-refining, and other requirements. Each of these uses produces an effluent that must be collected, treated, and discharged. These effluents include: mine waters; brines from ion exchange, reverse osmosis, filtration and other treatment processes; storm water runoff from the plant area; and various process waters. All of these effluents, except the mine waters and process waters, are normally found in other types of industrial operations and can be treated using conventional control technologies. However, the process waters (retort water and gas condensate) and mine waters are unique to oil shale retorting due to their volumes and/or composition and may represent a difficult treatment and disposal problem.

The purpose of this section is to develop background information on these effluents and wastewater treatment strategies which will enable unresolved technical issues and attendant research priorities to be identified.

EFFLUENTS

The oil shale industry must develop treatment methods and disposal options for three special wastewaters: retort water, gas condensate, and mine water. Each presents a unique set of challenges. Retort water and gas condensate, produced during retorting, are chemically complex and contain high concentrations of a large number of dissolved organic and inorganic constituents that may prove difficult to remove with conventional treatment technology. Mine waters, by contrast, are produced

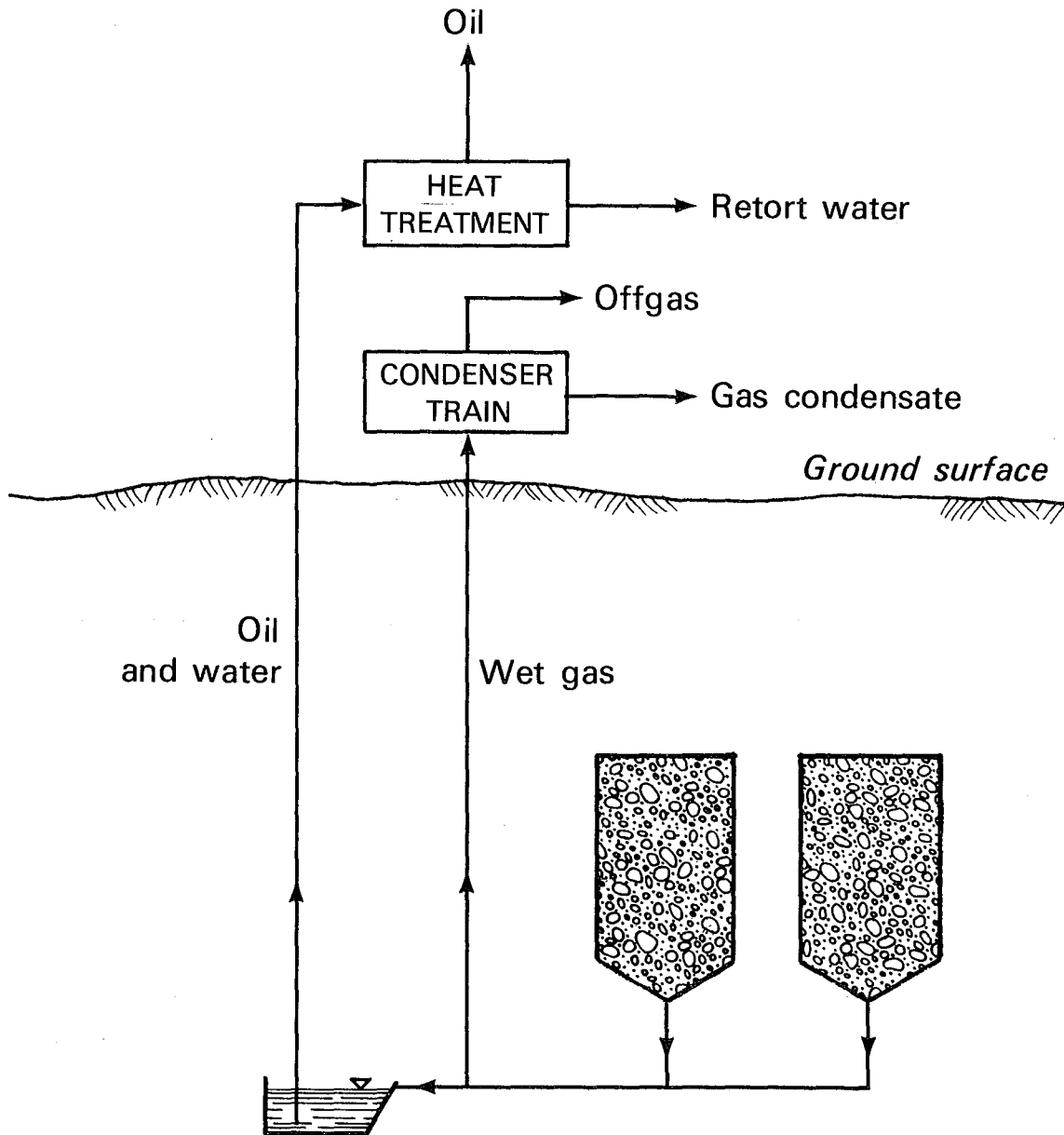
in very large volumes and are contaminated with dissolved inorganic substances.

Retort Water and Gas Condensate

Two unique types of water are produced from combustion, mineral dehydration, input steam, and groundwater intrusion during oil shale retorting: retort water and gas condensate. These waters are produced within the retort as a vapor that is condensed with the oil or gas. Retort water condenses in the retort with the oil or in the oil-gas separators and is separated from the oil by heat treatment and decantation (Burton, 1976; Nevens et al., 1979). Gas condensate is removed from the gas stream in a condenser train or in gas scrubbing systems (Hicks et al., 1980) (Figure 1).

These waters are produced in rather large volumes, and their combined production is 0.1 to 22 barrels of water per barrel of oil (Farrier et al., 1978). For a 500,000 barrel per day plant, about six percent of the 1977 U.S. crude oil production, this represents a total of about two million to 500 million gallons of water per day, depending on the type of process used and the plant location. Water produced by surface processes is at the lower end of this range [(0.10-0.30 barrels of water per barrel of oil (bbl/bbl))], while it is at the upper end for in-situ processes (0.4-22 bbl/bbl). The high value of 22 bbl/bbl is due primarily to groundwater inflow and is probably not realistic for a commercial industry if the site is carefully dewatered.

The relative proportion and composition of each type of water depend primarily on the exit gas temperature, retort operating conditions,



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Figure 1. Schematic showing the production of retort water and gas condensate during in-situ retorting.

and product collection system design and operation. Most of the water, particularly in surface processes, leaves the retort in the vapor phase with the offgases and is recovered as gas condensate (Nevens et al., 1979). In surface processes, the relative volumes of retort water and gas condensate can be controlled by operating the retort at a temperature high enough to keep the water in the vapor phase until it reaches the gas handling system (Nevens et al., 1979). This may have some decided advantages because retort water is more highly contaminated and more difficult and costly to treat than is gas condensate. However, in the co-current in-situ processes presently under development, condensation of water within the retort cannot be avoided because the vapors pass through the cold unretorted shale at the bottom of an in-situ retort before reaching the gas handling system (Fox, 1980b).

The compositions of retort water and gas condensate differ significantly; both depend largely upon retort and product collection system operation. Retort water is in intimate contact with oil and shale during its production and/or collection. In in-situ processes, retort water passes over raw or partially retorted shale in the cool portion of the retort, and thus may leach constituents from both the shale matrix and the oil.

Retort waters are brown to yellow, have a pH that ranges from 8 to 9, contain high levels of many inorganic and organic constituents, and are known to support bacterial growth when maintained at temperatures above 40°F (Farrier et al., 1977). The composition of retort waters is summarized in Table 1 which indicates that they have high concentrations of solids, NH_3 , HCO_3 , and SO_4 . The organic constituents are primarily

Table 1. Composition of retort water, gas condensate, and mine water (mg/l).

Parameter	Retort waters ^a	Gas condensate ^b	Mine water ^c
Alkalinity (as CaCO ₃)	18,000-111,000	25,000	70-4,500
Bicarbonate (as HCO ₃ ⁻)	4,200-74,000	-- ^d	85-25,000
Biochemical oxygen demand	350-5,500	500	-- ^d
Carbon, inorganic	2,000-19,000	--	--
Carbon, organic	2,000-19,000	1,100	1-70
Carbon dioxide	--	18,900	--
Carbonate (as CO ₃ ²⁻)	0.0-15,000	--	<1-2,000
Chemical oxygen demand	8,500-43,000	2,300-3,800	--
Conductivity (μmhos/cm)	15,000-193,000	--	600-45,000
Nitrogen, ammonia (as NH ₃)	2,000-13,000	7,600	<0.1-200
Nitrogen, organic (as N)	73-1,510	189	--
pH	8.1-9.4	8.6-8.8	6.0-9.3
Solids, dissolved	1,800-24,000	440-500	400-42,000
Solids, volatile	2,100-119,000	260	--
Sulfate (as SO ₄ ²⁻)	40-2,200	5.6	<4-900
MAJOR ELEMENTS (concentration > 0.1%)	C, H, N, S	--	C, H, S
MINOR ELEMENTS (concentration ≤ 0.1% to 1 ppm)	Al, As, Ca, Cl, Fe, K, Na, Ni, Zn, B, F	--	B, Ca, Cl, F, Mg, K, Si, Na, N
TRACE ELEMENTS (concentration < 1 ppm)	Ba, Br, Cd, Ce, Co, Cr, Cs, Cu, Eu, Ga, Ge, Hf, Hg, I, La, Mg, Mn, Mo, Pb, Sb, Se, Sm, Sr, Ta, Th, Ti, U, V, W, Y, Yb, Yb	--	Al, As, Ba, Br, Cr, Co, Cu, Ga, I, Fe, Pb, Li, Mn, Hg, Mo, Ni, Rb, Sc, Se, Ti, V, Zn

^a Summarized from Fox et al., 1978 and from Fox, 1980a.

^b Summarized from Hicks et al., 1980 and from unpublished LBL data for Occidental gas condensate.

^c Summarized from Fox, 1980b.

^d A dash signifies that no data are available.

polar, and the principal components are the monocarboxylic and dicarboxylic acids (Cook, 1971; Yen and Findley, 1967b; Ho et al., 1976; Fish, 1980). Other identified constituents include ketones, pyridines, pyrroles, lutidines, anilines, amines, indoles, and quinolines (Fish, 1980; Pellizzari et al., 1979). The environmentally significant elements are As, Se, B, F, Zn, and Ni.

Retort waters produced by surface retorts are typically more concentrated than waters from in-situ retorts because water production is lower. The elemental composition of surface retort waters is similar to in-situ retort waters, although the organic carbon and pH may be considerably higher in some surface retort waters.

The gas condensate, which leaves the retort as a vapor, contains lower concentrations of dissolved solids than retort water and higher concentrations of dissolved gases such as NH_3 , H_2S , and CO_2 (Table 1). Preliminary analyses at the Lawrence Berkeley Laboratory indicate that the organic constituents in gas condensate include phenols, nitriles, and aromatic amines; carboxylic acids have been identified but in much lower concentrations than in retort waters.

In a commercial oil shale plant, retort water and gas condensate will be collected and treated separately due to their different compositions. However, the design and operation of a commercial product collection system have not been investigated, and the effect of a system on water production and composition has not been studied. In laboratory and field experiments, which have provided the majority of the data on these process waters, these two types of waters usually have not been

distinguished; they generally have been combined into a single fraction or only the retort water has been collected.

Mine Waters

Oil shale in the Green River Formation is laced with groundwaters. Before mining and retorting operations can be carried out, these waters must be removed to prevent groundwater inflow into shafts, adits, mines, and rubblized retorts. Groundwater inflow during site preparation could impede construction progress and could lead to safety problems; during retorting, it could extinguish the combustion front. Thus, many sites must be dewatered prior to and during retorting. The resulting waters are called mine waters.

Large volumes of water, estimated to range from 5 to 15 ft³/sec for tracts C-a and C-b (Robson and Saulnier, 1980) or higher (Mehran et al., 1981), will be generated. Although some of this water could be used to meet projected water requirements, state water rights may prevent extensive consumption. Because of possible adverse effects on other existing water rights, stream flow augmentation or reinjection may be required.

Mine waters will have the same composition as water in the aquifers (Table 1) except that mine drainage may also include wastes from drilling and mine operations and therefore may contain more suspended solids and oil and grease. Table 1 indicates that mine waters from the upper and lower aquifers on tracts C-a and C-b will have total dissolved solids (TDS) that range from 400 to 42,000 mg/l. Similarly, Weeks et al. (1974) indicated that TDS concentrations of up to 60,000 mg/l have been reported in the Piceance Creek Basin. These high concentrations would require

special processing for use and disposal if encountered in actual practice. The principal ions in these waters are CO_3 , HCO_3 , SO_4 , Cl, Ca, Mg, K, Na, and Si. Most environmentally important trace elements, with the exception of B and F, occur at concentrations that are less than 1 ppm. The quality of mine waters will vary over time as the relative contributions of the aquifers change. In addition, modifications in the underground flow regime due to extensive dewatering may bring waters with very different compositions in from other parts of the aquifer.

WASTEWATER TREATMENT STRATEGIES

The effluents produced at an oil shale plant may be discharged into ground or surface waters or reused on site. Most of the disposal options require treatment to meet water quality standards and criteria. Most oil shale effluents will be reused and any residuals evaporated. This section discusses the treatment requirements for reuse and discharge standards.

General Treatment Considerations

Treatment is required for conventional raw water supplies and for effluents that are to be reused or discharged into receiving waters. The type and degree of treatment required depend on the water's characteristics and its use. Table 2 summarizes available water supplies, potential uses, disposal options, and factors that govern the quality required for each option. For example, if water is used for cooling tower makeup or boiler feedwater, a high quality water is necessary. This means that extensive treatment will be required for poor quality supplies, such as retort water, while minimal treatment will be needed for high quality supplies, such as local surface waters. Alternatively, if the water is to be used for dust control or spent shale disposal,

Table 2. Water supplies, disposal options, and governing water quality standards.

Potential water supplies	Disposal option	Factors that determine requisite quality
	<u>Use</u>	
Retort water	Backwash water	Varies with medium/resin used
Gas condensate	Domestic use	EPA 1975 Drinking Water Standards
Dewatering effluents	Mining	Public health criteria
Mine water		
Local surface waters	Retorting	Depends on application, i.e., for steam production, etc.
Local groundwater		
Domestic sewage	Spent shale disposal	Public health criteria
Storm water runoff	Revegetation	Irrigation water quality criteria
Cooling tower blowdown		
Boiler blowdown	Boiler feedwater	Boiler feedwater requirements
Filter and ion exchange backwash water	Cooling water makeup	Cooling water makeup requirements
Pre-refining process effluents	Pre-refining	Refinery process water requirements
	<u>Discharge</u>	
	Surface water discharge	Water quality standards and effluent limitations
	Groundwater discharge	Water quality standards and effluent limitations
	Evaporation	Public health criteria

a poor quality water is adequate, and many of the available supplies, such as mine waters, could be used directly without treatment.

Three factors will largely control water disposal decisions for an oil shale industry:

- Western shale deposits are located in the Colorado River Basin where water is a limited resource and water supply and water quality have long been issues of national and international importance. Thus, water supply and disposal are inextricably linked with decisions surrounding the use of the Colorado River.
- Oil shale processing produces a large volume of poor quality water (retort water, gas condensate, mine water); the volume of water produced is sufficient to meet some of the in-plant water needs if quality of the water can be improved.
- Existing water quality standards and effluent limitations require a high degree of treatment prior to discharge. Additional future limitations may be imposed.

These factors suggest that an oil shale industry will reuse most of the effluents produced during processing and evaporate the residuals. This will not only partially solve the water availability problem, it also will be economically attractive because treatment for discharge may be more costly than treatment for reuse.

Table 3 summarizes the estimated degree of treatment required for reuse and disposal of waters from various sources. Water supply sources are listed at the top of the chart; symbols in the body of the chart refer qualitatively to the amount of treatment required based on water

Table 3. Treatment requirements for reuse and disposal.

		Potential Water Sources								
		Local surface waters	Mine waters	Retort water	Raw domestic sewage	Cooling tower blowdown	Boiler blowdown	Storm water runoff	Prerefining process effluents	Gas condensate
Uses										
Discharge	Surface water discharge	N/A	●	●	○	●	○	○	●	○
	Ground water discharge	N/A	●	●	○	●	○	○	●	○
	Land treatment	N/A	○	●	○	○	○	○	○	○
	Evaporation	N/A	○	○	○	○	○	○	○	○
	Cooling water (3 cycles)	○	○	●	●	●	○	○	●	○
	Boiler feedwater (medium-pressure boilers)	○	●	●	●	●	●	○	●	●
Reuse	Domestic water	○	○	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Prerefining process water	○	○	●	○	●	○	○	○	○
	Revegetation	○	○	●	○	○	○	○	○	○
	Mining	○	○	●	●	○	○	○	○	○
	Spent shale disposal	○	○	○	○	○	○	○	○	○

● Extensive treatment

○ Moderate treatment

○ Minimal or no treatment

N/A not applicable or not recommended

quality standards and criteria for surface water discharge, groundwater discharge, and reuse as summarized in Table 2. Although local surface waters are the highest quality supply available, limited water supplies and the large volume of processing effluents to be disposed of provide strong motivation for using lower quality supplies to partially meet water requirements. Table 3 indicates that boiler blowdown, gas condensate, and storm water runoff are suitable for most uses with minimal to moderate treatment. Retort water and domestic sewage could be upgraded for most uses with a high degree of treatment; and mine waters, cooling tower blowdown, and pre-refining effluents require minimal to extensive treatment, depending on their eventual use. For most of these waters, the treatment required for reuse is equivalent to or less extensive than that required for discharge. Large-scale evaporation is unlikely due to large land requirements. Therefore, even though extensive treatment may be required to upgrade retort water, gas condensate, domestic sewage, and other process waters, such treatment for reuse may be economically attractive.

ISSUES AND RESEARCH PRIORITIES

Wastewater treatment and disposal options have been the subject of an oil shale research and development program sponsored by industrial developers of the technology, the Department of Energy's (DOE) Division of Environmental Control Technology, the Laramie Energy Technology Center (LETC), and most recently, by the Environmental Protection Agency (EPA). The purpose of this program is to develop economic and environmentally acceptable waste treatment methods for the oil shale industry. Several processes hold promise for treating oil shale effluents, but

considerable work is required to develop treatment goals and design criteria and to resolve a number of process-specific issues before these processes can be used commercially. Retort water treatment is a technically difficult problem and acceptable methods have not yet been identified, although progress continues to be made. Novel techniques, modifications in conventional treatment technology, or modifications in oil shale retorting processes may be required. Mine water and gas condensate treatment, by contrast, appear straightforward, and conventional technology may be adequate.

Oil shale retorting, as noted previously, produces three unique aqueous waste streams--retort water, gas condensate, and mine water--that require treatment and disposal. Stringent water quality standards suggest that these waters will probably be used on site and residuals evaporated. However, treatment and use of these waters produce various residues, concentrates, and sludges which also require treatment and disposal.

This section reviews the state of knowledge of retort water, gas condensate, and mine water treatment and disposal (Table 4). It also identifies key unresolved issues and the research needed to solve these problems. Emphasis is placed on basic and applied research required to identify or develop suitable treatment technologies rather than on engineering studies to select, cost, or design a system. This review focuses on research sponsored by federal agencies. Related research sponsored by industry is not presently publicly available.

Table 4. Summary of process-specific research on retort water, gas condensate, and mine waters.

	Retort Water	Gas Condensate	Mine Water
<u>SUSPENDED SOLIDS</u>			
Gravity Separation			
Filter Coalescence			
Coagulation/Flocculation	●		
Dissolved Air Flotation			
Filtration			
<u>DISSOLVED GASES AND INORGANICS</u>			
Stripping	●	●	
Ion Exchange	●		
Reverse Osmosis	?		●
Chemical Treatment	0		
Breakpoint Chlorination			
Spent Shale Treatment	●	●	
<u>DISSOLVED ORGANICS</u>			
Activated Sludge	?		
Anaerobic Fermentation	0		
Rotating Biodisc Contactor	0		
Activated Carbon Adsorption	●		
Resin Adsorption	0		
Chemical Oxidation	0		
Electrolytic Oxidation	0		
Reverse Osmosis	?		
Ultrafiltration			
Solvent Extraction	0		
Wet Air Oxidation	?		
Stripping	●	●	
<u>TRACE CONSTITUENTS</u>			
Chemical Treatment	0		
Ion Exchange			
Adsorption	?		
<u>COMBINED TREATMENTS</u>			
Reverse Osmosis	?		
Vapor Compression Evaporation	●		
Crystallization			
Solar Evaporation			

0 = experimental studies conducted; process not suitable for water and additional research not recommended.

● = experimental studies conducted; process appears suitable if certain operational problems are resolved.

? = research in progress; results inconclusive or incomplete.

RETORT WATER

Retort water will be the most difficult and costly oil shale waste stream requiring treatment and disposal. These waters are chemically complex and are produced in large volumes. Suspended solids, dissolved gases, dissolved organics, dissolved inorganics, and some trace constituents (Table 1) will have to be removed, depending on ultimate water use. Most anticipated uses will require removal of dissolved gases and organics while some other uses, such as cooling water and boiler feedwater, will require the removal of additional constituents. Treatment costs will be high due to the complex nature of these waters and the high concentrations of most constituents.

Generic Issues

During the past five years, a considerable amount of exploratory research has been devoted to treatment processes to remove suspended solids, dissolved gases, dissolved inorganics, and dissolved organics from retort waters. This work has identified several processes that may be used to treat retort water if certain operational problems, including fouling, plugging, and rapid breakthrough, can be solved. This section discusses general issues common to all processes and applicable to the entire area of retort water treatment. Because they relate to all treatment processes, resolution of these issues should be given top funding priority. In most cases, meaningful and definitive process-specific research cannot go forward without early solutions to these common issues. Process-related issues and research needs are discussed in a later section.

Characterization. Accurate water composition data are necessary to determine treatment requirements, to select suitable treatment processes, and to assess process performance in treatability studies. Although some characterization work has been completed (Fox et al., 1978; Fox, 1980a; Fish, 1980; Pellizzari et al., 1979), available characterization data are inadequate because of analytical problems, limited selection of waters studied, and the limited numbers of compounds measured. Fox et al. (1978) have demonstrated that many analytical methods are not suitable for retort waters due to chemical and other interferences. Consequently, much characterization data are inaccurate, and results of some treatability studies are misleading and inconclusive. High priority should be given to the development of accurate analytical methods for the measurements of major constituents in retort waters (Cl , SO_4 , CO_3 , HCO_3 , NH_3), environmentally important elements (As, F, B), and performance parameters for treatability studies (BOD, COD, organic C, and oil and grease). Molecular characterization of inorganic, organometallic, and organic compounds needs to be completed to identify specific compounds that must be removed. The EPA, for example, will regulate compounds of certain toxic elements, such as As and Se. Certain other compounds or classes of compounds may interfere with downstream treatment processes, i.e., they may be toxic to biological processes or may foul resins and membranes. Because retort waters are unique and chemically complex, biological tests, such as the standard bioassay and the Ames test, should be conducted on both untreated and treated waters to assess the performance of treatment processes and potential ecological impacts. Untreated and treated waters

from near-commercial and commercial surface and in-situ retorts need to be completely characterized using these procedures.

Samples. Sample selection and preservation are perhaps the most important and neglected aspects of retort water treatment studies. The majority of the characterization and treatability work that has been completed has used nonrepresentative simulated in-situ waters from LETC and Lawrence Livermore Laboratory (LLL) simulated retorts or field samples (Omega-9). Geokinetics and Paraho retort waters are the only near-commercial process waters that have been investigated (Mercer et al., 1980). Waters from Occidental field experiments are being used in studies now in progress. Because a variety of waters has been used, it is difficult to compare results obtained by various investigators using the same process.

Many of the tested simulated waters were a composite of gas condensate and retort water and therefore had much higher concentrations of dissolved gases than retort water alone. This has resulted in the rejection of some processes, such as weak acid cation exchange resins (Harding et al., 1978), that might be suitable for the lower concentrations of NH_3 and CO_2 found in retort waters. All of the samples tested were several months to several years old and had been exposed to a variety of storage conditions. We now know that sample composition, particularly organic components, varies over time, and that storage will remove suspended materials. Therefore, much of the suspended solids removal work and some of the biological treatment are inconclusive because of sample handling and storage. Furthermore, none of the samples tested has been truly representative of field or commercial processes because the tech-

nology itself is in transition. Product collection system design will determine the volumes and composition of retort water and gas condensate. Final designs are not available, and no work has been completed in this area. Retort water composition will vary throughout a run (Farrier et al., 1978), and water temperatures will be above the ambient levels used in treatability studies. Both of these factors will significantly affect the operation of some treatment processes and could lead to poor performance and frequent upset and failure.

Almost no treatment studies have been conducted on surface retort waters because it was previously anticipated that these waters would not require treatment since they are produced in small volumes intended for hot spent shale moisturization. However, a recent ruling by the state of Colorado may require the removal of organics from these waters, and recent concern about the escape of volatiles, including NH_3 , may require the removal of dissolved gases.

Therefore, more representative field samples should be used in future treatability and characterization studies. Large volume composite samples from field tests of all near-commercial processes should be prepared. LETC has initiated such a program, and it should be continued and expanded. Similar composites should be used by all investigators to enable results to be cross compared and validated. Reliable sampling, compositing, and storage procedures need to be developed and validated prior to large-scale sample preparation. Special samples of fresh retort water need to be made available on a case-by-case basis for treatability studies on nonconservative parameters such as suspended solids or oil

and grease. Field testing needs to be conducted at operating oil shale plants to assess the effect of water temperature, variable water composition, and climate on process performance. Programs in this latter area, initiated under EPA sponsorship at Monsanto, should be continued and expanded.

Process-Specific Issues

Much of the research conducted on treatment of retort waters during the last five years has been exploratory, and a large number of individual processes has been screened in simple batch experiments to determine their applicability to retort waters. Several processes--hot gas stripping, carbon adsorption, and reverse osmosis, for example--indicate potential for upgrading retort water; but none of these can be used for retort water treatment without resolution of operating problems such as foaming, fouling, rapid breakthrough, and toxicity. Furthermore, all processes require further testing.

Fundamental studies are required to resolve operating problems; and laboratory research is needed concerning the treatment of residues, brines, concentrates, and sludges produced during treatment as well as the blending of various waste streams to improve treatability. These investigations should include development of appropriate pretreatments and should involve chemical fractionation of waters and tests on individual fractions. Treatment and disposal of brines and solids from other processes, such as reverse osmosis or biological processes, need to be studied because they may be chemically unique and may be produced in large volumes. Other processes not yet investigated need to be screened to determine their applicability to oil shale retorting.

Promising processes from past and future studies need to be tested on a larger scale, sequenced in a total treatment system, and operated continuously to develop design data. Alternative treatment trains need to be evaluated, and cost data should be developed.

Exploratory research has been constrained by the lack of both treatment goals and representative samples. Treatment goals remain undefined because developers have been slow in investigating water management strategies. State and federal regulatory agencies have not defined specific effluent limitations or water quality standards that apply to an oil shale industry. Retorting processes have been in a state of flux and continued development. As a result of this uncertainty and the difficulty of retort water treatment, most research has focused on optimizing process performance. Regulatory agencies should define effluent limitations for the oil shale industry to lessen part of this uncertainty. Water reuse criteria should be developed based on related industrial experience. These standards should be used to determine treatment requirements, and processes and systems should be selected for their capability to comply with these standards.

This section discusses issues relevant to the five categories of treatment summarized in Table 4: removal of suspended solids, dissolved gases and inorganics, dissolved organics, and trace constituents and combined treatment. Source control is also discussed.

Suspended Solids Removal. Retort waters may contain three types of suspended material: oils and tars, raw and spent shale fines, and bacterial material (Fox, 1979). Measurements of suspended solids in several simulated in-situ waters indicate that these solids range from

about 200 to 3,000 mg/l (Fox, 1979). Oils and tars originate from intimate contact between shale oil and retort water. Although the oil-water emulsion is broken by heating (Burton, 1976), this process is not completely effective and residual oily and tarry material remains in the water phase. Raw and spent shale fines originate from contact between these materials and the oil-water emulsion during retorting. Bacterial material--cell debris and live bacteria--originates from bacterial growth following retorting (Farrier et al., 1977). These materials must be removed before retort waters can be discharged or reused because they interfere with downstream treatment processes by causing membrane and media fouling and plugging. They also may create surface films and shoreline deposits if the water is discharged.

Suspended solids may be removed by a number of physical and chemical processes including gravity separation, coagulation/flocculation, dissolved air flotation, filtration, or filter coalescence. The effectiveness of each process depends on the nature of the suspended material and the chemical composition of the water.

Little research has been conducted on removing suspended solids from retort waters. The only process studied is coagulation-flocculation (Blanc et al., 1980; Fox et al., 1980b; Mercer et al., 1980). A number of metal salts, polymers, and emulsion breaking chemicals have been screened and jar tested in laboratory studies using simulated and field in-situ waters that have been stored for from months to years. These studies indicate that ferric chloride, alum, and lime are not effective for removing suspended solids from retort water because of the high dosages required for moderate suspended solids reductions and the pro-

duction of pin flocs and sludge with poor settling capability. Cationic polymers and emulsion breaking chemicals are more effective although high dosages, 50 to 200 mg/l, are required to achieve good reductions. These studies have also indicated that current methods for analyzing oil and grease, components of the suspended material, give erroneous results (Fox et al., 1980b) and that fresh samples of water should be used due to sample changes during storage (Mercer et al., 1980; Fox et al., 1980b; and Blanc et al., 1980).

Because suspended solids must be removed before other treatments due to downstream fouling, immediate attention should be devoted to developing effective and economic methods to reduce these solids. Additional treatment methods for removing suspended solids--including gravity separation, dissolved air flotation, filtration, and filter coalescence--should be screened in laboratory studies using fresh samples of several surface and in-situ retort waters. Promising processes should be evaluated in bench-scale and pilot-scale continuous-flow systems and design criteria developed for a commercial system. Process selection and sequencing should be based on knowledge of the composition of the suspended material. Since this material consists of three distinct types of particles, two or more processes may have to be used in series. Combinations, such as gravity separation to remove raw and spent shale fines followed by coagulation-flocculation-filtration or dissolved air flotation to remove oil and grease, should be considered. Reliable analytical methods are needed for oil and grease analyses, and identification and validation of performance parameters for removing suspended solids are required.

Dissolved Gases and Inorganics. Retort waters are highly buffered and may contain from 1 to more than 10 weight percent dissolved solids. The majority of this material consists of the dissolved gases and inorganics, NH_3 , NH_4 , CO_2 , CO_3 , and HCO_3 . Chloride, Na, S_2O_3 , and SCN are also high in some waters. The NH_3 , CO_2 , and inorganic S compounds probably originate primarily from gases produced during retorting, while the other inorganic constituents result from contact between the water and raw or spent shale in the retort. Some of these constituents may be toxic to humans and to aquatic and terrestrial biota. Some also may interfere with downstream treatment processes or cause fouling and corrosion in boilers, cooling towers, and other end-use components. Therefore, various amounts of these compounds must be removed, depending on the end use of the water.

Removal of dissolved gases and inorganics may be achieved by air or steam stripping, ion exchange, breakpoint chlorination, biological treatment, chemical precipitation, or spent shale treatment. Research has been conducted on stripping, ion exchange, lime precipitation, and spent shale treatment. Since stripping and ion exchange simultaneously remove NH_3 and CO_2 while the other processes remove either one or the other of these gases, most of the research has been directed at the first two processes. Air and steam stripping have been screened in a number of simple laboratory experiments that have demonstrated that steam stripping holds promise for NH_3 and CO_2 reduction from in-situ retort waters if problems related to foaming and fouling can be solved (Harding et al., 1977, 1978; Hines, 1978; Water Purification Associates, 1979; Murphy, 1979; Mercer et al., 1980; Fox et al., 1980b). Heat

treatment, pH adjustment, and alkalinity addition may be required to obtain practical stripping rates. Greater than 99 percent NH_3 removal can be achieved with simultaneous reduction of 10 to 20 percent of the COD and over 50 percent of the CO_2 . Weak acid cation exchange resins, which remove essentially all of the NH_3 and CO_2 , hold promise for application to some waters (Harding et al., 1978, 1979). The water must have sufficient alkalinity to buffer the exchange reaction and a low enough NH_3 concentration to limit the frequency of resin regeneration. Spent shale treatment, which removes over 90 percent of the inorganic carbon (CO_2 , HCO_3 , CO_3), up to 60 percent of the organic carbon, and elevates the pH, may be used in combination with stripping or ion exchange (Fox et al., 1980a) to remove CO_2 and NH_3 without pretreatment. Lime precipitation is not practical due to the large doses of lime and huge quantities of sludge that are produced (Hubbard, 1971; Blanc et al., 1980).

The studies completed to date have indicated that steam stripping, ion exchange, and spent shale are all effective in removing NH_3 and/or CO_2 from some retort waters. Additional studies are required to identify appropriate pretreatments and to screen additional waters and treatment processes (i.e., clinoptilolite, locally available, and biological nitrification). The operational problems of foaming and fouling also must be resolved. These should be followed by process scale up to develop design parameters and economic data. Studies similar to those conducted by Hines (1978) on a synthetic retort water need to be repeated with several field surface and in-situ waters.

The removal of salinity and dissolved inorganics other than NH_3 and CO_2 species has not been extensively studied. It has been shown that reverse osmosis holds promise for salinity reduction (Hicks et al., 1980) and that activated sludge treatment will remove significant amounts of S_2O_3 and SCN (Mercer et. al., 1980). Additional work is required to identify and screen other methods to remove TDS and specific dissolved inorganics. Proper sequencing of these processes must be determined and adequate pretreatment provided. However, scale up and design of processes to remove dissolved inorganics can be delayed until similar work on suspended solids, organics, and dissolved gases removal is complete because these processes will be last in the treatment sequence and because some TDS reduction will occur upstream. Additionally, removing dissolved inorganics will not be required for all water uses.

Dissolved Organics. Although the removal of organics, presently the major technical constraint to developing a system to upgrade retort water, has received more study than any other parameter, results have generally been disappointing. This is attributed to the unique and complex nature of these waters and the lack of analytical methods to accurately characterize them (Fox et al., 1978). Retort waters contain a complex mixture of hundreds, perhaps thousands, of organic compounds, including organonitrogen compounds, carboxylic acids, hydrocarbons, and many others (Fish, 1980; Pellizzari et al., 1979). Dissolved organic carbon concentrations of 1 to 10 percent have been measured, and COD and BOD values are high. Organic carbon and specific organic compounds must be removed before these waters can be treated or used since these compounds foul or are toxic to downstream treatment processes and are

toxic if they reach the environment. Because some removal of organics will be required for all projected uses (Colorado has recently ruled that organics must be removed before retort water is used to moisturize spent shale), study of dissolved organics should be given very high research priority.

Dissolved organics may be removed by a large number of processes including aerobic and anaerobic biological treatment; solvent extraction; chemical, wet air, and electrolytic oxidation; reverse osmosis; and ultrafiltration. Most of the work completed to date has focused on in-situ waters and aerobic and anaerobic biological treatment and adsorption processes. Limited investigations have been conducted on chemical and electrolytic oxidation, solvent extraction, and reverse osmosis. Little work has been initiated on the removal of organics from surface retort waters. Many of these investigations have been hindered by the lack of adequate performance parameters. Both BOD and COD, which were used in most studies, are now known to yield results that are difficult to interpret due to chemical and other interferences (Fox et al., 1978; Wong and Mercer, 1981). Organic carbon should be used as a performance parameter in future studies, and work should be initiated to develop a good performance parameter for biological treatment (organic carbon is independent of the oxidation state). Other processes, including wet air oxidation, ultrafiltration, and pyrolysis, need to be evaluated, and a variety of processes needs to be screened using surface retort waters.

Exploratory studies of aerobic oxidation (activated sludge, rotating biodisc) using in-situ waters (Yen et al., 1977; Kaefer, 1979; Mercer

et al., 1980; Hicks et al., 1980; Water Purification Associates, 1980) indicate that up to 50 percent reduction in organic carbon can be achieved with long hydraulic and mean cell residence times, pH adjustment, ammonia removal, and nutrient addition. The process is very sensitive to water composition, and the activated sludge is highly dispersed in and not easily separated from the treated water. Addition of 300 mg/l or more of powdered activated carbon (PAC) (Mercer et al., 1980; Water Purification Associates, 1980) improved organic reductions and the settleability of the floc; alum also improved floc settling (Mercer et al., 1980). The low organic reductions and poorly settling floc suggest that system performance is limited by a toxicity problem and/or the presence of significant amounts of refractory organics.

These results are not encouraging and indicate that activated sludge may not be suitable for commercial application unless major research breakthroughs occur. Severe weather conditions in the oil shale region coupled with fluctuations in the quality of retort water, particularly during an in-situ burn, may result in frequent process upset and failure. The low organic reductions and long residence times will result in high treatment costs.

Because a properly functioning activated sludge process is one of the most economic methods of removing organics and because this process has been successfully demonstrated on other complex synfuel wastes, additional research should be conducted to improve the performance of activated sludge on retort waters. Fundamental research needs to be conducted to identify the cause for poor performance of the air activated sludge process. Two approaches should be used: (1) the development of

a strain(s) of bacteria to biodegrade the majority of the organics in retort waters and (2) the development of methods to remove toxic compounds or to convert refractory compounds to readily oxidizable forms. Strain development may take a long time and should be started immediately. Near-term success is more likely with the second approach. Toxic or refractory compounds should be identified by fractionating the waters and aerobically oxidizing each fraction. Fractions that are toxic or refractory should be characterized and specific methods selected to remove the offending compounds or groups of compounds. Additional exploratory studies need to be conducted on waters from field in-situ experiments and surface retorts.

Other aerobic processes--including trickling filters, rotating biodiscs, pure-oxygen activated sludge, multiple-stage activated sludge systems, and nitrifying activated sludge--should be screened and successful processes scaled up.

Exploratory studies of anaerobic fermentation (Yen, 1975; Yen and Findley, 1976a and 1976b; Ossio and Fox, 1980; and Mercer et al., 1980) are inconclusive, with performance generally depending on the water investigated. Successful digestion was achieved with some simulated in-situ waters while failure occurred with other simulated in-situ waters, field in-situ waters, and surface retort waters. These studies indicate that long hydraulic residence times, on the order of 50 days; pH adjustment; nutrient addition; and/or PAC addition are required to achieve successful digestion. The sensitivity of this process to water composition and the long hydraulic residence times suggest that the process may not be suitable for commercial application. Since more favorable results

have been achieved with aerobic processes, biological treatment research on anaerobic processes should be discontinued.

Resin and activated carbon adsorption evaluated by Harding et al. (1978) and Mercer et al. (1980) indicate that granular activated carbon and four macroreticular resins did not effectively remove organic carbon due to fouling, bleeding, and rapid breakthrough. However, activated carbon may be effective as a polishing step following biological treatment (Mercer et al., 1980). Similarly, reverse osmosis (Hicks et al., 1980) also achieved good organic reductions but low membrane fluxes suggested a possible membrane fouling problem. Additional studies are required to identify pretreatments and to properly sequence these processes; to screen additional waters, membranes and resins; and to resolve the operational problems of fouling, bleeding, and rapid breakthrough. Waters should be fractionated and fractions tested to identify groups of compounds responsible for operational problems. These data should then be used to identify pretreatments and to properly sequence these processes into a complete treatment system. Desorption, which may be hindered by chemical bonding, should be evaluated experimentally. Promising processes or sequences of processes should be scaled up and design criteria and cost data developed.

Exploratory studies have also been conducted on chemical (Cl_2 , O_3 , KMnO_4) oxidation (Blanc et al., 1980; Anselmi, 1976), electrolytic oxidation (Wen, 1976; Wen and Yen, 1977), and solvent extraction (Hicks, June 1980). These processes do not appear suitable for organic carbon reduction due to poor removals and high chemical costs. However, they may be used as pretreatments for other organic reduction processes, such as

biological treatment or adsorption. These and other processes may be used to convert some organics to forms that are readily biodegraded, or they may be used to selectively remove classes of compounds that foul resins and membranes. These and other similar processes should be evaluated as pretreatment steps for biological and adsorption processes and successful processes scaled up.

Trace Constituents. Retort waters contain a complex mixture of organic and inorganic compounds. Hundreds of organic, organometallic, and inorganic compounds have been identified in these waters, including such compounds as arsenate, methylarsonic acid, mono- and dicarboxylic acids, pyridines, pyrroles, lutidines, aliphatic aromatic hydrocarbons, and most elements in the periodic table (Fish, 1980; Fox, 1980a; Pellizzari et al., 1979). Some of these compounds occur at concentrations that may interfere with downstream treatment processes or projected end uses of the water. For example, low-boiling organics may have to be removed before the water is used to wet hot spent shale or is ponded; other toxic organics and inorganics may have to be removed prior to use for irrigation or dust control.

A large number of processes may be used to remove trace constituents, including adsorption, ion exchange, and chemical methods. Very little work has been conducted in this area. Hines (1978) investigated the removal of phenol and benzoic acid by resin adsorption in model compound studies, and Mercer et al. (1980) studied the removal of As by ferric hydroxide scavenging. Manahan et al (1978) investigated the removal of benzo(a)pyrene, naphthalene, phenol, benzoic acid, octanoic acid, carbonate, and KCN by treatment with lime and lime-plus-coal humic acids.

None of these processes were successful due to low removals and/or high chemical costs.

Except for pretreatment uses, there should be no additional research in this area until water uses and quality requirements are established and methods have been developed to remove the major components (suspended solids, gases, dissolved inorganics, and dissolved organics). Because many trace components may be removed in these processes, additional removal may not be required. Trace constituent removal in the near future should focus on pretreatment to eliminate toxicity, fouling, or foaming problems in downstream processes. The compounds that need to be removed should be identified using bioassay and toxicological test methods and standard engineering analyses, and maximum acceptable levels should be established for the treated water.

Combined Treatments. Previous sections have discussed the removal of specific compounds or classes of related compounds such as suspended solids, organics, gases, and dissolved inorganics by a single process such as activated sludge or steam stripping. Some treatment processes, such as crystallization, vapor compression evaporation, and reverse osmosis, may remove the majority of the organic and inorganic contaminants in a water in a single step that may or may not require minimal pretreatment or polishing. Typically, these processes are very expensive, costing from \$5 to \$20 per 1000 gallons and are considered only when a more conventional system, consisting of several unit processes in series, is technically or economically impractical.

The high cost of retort water treatment by a conventional system, projected to range from \$5 to \$50 per 1000 gallons, and the poor per-

formance of many conventional processes suggest that these single-step treatments may be economically attractive. This has been recognized recently, and some work is now underway to evaluate these processes. Preliminary results are encouraging and suggest that evaporation (Peters, 1980) and reverse osmosis (Hicks et al., 1980) may be effective in removing major organic and inorganic compounds and some trace constituents from retort waters. Preliminary cost estimates indicate that these single-step processes may be more economic than a conventional multi-staged system and that effluent quality is better.

Future research should focus on these combined treatments due to the favorable economics and performance. Laboratory screening studies using several surface and in-situ retort waters need to be conducted on all commercially available processes to assess their performance and identify potential operating problems. Pretreatment and polishing requirements need to be determined, and disposal of brines and sludges investigated. Promising processes should be scaled up and design criteria and cost data developed.

Source Control. Work completed to date and reviewed in previous sections indicates that treatment of retort water by conventional technology is costly and that a number of technical difficulties remain. It may be feasible to eliminate some of these by modifying process operating conditions. This may lessen the total volume of water produced, alter the relative volume of retort water and gas condensate, and alter water composition. Operating conditions that may be important include retorting rate, maximum retorting temperature, input gas composition (steam significantly increases the amount of water that must be

treated), residence time of water in collection sumps and separation devices, and temperature of oil-water separation. There has been no investigation of source control, and such a program should be developed.

Work completed by Fox (1980a) suggests that the composition of in-situ retort water is controlled by its contact with gases, oil, and raw or partially retorted shale ahead of the reaction zone. During and after retorting, organic and inorganic compounds are partitioned from these phases to the water. The length of time that the water is in contact with these phases and the prevailing temperatures in the cool zone of the retort and in the oil-water separator will determine water composition. These residence times and temperatures are controlled by retort and product collection system operation. If the contact times and temperatures could be lessened, it might be possible to improve the composition of retort water.

Alternatively, Nevens et al. (1979) noted that the relative volume of retort water and gas condensate can be controlled by varying maximum retorting temperature. If the retort is operated at a sufficiently high temperature, it may be possible to keep the water in the vapor phase until it reaches the gas handling system. This could largely eliminate retort water in surface retorts, producing a larger gas condensate stream. This would be a decided advantage because gas condensate is easier to treat than retort water and is less contaminated because the water has not been in contact with the oil and shale.

These methods and others should be investigated in laboratory and computer modeling studies. The goal of this work should be to minimize

the volume of retort water and to improve its quality by modifying retort operating conditions. Studies should be performed to assess the effect of any recommended process changes on oil yield and, hence, process economics.

GAS CONDENSATE

Gas condensate is removed from the gas stream in the product collection system or air pollution control system and is chemically less complex than retort waters. Limited analyses of these waters (Hicks et al., 1980) indicate that they contain high concentrations of NH_3 , CO_2 , and organic carbon and low concentrations of dissolved inorganics (Table 1).

Gas condensate was only recently recognized as a waste stream (Nevens et al., 1979). Previous work had overlooked this water because it was not separated during simulated in-situ retorting experiments and was combined with the retort water. Therefore, little gas condensate research has been conducted. However, preliminary studies suggest that gas condensate treatment will be straightforward. Hicks et al. (1980) achieved 90 percent removal of organics and 98 percent removal of NH_3 in batch stripping experiments of an Occidental field sample; and Lewis et al. (1980) obtained simultaneous removal of alkalinity, NH_3 , and H_2S in a single-stage, continuous-flow steam stripper. Lewis' work suggests that a high liquid-to-gas ratio may be required to achieve high removals of alkalinity and NH_3 . Using spent shale treatment, Fox et al. (1980a) removed 65 to 99 percent of the inorganic carbon and 49 to 75 percent of the conductivity in batch experiments on an LLL gas condensate.

Since treatment of this waste stream is not expected to create any significant technical problems, government-sponsored research in this area should be minimized. Industry should be able to design gas condensate treatment systems using existing technology. If subsequent field experience identifies technical problems, research should then be initiated.

MINE WATERS

Mine waters are produced in large volumes from site dewatering throughout a plant's operational life. As noted previously, they are saline, contain elevated concentrations of some trace constituents such as F and B, and may vary greatly in composition. These waters may be upgraded for on-site use, used for stream flow augmentation to protect downstream water rights, or reinjected. All of these options may require treatment to remove salinity and certain trace constituents.

Very little research has been conducted in this area. Sinor (1977) evaluated a number of options for the disposal of excess mine water from lease tract C-b, including evaporation via sprinkler irrigation, deflourination via ion exchange, and reinjection. Reinjection was the preferred method due to its great flexibility. Hicks et al. (1980), in the only experimental work conducted on mine water, demonstrated that reverse osmosis achieves adequate TDS and F removal from tract C-b waters.

Although treatment of these waters appears straightforward at the present time, treatment requirements have not been adequately defined. Consequently, a number of operational problems may be expected, and treatment costs may be high. Mine water quality will vary over the life of a plant (Robson and Saulnier, 1980), and large volumes of water may have to be treated to meet very high water quality standards.

Therefore, additional research should be conducted to identify cost-effective treatment methods and to determine the effect of varying water compositions on process operations.

SUMMARY

This paper has reviewed wastewater treatment strategies for an oil shale industry and has identified key issues and research priorities that require resolution before a large-scale commercial industry develops. It focuses on treatment of waters that are unique to an oil shale industry: retort water, gas condensate, and mine water.

This review indicates that water management in the oil shale industry is in the development stage. There are many unresolved issues, ranging from the anticipated on-site uses of water to treatment criteria to identification of processes capable of upgrading the effluents. Much of this uncertainty is due to the absence of a commercial industry. The retorting processes that may be used are in transition. The research community has been faced with developing treatment methods for waste streams that have not yet been produced. Waters from simulated retorts have been substituted with varying degrees of success. The regulatory agencies are faced with a similar dilemma; they cannot develop regulations for effluents that have not been generated. The lack of accurate characterization data, because of chemical and other interferences with standard analytical methods, has compounded the problem.

Accelerated research in this area in the past five years has produced some encouraging results and has identified areas that require additional study. The treatment of gas condensate and mine waters appears to be straightforward; significant additional research in this

area is not recommended. Retort water treatment, by contrast, is complex, and a suitable treatment system has yet to be developed. Some processes hold promise if certain operational problems, including foaming, fouling, and rapid breakthrough, can be solved, and if costs can be lowered. Cationic polymers and emulsion-breaking chemicals are effective in removing suspended solids at high dosages. Steam stripping, weak acid ion exchange resins, and spent shale treatment are capable of removing the dissolved gases and certain inorganics from some retort waters. Activated carbon is an effective polishing step for organics and inorganics. Certain other processes do not appear suitable for retort water treatment. These include: chemical treatment for the removal of dissolved gases, inorganics, or trace constituents; anaerobic fermentation; rotating biological contactors; chemical or electrolytic oxidation; and solvent extraction for removal of dissolved organics. Still other processes, such as gravity separation, dissolved air flotation, filtration, ultrafiltration, and wet air oxidation, have not been evaluated.

Additional research is required to develop a treatment system for retort water. Emphasis should be placed on the single-step treatments such as vapor compression evaporation, crystallization, and reverse osmosis because of their favorable economics and good performance in preliminary studies. Parallel studies should be conducted to develop an economic conventional treatment system for retort water consisting of individual unit processes to remove suspended solids, dissolved gases, dissolved inorganics, dissolved organics, and trace constituents. Major emphasis in this latter program should be placed on the

removal of dissolved organic compounds. Exploratory treatability studies should be phased out in the near future and promising processes scaled up to obtain design and cost data. Representative samples of waters from near-commercial processes should be used in this research, and accurate analytical methods should be used to obtain characterization and performance data. Treatment methods and disposal options for the various residues, concentrates, and sludges produced by retort water treatment should be developed. Some of these streams--such as blowdown from a low-pressure boiler using retort water as makeup, brines from reverse osmosis processes, or bottoms from a distillation step--may be more difficult to treat and dispose of than the original waters, i.e., retort water, gas condensate, and mine waters.

To date, the developing oil shale industry has given research priority to perfecting retorting and refining processes. Little if any emphasis has been placed on investigation of wastewater treatment. The high volume of aqueous waste, the stringent state and federal regulations governing discharge of waste into local waters, and the limited water supplies in the oil shale area make mandatory the development of adequate treatment methods to upgrade these wastewaters. This requirement is further strengthened by the fact that future contamination of surface and ground waters can be prevented only by necessary treatment of oil shale waste products. Consequently, both government and industrial oil shale research should place high priorities on the development of adequate treatment processes.

REFERENCES

- R. T. Anselmi, Oxidation of Shale Process Waters, Report to Laramie Energy Technology Center (Dec. 1976).
- F. C. Blanc, J. C. O'Shaughnessy, I. W. Wei, and F. E. MacNevin, "In-Situ Oil Shale Retort Wastewater Pretreatment Using Coagulation and Oxidation," Proceedings of the 35th Purdue Industrial Waste Conference (May 1980).
- R. S. Burton, III, "Method of Breaking Shale Oil-Water Emulsion," U. S. Patent 4,109,718 (Aug. 1976).
- E. W. Cook, "Organic Acids in Process Waters from Green River Oil Shale," Chem. and Ind., 1, 485 (1971).
- D. S. Farrier, R. E. Poulson, Q. D. Skinner, J. C. Adams, and J. P. Bower, "Acquisition, Processing and Storage for Environmental Research of Aqueous Effluents from In-Situ Oil Shale Processing," in Proceedings of the Second Pacific Chemical Engineering Congress, Denver, Colo., v. II, p. 1031 (1977).
- D. S. Farrier, J. E. Virgona, T. E. Phillips, and R. E. Poulson, "Environmental Research for In-Situ Oil Shale Processing," in Proceedings of the 11th Oil Shale Symposium, Colorado School of Mines (1978).
- R. H. Fish, "Speciation of Trace Organic Ligands and Inorganic and Organometallic Compounds in Shale Oil Process Waters," in Proceedings of the 13th Oil Shale Symposium, Colorado School of Mines (1980).
- J. P. Fox, "Retort Water Particulates," Oil Shale Symposium, Sampling, Analysis and Quality Assurance, EPA-600/9-80-022 (1979).
- J. P. Fox, The Partitioning of Major, Minor, and Trace Elements During Simulated In-Situ Oil Shale Retorting, Ph.D. Dissertation, University of California, Berkeley, Lawrence Berkeley Laboratory Report LBL-9062 (1980a).
- J. P. Fox, Water-related Impacts of In-Situ Oil Shale Processing, Lawrence Berkeley Laboratory Report LBL-6300 (1980b).
- J. P. Fox, D. S. Farrier, and R. E. Poulson, Chemical Characterization and Analytical Considerations for an In-Situ Oil Shale Process Water, Laramie Energy Technology Report LETC/RI-78/7 (1978).
- J. P. Fox, D. E. Jackson, and R. H. Sakaji, "Potential Uses of Spent Shale in the Treatment of Oil Shale Retort Waters," in Proceedings of the 13th Oil Shale Symposium, Colorado School of Mines (1980a).

- J. P. Fox, D. E. Jackson, R. H. Sakaji, C. G. Daughton, and R. E. Selleck, Spent Shale as a Control Technology for Oil Shale Retort Water, Annual Report for Period Oct. 1, 1978-Sept. 30, 1979, Lawrence Berkeley Laboratory Report LBL-10746 (1980b).
- B. L. Harding, K. D. Linstedt, E. R. Bennett, and R. E. Poulson, "Removal of Ammonia and Alkalinity from Oil Shale Retort Waters by the Use of Weak Acid Cation Exchange Resins," in Proceedings of the Second Pacific Chemical Engineering Congress, p. 442 (1977).
- B. Harding, K. D. Linstedt, E. R. Bennett, and R. E. Poulson, "Study Evaluates Treatments for Oil-Shale Retort Water," Industrial Wastes, 28 (Sept/Oct. 1978).
- B. L. Harding, K. D. Linstedt, and E. R. Bennett, Removal of Ammonia and Alkalinity from Oil Shale Retort Waters, Laramie Energy Technology Center Report LETC-3096-1 (April 1979).
- R. E. Hicks, Water Purification Associates, Cambridge, Mass., personal communication to T. Phillips (June 1980).
- R. E. Hicks, R. F. Probststein, I. Wei, D. S. Farrier, J. Lotwala, and T. E. Phillips, "Wastewater Treatment and Management at Oil Shale Plants," in Proceedings of the 13th Oil Shale Symposium, Colorado School of Mines (1980).
- A. L. Hines, The Role of Spent Shale in Oil Shale Processing and the Management of Environmental Residues, Final Technical Report, Sept. 1976-Dec. 1977, U.S. Dept. of Energy Report TID-28586 (1978).
- C. H. Ho, B. R. Clark, and M. R. Guerin, "Direct Analysis of Organic Compounds in Aqueous By-Products from Fossil Fuel Conversion Processes: Oil Shale Retorting, Synthane Coal Gasification and COED Coal Liquefaction," J. Environ. Sci. Health, A11 7, 481 (1976).
- A. B. Hubbard, "Method for Reclaiming Waste Water from Oil Shale Processing," ACS Division of Fuel Chemistry Preprint, 16, No. 1, 21 (1971).
- J. R. Kaefer, The Acclimation of Oil Refinery Activated Sludge to Oil Shale Retort Water, Master of Science Thesis, University of Arizona (1979).
- R. S. Lewis, B. O. Desai, and G. D. Rawlings, Steam Stripping of Occidental Petroleum Retort No. 6 Gas Condensate, Preliminary Report from Monsanto to U.S. Environmental Protection Agency under Contract No. 68-03-2801 (1980).
- S. E. Manahan, R. E. Poulson, J. B. Green, and D. S. Farrier, Coal Humic Substances and their Application to Pollution Control in the Synthetic Fuels Industry, Laramie Energy Technology Report LETC/RI-78/5 (Sept. 1978).

M. Mehran, T. N. Narasimhan, and J. P. Fox, An Investigation of Dewatering for the Modified In-Situ Retorting Process, Piceance Creek Basin, Colorado, Lawrence Berkeley Laboratory Report Number LBL-11819 (1981).

B. W. Mercer, M. J. Mason, R. R. Spencer, A. L. Wong and W. Wakamiya, Evaluation of Physical-Chemical and Biological Treatment of Shale Oil Retort Water, Draft Report, Battelle Pacific Northwest Laboratory, Richland, Wash. (May 1980).

C. L. Murphy, Hot Gas Stripping of Ammonia and Carbon Dioxide from Simulated and Actual In-Situ Retort Waters, Colorado School of Mines (1979).

T. D. Nevens, W. J. Culbertson, Jr., J. R. Wallace, G. C. Taylor, A. P. Jovanovich, and C. H. Prien, "Predicted Costs of Environmental Controls for a Commercial Oil Shale Industry, Volume I. An Engineering Analysis" in Environmental Control Costs for Oil Shale Processes, U. S. Department of Energy Report Number DOE/EV-0055 (October 1979).

E. Ossio and J. P. Fox, Anaerobic Biological Treatment of In-Situ Retort Water, Lawrence Berkeley Laboratory Report LBL-10481 (1980).

E. D. Pellizzari, N. P. Castillo, S. Willis, D. Smith, and J. T. Bursley, "Identification of Organic Components in Aqueous Effluents from Energy-related Processes," in Measurement of Organic Pollutants in Water and Wastewater, ASTM Special Technical Publication 686, C. E. Van Hall (ed.), ASTM, Philadelphia, PA (1979).

H. H. Peters, Shale Oil Waste Water Recovery by Evaporation, Final Report to Battelle Pacific Northwest Laboratory by Resources Conservation Company, Seattle, Wash. (Jan. 1980).

S. G. Robson and G. J. Saulnier, Jr., Hydrogeochemistry and Simulated Solute Transport, Piceance Basin, Northwest Colorado, U. S. Geological Survey Open-File Report 80-72 (1980).

J. E. Sinor, "Disposal of Mine Water from a Deep Oil Shale Mine," in Proceedings of the Second Pacific Chemical Engineering Congress, Vol II, (Aug. 1977).

Water Purification Associates, A Study of Aerobic Oxidation and Allied Treatment for Upgrading In-Situ Retort Waters, Quarterly Status Report for the Period May 1, 1979-August 31, 1979, Cambridge, Mass. (1979).

Water Purification Associates, A Study of Aerobic Oxidation and Allied Treatment for Upgrading In-Situ Retort Waters, Quarterly Status Report for the Period March 1-May 31, 1980, Cambridge, Mass. (1980).

J. B. Weeks, G. H. Leavesley, F. A. Welder, and G. J. Saulnier, Jr., Simulated Effects of Oil Shale Development on the Hydrology of Piceance Basin, Colorado, U.S. Geological Survey Professional Paper 908 (1974).

C. S. Wen, Electrolytic Processes of Oil Shale and its Derivatives, Ph.D. Dissertation, University of Southern California (1976).

C. S. Wen and T. F. Yen, "Purification and Recovery of Economic Materials from Oil Shale Retort Water by an Electrolytic Treatment Process," in Proceedings of the Second Pacific Chemical Engineering Congress, August 28-31 (1977).

A. L. Wong and B. W. Mercer, "Contribution of Thiosulfate to Chemical and Biological Demand in Oil Shale Process Wastewater," in Analysis of Waters Associated with Alternate Fuel Production, ASTM STP 720, L. P. Jackson and C. C. Wright, Eds., American Society for Testing and Materials (1981).

T. F. Yen, Annual Report on Biological Degradation of the Soluble Organic Components in Retort Water, Los Angeles USC (Dec. 1975).

T. F. Yen and J. Findley, Progress Report on Retort Water Project for Quarter Ending February 29, 1976, Los Angeles, USC (1976a).

T. F. Yen and J. Findley, Progress Report on Retort Water Project for Quarter Ending June 30, 1976, Los Angeles, USC (1976b).

T. F. Yen et al., Degradation of the Organic Compounds in Retort Water, Final Report to LETC for Contract No. E(29-2)-3758 (1977).

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