United States
Environmental Protection
Agency

Industrial Environmental Research Laboratory Cincinnati OH 45268

Research and Development

EPA-600/D-84-036 Mar. 1984



ENVIRONMENTAL RESEARCH BRIEF

Oil Shale—Potential Environmental Impacts and Control Technology

E. R. Bates, W. W. Liberick, and J. Burckle

Introduction

Since 1973, the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory in Cincinnati, Ohio (IERL-Ci) has performed research related to oil shale processing and disposal. This research is in support of the Clean Air Act, the Federal Water Pollution Control Act, the Resource Conservation and Recovery Act, the Safe Drinking Water Act, and the Toxic Substances Control Act. Potential environmental impacts from oil shale development activities have been identified and potential control technologies are being evaluated through a combination of laboratory and field tests on actual oil shale waste streams. This paper discusses recent results from the oil shale program. Included are field test results on control of sulfur gases at Occidental Oil Shale's Logan Wash Site and Geokinetic's Kamp Kerogen Site; wastewater treatability studies on retort water and gas condensate at Logan Wash; and results of laboratory and field testing on raw and retorted oil shales.

Air Pollutants and Controls

Potentially, the mining and processing of oil shale to produce a refined shale oil product might produce a variety of air pollutants, many of which could have a significant adverse environmental impact if not properly managed. Such pollutants include those shown in Table 1: fugitive emissions from mining, transportation, and materials handling; process emissions from materials preparation such as sizing for indirect-fired retorting; process emissions from oil upgrading and storage facilities; fugitive emissions from waste handling and disposal; process emissions from utility generation; and process and fugitive emissions from infrastructure development and secondary pollution sources.

Processes for removal of reduced sulfur and carbon dioxide from gases are known as acid-gas removal or gas-sweetening processes which involve either adsorption and chemical conversion (direct processes), or adsorption and stripping, to form a more concentrated stream which is then processed for sulfur conversion and recovery (indirect processes). More than 30 such commercial processes exist. IT Environscience conducted an in-depth evaluation of a number of emissions reduction systems to determine applicability for removal of hydrogen sulfide from retort off-gases (Lovell, et al., 1982). The study found that because gases from direct-fired retorts have a high content of carbon dioxide relative to hydrogen sulfide and also contain large amounts of ammonia and unsaturated hydrocarbons, they are significantly different from gases encountered in commercial applications of desulfurization technologies. Hence, such technologies cannot be simply applied at full scale through technology transfer; such transfer must be achieved through an application research program to minimize risk and maximize success.

Since retort off-gases will be produced in very large volumes at near atmospheric pressure, many desulfurization processes cannot be economically applied. The high concentration of CO₂, and CO₂/H₂S ratios, and the presence of oxygen, unsaturated hydrocarbons, or organic sulfur species also make application of a number of desulfurization techniques impractical.

Of the systems studied, the Stretford, EIC, MDEA (Select-samine and Adip), Benfield, Diamox, and Selexol appear to have the potential for the greatest H₂S selectivity for application to direct-fired retorts. Except for the Diamox process, these systems should be capable of controlling H₂S to about 10 ppmy, resulting in an H₂S control efficiency of 99+ %. However, organic sulfur compounds, principally COS, are not significantly removed or are only partly removed by the various processes. Therefore, the presence of such compounds may lower the overall reduced sulfur control efficiency to about 98% (Table 2).

When discussing reduction of emissions from oil shale retorting operations, it is useful to classify the retorting processes as direct-fired (where the combustion occurs

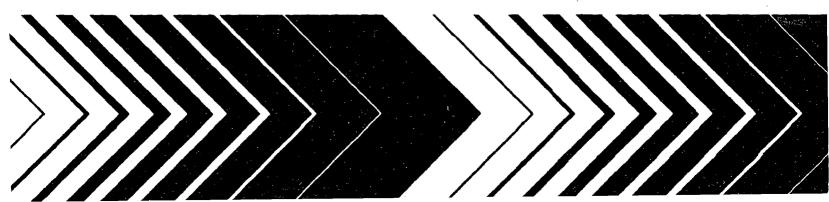


Table 1. Potential Pollutants from Oil Shale Mining and Processing

Criteria	Hazardous	Other
Pollutants	Pollutants	Pollutants
Particulate	Asbestos	Ammonia
Sulfur dioxide	Arsenic	Hydrogen sulfide
Nitrogen oxides	Beryllium	Trace metals
Carbon monoxide Hydrocarbons Lead	Mercury Polycyclic Organics Radionuclides	Reduced organic sulfides

within the retort itself) or as indirect-fired (where combustion to produce the heat required for retorting occurs outside of the retort). This distinction is important because it influences the nature of the retort off-gas to be treated (Table 3) and hence poses distinctly different duty requirements which must be considered in the selection of an emissions reduction technology. The predominant factor in the selection process is the CO_2/H_2S ratio. Direct-fired retorts have CO_2/H_2S ratios ranging from 75 to more than 165. Such high ratios require a process that selectively removes H_2S in preference to CO_2 , in order to prevent excess consumption of reagent capacity by the CO_2 , and the resulting increase in processing costs. Indirect-fired retorts produce off-gases having a CO_2/H_2S ratio in the range of 4.5 to 5, which permits the use of a nonselective process.

Based upon a cost evaluation of a model case, the Stretford process appears to be the most cost-effective approach for direct-fired retorts (Lovell, et al., 1982). In Table 4 the relative costs for using the Stretford, MDEA selective absorption followed by Stretford or Claus sulfur recovery systems, and the Diamox process are compared. The estimated cost for sulfur control using the Stretford process directly is fifty cents per barrel of oil, which is less than half that of the indirect sulfur removal process.

Based upon the results of this study, EPA funded the design and construction of a Stretford pilot unit which has been utilized in three series of tests. These three test series were conducted at Occidental's Logan Wash retorts 7 and 8 (OXY—6/17/82 to 7/1/82), Geokinetics' Kamp Kerogen (GKI—9/15/82 to 10/1/82), and the U.S. Bureau of Mines coal gasification facility at Twin Cities Research Center (TCRC—11/5/82 to 11/22/82). The results are summarized in Table 5.

Table 3. Concentration of Major Sulfur Species in Retorted Off-Gas

Species	Direct-Fired	Indirect-Fired		
H ₂ S	0.1 - 0.6 percent v	1.0 - 5.0 percent v		
cos	100 - 600 ppmv	100 - 1000 ppmv		
CS ₂	100 - 600 ppmv	100 - 1000 ppmv		
CH ₃ - SH	50 - 300 ppmv	50 - 500 ppmv		

Table 4. Relative Costs of Various Gas Desulfurization Options*

Category	Stretford Direct Process with Purge Stream Disposal	Direct Process with Purge Stream	1-Step MDEA Selective Adsorption with Stretford Sulfur Recovery	3-Step MDEA Selective Absorption with Claus Sulfur Recovery	Diamox Process with Claus Sulfur Recovery
Installed capital	-				
cost	1.00	1.11	1.29	1.17	2.46
Utility costs	1.00	1.51	5.90	9.88	16.79
Total operating costs	1.00	1.13	1.88	2.15	3.90
Value of sulfur recov-					
ered Net	0.92	0.95	0.96	1.00	0.98
annual cost	1.00	1.15	2.05	2.37	4.47
Cost effective-					
ness	1.00	1.15	2.04	2.34	4.54

*Based on a plant processing 10.2 million sm³ of Paraho gas per day. The most effective or least costly option in each category is shown as unity (1.00). The relative costs of the other options are shown as a ratio to the most effective or least costly system.

Source: Lovell, et al, 1982.

Table 2. Variation of Process Effectiveness with Amount of COS in Raw Gas*

						Estimated Overall Emissions			
	H ₂ S	cos		Sulfur		Total Sulfur		SO ₂ Equivalent	
	Remaining (ppmv)	Reduction (wt %)	Reduction (wt %)	Remaining (kg/hr)	kg/hr	(tonnes/day)	(kg/hr)	(kg/bbl of oil)	Reduction (wt %)
Stretford	10	Nil	98.0-99.3	19-58	19-58	0.45-1.35	38-115	0.02-0.05	98.0-99.3
MDEA - 1 stage with Stretford	10	60	99.2-99.5	13-29	20-59	0.45-0.90	40-117	0.02-0.05	98.0-99.3
MDEA - 3 stages with Claus/ SCOT	10	60	99.2-99.5	13-29	20.4-36	0.45-0.90	41-72	0.02-0.04	98.0-99.3
Diamox with Claus/BSPR	63	Nil	96.3-97.6	70-109	75-114	1.81-2.70	151-228	0.07-0.11	96.1-97.4

^{*}Based on a Paraho plant producing 8,000° of oil per day, with COS ranging from 10 to 50 ppmv in the raw gas.

Table 5. EPA Stretford Field Tests

Site	H₂S Removal Efficiency
Logan Wash, MIS Retorts 7 & 8	20 - 60%
Geokinetics, in situ Retorts	60 - 90+%
U.S. Bureau of Mines (coal gas)	75 - 99.7%

During the OXY test series, the H₂S control efficiency ranged from 20% at startup to approximately 60% at the end of the test. A major field modification of the venturi absorber was made to improve the gas-liquid contacting; almost all of the improvement in performance is attributed to this measure. Analysis of the resulting test data identified gas/liquid contacting and Stretford solution chemistry as the targets for further efforts to improve performance.

In the GKI test series, the H₂S removal efficiency ranged from about 60% to approximately 85%, with brief periods in the mid to high 90's. During the first phase of the test, the effectiveness of gas/liquid contact using the venturi and an inline static mixer was investigated with no noticeable difference in removal efficiency. During the balance of the test, various experiments were conducted to evaluate solution chemistry. First, an increase in the vanadium content of the Stretford solution improved H₂S removal. Second, it was suspected that the reaction vessel retention time was too short to permit the completion of the Stretford solution reactions, thereby permitting recycling of incompletely regenerated Stretford solution to the venturi scrubber. To verify this effect, the liquid in the reaction tank was raised to its maximum level with the observed effect of improved H₂S removal. Additionally, it was noted that a 99+ percent H₂S removal was obtained whenever the unit was restarted after an extended down-time and during periods of low retort off-gas flow through the venturi.

In a subsequent test series, performed on a coal gasification off-gas at the USBM Twin Cities Research Center, improved results for given operating conditions were achieved as predicted from the GKI tests. The only change in operation from the GKI tests was a reduction in the gas flow rate into the pilot unit through the addition of a gas bypass arrangement. This change allowed operation at lower liquid flow rates, while maintaining the required L/G ratio at the scrubber, and resulted in the increase in residence time in the reaction tank needed for complete regeneration of the Stretford solution. Through this change, H2S removal efficiencies of 75% at the start of the test were increased under controlled experimental conditions to 99.7%. Still remaining to be demonstrated is that high removal efficiency under sustained operation is possible on the off-gas from a direct-fired retort.

In a cooperative program with the Department of Energy's Laramie Energy Technology Center (LETC), EPA sponsored tests for the control of oily particulates remaining in the off-gas from LETC's 150-ton simulated in situ retort after oil and heat recovery. In September 1980, Monsanto Research Corporation conducted the tests using EPA's mobile scrubber pilot unit.

The particle size (weight basis) measured indicated that about 60% of the particles were less than 15 μ m, 50% were less than 5 μ m, and the distribution was bimodal with approximately one-third of the catch reporting to both the greater than 20 μ m and to the 1.0 to 2.0 μ m fractions.

Qualitative observation of the glass fiber substrates used for particle collection indicated the presence of a strawcolored oil material and a black, dust-like material.

The control efficiency as measured by the front half of the Method 5 Procedure varied from 67% to 94%. No correlation of control efficiency with the liquid to gas ratio (L/G) was found within the relatively narrow experimental range.

Analysis of the "back half" of the Method 5 train indicated the presence of considerable condensible material compared to the "front half," resulting in back-to-front ratios ranging from 2.7 to 5.5 at the scrubber inlet and 3.7 to 22 at the scrubber outlet. The measured control efficiency for these condensible materials ranged from 40% to 83%, much less overall than the front-half materials. These data indicate the need for careful evaluation of the potential impact of such fine particulate emissions upon visibility, since visibility reduction is generally dominated by particles 0.1 to $2 \mu m$ in size which tend to be formed by condensation.

Retort off-gas content of ammonia, hydrogen sulfide, carbon monoxide and the C_1 - C_6 hydrocarbons were substantial, that is, greater than those measured for particulate emissions. Emissions characterization showed that venturi scrubbing had no effect on other pollutants contained in the emission except for ammonia.

Surprisingly, some 50% to 75% (mass basis) of the ammonia was removed, primarily because of the rapid adsorption of the ammonia by the water. This unexpected result led to consideration of ammonia-bearing retort wastewater for H₂S control. A second test was conducted to explore the feasibility of this concept. As expected, H₂S removal was achieved at reasonable efficiencies with operation at appropriate L/G ratios, scrubbing fluid pH, and NH₃/H₂S molar ratio. Particulate control efficiency was also found to be enhanced by some 2% to 5% by the addition of NH₃.

EPA is currently investigating approaches to improve procedures for testing a variety of chemical systems controlling both oxidized and reduced forms of sulfur emissions from both direct and indirect-fired oil shale retorts. The mobile scrubber research unit is currently undergoing modifications to incorporate capabilities for ammonia and caustic scrubbing of the off-gases prior to their use as fuel. EPA is also planning additional tests to better define the efficiency of the Stretford system in removing H₂S from retort off-gas.

Wastewater Pollutants and Controls

Over the past several years, EPA has assessed the potential environmental impact of oil shale development, particularly in the Western Regions of the U.S. (Colorado and Utah). Detailed development plans submitted by the prospective developers indicate that, in the semi-arid region in which the major development will take place, the industry will be "water consumptive." This means that oil shale plants will have to import water to satisfy their process needs; therefore they will have no wastewater discharges ("zero discharge"). Because of the scarcity of water, these facilities will have to reuse water and be very conscious of optimizing the "partial treatment" of selective wastewater

streams for their "next best use." Developers have proposed that any "unusable" waste streams should be mixed with spent shale for moisturizing and ultimate disposal in the solid waste piles. This concept leads to the question of what should be the wastewater quality requirements for spent shale moistening, a question which cannot be answered at this time. EPA is investigating the wastewaters from various processing technologies (i.e., in situ, modified in situ, direct and indirect surface retorting) and will continue to sample wastewaters to further understand potential treatment problems. To date, EPA's most significant sampling and analytical effort to determine wastewater treatment efficiency was the field testing at Occidental's Logan Wash 7 and 8 burns during the summer of 1982.

These MIS oil shale retorts generate gases and an oil/water mixture from shale pyrolysis, combustion of carbonaceous residues, and decomposition of inorganic carbonates. Off-gases generated exit from the retort bottom and are brought to the surface for treatment. The retort oil/water mixture accumulates in the product collection sump at the retort bottom and is subsequently pumped out and treated for recovery of the bulk of the shale oil. The separated gas condensate and retort waters are the wastewaters which were studied at the Logan Wash field site.

At Logan Wash, treatability studies were conducted for three weeks on retort water using filter coalescing, flocculation/clarification, and steam stripping technologies (Figure 1). Also, studies were conducted for 14 weeks on gas condensate wastewater using filter coalescing, steam stripping, conventional and powdered activated carbon (PAC) activated sludge treatments, sand filtration, and granular activated carbon adsorption technologies (Figure 2).

Retort Water

Raw wastewater characterization data collected over the 16 days of retort water treatment tests are summarized in Table 6. As expected, the raw retort water contained high concentrations of total dissolved solids (TDS), ammonia, total Kjeldahl nitrogen (TKN), organics, sulfide, alkalinity, phenols, chlorides, and fluorides.

Ammonia and alkalinity were readily stripped from retort water (see Table 7). As expected, removals of these two

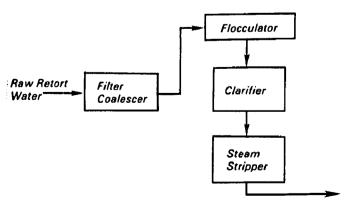


Figure 1. Retort water treatment scheme. Source: Day, 1983.

pollutants increased as the G/L ratio increased. Greater than 97% ammonia and 47% alkalinity removals were achieved with G/L ratios equal to or greater than 0.18 kg of steam per liter of feed water (1.5 lb/gal). TKN removals resembling ammonia removals (>99%) at G/L ratios as low as 27% to 54%, were also achieved and the TKN removals appear to depend on G/L ratio and feed phenol concentration. Using the G/L ratios between 0.07 kg/L (0.6 lb/gas) and 0.30 kg/L (2.5 lb/gas), incidental removals of organics ranged from 0 to 25% for dissolved organic carbon (DOC), 5% to 11% for soluble BOD₅, and 16% for COD.

Primarily, retort water was treated to remove oil and grease, suspended solids, ammonia, and alkalinity. The filter coalescer, flocculator/clarifier, and steam stripper in series were used to remove these pollutants. The overall treatment scheme was very effective for removal of ammonia and alkalinity. Relatively high sulfide, TKN, and phenols removals were also achieved. Due to low levels of oil and grease and suspended solids, the scheme was not effective in removing these pollutants, nor was it critical that these low levels be further reduced prior to the next series of treatment.

Gas Condensate

Raw gas condensate wastewater was analyzed for conventional pollutants during 14 weeks of gas condensate trials. The results of these analyses are summarized in Table 8. As expected, the raw gas condensate contained high concentrations of ammonia, TKN, organics, alkalinity, phenols, and sulfide. Analytical results for GC/MS organic compounds, metal, and DOC fractionation are presented in Reference 2.

Filter coalescing, steam stripping, conventional activated sludge treatment, sand filtration, and GAC adsorption comprised the overall treatment scheme for the gas condensate. The scheme was very effective in removing ammonia, organics, sulfide, alkalinity, and solids from the gas condensate (Table 9).

The other treatment scheme utilized coalescing, steam stripping, and GAC adsorption. The scheme was effective for removal of ammonia, organics, sulfide, alkalinity, and solids from the gas condensate. However, the performance of granular activated carbon adsorption was relatively poor and this scheme was apparently less effective for pollutant removal than was the scheme which included an activated sludge system.

In summary, pilot-scale field treatability studies on realtime oil shale wastewaters from Occidental in situ MIS retorts demonstrated that retort water had high concentrations of ammonia, TKN, alkalinity, dissolved organics, phenols, sulfide, and TDS; and gas condensate had high concentrations of ammonia, TKN, dissolved organics, alkalinity, phenols, and sulfide. Steam stripping was effective for removal of ammonia and alkalinity from the retort water. Steam stripping, activated sludge treatment (both conventional and PAC), sand filtration, and GAC adsorption effectively removed ammonia, alkalinity, TKN, nitrate, soluble COD, soluble BODs, DOC, phenols, sulfide, and TSS from the gas condensate. Pollutant-removal efficiencies across individual treatment units for retort water and gas condensate treatment schemes are presented in Tables 7 and 9, respectively.



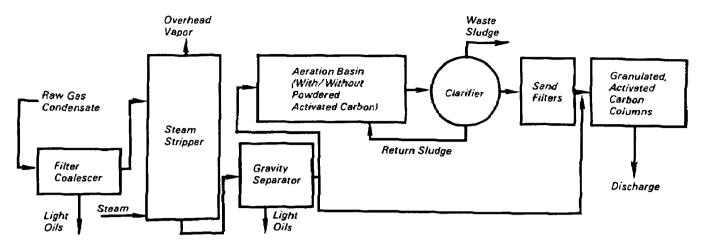


Figure 2. Gas condensate wastewater treatment schemes. Source: Day, 1983.

Table 6. Raw Retort Wastewater Characteristics*

	Number of analyses	Concentration, mg/L		
Parameter	performed	Range	Average	
Total COD	4	3,400-6,000	4,700	
Soluble COD	4	3,100-5,400	4,100	
Total 80Ds	4	2,200-4,000	3,200	
Soluble BODs	4	1,900-2,200	2,000	
Dissolved organic carbon (DOC)	5	1,400-2,300	1,700	
il and grease	(5)	(50-170)	(110)	
VH ₃ -N	6(5)	1,600-3,900	2,200	
		(1,700-3,700)	(2,200)	
KN	6(2)	1,700-3,000	2,100	
		(2,100-2,200)	(2,100)	
IO ₃ -N	5	3,0-4.8	4.3	
lkalinity as CaCO₃ to pH 4.5	6(4)	12,000-17,000	14,000	
		(13,000-16,000)	(14,000)	
ulfide	3	50-130	90	
hosphorus	4	0.8-2.1	1.5	
yanide	(4)	(<0.02-0.08)	(0.05)	
henols	(5)	(47-70)	(56)	
luorides	7	36-63	45	
hlorides	6	500-1,000	800	
SS	8	27-93	<i>59</i>	
SS	6	23-78	5 4	
os -	6(1)	10,000-15,500	14,000	
	·	(15,000)	(15,000)	
⊬°	(10)	(8.6-9.4)	(8.8)	
emperature ^c	(10)	(21-46)	(35)	

Data reported in parentheses are from grab samples. The rest of the data are from composite samples.

Source: Day, 1983.

PpH is reported in standard pH units. *Temperature is reported in °C.

Table 7. Pollutant Removal Efficiencies Across Individual Units for Retort Water Treatment Scheme^{a,b}

Parameter	Filter Coalescer	Flocculation/ Clarification ^c	Steam Stripper ^d
Oil and grease	6		
Ammonia			<i>97</i>
TKN			88
Soluble BODs			5
DOC			4
Phenols			32
TSS	21	0	
VSS	20		
Alkalinity as CaCO ₃ to pH 4.5			47
Fluorides		7	
Chlorides		11	

[&]quot;Average removal efficiencies are reported.

Source: Day, 1983.

Solid Waste Environmental Impacts and Control

Analysis of solid waste environmental impacts and controls for an oil shale facility presents unique problems caused by the very large volume of waste produced. A typical 50,000 bbl/day (7,949 m³/day) facility fed by 30 gal/ton (103 L/10³ kg) shale will produce 22-26 million tons/year (20-24 x 10³ kg/yr) of spent shale alone, which over an operating life of 30 years, would cover an area of 3.5 square miles (9 km²) to a depth of 150 feet (45.7m). (Bates and Thoem, 1980.) Hence, even though this waste may not be hazardous, it will require special handling and control to prevent environmental impacts which would include:

- Degradation of surface water quality by runoff.
- Degradation of air quality by release of vapors or dust.
- Siltation of surface streams by erosion.
- Degradation of air quality from auto ignition,
- Aesthetic impact.
- Mass failure of disposal piles threatening life or property.
- Degradation of surface and groundwater quality by leachates.

Technologies to prevent or control most of these problems have already been developed for other mining industries, or have been demonstrated on a small scale for oil shale. Runoff can be collected and treated, infiltrated or evaporated, and if the disposal site is top soiled and revegetated,

Table 8. Raw Gas Condensate Wastewater Characteristics

	Number of analyses	Concentratio	on mg/l
Parameter	Performed	Range	Average
Total COD	2	2,000-4,100	3,100
Soluble COD	37 (13) *	1,400-4,100	2,700
		(2,000-4,200)	(2,800)
Soluble BODs	8	600-1,000	800
DOC	<i>33</i>	500-1,400	890
Oil and grease	(13)	(1.8-76)	(18.6)
NH ₃ -N	40 (33)	6,100-14,000	9,000
		(4,800-11,000)	(8,200)
7KN	21	1,300-9,700	6.800
NO ₃ -N	16	0.3-3.0	1.1
Alkalinity as CaCO ₃ to pH 4.5	27 (19)	1,000-37,000	31,000
		(22,000-40,000)	(31,000)
Suffide	17	18-190	72
Phosphorus	6	<0.01-1.3	0.26
Cyanide	(4)	(<0.02-0.11)	(0.04)
Phanois	(21)	(70-150)	(120)
Fluorides	9	0.07-1.05	0.43
TSS	8	<5-14	7
VSS	8	<5-6	5
TDS	6	48-140	98
ρH ^b	(~560)	(8.3-8.7)	(8.5)
Temperature ^c	(~560)	(26-45)	(34)

^{*}Data reported in parentheses are from grab samples. The rest of the data are from composite samples. * *pH is reported in standard pH units.

Source: Day, 1983.

Blanks indicate data not collected.

^cLime dosage at 90 mg/L.

 $^{{}^{}d}G/L = 0.18 \, kg/L \, (1.5 \, lb/gal).$

^cTemperature is reported in °C.

Table 9. Pollutant Removal Efficiencies Across Individual Units for Gas Condensate Treatment Scheme^{a,b}

Parameters	Filter Coalescer	Steam Stripper ^c	Activated Sludge Treatment ^d	Sand Filter	GAC Adsorption Column*
Oil and grease	28				
Ammonia		<i>99</i>	6		
TKN		96			
Soluble COD		56	<i>59</i>		<i>95</i>
Soluble BOD ₅			91		70
DOC		60	<i>52</i>		8 9
Phenols		29	93		99.5
Sulfide		97			
<i>1SS</i>				70	
Alkalinity as CaCO ₃ to pH 4.5		99			

^{*}Average removal efficiencies are reported.

Source: Day, 1983

runoff will be of a quality equivalent to that from undisturbed areas. Emission of vapors can be prevented by removal of volatiles from wastewater disposed with the shale and by cooling the shale prior to disposal. Fugitive dust can be controlled with water sprays or chemical binders during placement, and by vegetation after reclamation. Technology to revegetate spent shale, through the use of top soil covers, irrigation, water harvesting techniques, fertilization, and use of selected plant species has been demonstrated in small-scale field studies. Good reclamation techniques will substantially improve the appearance of the disposal sites and will control erosion and prevent generation of wind blown fugitive dust. Presently EPA studies are assessing the auto ignition potential of carbonaceous retorted shales and fine grained raw shale wastes. Preliminary indications from these studies are that these materials have about the same or less potential for auto ignition than do bituminous coals. Good engineering design similar to that used for earth-filled dams might prevent mass failure of disposal piles if moisture movement within the piles can be controlled. The extent and nature of moisture movement within the spent shale disposal pile remains unknown and is the subject of much controversy.

When precipitation falls on a disposal site, some runs off, some evaporates, and some infiltrates. Of the moisture which infiltrates, most, and perhaps all, will be transpired by plants on the reclaimed disposal site. However, any moisture which infiltrates too deeply to be transpired will become net infiltration into the retorted shale. The quantity of this net infiltration into the disposal pile in conjunction with the hydraulic properties of the retorted shale are particularly significant because they determine the quantity of leachate produced, and the potential for a portion of the disposal pile to become saturated and fail. Care must also be taken in spent shale pile location and design to prevent groundwater, springs, and streams from infiltrating the pile.

In cooperation with the oil shale industry, EPA is currently sponsoring laboratory studies at Colorado State University to determine the hydraulic properties of spent oil shales; soon to be initiated are studies of codisposal of wastewaters with retorted shale. Field determinations of the quantity of net infiltration for western Colorado disposal sites will also be initiated. Current laboratory studies are focused on determining the nature of leachate produced from various retorted and raw shales, and the permeability and water holding capacity of retorted shales for various compactive efforts and loading conditions.

Retorted oil shales will be placed in disposal sites at relatively low moisture contents, generally between 5% and 20%, as required for dust control, and to achieve desired compaction. As water penetrates into the pile from initial irrigation or seasonal precipitation, a portion of the water will be in storage behind the wetting front. The water thus held in storage is not available to extend the wetting front deeper into the pile. Given the huge size of proposed spent shale disposal piles and the relatively low precipitation in western Colorado and Utah, this water holding capacity will be a signiificant factor influencing moisture movement in the shale pile. Table 10 shows water holding capacities for three retorted shales. Water holding capacities are quite large but are inversely related to initial compaction and to loading pressures. These values are important, not only as a measure of sorptive capacities for net infiltration, but also as an indication of whether the bottom of a disposal pile will saturate from loading pressures given an initial moisture content and compactive

In addition to waterholding capacity, the hydraulic conductivity or permeability is obviously important in assessing potential moisture migration in a retorted shale pile. An apparatus for measuring hydraulic conductivity for various compactive efforts and loading pressures is illustrated in

Blanks indicate data not collected.

 $^{^{}c}G/L = 0.19 \text{ kg/L } (1.6 \text{ lb/gal)}$ average.

⁴Hydraulic retention time = 16 hours, sludge age = 32 days.

^{*}Contact time = 19 minutes.

Table 10. Water Holding Capacity of Retorted Shales (Expressed as Weight % Water/Dry Solid)

Sample	14.7 psi 0.10 MPa	44.1 psi 0.30 MPa	73.5 psi 0.51 MPa	147 psi 1.01 MPa	200 psi 1.38 MPa
LURGI				22.4	50.5
No Compaction (Ash)	73.6	62.0	<i>64.5</i>	<i>63.1</i>	<i>59.5</i>
No Compaction	27.5	27.6	<i>26.9</i>	25 .3	1 <i>5.5</i>
1.30 g/cc (Ash)	62.4	62.3	62.2	<i>62.0</i>	61.7
1.45 g/cc (Ash)	60.2	58.7	<i>55.6</i>	<i>55.</i> 5	55.2
1.60 g/cc (Ash)	47.2	46.3	45.8	44.4	43 .7
1.60 g/cc	20.7	20.2	19.8	19.8	19.0
TOSCO II					
No Compaction	48.0	45.8	45.9	43.8	44.7
1.30 g/cc	42.2	42.0	41.9	41.6	41.4
1.45 g/cc	36.0	33.8	<i>32.9</i>	32.1	<i>30.5</i>
1.60 g/cc	34.6	33.5	32.1	30.8	30.5
HYTORT					
1.30 g/cc	35.2	33 .7	32. <i>6</i>	31.8	31.0
1.45 g/cc	31.0	27.6	<i>25.3</i>	23.8	23.2
1.60 g/cc	30.5	30.3	28.9	25.4	24.6

Source: McWhorter, 1982a.

Figure 3. Table 11 presents permeability values for several given initial moisure contents and compactive efforts as these samples were subjected to increasing loading pressures. Generally, the hydraulic conductivity decreases sharply with increased initial compaction but decreases only slightly with increased loading pressures. This indicates that the desired permeability values should be achieved by initial compaction at the time of placement rather than depending upon secondary compaction through loading.

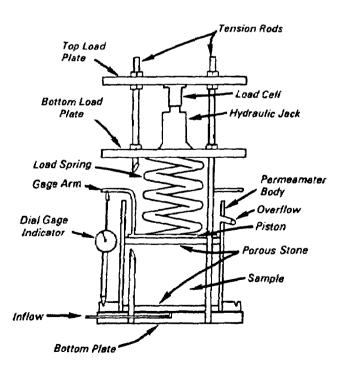


Figure 3. Schematic of permeameter. Source: McWhorter, 1982a.

As previously discussed, net infiltration, as well as water holding capacity and permeability, are influenced by engineering design and will be important in determining the quantity of leachate produced. Also of interest is obtaining an estimate of quality of leachate from either raw shale storage piles or retorted shale disposal sites. Standardized tests such as the RCRA EP (acetic acid) or ASTM (water) shaker tests as well as various column leaching tests have been used for this purpose. Tables 12 and 13 present major ion concentrations in leachate from raw shale, retorted shale, and when available, field lysimeters. The apparatus for producing leachate from constant rate injection into a dry packed column is illustrated in Figure 4. Column leachate data varies depending upon the quantity (pore volumes) of water that has passed through the material. Data presented are for initial leachate produced and for leachate produced after approximately one pore volume (PV) has passed through the material. (Note that the material has been contacted by one more pore volume than shown since the column must be wetted with one complete pore volume before any leachate is eluted.)

The data in Tables 12 and 13 indicate that none of the laboratory methods employed provides a good indication of what happened under field conditions. Generally, the ASTM and RCRA shaker tests seem to correlate more closely with the column-produced leachate after one or more pore volumes, while the initial column-produced leachate correlates more closely with the field data. Logically, this might be expeted since the RCRA and ASTM tests contact the shale with much more water than occurs under field conditions. Generally, all the laboratory methods are indicative of what will be leached but do not provide a good indication of the concentration of species in solution. Hence, the results of laboratorty leaching tests on raw or retorted oil shales should be interpreted with caution because results form actual disposal may be significantly different. Presently column tests are being conducted with the material being packed into the columns in a pre-wetted state rather than dry as it is felt this may better reflect field conditions. Results from this procedure will be reported in subsequent papers.

Table 11. Summary of Hydraulic Conductivity Measurements (Constant Head)

Material	Water			Permeability cm/s		
	%	g/cm³	50 psi 0.34 MPa	100 psi 0.69 MPa	200 psi 1.38 MPa	
TOSCO II	20.8	1.56	6.8 x 10 ⁻⁶	6.2 x 10 ⁻⁶	5.6 x 10 ⁻⁶	
	11.0	1.39	5.6 x 10 ⁻⁵	4.6 x 10 ⁻⁵	3.9 x 10 ⁻⁵	
	11.4	1.29	6.7 x 10 ⁻⁵	4.0×10^{-5}	2.5 x 10 ⁻⁵	
LURGI-RG-I	26.6	1.41	1.0 x 10 ⁻⁶	6.5×10^{-7}	6.5 x 10 ⁻⁷	
	10.4	1.33	3.0 x 10 ⁻⁵	1.9 x 10 ⁻⁵	2.0 x 10 ⁻⁵	
*LURGI-ULG-I	dry	1.81	8.3 x 10 ⁻⁵			
*LURGI-RB	dry	1.22	1.2 x 10 ⁻⁵			
PARAHO	20.0	1.67	4.7 x 10 ⁻⁷	4.2×10^{-7}	4.5×10^{-7}	
	10.0	1.36	9.7 x 10 ⁻⁴	7.1 x 10 ⁻⁴	2.5 x 10 ⁻⁴	
*PARAHO	dry	1.09	4.6 x 10 ⁻⁴			
*TOSCO II	dry	1.46	2.8 x 10 ⁻⁵			

^{*}Leaching columns (Constant Rate Injection).

Source: McWhorter, 1982a.

Table 12. Raw Shale Leachates by Leaching Method (mg/L)

Location		C-b			С	-8	
Test	RCRA	ASTM	Field (mean)	ASTM	Column*	Column	Field (mean)
Pore Volume					Initial	.73 PV	<u>, </u>
pН	7.67	8.57	7.7	8.22	8.17	8.08	7.5
Ec (μS/cm at 25°C)	4,350	85 0	7,000	2,500	39,000	5,800	20,000
HCO ₃	2,461	141	177	150	183	86.9	384
CO ₃	4.9	2.2		1.1	1.16	0.45	
TDS	5,884	710	6,450	2,430		••	30,080
CI	1.9	2.8	14.2	84.5	2,433	16	163
SO ₄	154	315	3,680	1,480	25,224	4,110	20,500
F		2.4	7.8	1.5	18.5	5.8	10.4
Mg	252	38	218	173	6,465	680	4,490
Na	36	76	1,045	117	4,660	236	880
Ca	1,092	50	451	350	430	472	633
K	3.5	14	7.8	7.0	53	4.0	7.8

^{*}Column leaching by constant rate injection method initial values and after 0.73 pore volumes.

Source: McWhorter, 1982b.

Shale Paraho	Parameter Pare Volume	Field	RCRA	ASTM	Column Initial	Column 0.918
	pH Ec (μS/cm	9.57	9.27	12.05	11.55	12.35
	at 25°C)	21,100	4,600	2,800	9,230	6,250
	HCO ₃		2,723	2,800 5	15.3	4.8
	CO3		217	2 3 6	232	463
	SO ₄	12,350	226	536	3,840	2,045
	C/	<i>526</i>	29	7	49	14
	F	11.9		13.5	21	11.4
	Mg	<i>7.</i> 7	484	0.5	1.6	1.7
	Na	5.591	37	145	1,500	285
	Ca	421	724	266	610	670
	K	834	6.5	31	140	38
TOSCO II	Parameter Pore Volume	Field	RCRA	ASTM	Column Initial	Column 1.03
	PH	<i>8</i> -9	7.72	8.69	9.24	9.21
	Ec IµS/cm					
	at 25°C)	10,000	5,710	2,650	35,080	5,180
	HCO₃		3,325	191	619	188
	CO ₃				46	13
	SO ₄	30,270	229	1,130	25,000	2,470
	C1	••	22	10	178	13
	F	13		20.2	27	29.5
	Mg	156	81	35	628	60
	Na	10,270	131	545	10,095	945
	Ca	463	1,872	31	545	83
	K	110	3.9	8	89	11
LURGI*	Parameter Pore Volume	Field	RCRA	ASTM	Column Initial	Column 0.621
	PH		8.67	11.85	12.24	11.93
	E (μS/cm at 25°C)	·-	5,650	4,270	59,500	4,250
	HCO ₃		2,940	6.9	10.5	7
	co,		59	210	775	203
	SO ₄		880	2,290	34,000	2.070
	CI		19	17	2,250	15
	F	••		6.3	26.4	7.6
	Mg		430	0.4	3.5	0.3
	Na	••	<i>55</i>	275	18,770	325
	Ca		1,479	713	535	575
	K		11	64	1,464	150

^{*}Several Lurgi shales have been tested and results differ slightly. Example provided is Lurgi shale provided by Rio Blanco Oil Shale.

Source: McWhorter, 1982a, for laboratory data. Bates & Thoem, 1980, for Paraho field data. Metcalf & Eddy Engineers, 1975, for TOSCO field data.

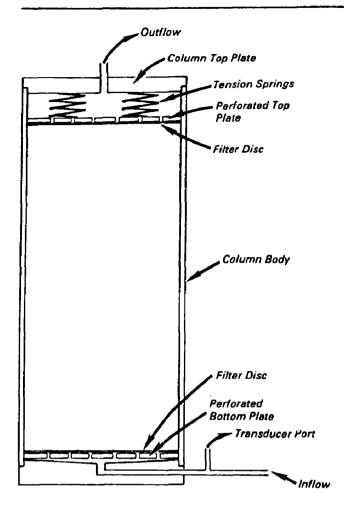


Figure 4. Schematic of leaching column—constant rate injection tests. Source: McWhorter, 1982a.

References

Lovell, R. J., S. W. Dylewski, and C. A. Peterson, IT Environscience, *Control of Sulfur Emissions from Oil Shale Retorts*, EPA-600/7-82-016, U.S. EPA, Cincinnati, OH 45268, 1982.

Day, Duane R., Desai, Bharat O., and Liberick, Walter W., The Treatability of Wastewaters Produced During Oil Shale Retorting, 16th Oil Shale Symposium Proceedings, Colorado School of Mines Press, Golden, CO, August 1983, pages 512-533.

Bates, E. R. and Thoem, T. L., Editors, 1980, Environmental Perspective on the Emerging Oil Shale Industry, EPA-600/2-80-205a, U.S. EPA, Cincinnati, OH 45268, page 85.

McWhorter, D. B., 1982a, Leaching and Hydraulic Properties of Retorted Oil Shales, unpublished report, U.S. EPA, Cincinnati, OH 45268.

McWhorter, D. B., 1982b. Quality and Quantity of Leachate from Raw Mined Colorado Oil Shale-Interim unpublished report, U.S. EPA, Cincinnati, OH 45268.

Metcalf & Eddy Engineers, 1975. Water Pollution Potential from Surface Disposal of Processed Oil Shale from the TOSCO II Process, A Report to Colony Development Operation at Atlantic Richfield Company, Operator, Volume 1, page A4-6, mean values for twelve samples.