

EVALUATION OF POTENTIAL CONTROL TECHNOLOGIES
FOR SHALE OIL RECOVERY OPERATIONS

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INTRODUCTION

For the past several years, under contract to the U.S. Environmental Protection Agency (Industrial Environmental Research Laboratory) in Cincinnati, TRW and Denver Research Institute have studied various aspects of shale oil development. These studies have included emissions testing and laboratory analysis, environmental assessment, and evaluation of existing environmental control technologies. This paper presents a summary of findings obtained for specific environmental control needs of oil shale operations.

The following discussion is limited to evaluation of technologies for control of: gases exiting from the retort; mining, crushing and material-handling particulate emissions; and process wastewaters, containing ammonia and sulfur. Many processes are available or under development for the extraction of oil from shale. Rather than use specific technologies, general extraction technology types (including above ground, and modified in situ retorts) are used for emission characterization.

CONTROL OF SULFUR EMISSION IN GASES EXITING FROM THE RETORT

Depending upon the process employed, oil shale retorting yields either large quantities of low-Btu (900 kcal/m^3) or lesser amounts of high-Btu (7000 kcal/m^3) gas. The main constituents to be removed, before the gas can be used as fuel, include hydrogen sulfide (H_2S) and ammonia (NH_3). The majority (99%) of the ammonia and a small amount

of hydrogen sulfide (a few %) are separated out in the condensate from the product cooling unit following the retort. The remaining H_2S must be removed by a separate control process. The presence of other sulfur compounds (besides H_2S , such as carbonyl sulfide and carbon disulfide), which have not been confirmed, would greatly increase the difficulty of controlling this stream.

A variety of processes for concentration and removal of H_2S from gas streams have been used in the petroleum, chemical, and natural gas industries, and new processes (some specifically designed for application to synthetic fuels processes) are under development. The enriched stream can be fed to a downstream process (such as Claus or Stretford) for recovery of the sulfur. Tail gas from these sulfur recovery processes sometimes requires further treatment before it is environmentally acceptable for release to the atmosphere. Choice of which H_2S removal, sulfur recovery and tail gas treatment process is to be used for a particular retort gas will depend upon: the concentration of H_2S in the retort off-gases, concentration of H_2S in the removal process gas stream, local environmental regulations, and the presence of constituents that would contaminate or interfere with a process operation.

Processes for the removal of H_2S from the retort-exiting gases include: the various amines (e.g., MEA, DEA, etc.); physical solvents (e.g., selexol); carbonates (e.g., Benfield); mixed solvents (e.g., sulfinol), and redox (e.g., Stretford). Each of these

offers both advantages and disadvantages. In order to evaluate the potential of each of these process types in oil shale development, retort-exiting gas compositions were examined. Table 1 presents the composition of typical gases for both a low and a high Btu gas (Jones, 1976 and Cotter et al., May 1977).

Table 1. Composition of retort exiting gases.

RETORT OFF GAS COMPOSITION		
CONSTITUENT	LOW-BTU GAS VOL. %	HIGH-BTU GAS VOL. %
H ₂ S	0.2	2.4
CO ₂	17.9	10.6
CH ₄	1.9	22.5
C ₂ ⁺	3.3	15.8
CO	1.6	1.9
H ₂	3.6	17.4
N ₂ , O ₂ , & Ar	53.6	0.3
NH ₃	0.2	0.9
H ₂ O	17.6	28.1

The removal of CO₂ from retort-exiting gases will not be required for the gas to be used on-site. The cost of CO₂ removal would far exceed the benefit derived from the higher heating value of the gas. Many of the H₂S removal processes are not selective towards H₂S and remove CO₂ as well. CO₂ removal would also produce a more dilute H₂S stream than a selective removal process, thereby increasing sulfur recovery costs. For the low-Btu gas case, H₂S concentration in the off-gas from acid gas treatment would be 1.1 percent versus 0.2 percent in untreated gas.

Amine solvents are generally not selective between H₂S and CO₂. Physical solvents are more selective; however, they are most effective and economical when high partial pressures of H₂S are encountered. Carbonates, likewise, are partially selective toward H₂S but, like physical solvents, require moderate to high pressures for economical operation. Mixed solvents offer little H₂S selectivity. Redox processes

offer the advantage of combined H₂S removal and sulfur recovery in one step. The economics of a Stretford redox process applied to a low-Btu retort gas are shown in Table 2 (Cotter and others 1977).

Disadvantages of the Stretford include: solution degradation when certain contaminants are present (HCN causes thiocyanate

Table 2. Estimated annual Stretford unit operating costs (Basis 168,000 m³/hr of low-Btu gas).

CAPITAL INVESTMENT COST	\$6,300,000
OPERATING COST	
CAPITAL CHARGE (15%)	942,000
LABOR	90,400
SUPERVISION	30,100
PAYROLL BENEFITS	30,100
MAINTENANCE	188,400
ELECTRICITY	240,100
FUEL	7,800
CATALYSTS AND CHEMICAL	198,900
OVERHEAD	154,500
	<u>\$1,882,300</u>

formation without pretreatment); larger absorbers are required where high CO₂ concentrations are present; and inability to remove COS and CS₂ when present. Sulfur compounds such as these can be treated by processes such as the Beavon process. All sulfur compounds are converted to H₂S in the Beavon process and then removed in a conventional Stretford unit.

PARTICULATE EMISSION CONTROL FROM MINING, CRUSHING, AND MATERIAL HANDLING

Particulate emissions from mining, crushing, and material handling operations are roughly proportional to the amount of material handled and the size of feed required. It is estimated, therefore, that open pit mines and processes using fine shale feed would involve the largest particulate emissions. For instance, open pit mining has large particulate emissions due to both mining of the overburden, as well as the shale, and the open nature of the mining operations. Modified in situ mining,

with its rubblizing operation, is less well understood from a particulate emissions standpoint. However, large amounts of particulates may be released during the rubblizing operations. It is unknown how much of these particulates will reach the above-ground environment.

Only those operations which lend themselves to being enclosed (e.g., crushing), are considered. The quantities of particulates from the various crushing and handling operations required for surface retorting that must be removed are presented in table 3. Table 4 presents annual operating cost comparisons for baghouses vs. wet scrubbers when designed to satisfy the design requirements indicated in table 3. Settling tanks and recirculation loops have been made an integral part of the wet-scrubber alternative; their costs have been included in the comparison.

An investigation of appropriate fabrics determined that dacron is a suitable material for all baghouse collection systems except the retorted shale discharge and moisturizer exhaust of an above-ground retort. The retorted shale discharge would be hotter than the dacron limit of 121°C; the gas would contain SO₂, ammonia and hydrocarbons. Teflon may be an appropriate material for the discharge application. The moisturizer exhaust would not be an acceptable baghouse application, since the stream would be satur-

ated with water vapor. Electrostatic precipitators have not been evaluated in detail due to the need for further data on the resistance characteristics of both raw and spent shale.

SULFUR AND AMMONIA REMOVAL FROM PROCESS WASTEWATERS

Process waters containing hydrogen sulfide and ammonia originate from: the pyrolysis of kerogen, the release of free and inorganically bound water from raw shale and the combustion of organic material in shale. Many other components will also be present in these waters (e.g., carbonates, bicarbonates, solids, etc.) (Cotter and others 1977). However, only control technologies for sulfur and ammonia removal will be discussed here.

Process waters will contain high concentrations of ammonia (14,000-17,000 mg/l) and lesser amounts of the dissolved H₂S (0-400 mg/l) (Cotter and others 1977). These contaminants may be readily removed by application of steam stripping - a method widely used in industry for control of these components. The common stripping approach is the counter-flow method in which the sour water moves downward through a tray or packed tower while an ascending flow of stripping steam removes NH₃ and H₂S from the wastewater. The exit gases will need treatment to recover ammonia and sulfur

Table 3. Summary of estimated dust mass rates.

SUMMARY OF ESTIMATED DUST MASS RATES (16,000 CUBIC METERS PER DAY PRODUCTION RATE)			
EMISSION STREAM	INLET, KG/HR	OUTLET, KG/HR	DESIGN COLLECTION EFFICIENCY, %
RAW SHALE BLDG.	292	0.9	99.7
SECONDARY CRUSHING	1,870	5.6	99.7
SURGE BINS	921	2.8	99.7
TERTIARY CRUSHING	8,415	25.2	99.7
RETORT FEED	8,415	25.2	99.7
RETORT DISCHARGE	10,682	22.9	99.7
MOISTURIZERS		41.1	

Table 4. Estimated twenty-year cost comparison.

ESTIMATED TWENTY YEAR COST COMPARISON, BAGHOUSE AND WET SCRUBBERS		
EMISSION STREAM	BAGHOUSE \$M	WET SCRUBBER/SETTLING TANKS \$M
RAW SHALE BLDG.	932	935
SECONDARY CRUSHING	525	518
SURGE BINS	474	605
TERTIARY CRUSHING	1597.5	2,331
RAW SHALE FEED	3108	3,308
RETORTED SHALE DISCHARGE	3108	3,308
TOTAL	9744.5	11,005

before discharge to the atmosphere. The addition of mineral acid is sometimes practiced to enhance the removal of fixed ammonia from wastewaters. Table 5 presents an estimate of capital costs and utility requirements for a stripping tower, to handle typical process water streams (Bonham and Atkins 1975). Water, acceptable for ponding and/or evaporation, may be produced after steam stripping. An effluent with less than 50 ppm NH_4^+ and 10 ppm H_2S should be achievable.

Table 5. Capital costs and utility consumption for stripping and ammonia recovery.

CAPITAL COSTS AND UTILITY CONSUMPTION FOR STRIPPING AND AMONIA RECOVERY (ANNUAL COSTS, BASIS: 2536 l/min, CONTAINING 4800 mg/l, NH_3 ; 350 mg/l, H_2S)		
	STRIPPING TOWER	CHEVRON
CAPITAL COST (MILLION \$)	0.91	2.44
ELECTRICAL REQUIREMENTS (KW)	142.00	406.00
STEAM: MEDIUM PRESSURE (10 MPa) (KG/HR)	-	19,080.00
LOW PRESSURE (3.4 MPa) (KG/HR)	61,720.00	53,400.00
COOLING WATER (l/min)	1,510.00	610.00
VALUE OF AMONIA RECOVERED (@ \$330/tonne)	-	94,000.00

Treatment processes, such as the Chevron or Phosam wastewater treatment, may also be applicable where recovery of the ammonia is important. In this process, the sour water is first sent to the sour water stripper where steam is heated under pressure and contacted with the wastewater. The overhead vapor contains H_2S essentially free from NH_3 . This stream can be combined with other gas streams and treated in the Stretford unit for sulfur recovery. The bottom liquid, containing ammonia and some H_2S , is withdrawn and sent to the ammonia stripper.

In the ammonia stripper, the vapor stream is partially condensed yielding an ammonia-enriched vapor. A portion of the condensate is returned to the H_2S stripper. The enriched vapor is once again partially condensed to form a vapor essentially free of H_2S .

The H_2S -free ammonia stream is sent through a scrubber, condensed and dried,

resulting in a final anhydrous liquid ammonia. Estimated costs and utility requirements for Chevron ammonia recovery are shown in table 5 (Bonham and Atkins 1975). As can be seen in table 5, much of the higher operating cost of the Chevron process, compared to conventional steam stripping, may be offset by sales of the recovered ammonia.

AREAS REQUIRING FURTHER STUDY

Further study is required in both the process effluents and emissions characterizations and in demonstrating control technologies before detailed studies of control technology effectiveness and costs can be made.

Demonstrations are needed to provide assurance of control technology effectiveness and reliability as well as investigating low cost alternatives. Fine particulate control devices have been identified as an especially critical need. Processes for the removal of organic constituents from both in situ and above-ground retort water need to be evaluated.

A number of tentative conclusions reached in the TRW-DRI studies have necessarily been based on information reported by process developers as well as field measurements conducted during the course of the investigation. Much more definitive process information is needed to support further environmental studies. Further studies on emissions from mining, crushing, and material handling (both size distributions and quantities) need to be undertaken. Sulfur species present in retort-exiting gases, as well as other components, need better definition. Treatability studies of process waters will also need investigation if accurate definition of environmental problems and solutions is to be accomplished.

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