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CONTROL OF SULFUR EMISSIONS  
FROM OIL SHALE RETORTING USING  
SPENT SHALE ABSORPTION  
PILOT PLANT TESTING

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NOTICE

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A. BACKGROUND

Control of sulfur emissions constitutes a major portion of the environmental control cost for oil shale facilities. For example, the Denver Research Institute estimated costs (in 1980 dollars) in the range of \$1 to \$3 per barrel of shale oil produced(1,2,3.). These substantial sulfur control costs have encouraged developers to seek less costly but equally or more effective methods for limiting sulfur emissions. Recently, a strong industry trend has been to look toward the potential for combusting carbonaceous retorted shale to recover its energy value (a plus in terms of economics and resource conservation), while exploring the possibility of absorbing the sulfur gases produced during retorting onto the calcined carbonate material present after combustion of retorted western oil shale.

EPA awarded a contract to J & A Associates to investigate the environmental advantages/disadvantages of absorbing SO<sub>2</sub> onto combusted

retorted oil shale. The objective of this program was to obtain more information in support of its PSD (Prevention of Significant Deterioration) permitting decisions on sulfur control and to investigate whether emission of other pollutants such as nitrogen oxides (NO<sub>x</sub>) and trace elements might be significantly increased in the process. The program was done in two phases. Phase I developed an engineering assessment and costs for application of this sulfur absorption process to selected leading retorting processes. In Phase II, experimental work in an integrated oil shale pilot plant defined operability and proof of principle and defined trace element emissions.

B. THE ASSP CONCEPT

The ability of combusted carbonate-containing spent shale to absorb SO<sub>2</sub> gives rise to a novel concept for controlling sulfur emissions in oil shale plants. This concept will be referred to as ASSP which stands for Absorption on Spent Shale Process.

The ASSP concept has several potential advantages over conventional sulfur removal technologies:

- o The sorbent is cheap and inherently abundant in oil shale plants.
- o The process requires combustion of the spent shale which is already incorporated into several of the retorting technologies or which would be a useful add-on to recover residual carbon values.
- o Since non-H<sub>2</sub>S compounds are converted to SO<sub>2</sub> by combustion, ASSP could represent a more efficient removal relative to gas sweetening processes which only remove H<sub>2</sub>S.

The ASSP concept uses a fluidized transport system to combust either raw or retorted shale, thereby providing the vehicle for converting sulfur compounds to SO<sub>2</sub> and absorbing the SO<sub>2</sub> in the shale matrix. The concept envisions either a conventional dense-phase fluidized bed or a dilute-phase contactor (lift pipe). Key elements of the process are shown in Figure 1.

### C. PHASE I: CONCEPTUAL DESIGN AND ECONOMICS

For evaluation purposes, specific projects were chosen as representative of the three retort types:

- o Direct heated - Modified In-Situ (MIS) with Unishale C - Cathedral Bluffs
- o Indirect heated - Unishale B - Union Oil
- o Integral Combustor - Lurgi - Rio Blanco  
- Unishale C - Union Oil

This study assumed that MDEA (Methyldiethanolamine) absorption is used to remove acid gases from indirect heated retort gases and that regenerated acid gases are burned in the ASSP combustor. MIS gases were assumed to be processed in the ASSP combustor without pretreatment.

For comparison purposes, conventional sulfur removal processes were evaluated:

- o Direct heated - Case A: Unisulf + Flue Gas Desulfurization on MIS gases  
Case B: Unisulf + Stretford on MIS gases
- o Indirect heated - Unisulf
- o Integral Combustor - DEA + Stretford on Lurgi  
- Unisulf on Unishale C

TABLE 1. COST COMPARISON FOR ASSP

Retort Type	Direct Heated		Indirect Heated	Integral Combustor	
	Case A	Case B		Lurgi	Unishale C
Retorting Process	MIS/Unishale C	Unishale B	Lurgi	Unishale C	
ASSP Incremental Capital Cost, \$10 <sup>6</sup>	-71.2	63.2	+90.2	-13.0	-32.1
ASSP Incremental Annual Operating Cost, \$10 <sup>6</sup> /yr.	+10.83	+12.07	-19.21	-2.29	-1.56
Plant Capacity TPSD (kg/sec)	36,200 (380)	13,600 (143)	27,200 (286)	119,000 (286)	27,200 (1251)

Source: Reference (4).  
TPSD: Tons Per Stream Day.

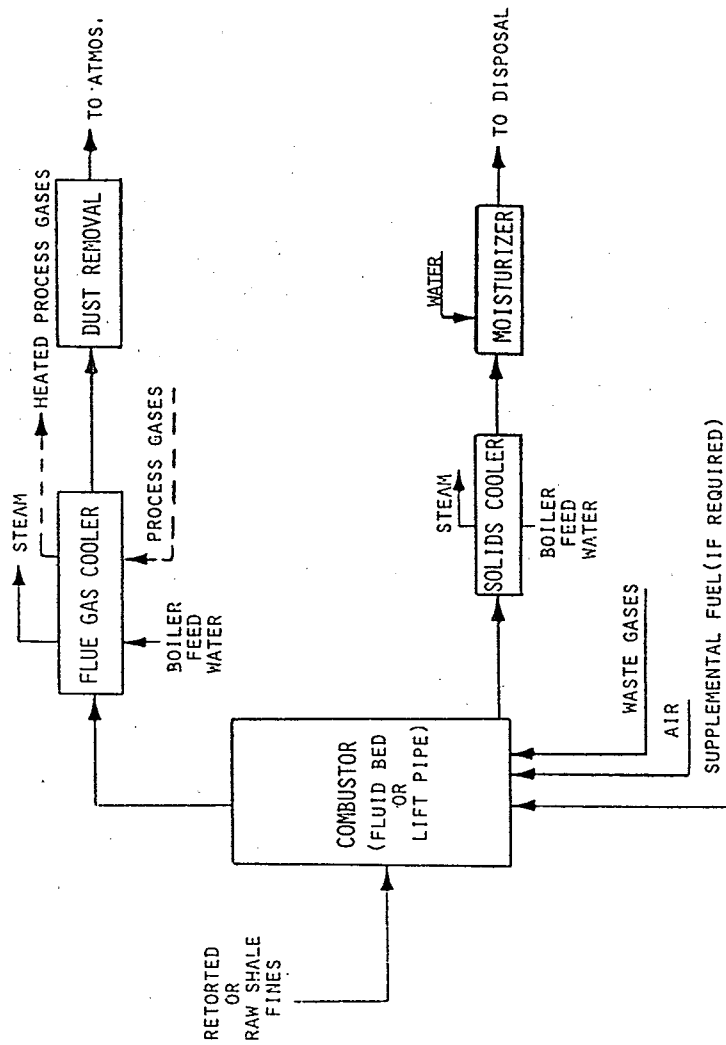


Figure 1. ASSP Process Flow Diagram

Major equipment costs were taken from EPA Pollution Control Technical Manuals (PCTMs)(1,2). ASSP equipment was sized and costs factored from in-house data and PCTMs. Costs were factored to first quarter 1985.

A discussion of the Phase I work is given in more detail in a previous paper.(4)

Results of the cost study showed changes in incremental capital and operating costs for ASSP relative to conventional processing in Table 1.

These cost comparisons show that the best potential for application of ASSP are those processes which already have a spent shale combustor integrated into the retorting process (e.g., Lurgi, Unishale C, Chevron STB, and Tosco HSP). Capital and operating cost savings for Unishale C and Lurgi are primarily a result of deleting the Unisulf and Stretford plants.

Economics for the indirect and direct heated retorts are good to marginal. Factors which will affect the economics are:

- o How effectively combustor heat can be utilized (simple steam raising is the least desirable).
- o The value of steam.
- o The use of fast or circulating fluid beds to reduce investment in combustor equipment.

#### D. PHASE II: PILOT PLANT TESTING

##### 1. Description of the Pilot Plant

The test facility used in Phase II was a pilot plant built by Tosco Corporation to develop their Hydrocarbon Solids Process (HSP)(5). The pilot plant has a nominal capacity of 6 tons per day (63 g/sec) of oil shale and contains a fluidized bed combustor which is 18 in. (0.46m) in diameter. Figure 2 is a process flow diagram of the plant. A description of the process is given below.

Raw oil shale, crushed to minus 1/4-in. (0.0064m) and smaller, is pneumatically lifted to the shale feed weigh hopper system from which shale is metered into the retort at a constant rate. The raw shale from the weigh hopper is preheated up to 300 to 500°F (421-533K). The retort is an inclined rotating cylinder in which oil shale and hot heat carrier solids (from the fluid bed combustor) are mixed. The mixture of heat carrier and oil shale is conveyed concurrently through the retort to the retort accumulator. The feed rates of raw oil shale and heat carrier are adjusted to maintain the desired temperature in the retort, approximately 900°F (755K).

The mixture of spent shale and heat carrier from the retort, called retorted solids, is pneumatically conveyed from the accumulator discharge screw into the fluid bed combustor using superheated steam. The fuel residue on the spent shale (primarily organic carbon and hydrogen) is combusted to provide part or all of the heat required to pyrolyze the oil shale. Combusted solids, which constitute the heat carrier, are drawn off from the fluid bed combustor and are recycled to the retort.

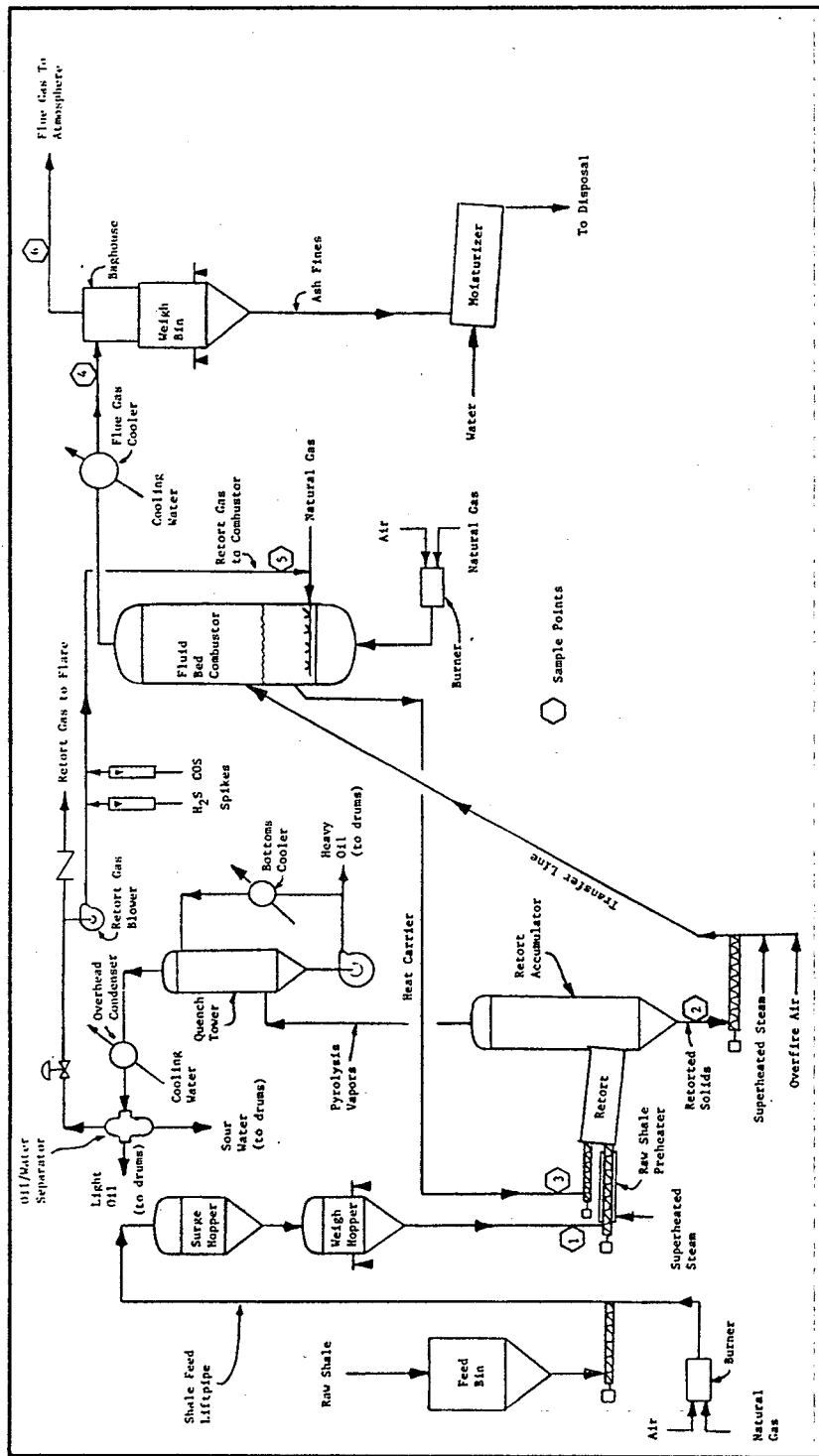


Figure 2. Pilot Plant Process Flow Diagram

The combustor is an atmospheric, dense-phase, bubbling, fluidized bed. The spent shale fuel is supplemented as needed by injection of natural gas or retort gas into the bed. Solid fuels such as raw oil shale can also be used. The bed is fluidized by air and/or hot flue gases from an external burner. Flow rates of air and flue gas are adjusted to maintain bed fluidization, bed temperature, and oxygen concentration in the combustor flue gas.

Flue gas and entrained shale ash from the combustor are cooled in a heat exchanger, and the ash is separated from the flue gas in a baghouse. From the baghouse weigh bin the ash flows to a moisturizer where it is mixed with water prior to disposal. The clean flue gas flow is measured with an orifice meter prior to being vented to the atmosphere.

Pyrolysis vapors from the retort are cooled and the oil and water condensed in a quench tower and overhead condenser. The non-condensed retort vapors are either metered and sent to a flare or are diverted to the fluid bed combustor through a blower used to overcome the pressure in the bed. For the majority of the pilot plant tests, retort gas was burned in the fluid bed to supply the H<sub>2</sub>S and non-H<sub>2</sub>S sulfur compounds. In addition, H<sub>2</sub>S and COS from pressurized cylinders were used to "spike" the retort gas to allow significantly higher sulfur concentrations in the injected retort gas than would have been possible with only retort gas.

## 2. Test Objectives

Key questions addressed in the Phase II test program included:

- o How effective is ASSP in controlling sulfur emissions?
- o Will ASSP produce large quantities of H<sub>2</sub>S?
- o What are the most favorable operating conditions to achieve maximum sulfur control while holding NO<sub>x</sub> emissions to minimum?
- o Will retorted or raw oil shale combustor produce significant emissions of trace elements such as mercury or cadmium?

## 3. Experimental Procedure

Parachute Creek oil shale obtained from the Colony mine was used in the pilot plant program. This shale was crushed to minus 1/4-in. (0.0064m) particle size and had a nominal richness of 34-37 gal. per ton (142-154 L/Tonne). The shale used is similar to shale being processed by the Union Oil commercial plant. This shale has significant amounts of calcium and magnesium carbonates, which (when decomposed to the oxides) are available for sulfur absorption.

The pilot plant was operated for 10 days between October 14 and 24, 1985. A total of 44 "tests" were conducted during which plant operating data were recorded.

Some of the key process variables evaluated in the pilot plant program were:

- o Bed temperature
- o Solids residence time (bed depth and solids circulation rate)
- o Gas residence time (superficial velocity)
- o Ca/S mole ratio
- o Flue gas oxygen concentration
- o Raw shale/spent shale ratio
- o Single stage and two stage combustion

During single stage combustion tests, all combustion air flowed through the fluid bed and superheated steam was used to pneumatically convey retorted solids to the combustor via the transfer line. In this mode, the bed was normally oxygen-rich.

During two stage combustion tests, combustion air to the bed was reduced until the flue gas oxygen concentration fell to zero. Then, overfire air was added to the retorted solids transfer line while simultaneously reducing superheated steam flow until the desired flue gas O<sub>2</sub> level was achieved. Since the transfer line does not enter the fluid bed, overfire air and superheated steam do not pass through the bed. Thus overfire air can combust CO and trace hydrocarbons in only the freeboard portion of the combustor.

#### 4. Discussion of Results

The range of key operating conditions for the 44 tests performed are summarized in Table 2.

Over this range of conditions, flue gas composition and organic carbon combustion efficiency ranged as shown in Table 3.

To increase the sulfur concentration in the retort gas, H<sub>2</sub>S and COS from pressurized cylinders were injected into the retort gas upstream of the sample point. This increased the H<sub>2</sub>S concentration from an initial concentration of about 0.4 - 0.5 vol % to 4 vol % and in some tests, nearly 10 vol %. The retort gas was spiked with H<sub>2</sub>S and COS in 33 of the 44 tests.

#### 5. Process Variable Correlations

Correlations of emissions (SO<sub>2</sub>, NO<sub>x</sub>, CO, trace HC)

TABLE 2. RANGE OF OPERATING CONDITIONS AND PROCESS VARIABLES

Bed Temperature, °F (K)	1127-1558	(881-1121)
Freeboard Temperature, °F (K)	1273-1593	(962-1140)
Retorted Solids to Combustor, lb/hr (g/sec)	2487-3615	(315-458)
Raw Shale to Combustor, lb/hr (g/sec)	0- 133	( 0-17)
Retort Gas to Combustor, scfm (Nm <sup>3</sup> /sec)	0-6.66	( 0-11.3)
H <sub>2</sub> S in Retort Gas, vol %	0.43-9.28	
Bed Depth, ft (m)	3.27-4.28	( 1-1.3)
Solids Residence Time, min.	8.07-18.72	
Gas Superficial Velocity, ft/sec (m/sec)	3.78-7.20	(1.15-2.19)
Gas Residence Time, sec	0.46-1.13	
Flue Gas Oxygen, vol %	0-6.25	
Carbonate Decomposition, %	45.5-83.3	
Ca/S Mole Ratio	6.20-10.25	

TABLE 3. RANGE OF FLUE GAS COMPOSITION AND ORGANIC CARBON COMBUSTION EFFICIENCY

<u>Flue Gas Composition</u>	<u>Range</u>
SO <sub>2</sub> , ppmv	1-38
NO <sub>x</sub> , ppmv	80-670
CO, vol %	0.05-1.80
Trace Hydrocarbons, ppmv	51-8465
Organic Carbon Combustion Efficiency, %	57.5-100.0

with key process variables indicated that the only significant factor which affected emissions was flue gas oxygen concentration. Smoothed curves of the experimental data are shown in Figures 3 and 4. Note that the NO<sub>x</sub> curve is presented as a band reflecting substantial data scatter.

Key findings of the test program were:

- o SO<sub>2</sub> emissions were easily controlled to low levels at virtually all conditions tested, probably as a result of the high Ca/S ratios used. Thus the inlet sulfur concentration is immaterial providing the Ca/S ratio is adequate.
- o Reasonably good NO<sub>x</sub> control could be obtained with flue gas oxygen concentrations below about 3 vol %. The lowest NO<sub>x</sub> concentrations were seen at O<sub>2</sub> levels approaching zero but at the expense of higher CO and trace hydrocarbon emissions.
- o Good control of CO and trace hydrocarbon emissions could be obtained at O<sub>2</sub> levels above about 2 vol %.

Emissions of NO<sub>x</sub> move in a direction opposite to SO<sub>2</sub>, CO, and trace hydrocarbon emissions. Thus, finding a set of operating conditions which minimize all four represents a compromise. One test was run which produced nearly optimum results. Conditions for this test were:

Bed Temperature	1227°F	(937K)
Solids Residence Time	9.4 min.	
Gas Residence Time	0.9 sec	
Gas Superficial Velocity	4.4 ft/sec	(1.3 m/sec)
Flue Gas O <sub>2</sub>	2.6 vol%	
Ca/S Mole Ratio	10.3	
Raw Shale/Spent Shale Ratio	1:36	

At these conditions the following results were obtained:

SO <sub>2</sub>	11 ppmv
NO <sub>x</sub>	160 ppmv
CO	0.27 vol%
Trace Hydrocarbon	388 ppmv
Combustion Efficiency	89%

#### 6. Design Recommendations

Based on the pilot plant data obtained in this study, fluid bed operating conditions are recommended to optimize SO<sub>2</sub> and NO<sub>x</sub> control. In general, conditions that favor low SO<sub>2</sub> emissions also favor low CO and trace hydrocarbon emissions but do not favor low NO<sub>x</sub> emissions. The general ranges of operating conditions which produced reasonable results from both an operating and emissions viewpoint are given below. Conditions used in the Phase I conceptual design work are shown for comparison in Table 4. This comparison indicates that the conditions chosen for the conceptual design are reasonable and in most cases conservative.

TABLE 4. RECOMMENDED FLUID BED COMBUSTOR OPERATING CONDITIONS

Operating Conditions	Recommended		Conceptual Design
	1150-1550	(897-1116)	1350 (1005)
Fluid Bed Temperature, °F (K)	11-14		14
Solids Residence Time, min	0.5-1.0		1.0
Gas Residence Time, sec	7+	(2.1+)	5.0 ( 1.5)
Gas Superficial Velocity, ft/sec (m/sec)	2+		3.0
Flue Gas Oxygen, vol %	45+		60
Carbonate Decomposition, %	6+		23
Ca/S Mole Ratio	3/97		7/93



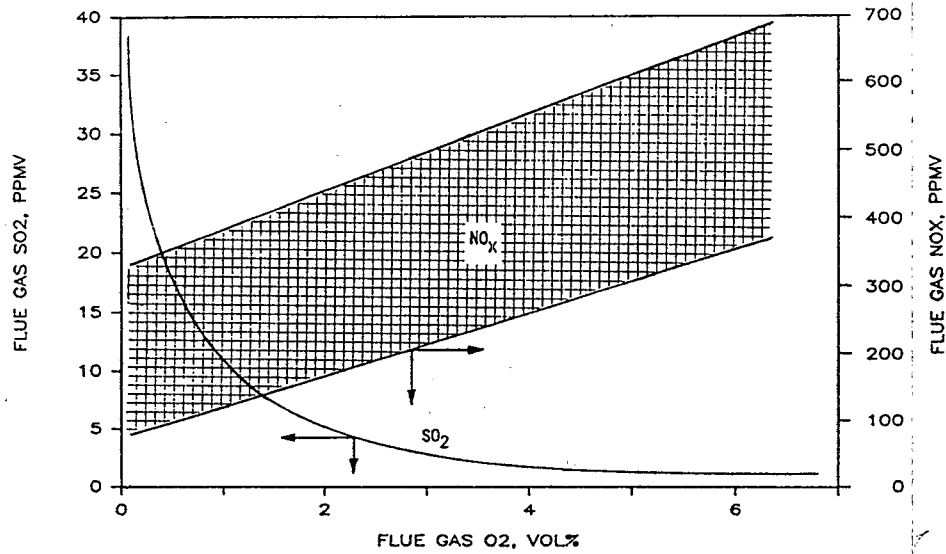


FIGURE 3. EFFECT OF FLUE GAS OXYGEN ON  $SO_2$  AND  $NO_x$  EMISSIONS.

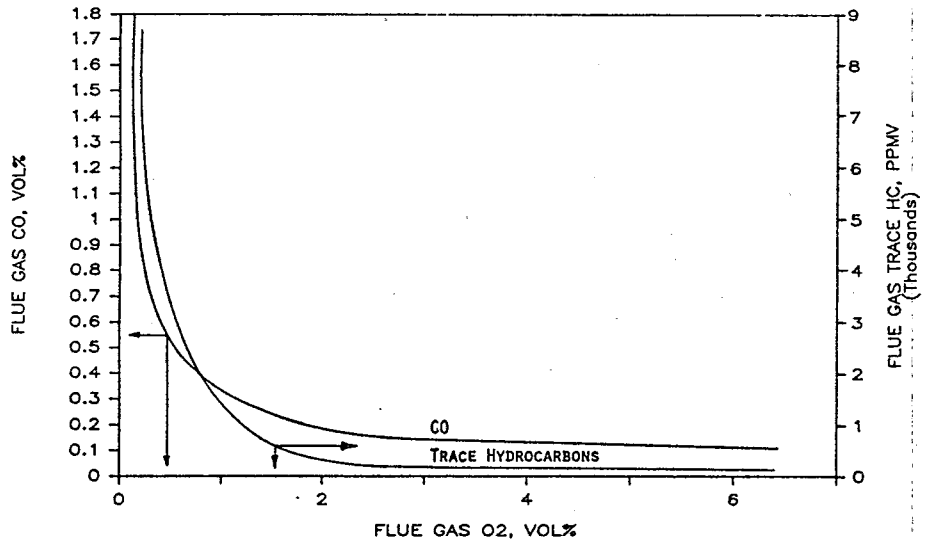


FIGURE 4. EFFECT OF FLUE GAS OXYGEN ON CO AND TRACE HYDROCARBON EMISSIONS.

## 7. Trace Element Sampling and Analysis

Selected process streams were sampled and analyzed for the following trace elements: arsenic, cadmium, mercury, beryllium, lead and fluorine (as fluoride). The streams sampled and analyzed were raw shale, retorted solids, heat carrier, baghouse ash, retort gas, and combustor flue gas. Oil and retort water were not analyzed. The primary goal was to determine the trace element concentration in the retort gas and flue gas.

Previous investigators(6-12) measured trace element concentrations in various process streams from laboratory and simulated in-situ retorts. Mercury concentrations of from less than 0.2 to 8,200  $\mu\text{g}/\text{m}^3$  have been reported in retort gases. Cadmium concentrations of from 1 to over 1000  $\mu\text{g}/\text{m}^3$  have been reported in retort gases. Arsenic concentrations from 5 to 155  $\mu\text{g}/\text{m}^3$  have been reported in gas streams from oil shale retorts. No data have been reported on lead, beryllium, and fluoride in oil shale processing gas streams.

Retort gas and combustor flue gas were sampled during three pilot plant tests: Tests 7, 12, and 19C.

Retorting and combustion temperatures were varied for these three tests; average temperatures are given:

Test Number	Average Retorting Temp, °F (K)		Average Combustion Temp, °F (K)	
	7	1015	(819)	1550
12	930	(772)	1430	(1050)
19C	860	(733)	1240	(944)

During Test 12, an aqueous spike solution containing 3 g/L Hg and 3 g/L Cd (prepared from the nitrate salts) was pumped into the bottom of the combustor to determine their fate in the combustor. The amount of mercury and cadmium fed in the spike represents about 4700 times and 170 times, respectively, of the amounts of mercury and cadmium entering the system in the raw shale during the 2-hour spike period.

A summary of analytical results is given in Table 5. Table 6 gives the percentage of trace elements present in the raw shale feed which was found in the retort gas and flue gas. In Test 12 the amount of mercury and cadmium added to the combustor is included as part of the total. Note that, although the trace elements were fed to the combustor, significant amounts of mercury (106 micrograms/ $\text{m}^3$ ) were found in the retort gas. Mercury and possibly some cadmium were probably deposited on the heat carrier in the combustor and recycled to the retort where they were re-volatilized.

TABLE 5. TRACE ELEMENT ANALYTICAL RESULTS

Test	Stream	Concentration, micrograms/ $\text{m}^3$					
		Hg	Cd	As	Pb	Be	F
7	Retort Gas	4	184	115,355	2,546	2	35
	Flue Gas	4	26	8	113	9	35
12	Retort Gas	106	264	88,103	146	2	35
	Flue Gas	24,720	25	9	6	2	35
19C	Retort Gas	4	2	49	9	2	35
	Flue Gas	22	15	9	9	2	35

TABLE 6. PERCENTAGE OF TRACE ELEMENTS PRESENT IN RAW SHALE  
FOUND IN RETORT GAS AND FLUE GAS

<u>Test 7</u>	<u>% Found In Retort Gas</u>	<u>% Found In Flue Gas</u>
Hg	ND	ND
Cd	2	7
As	13.8	0.03
Pb	0.65	0.8
Be	ND	2.7
F	ND	ND
<u>Test 12</u>		
Hg(a)	0.01	41.3
Cd(a)	0.02	0.005
As	11.2	0.03
Pb	0.03	0.04
Be	ND	ND
F	ND	ND
<u>Test 19C</u>		
	<u>% Found In Retort Gas</u>	<u>% Found In Flue Gas</u>
Hg	(b)	(b)
Cd	(b)	(b)
As	0.004	0.03
Pb	0.001	0.7
Be	ND	ND
F	ND	ND

ND = Not detected

(a) = Includes metal spikes

(b) = Not applicable due to unknown amount of Hg and Cd still present from the spiking of these metals in Test 12

Results of the trace element tests indicated some relative trends with regard to emissions but because of the short duration of the sampling, no hard conclusions can be reached which would allow extrapolation of results to long term steady-state operations. Some of the key observations were:

- o Lead, beryllium and fluoride were found to have low volatility. That is, of the amounts present in raw shale, only very small percentages were volatilized to the gas streams.

- o Arsenic was found in significant concentrations in the retort gas (100-400 ppmv), although the amount of arsenic represented less than 15% of that in the raw shale.

- o So little mercury was present in the raw shale that mercury emissions could not be characterized with high accuracy. Mercury emissions were very low except during the spike, indicating that mercury, if present in higher concentrations in the raw shale, could possibly pose emissions problems.

- o Cadmium demonstrated moderate volatility at higher retort and combustor temperatures but emissions represented less than 10% of cadmium present in raw shale.

There is some evidence that mercury and cadmium introduced to the combustor during the spike test condensed within the retort equipment and re-volatilized over time. However, because of the limited number of samples taken, it would not be prudent to draw any hard conclusions. Longer term steady-state operations would have to be studied to determine the fate of mercury and cadmium with more certainty.

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