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Project Summary

Control of Sulfur Emissions from Oil Shale Retorting Using Spent Shale Absorption

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This study investigated the environmental advantages/disadvantages of absorbing SO_2 onto combusted retorted oil shale. The objective of this program was to obtain more information in support of Prevention of Significant Deterioration (PSD) permitting decisions on sulfur control and to determine if emission of other pollutants such as nitrogen oxides (NO_x) and trace elements might be significantly increased by the combustion process. The program consisted of two phases: Phase I developed an engineering assessment and costs for application of this sulfur absorption process to selected leading retorting processes, and Phase II was experimental work in an integrated oil shale pilot plant to define operability, proof of principle, and trace element emissions.

Based on the pilot plant data obtained in this study, fluid bed operating conditions are recommended to optimize SO_2 and NO_x control. In general, conditions that favor low SO_2 emissions also favor low CO and trace hydrocarbon emissions but do not favor low NO_x emissions. The general ranges of operating conditions which produced reasonable results from both operating and emissions viewpoints are given in the report. Results of the trace element tests indicated some relative trends with regard to emissions but, because of the brevity of the sampling, no hard conclusions can be reached which would allow extrapolation of results to long-term steady-state operations.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Background

Control of sulfur emissions constitutes a major portion of the environmental control cost for oil shale facilities. For example, Denver Research Institute estimated costs (in 1980 dollars) in the range of $1 to $3 per barrel of shale oil produced. 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.

The ASSP Concept

The ability of combusted carbonate-containing spent shale to absorb SO_2 gives rise to a novel concept for controlling sulfur emissions in oil shale plants. This concept is the Absorption on Spent Shale Process (ASSP).

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

- The sorbent is cheap and inherently abundant in oil shale plants.
- 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.

- Since non-H_2S compounds are converted to SO_2 by combustion, ASSP could represent a more efficient removal relative to gas sweetening processes which remove only H_2S.

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_2 and absorbing the SO_2 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.

Phase II—Pilot Plant Program

Phase II involved pilot scale experimental testing of the ASSP concept in a pilot plant used by Tosco Corporation to develop their Hydrocarbon Solids Processing (HSP) process. The pilot plant has a nominal capacity of 6 tons (5440 kg) per day of oil shale and contains an 18 in. (46 cm) diameter fluidized bed combustor.

Key questions addressed in the Phase II tests were:

- How effective ASSP in controlling sulfur emissions?
- Will ASSP produce large quantities of NO_x?
- What are the most favorable operating conditions to achieve maximum sulfur control while holding NO_x emissions to a minimum?
- Will retorted or raw oil shale combustion produce significant emissions of trace elements such as mercury or cadmium?

The pilot plant was operated for 10 days between October 14 and 25, 1985. A total of 44 tests were conducted during which plant operating data were recorded.

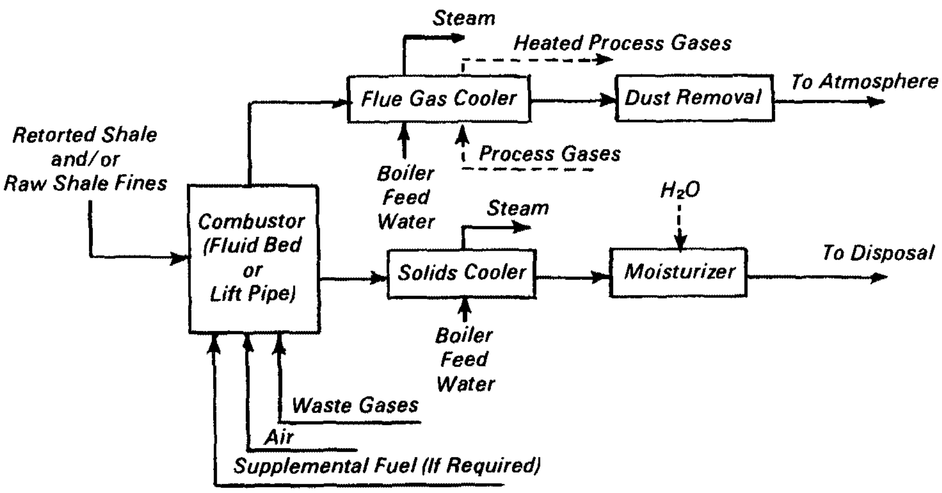

Figure 1. ASSP Process flow diagram.

Phase I—Engineering Evaluation/Conceptual Process Designs

The engineering assessment of the ASSP concept evaluated three types of retorting processes: direct heated, indirect heated, and indirect heated with combustion integrated into the process.

Specific retorting technologies and sites were selected as representative of these three retort types:

Retort Type	Process	Site
Direct heated	Modified In-situ with Unishale C	Cathedral Bluffs (Tract C-b)
Indirect heated	Unishale B	Union Oil (Parachute Creek)
Integral combustor	Lurgi	Rio Blanco (Tract C-a)
Integral combustor	Unishale C	Union Oil (Parachute Creek)

Selected process variables were correlated with their effect on SO_2 and NO_x emissions and other key dependent variables. Recommendations on the design and operation of a fluid bed combustor for SO_2 or NO_x control are given. Quality assurance/quality control procedures, as applied to sampling and analysis, are discussed.

Summary and Conclusions

The results of the Phase I study indicate that the ASSP concept is technically and economically viable compared to conventional sulfur removal technologies for most oil shale retorting processes. The Phase II results indicate that the ASSP concept is quite effective in controlling sulfur emissions and, with carefully controlled operating conditions, NO_x emissions can also be reduced by more than 85%. The pilot plant program also determined that some trace elements are volatilized by fluid bed temperatures in the range of 670 to 840°C.

Phase I Conceptual Design and Economics

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

- Direct heated —Modified In-situ with Unishale C—Cathedral Bluffs site
- Indirect heated —Unishale B—Union Oil site
- Integral combustor —Lurgi—Rio Blanco site
  —Unishale C—Union Oil site

The study assumed that methyldiethanolamine (MDEA) 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:

- Direct heated —Case A; Unisulf + flue gas desulfurization on combusted MIS gases
  —Case B; Unisulf + Stretford on MIS gases

- Indirect heated —Unisulf on Unishale B gases
- Integral combustor —DEA + Stretford on Lurgi gases
  —Unisulf on Unishale C gases

Major equipment costs were taken from EPA Pollution Control Technical Manuals (PCTMs). ASSP equipment was sized and costs factored from inhouse data and PCTMs. Costs were factored to first quarter 1985.

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

These cost comparisons show that the best potential for application of ASSP are processes that 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:

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

Phase II Pilot Plant Testing

Pilot plant tests were performed in a bubbling fluid bed combustor of the type which is integrated into the retort process. A total of 44 individual tests were performed. Variables evaluated were combustor temperature, solids residence time, gas residence time, oxygen concentration, inlet gas sulfur concentration, staged combustion, and raw shale injection. Over the entire range of conditions tested, emissions of primary pollutants were:

Component	Range
SO_2	1-38 ppmv
NO_x	80-670 ppmv
CO	0.05-1.80 vol %
Trace Hydrocarbon	51-8465 ppmv

Key findings of the tests were:

- SO_2 emissions were easily controlled to low levels at virtually all conditions tested, probably as a result of the high Ca/S ratios used.
- NO_x emissions were primarily sensitive to oxygen concentration, as were SO_2 emissions to a lesser extent (Figure 2). Reasonably good NO_x control could be obtained with flue gas oxygen concentrations below about 3 vol %. The lowest NO_x concentrations were seen at O_2 levels approaching zero but at the expense of higher CO and trace hydrocarbon emissions.
- CO and trace hydrocarbon emissions were primarily sensitive to flue gas oxygen concentration (Figure 3). Good control of both could be obtained at O_2 levels above about 2 vol %.

Emissions of NO_x move in a direction opposite to SO_2, CO, and trace hydrocarbon emissions. Thus, operating conditions that minimize all four represent a compromise. One test was run which produced nearly optimum results.

Conditions for this test were:

Bed Temperature	664°C
Solids Residence Time	9.4 min
Gas Residence Time	0.9 sec
Gas Supply Velocity	134.1 cm/sec
Flue Gas O_2	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_2	11 ppmv
NO_x	160 ppmv
CO	0.27 vol %
Trace Hydrocarbon	388 ppmv
Combustion Efficiency	89 %

During selected tests, both combustor flue gas and retort gas were sampled and analyzed for selected trace elements: mercury, cadmium, arsenic, lead, beryllium, and fluorine. During these tests, solids streams were also analyzed for trace elements in an attempt to determine where trace elements go. One run was performed where a spike solution of mercury and cadmium was added to the combustor.

Results of the trace element tests indicated some relative trends with regard to emissions but, because of the brevity 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:

- Lead, beryllium and fluorine were found to have low volatility; i.e., of the amounts present in raw shale, only very small percentages were volatilized to the gas streams.
- Arsenic was found in significant concentrations in the retort gas (100-400 ppmv), although the amount of arsenic found represented less than 15% of that in the raw shale.
- 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.
- Although significant amounts of cadmium was found in the gases at higher retort and combustor temperatures, 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 revolatilized over time. However, because of the limited number of samples taken, it would not be prudent to draw any conclusions. Longer term steady-state operations would have to be studied to determine the fate of mercury and cadmium with more certainty.

Table 1. *Cost Comparison For ASSP*

Retort Type	*Direct Heated Case A, Case B*		*Indirect Heated*	*Integral Combustor*	
Retorting Process	*MIS/Unishale C*		*Unishale B*	*Lurgi*	*Unishale C*
ASSP Incremental Cap. Cost, $\$10^6$	*−71.2*	*−63.2*	*+90.2*	*−13.0*	*−32.1*
ASSP Incremental Annual Oper. Cost, $\$10^6$/yr	*+10.83*	*+12.07*	*−19.21*	*−2.29*	*−1.56*

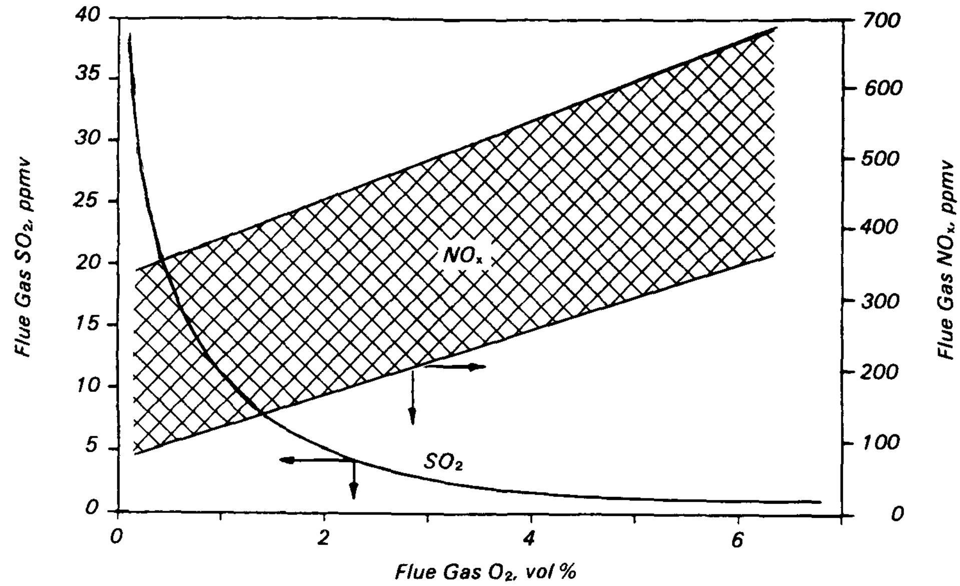

Figure 2. *Effect of flue gas oxygen on SO_2 and NO_x emissions.*

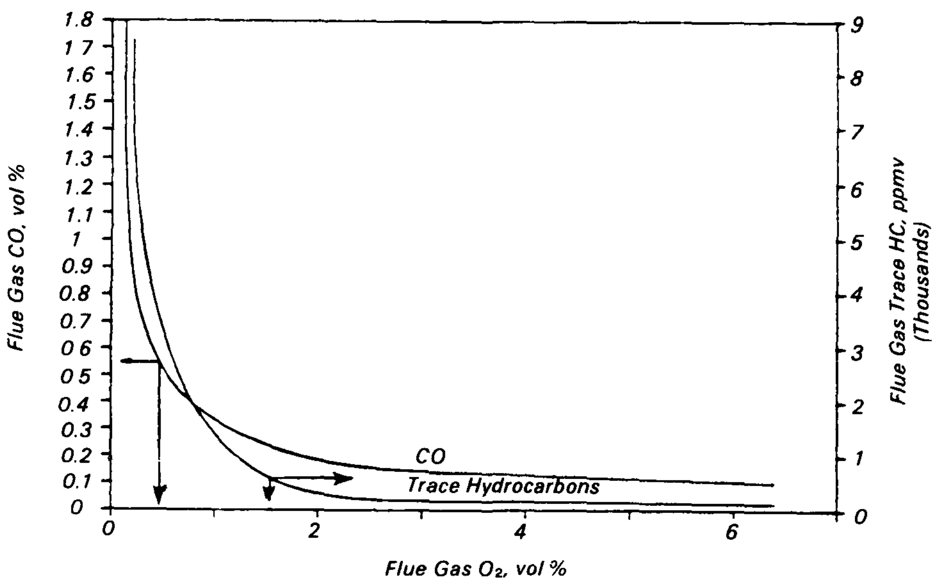

Figure 3. *Effect of flue gas oxygen on CO and trace hydrocarbon emissions.*

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The complete report, entitled "Control of Sulfur Emissions from Oil Shale Retorting Using Spent Shale Absorption," (Order No. PB 87-110 516/AS; Cost: $18.95, subject to change) will be available only from:
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