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# Project Summary

# Control of Sulfur Emissions from Oil Shale Retorts

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**The objectives of this study were to determine the most applicable technology for control of sulfur emissions from oil shale processing facilities and then to develop a design for a mobile slipstream pilot plant that could be used to test and demonstrate that technology.**

**The work conducted included an in-depth evaluation of available gas characterization data from all major oil shale development operations in the United States. Data gaps and inconsistencies were identified and corrected where possible through working with the developers or researchers in the field. From the gas characterization data, duty requirements were defined for the sulfur removal systems. Based on this information, Stretford gas sweeting technology was recommended, and the design of a 1000 CFM pilot plant was completed.**

***This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, 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

The future beneficial use of the nation's extensive oilshale resources depends not only on the development of suitable process economics but also on the development of suitable environmental controls. Even though the sulfur content of the oil that would be produced is comparatively low, sulfur emissions from large-scale production of shale oil could be enormous. Oil shale contains up to 2% sulfur. A typical shale in the Green River Formation in Colorado contains about 0.7% sulfur. When the shale is retorted, somewhere between 16 and 30% of the sulfur is liberated to the gas stream, and the majority remains with the spent shale. The emissions from a 400,000-barrel/day oilshale industry could be as high as 760 to 1400 tons per day if controls were not applied. If conventional flue-gas scrubbing systems were used to control the emissions (the average reduction is about 90%), the controlled emissions would be 76 to 140 tons/day. However, if the sulfur could be removed before the gas is burned (the average reduction here is about 98%), the controlled emissions would be in the order of 15 to 28 tons/day.

The viability of the oilshale industry hinges on a sulfur-removal process compatible with environmental concerns. Although there are no federal standards for emissions for the oilshale industry at this time, the State of Colorado has enacted legislation that limits emissions to less than 0.3 lb of sulfur dioxide per barrel of oil produced and an equal amount per barrel of oil refined. To meet this standard, at least 95% of the sulfur in the gas would have to be removed.

The area of air pollution compliance that is of the greatest concern to industry and government is the Prevention of Significant Deterioration (PSD) requirements of the Federal Clean Air Act. This concept was enacted to prevent the addition of specified pollutants above a prescribed baseline value in specified air regions. Colorado adopted a more stringent plan which limits the maximum level of sulfur dioxide in the air to an annual average of 10 $\mu g/m^3$. Thus the maximum quantity of shale oil that can be produced will be limited by the effectiveness of the sulfur emission control system used.

Gases produced by direct-fired retorts, either above ground or in-situ, are different enough from gases normally encountered in application of desulfurization technology that the technology cannot just be transferred. Gases from direct-fired retorts contain large amounts of inert components and have a high ratio of carbon dioxide ($CO_2$) to hydrogen sulfide ($H_2S$); they also contain large amounts of ammonia and unsaturated hydrocarbons such as acetylene, ethylene, propylene, butylene, and butadiene. The gases are saturated with water and contain some oxygen and trace amounts of sulfur species other than $H_2S$.

The large amounts of $CO_2$ in the gases and the high $CO_2$ to $H_2S$ ratios make it impractical to employ many of the desulfurization technologies. Since the gases are produced in huge volumes at near-atmospheric pressures, many other desulfurization processes cannot be economically applied. The applicable processes may perform only marginally because $CO_2$ is present in large quantities. Oxygen and unsaturated hydrocarbons may be present in the gases, or the gas may contain a large quantity of organic sulfur.

Oilshale developers are involved in many significant pilot-scale activities to devise retorting process technology. They have indicated their willingness to cooperate with the U.S. Environmental Protection Agency (EPA) on projects for sulfur control technology evaluation. To capitalize on this opportunity and to explore the possibility that sulfur emission control will be more of a problem than was originally thought, EPA contracted with IT Enviroscience, Inc., to investigate the various commercial sulfur-removal technologies and to propose a pilot-plant design based on the most cost-effective process for removing gaseous sulfur compounds from oilshale retort gases.

The objectives of this study were to determine the most applicable control technology for control of sulfur emissions from oil shale processing facilities and then to develop a design for mobile slip-stream pilot plant that could be used to test and demonstrate that technology.

## Approach

The work included an in-depth evaluation of available gas characterization data from all major oilshale development operations in the United States. Data gaps and inconsistencies were identified and corrected where possible through working with the developers or researchers in the field. From the gas characterization data, duty requirements were defined for the sulfur removal systems. It was found that oilshale retorting processes fall into two broad categories; direct-fired-retort process and indirect-heated-retort processes, each category having distinct duty requirements.

The overriding factor separating the two categories of retorting processes and determining which desulfurization technology to apply is the $CO_2$ to $H_2S$ ratio of the gas produced from the retort. Those from direct-fired retorts have $CO_2$ to $H_2S$ ratios ranging from 76 to over 165, thus requiring that the process selectively remove $H_2S$ in the presence of large amounts of $CO_2$. Indirect-heated retorts produce gases with $CO_2$ to $H_2S$ ratios in the range of 4.3 to 5, which would allow a nonselective process to be used.

During this study, it was determined that the greatest immediate concern is control of sulfur emissions from direct-fired oilshale retorting processes and that the pilot-plant design should be applicable to these retorting methods. Since application of desulfurization technology to gases from direct-fired-retorting processes is more limiting, the screening of available process technologies was based on the duty requirements for those gases.

## Recommended Available $H_2S$ Control Technology

The class of processes that remove $H_2S$ and $CO_2$ from fuel gases is generically called acid-gas removal or gas-sweeting. Acid gas or other gaseous impurities are removed from gas streams either by direct chemical conversion to a compound more easily separated from the gas stream, by absorption into liquid, or by adsorption onto a solid. Because large volumes of gas must be processed in a typical oilshale plant, desulfurization technology will be applied only to high-capacity, liquid-phase processes. Since $CO_2$ is absorbed to some extent by all liquid-phase processes, the high $CO_2$ to $H_2S$ ratio of the gas limits the choice to those processes that selectively absorb sulfur compounds in the presence of large amounts of $CO_2$.

Of the processes that remove $H_2S$ by directly converting it to elemental sulfur, the Stretford process is the most effective. Of the indirect processes that remove $H_2S$ by separating it as a concentrated acid-gas stream, the following processes were most effective: The Selectamine and the Adip processes, which use MDEA as the absorbent, the Benfield, the Selexol, and the Diamox processes. The Benfield and Selexol processes require the gas to be at high pressure and thus were eliminated, since the compression of the gas for desulfurization cannot be economically justified.

Except for the Diamox process, all the candidate processes can remove $H_2S$ down to about 10 ppmv. However, organic sulfur compounds, principally COS, which exist in only trace amounts in the gas, are not significantly removed by the various processes. The presence of those compounds may reduce the overall effectiveness to 98%.

The Stretford process is most cost-effective for desulfurization gases from direct-fired oilshale retorts. In the model case used to evaluate the processes the total estimated cost of sulfur removed by the Stretford process is about $0.50 per barrel of oil produced, less than half that projected for the best of the other processes evaluated.

The Claus process recovers sulfur from the acid gas produced by indirect sulfur-removal. Because of the large quantity of $CO_2$ in the gas, the best indirect processes can only marginally produce an acid gas rich enough in $H_2S$ for the Claus process. Thus, to apply the Claus process, multiple stages of selective absorption would be required to handle the gas produced by many of the direct-fired retorts.

The Stretford direct process, on the other hand, is only minimally affected by the quantity of $CO_2$ in the gas and therefore is adaptable to the full range of gases produced by direct-fired retorts.

## Design of Pilot Plant

The pilot-plant design is based on the current state-of-the-art technology for commercial application of the Stretford process. The maximum design capacity of the unit is 1000 scfm of feed gas and 14.6 lb of sulfur per hour. The plant should be capable of reducing the $H_2S$ content of the gas to 10 ppmv or less, and $CO_2$ to $H_2S$ ratios as high as 200:1 should be possible.

The pilot plant is sized primarily to remove $H_2S$ from oilshale gas produced by direct-fired retorts. However, use of an ejector-venturi gas-scrubbing system affords wide gas turndown capability for the system. The pilot plant can thereby operate on a slip stream from any of the currently proposed direct or indirect oil shale retorting processes in the United States.

To function properly, the feed gas to the pilot plant must be 120°F or less, with most of the ammonia removed. A gas cooling column has been incorporated into the pilot design for cooling and removing the ammonia from the feed gas.

The estimated cost of the pilot plant with all equipment, instruments, and controls, assembled on skid mountings as a complete and operable unit, is as follows:

| Range | With Cooler | Without Cooler |
|---|---|---|
| High | $520,000 | $338,000 |
| Average | 400,000 | 260,000 |
| Low | 308,000 | 200,000 |

## Conclusions

The Stretford direct gas desulfurization process may be the only currently available commercial process capable of effectively removing $H_2S$ from gases produced by direct-fired retorts. Application of the Stretford process to the treatment of these gases would extend the technology of the Stretford process into areas in which no experience is available. Many questions need to be answered before the process can be applied with confidence to a full-scale commercial shaleoil production facility.

The principal areas of concern for Stretford technology are as follows:

1. absorption of $CO_2$ versus gas characteristics,
2. capacity of the solution for absorbing sulfur versus gas characteristics,
3. rate of by-product thiosulfate formation versus gas characteristics,
4. disposition of COS and other organic sulfur compounds in the feed gas, and
5. effects of unsaturated hydrocarbons in the feed gas on process operation, life of the Stretford chemicals, and quality of the sulfur produced.

Unless the Stretford process can be demonstrated as an effective and reliable process for treatment of direct-fired oilshale gases, industry may have to resort to combusting the gas first and then using less effective flue-gas desulfurization techniques. Because of the stringent PSD requirements, any increase in sulfur emissions could result in reduction of the potential production capacity of the shaleoil industry.

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*The complete report, entitled "Control of Sulfur Emissions from Oil Shale Retorts," (Order No. PB 82-231 945; Cost: $16.50, subject to change) will be available only from:*
*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*
*The EPA Project Officer can be contacted at:*
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