United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S7-81-021 Apr. 1981

EPA

Project Summary

Environmental Characterization of Geokinetics' *In situ* Oil Shale Retorting Technology

Gerald M. Rinaldi, Jean L. Delaney and William H. Hedley

The objective of this research program was to physically, chemically, and biologically characterize air emissions and water effluents from *in-situ* oil shale retorting. Geokinetics, Inc., agreed to allow Monsanto Research Corporation to sample and analyze emissions and effluents from Retort No. 17, a pilot-scale unit producing 30 barrels of crude shale oil per day and located at the "Kamp Kerogen" site in Uintah County, Utah. The potential pollution sources tested were the retort off-gases before and after mist elimination, the exhaust from thermal incineration of the demister outlet gases, fugitive gas seepage through the retort surface and around well casings, retort water after oil separation, and evaporation pond water.

The three stack gas streams were analyzed for criteria pollutants (carbon monoxide, hydrocarbons, oxides of nitrogen and sulfur, and particulate matter) as well as ammonia, arsine, hydrogen cyanide, and trace elements. Carbon monoxide, total hydrocarbons, and C_1 through C_6 hydrocarbon fractions were quantified in the fugitive emission samples. Conventional pollutants and water quality parameters, organic priority pollutants, and trace elements were measured in the samples of retort water and evaporation pond water. Selected air and water pollution samples were tested for biological activity, using the Ames mutagenicity assay, the Chinese hamster ovary (CHO) clonal toxicity assay, and the rabbit alveolar macrophage (RAM) cytotoxicity assay.

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

Oil shale has been recognized as a potentially substantial energy resource in the United States for more than 100 years. Recently, increasing dependence on foreign oil supplies and rapidly escalating oil prices have provided new incentive for shale oil recovery from deposits in Colorado, Utah, and Wyoming. At least four domestic firms (Colony Development Operation, Paraho Development Corporation, Superior Oil Company, and Union Oil Company) have developed surface retorting processes, in which oil shale is mined and crushed prior to thermal processing in aboveground facilities. The costs associated with mining and transporting voluminous quantities of raw shale and the environmental impacts of spent shale disposal may limit commercial application of surface retorting technology.

Considerable research is currently being directed toward the development of true or modified *in-situ* retorting processes. True or modified *in-situ* technologies, in which the shale bed is hydraulically or explosively fractured and retorting is carried out underground, are now being developed by Dow Chemical Company, Equity Oil Company, Geokinetics, Inc., Rio Blanco Oil Shale Company, and Occidental Oil Shale, Inc.

Despite the benefits of shale oil as an alternative energy source, air emissions, water effluents, and solid wastes associated with retorting could have adverse impacts on the environment if uncontrolled. Byproduct gases released during the retorting process may contain a complex mixture of so-called "criteria" pollutants (carbon monoxide, hydrocarbons, lead, oxides of nitrogen and sulfur, and particulate matter) and other non-criteria pollutant materials, such as ammonia, hydrogen cyanide, and hydrogen sulfide, all of which could have a deleterious effect on the West's pristine air quality. Similarly, contaminated wastewaters from oil shale processing operations might degrade the existing water quality if discharged without proper treatment. Reliable, comprehensive characterizations of air emissions, water effluents, and solid wastes must be performed now so as to identify suitable control strategies prior to commercialization of an oil shale industry.

In order to gather some of the necessary data on potential environmental impacts, the Environmental Protection Agency's Industrial Environmental Research Laboratory (IERL), Cincinnati, Ohio, contracted with Monsanto Research Corporation (MRC) to study air emissions and water effluents from horizontal *in-situ* oil shale retorting. To meet this objective, MRC obtained permission from Geokinetics, Inc., and the Department of Energy's Laramie Energy Technology Center to conduct a sampling and analysis program at Geokinetics' "Kamp Kerogen" site in Uintah County in northeast Utah. Studies of this nature may serve as a basis for determining additional testing needs and other efforts to define cost-effective solutions to potential pollution problems. This publication is a summary of the complete project report, which can be obtained from IERL's Energy Pollution Control Division along with further information on environmental aspects of oil shale processing.

In-situ *Retorting*

Crude oil can be recovered from shale by using heat to liquify a powdery organic solid known as "kerogen." *In-situ* retorting is the generic name given to recovery processes in which underground shale deposits are heated in place after increasing the permeability of the rock by fracturing and, in some cases, partial mining. Geokinetics, Inc., is currently developing a true *in-situ* process, that is, one which does not involve any mining, that employs a horizontally-moving flame front to retort oil shale deposits located beneath shallow overburden. Investigations of this novel shale oil recovery technique through privately funded laboratory and field work date back to 1973, and a cooperative agreement between Geokinetics and the Department of Energy has been in effect since 1977.

In the Geokinetics horizontal *in-situ* retorting process, a pattern of blastholes is drilled from the surface, through the overburden, and into the oil shale bed. The holes are loaded with explosives and then fired using a carefully planned blast system. The blast yields a well-fragmented mass of rock, with high permeability, and also a sloped-bottom bed which allows shale oil and co-produced water to drain to a sump for recovery by production wells; the result is shown in Figure 1. After "rubblization" of the shale deposit is completed, surface equipment such as that shown in Figure 2 is installed to process the product gases released during the retorting process.

The oil shale is ignited with burning charcoal at the air inlet wells which are drilled at one end of the retort. Injected air establishes and maintains a horizontally-moving burn front that occupies the entire cross-section of the rubblized bed. Off-gases containing oil mist exit through output holes at the downstream end of the retort. During Geokinetics' ongoing process development efforts, these off-gases, once above ground, are passed through a three-chamber, packed-tower mist eliminator to remove entrained oil and water, prior to combustion in a thermal incinerator. Provisions are made for firing propane as a supplemental fuel for the incinerator if the heat content of the demisted gases is insufficient to maintain combustion. For commercial-scale operations, instead of being incinerated after mist elimination, the retort off-gases will be either recycled to the air inlet wells or fed to a gas turbine to generate electricity.

The mixture of shale oil and water which collects in the sump at the retort's bottom is pumped by aboveground wells to an oil-water separator tank, along with the liquid recovered in the mist eliminator described above. From the separator, the aqueous layer is sent to an evaporation pond, and the crude shale oil is pumped to storage tanks for holding prior to refining into marketable products.

The specific oil shale retort selected for testing in this sampling and analysis program was designated as No. 17 by Geokinetics. This retort, blasted in May 1978, contained 13,000 tons of fragmented oil shale, in a bed 17 feet thick, 72 feet wide, and 156 feet long, situated under an average of 26 feet of overburden. Retort No. 17 was ignited in mid-April 1979, and MRC personnel per-

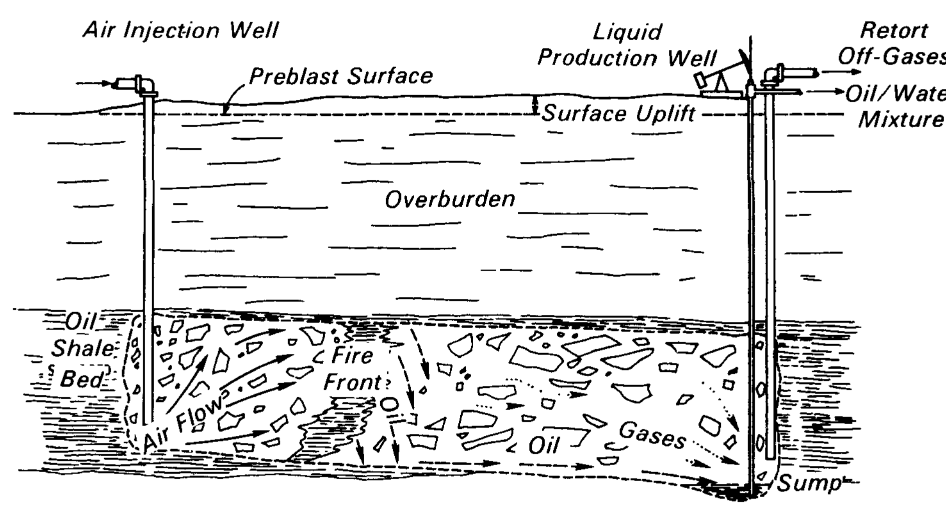

Figure 1. Sectional view of a Geokinetics horizontal in-situ *oil shale retort.*

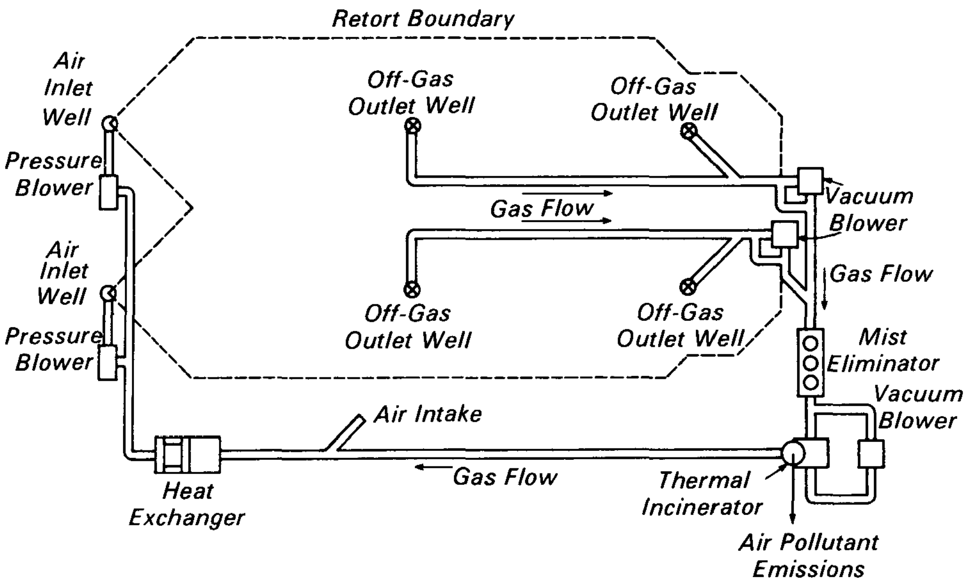

Figure 2. *Overhead view of surface equipment for handling off-gases from Geokinetics Retort No. 17.*

formed field sampling and analysis from July 16 to July 26. During that time period, the flame front advanced approximately 6 inches per day, and the crude shale oil production rate was 30 barrels per day. For comparison, Geokinetics' projected full-scale operations will produce on the order of 2,000 barrels of shale oil each day, and other developers have proposed commercial facilities as large as 50,000 barrels per day.

Stack Gas Sampling

EPA-approved methods were used to collect samples of retort off-gases after mist elimination (demister outlet) and of the thermal incinerator exhaust gases for quantification of air emissions. Investigation of the demister outlet gases, an essentially untreated stream, provided information that would enable the EPA to evaluate the potential of pollution control methods other than that implemented by Geokinetics, namely incineration. Numerical results from chemical analyses of the two types of stack gas samples are summarized in Table 1.

The amount of carbon monoxide in the demister outlet gases, that is, in the gases produced by the burning oil shale retort, was greater than that of any of the other air pollutants measured. However, because of essentially complete combustion in the thermal incinerator, the concentration of this criteria pollutant in the exhaust to the atmosphere was less than the detection limit of 0.1 percent by volume. Inspection of the data indicates that incineration is also a very effective control technique for hydrocarbons. Even particulate matter emissions are reduced somewhat due to the fact that a substantial fraction of the material that passes through the mist eliminator consists of condensed organic compounds which will burn. Nevertheless, the residual emissions in the incinerator exhaust implies that inorganic solids, such as shale dust, account for some of the particulate mass. Extrapolating the pilot-scale conditions and emission rate to Geokinetics' commercial-scale production of 2,000 barrels of shale oil daily, particulate emissions from incineration would amount to nearly 300 tons per year.

Contrary to the behavior of the other air pollutants, the emissions of nitrogen and sulfur oxides are increased, relative to amounts in raw retort off-gases, by incineration. The concentration of nitrogen oxides in the incinerator exhaust cannot be fully accounted for by the reaction of nitrogen and oxygen from the combustion air. However, nitrogen oxides may also be formed during incineration if nitrogenous compounds such as ammonia are present in the feed stream, as was the case at Geokinetics Retort No. 17. This hypothesis was confirmed by the disappearance of ammonia present in the demister outlet gases. The substantial emissions of sulfur oxides from the thermal incinerator can be similarly explained, due to oxidation of hydrogen sulfide (H_2S) and other sulfur compounds typically generated during oil shale retorting. Again extrapolating, predicted sulfur dioxide emissions from Geokinetics' commercial facility amount to 5,400 tons annually, which may require some sort of flue gas desulfurization for control. At the other extreme, emissions of hydrogen cyanide and trace elements, such as arsenic, lead, and mercury, from oil shale retorting were measurable but only at or near the detection limits of available analytical instrumentation.

Samples of the demister outlet gases from Geokinetics Retort No. 17 were also subjected to tests for biological activity in order to assess potential health and ecological effects. Using standardized experimental procedures, the oily particulate matter was demonstrated to be mutagenic, that is, it contained chemical substances that may increase the risk of cancer. This

Table 1. *Chemical Analyses of Stack Gas Samples from a Pilot-scale* In-situ *Oil Shale Retort*

Stack gas component	*Mass flow rate, lb/hr* Demister outlet	*Incinerator exhaust*
CRITERIA POLLUTANTS		
Carbon monoxide (CO)	130	<8.4
Hydrocarbons, total	37	1.3
Particulate matter	2.4	0.9
Nitrogen oxides (NO_x)	0.01	2.0
Sulfur oxides (SO_x)	<0.03	18
NON-CRITERIA EMISSIONS		
Ammonia (NH_3)	2.9	<0.06
Hydrogen cyanide (HCN)	0.01	<0.01
Trace elements	<0.01	<0.01

observation must be taken into consideration if oil shale developers are to select and implement appropriate treatment facilities for retorting emissions.

Fugitive Emissions

In addition to point-source emissions such as those from the thermal incinerator stack at Geokinetics Retort No. 17, oil shale processing operations may also give rise to so-called fugitive emissions. Fugitive emissions consist of diffuse, unconfined releases of particulate matter, hydrocarbons, or other pollutants into the atmosphere, usually as a result of equipment leaks.

Geokinetics' explosive fragmentation of an oil shale deposit causes the surface of the retort overburden to undergo noticeable uplift, creating ground cracks of various sizes. Plant personnel routinely seal the larger cracks by filling with mud before retorting begins, but all means of escape of fugitive emissions are not eliminated. Additional sources of fugitive emissions are created by drilling instrumentation wells into the oil shale bed. It has been estimated that as much as one-third to one-half of the total volume of gas injected into Geokinetics' *in-situ* retorts is not recovered at the outlet wells but rather lost in the form of fugitive emissions. Samples were collected using a novel technique that combined the applicable features of methods previously used to measure fugitive emissions from sources as diverse as growing or decaying vegetation and petroleum refineries.

Fugitive hydrocarbon emission rates due to ground seepage at Geokinetics Retort No. 17 ranged from 0.001 to 0.09 pound per square foot of surface area per day, a seemingly negligible amount. However, accounting for the entire retort surface as well as the contribution from well leaks, the total fugitive hydrocarbon emissions of about 13 pounds per hour are ten times more than those released to the atmosphere from the incinerator stack. In addition, fugitive emissions of carbon monoxide were measured to be as much as 40 pounds per hour, posing a potential health hazard to personnel working on the retort surface. The implications of extrapolating this data on fugitive emissions to commercial-scale facilities, which may be 100 to 1,000 times larger than Geokinetic's pilot retort, are that additional research into methods for both measurement and control is necessary.

Water Pollutant Sampling

Water collected along with the product oil from Geokinetics' *in-situ* shale retorts is contaminated with a number of potentially harmful pollutants. Samples of this "retort water" were analyzed by standard methods in order to identify the major chemical species present. Development of new analytical technology to resolve an ongoing controversy among researchers regarding method interferences due to the complex water pollutant matrix was considered beyond the scope of this project.

Table 2 lists the analytical results for the pollutants and water quality parameters observed at the largest concentrations in Geokinetics' retort water. As is typical of wastewaters for oil shale retorting, the data show the presence of significant quantities of a wide variety of pollutants. More specifically, this retort water sample contained nitrogen compounds (for example, ammonia), sulfur compounds, soluble solids, and organic compounds. As shown in Table 3, the retort water collected at Geokinetics also contained certain "organic priority pollutants" (acrylonitrile, benzene, phenol, toluene) and trace elements (arsenic, boron, iron, strontium) in amounts on the order of one part per million. The presence of these potentially toxic materials makes treatment of oil shale retorting wastewaters for discharge or process recycle, already difficult because of the number and amount of "conventional" pollutants present, a truly formidable challenge for both the EPA and industry.

Conclusion

Treating shale to recover crude oil may soon be an economically viable alternative to continued depletion of conventional petroleum reserves. Pilot-scale process development research by companies such as Geokinetics has begun to provide the information necessary for design and construction of large commercial shale oil production facilities. However, characterization of emissions and effluents from oil shale retorting has shown that significant numbers and quantities of pollutants present pose a complex environmental control problem. Additional measurement studies and technical and economic evaluations of treatment alternatives are necessary to prevent potential adverse impacts by integrating pollution control with oil shale development.

Table 2. *Analysis of Wastewater from Geokinetics' Pilot-scale Oil Shale Retort*

Parameter	*Concentration, mg/L**
Alkalinity (as $CaCO_3$)	*16,600*
Biological Oxygen Demand (BOD)	*2,000*
Bicarbonate (HCO_3^-)	*5,400*
Carbon, Total Inorganic (TIC)	*1,100*
Carbon, Total Organic (TOC)	*2,200*
Chemical Oxygen Demand (COD)	*7,200*
Chloride (Cl^-)	*1,100*
Nitrogen, Ammonia (NH_3)	*1,100*
Solids, Total Dissolved (TDS)	*9,400*
Sulfur, Total (as S)	*1,200*

**1,000 milligrams per liter (mg/L) is equivalent to a 1% solution.*

Table 3. *Organic Priority Pollutants and Trace Elements in Geokinetics' Retort Water*

Component	Concentration, mg/L*
ORGANIC PRIORITY POLLUTANTS	
Acrylonitrile	*0 25*
Benzene	*0 37*
Phenol	*0.67*
Toluene	*0 28*
TRACE ELEMENTS	
Arsenic (As)	*1.6*
Boron (B)	*61*
Iron (Fe)	*0.8*
Strontium (Sr)	*0.7*

**Milligrams per liter.*

Gerald M. Rinaldi, Jean L. Delaney, and William H. Hedley are with Monsanto Research Corporation, Dayton, OH 45407.
***Robert C. Thurnau** is the EPA Project Officer (see below).*
The complete report is in two parts:
"Environmental Characterization of Geokinetics' In situ *Oil Shale Retorting Technology," (Order No. PB 81-163 727; Cost: $9.50)*
Environmental Characterization of Geokinetics' In situ *Oil Shale Retorting Technology: Field and Analytical Data Appendices," (Order No. PB 81-163 735; Cost: $3.50 (microfiche only))*
These reports will be available only from: (costs subject to change)
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