

DOE/MC/11076 -- 5057  
(DE96000596)  
Volume I

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**Research Investigations in Oil Shale, Tar Sand,  
Coal Research, Advanced Exploratory Process  
Technology, and Advanced Fuels Research  
Volume I -- Base Program**

**Final Report  
October 1986 - September 1993**

Verne E. Smith

May 1994

Work Performed Under Contract No.: DE-FC21-86MC11076

For  
U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
Morgantown, West Virginia

By  
University of Wyoming Research Corporation  
Laramie, Wyoming

**MASTER**

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RESEARCH INVESTIGATIONS IN OIL SHALE, TAR SAND, COAL  
RESEARCH, ADVANCED EXPLORATORY PROCESS TECHNOLOGY,  
AND ADVANCED FUELS RESEARCH  
VOLUME I -- BASE PROGRAM

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Western Research Institute  
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## **FOREWORD**

This report summarizes the major research investigations conducted by the Western Research Institute under Cooperative Agreement DE-FC21-86MC11076 with the U.S. Department of Energy (DOE) over the period October 1986 through September 1993. In 1989 a Jointly Sponsored Research Program (JSRP) was incorporated into the agreement whereby some of the investigations were conducted as part of the Base Program and some were undertaken with cosponsorship from the commercial sector or other government agencies in the JSRP.

This report is divided into two volumes: Volume I consists of 28 summaries that describe the principal research efforts conducted under the Base Program in five topic areas. Volume II describes tasks performed within the JSRP. Research conducted under this agreement has resulted in technology transfer of a variety of energy-related research information. A listing of related publications and presentations is given at the end of each research topic summary. More specific and detailed information is provided in the topical reports referenced in the related publications listings.

## **ACKNOWLEDGEMENTS**

Funding for this research has been provided under U.S. Department of Energy Cooperative Agreement DE-FC21-86MC11076 and by numerous JSRP cosponsors. In addition to the efforts of the authors who prepared the topic summaries, the considerable efforts of the many researchers and support people at WRI who provided essential assistance in the design, conduct, and reporting of the work are greatly appreciated. Special thanks is due the individuals in DOE who have provided input and direction to the research studies and for their review and comments on completed studies.

## **EXECUTIVE SUMMARY**

Numerous studies have been conducted under Cooperative Agreement DE-FC21-86MC11076 since its initiation in October 1986. Program direction at that time was broken into five principal areas: oil shale, tar sand, underground coal gasification, advanced process technology, and advanced fuels research. In subsequent years, research emphasis changed in accordance with changes in the mission of DOE. As an example, underground coal gasification was broadened to be coal research, under which several research activities were conducted that related to coal processing.

The most significant change occurred in 1989 when the agreement was redefined as a Base Program and a Jointly Sponsored Research Program (JSRP). Research topics within the Base Program continued in the same areas, with an emphasis given to exploratory research that might lead to further development under the JSRP.

Investigations were conducted under the Base Program to determine the physical and chemical properties of materials suitable for conversion to liquid and gaseous fuels, to test and evaluate processes and innovative concepts for such conversions, to monitor and determine environmental impacts related to development of commercial-sized operations, and to evaluate methods for mitigation of potential environmental impacts.

In some of the most carefully controlled experiments ever done on the thermal decomposition of oil shale to oil, gas, and residue products, it was determined that a significant fraction of the kerogen in western oil shales is converted to an intermediate bitumen, whereas only a small portion of the kerogen was converted to bitumen in eastern oil shale. The maximum amount of extractable bitumen was found to increase with temperature and heating rate. In the characterization of reference oil shales it was found that the combination of nuclear magnetic resonance (NMR) measurements with material balance Fischer Assay data provides an indication of undesired coke formation. This basic information is of importance to the development and optimization of process systems.

The most commercially viable use for shale oil in the present market is as an additive to petroleum asphalt for paving applications, for which WRI holds a patent. In a study of other such applications, western shale oil was found to provide improved physical properties when used as an asphalt recycling agent. When used for crack and joint sealant the asphalt sealant was improved, but the material was not as good as more expensive, rubber-modified sealants.

Extensive organic and inorganic characterization was done on retorted oil shale that resulted in useful information for waste management planning for disposal of spent shale. Similarly, studies on ion speciation of materials in process waters and leachates have advanced the methods for measurement of chemical species of environmental concern related to fossil fuel processes.

Because oil shale products are not competitive as transportation fuel in the present market, alternative uses were evaluated. A viable market does exist for shale oil as an additive to petroleum asphalt for paving applications. Economic evaluation of a small commercial operation indicates that the return on investment would be in the 18 to 26% range.

Process studies were conducted on several tar sand resources. One-dimensional and three-dimensional tests were run to simulate in situ combustion processes. The problem of plugging was overcome in an extremely heavy tar sand by using steam-oxygen combustion. The different results obtained for different resources indicates that accurate extrapolations of process results cannot be made between resources.



WRI has developed the Recycle Oil Pyrolysis and Extraction (ROPE<sup>TM</sup>) process, for which one of the applications is to tar sand. Two long-term tests were conducted to evaluate steady-state process conditions. These conditions were reached within 2 days when the starting recycle oil was from the material being processed. Oil yields slightly greater than Fischer Assay were obtained. Also, an inclined liquid fluid-bed reactor was constructed and tested for the ROPE process. Some problems were encountered that could be resolved with modifications to the system.

Some of the oils produced in tar sand process tests were evaluated for their potential end use. Distillate from an oil from an Asphalt Ridge (Utah) tar sand that was produced by a forward combustion process was found to be potentially suitable for use as high-density or endothermic aviation fuel. The residue oil is suitable for use as an asphalt. Processed distillates of oil from a California tar sand were found to be suitable diesel fuels.

WRI participated in an underground coal gasification demonstration project that was primarily funded and directed by the Gas Research Institute and other DOE sources. Subsequent to the burn operations, WRI injected steam into the cavities to vent, flush, and cool them. This was followed by two pumping and treatment operations. The venting and flushing was effective in controlling and containing contaminants. The pumping and treatment operations were effective in restoring groundwater quality, as was observed in the groundwater monitoring that was conducted for the 5 years after the test burn.

A process called COMPCOAL<sup>TM</sup> has been developed to produce a premium-quality, solid fuel from low-rank coal. Tests run with the process have shown that pitch can be deposited on char produced by drying and mild gasification of the coal, resulting in a product that is dry, contains less dust, and is less susceptible to reabsorption of moisture.

Enhancement of liquid yields from coal hydroprocessing was investigated using an integrated approach applying coal drying and coprocessing, followed by hydroprocessing. Coal was dried in an inclined fluidized-bed dryer and immediately immersed in an oil bath composed of a coal derived liquid. The resulting coal slurry was subjected to coprocessing in an inclined-screw pyrolysis reactor. The product from coprocessing was hydroprocessed in tubing bombs to determine the liquid yield. These investigations used an Illinois No. 6 coal (Herrin No. 6), a Pittsburgh No. 8 coal, and a coal-derived liquid from mild gasification of Powder River Basin coal. The drying stage had only a small effect on the fixed carbon, but the coprocessing stage significantly increased the fixed carbon in the solid product. Coprocessing of the coals decreased the yield of liquid products from hydroprocessing of the solid product as compared to coals that were only dried.

An investigation was conducted to evaluate coal pretreatment prior to hydroprocessing, characterize coke deposits on supported catalysts after coal liquefaction, and evaluate modes of hydrogen utilization during coal liquefaction. The coal pretreatment studies were based on evaluating solvent induced swelling and low-temperature hydrogenation as pretreatment methods. The effectiveness of the pretreatment was measured by changes in liquid product yield from hydroprocessing the coal with Lloydminster crude oil. A significant increase in product was observed from pretreatment of Powder River Basin coal than from Illinois No. 6 coal. Coke deposited on supported catalysts after exposure to coal liquefaction was characterized by <sup>13</sup>C solid-state NMR. A linear relationship was identified between the catalyst pore volume and the size of the aromatic cluster of the coke using this technique. Solid-state and liquid-state NMR techniques were on samples from selected coal liquefaction tests to evaluate hydrogen utilization. Results from these measurements on one of the test materials indicated about 13% of the aromatic carbons in Illinois No. 6 coal was hydrogenated, and gas production accounted for 90% of the hydrogen consumption during the test.

In advanced exploratory research, the technical and economic feasibility of using oil shale as a sulfur sorbent in power plant coal combustion was studied. Oil shale does adequately reduce sulfur in coal combustion emissions and also provides energy from the kerogen. Depending on the mining and delivery costs for oil shale and the type of coal used, oil shale can be more economical to use than limestone.

Studies on the mathematical modeling of petroleum reservoirs (1) developed an improved method for determining well-block pressure and (2) extended the capabilities of WRI's mathematical thermal reservoir simulator to field-scale applications.

The Contained Recovery of Oily Wastes (CROW<sup>TM</sup>) process developed by WRI promises to be applicable to a number of environmental mitigation problems (see Volume II for descriptions of field demonstrations.) A study was conducted to evaluate the effectiveness of using chemicals, primarily surfactants, to enhance the removal of organic materials from soils. The addition of chemicals was found to be effective, especially in sandy soils.

An examination and evaluation of possible chemical additives for steamflooding applications to petroleum reservoirs found that a surfactant was more effective than selected polymers. Three-dimensional testing of the surfactant indicated that sufficient velocity of the steam and water volume in the steam are essential to the additive's effectiveness.

A problem related to the economical removal of nitrogen from natural gas by pressure swing adsorption is the regeneration of the adsorbent. A study was done to determine if microwave energy could be used to regenerate a zeolite adsorbent and improve the desorption phase of the process. It was determined that it is possible to do the regeneration, but there is excessive heating of the adsorbent. Using microwave energy for desorption may prove useful where minimal dilution is necessary.

The purpose of the advanced fuels research was to determine the feasibility of producing intermediates in the production of high-density aviation turbine fuel from western and eastern shale oil and a coal-derived liquid. The processes evaluated included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Only Attapulugus clay treatment and hydrogenation of the middle distillate from western shale oil produced intermediates that were evaluated for the production of high-density turbine fuel. However, the intermediates from both processes contained excessive amounts of alkanes. It was concluded that because of the paraffinic nature of western shale oil, it would be quite difficult or expensive to use it as a feedstock for the production of a high-density aviation turbine fuel. None of the five processes investigated produced intermediates from the eastern shale oil and coal-derived liquid that were suitable for further evaluation as a high-density turbine fuel. Single-stage hydrogenation of the distillates resulted in process intermediates that still contained significant amounts of aromatics and olefins. It was determined that the aromatics were composed of high concentrations of indanes/tetralins. However, hydrogenation of these species to dicyclic alkanes results in a class of compounds that are necessary for the production of high-density turbine fuel. Consequently, it is believed that a process that includes two-stage hydrogenation can be employed to produce a high-density turbine fuel from these two fossil fuels that would meet the requirements of the U.S. Air Force.

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**OIL SHALE**

# KEROGEN DECOMPOSITION

Francis P. Miknis

## Background

The kerogen in oil shales exists in a variety of structural assemblages, so that understanding the chemistry of kerogen decomposition requires investigations of the thermal decomposition of several different types of kerogens. Eastern U.S. oil shales have a more aromatic kerogen structure than western U.S. oil shales and produce about half as much liquid product during pyrolysis compared to western oil shales. Therefore, understanding the chemistry of pyrolysis of these aromatic shales is an important factor for the development of general chemical kinetics models of kerogen decomposition.

A common feature of oil shale decomposition models is the bitumen intermediate. Although bitumen is usually considered an important intermediate in kerogen decomposition, its chemical and physical properties have not been thoroughly investigated. Therefore, the role of a bitumen intermediate in oil shale decomposition is not satisfactorily understood. Eastern Devonian and Mississippian shales have a more aromatic kerogen structure than do the Tertiary oil shales from the Green River Formation. Little attention has been paid to whether the bitumen is a significant reaction intermediate in the pyrolysis of these more aromatic shales.

## Objective

The objective of this research effort was to explore the chemistry of kerogen thermal decomposition in relationship to kerogen structure. Since the kerogen in oil shales exists in a variety of structural assemblages, understanding the chemistry of kerogen pyrolysis requires investigations of the pyrolysis kinetics of several different types of kerogens. Knowing the chemistry of the pyrolysis of shales having different aromatic and aliphatic carbon distributions is necessary for the development of a

general chemical kinetics model of kerogen decomposition. Also, by understanding these relationships it may be possible to improve the efficiency of the conversion processes or to develop novel approaches for greater conversion of kerogen to oil.

## Procedures

The oil shales investigated in this study were a New Albany oil shale (Clegg Creek Member) from Bullitt County, Kentucky, a Mahogany zone (Parachute Creek Member) Green River Formation shale from the Exxon Colony mine in Colorado, and a Tipton Member, Green River Formation oil shale from an outcrop near Rock Springs, Wyoming. These shales have been designated as reference shales in the U.S. Department of Energy (DOE) oil shale research program.

The shales were crushed to pass a 20-mesh (841 $\mu$ ) screen and the 20-45-mesh (841 $\mu$ -354 $\mu$ ) fraction was separated for decomposition studies. An initial 1500-g fraction of each shale was thoroughly mixed and was then split eight ways in two stages to yield 64 samples each weighing about 22 g. Twenty-gram samples were weighed from these for kinetic measurements.

A heated sand-bath reactor system was used for the isothermal decomposition experiments. This system gave rapid heat-up and reliable temperature control. Typically, 20-g samples were used so that sufficient products were generated for other analyses such as nuclear magnetic resonance (NMR), elemental analysis, and molecular weights. The isothermal experiments were conducted in the temperature range of 375 to 425°C (707 to 797°F).

Quenched nonisothermal pyrolysis experiments were conducted at heating rates of 2 and 10°C/min to 500°C (932°F) on a Cahn 131 thermogravimetric analyzer.

## Results

The temperature dependence of the bitumen is shown in Figure 1. The data show that in the temperature range of 375 to 425 °C (707 to 797 °F), the maximum amount of extractable bitumen from the Kentucky New Albany shale is about 14% of the original kerogen (425 °C [797 °F] data). However, the Colorado and Wyoming oil shales show greater amounts of extractable bitumen, reaching maximum values between 40 and 60% at 425 °C (797 °F). The lower maximum value at 440 °C (824 °F) for the Exxon-Colony is probably due to experimental constraints that prevent rapid heating and quenching of the shale in a time sufficiently short to observe the maximum value at this temperature. The differences in carbon structure and conversion to oil between the shales suggest that bitumen formation may be a function of the original kerogen structure (i.e., the more aliphatic the oil shale, the

more bitumen that is formed during pyrolysis). The maximum value of the bitumen increases with temperature. The implication of this observation is that the activation energy of kerogen decomposition is greater than the activation energy of bitumen decomposition.

A reasonable explanation for the low bitumen yields of the New Albany shale is that direct kerogen conversion to residue, oil, and gas competes with bitumen formation. Because the overall carbon conversion of the New Albany shale is about 35 and 56% to oil and residue, respectively, during Fischer assay, direct residue formation appears to be a major pathway for kerogen decomposition in this shale. It is also possible that for the New Albany shale, given the high aromatic carbon content, a certain portion of the original kerogen resembles a residue product.

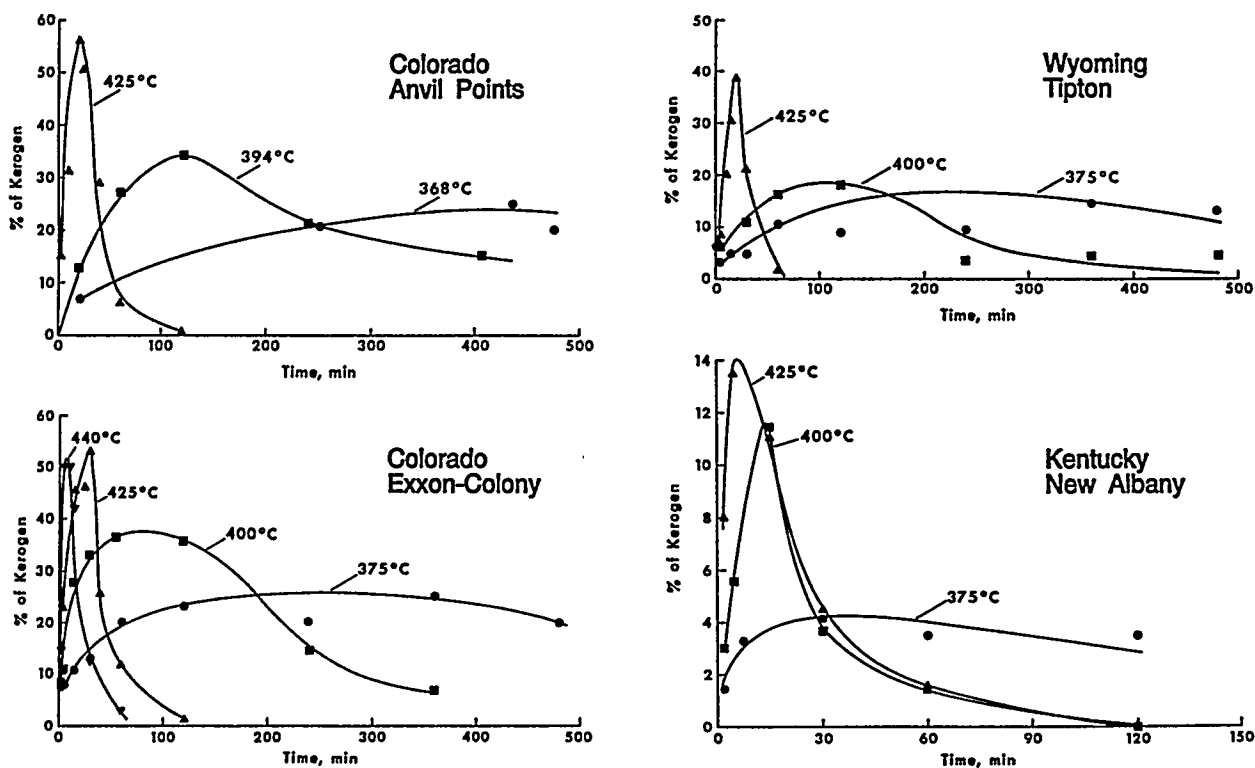


Figure 1. Time and Temperature Dependence of Bitumen

A significant finding from the 425°C (797°F) liquid product data for the western oil shales is that maxima in the oil plus bitumen curves are obtained. By quenching the reaction at the time of the maximum (~30 minutes), 85 to 95% of the carbon in the kerogen is recoverable as soluble products. For longer times, lesser amounts of soluble products are recoverable due to coking of the bitumen. Ultimately, the liquid yields will be that of the oil only, since the bitumen will have decomposed to form oil, gas, and residue products.

The behavior of the bitumen and kerogen under nonisothermal heating supported the notion that the activation energy of kerogen decomposition is greater than the activation energy of bitumen decomposition.

Hydrogen-to-carbon (H/C) ratios and molecular weights were determined for the oils and bitumens produced from isothermal decomposition of the Colorado Exxon and Kentucky New Albany oil shales. For the shale oils, the H/C ratios and molecular weights were remarkably constant at all times and temperatures for each type of shale oil.

Chemical property measurements of the bitumen were limited by the small amounts of bitumen extracted from the 20-g samples of shale. This was especially true for the Kentucky oil shale in which little bitumen was extracted throughout the decomposition, and for the Colorado oil shale at longer reaction times where little bitumen remained. In general, the composition and properties of the bitumen changed during the course of the reaction. This was most evident from the molecular weight data which showed that the bitumen molecular weight passed through a maximum during the decomposition.

### **Conclusions**

Isothermal pyrolysis studies found that the maximum amount of extractable bitumen in the New Albany shale was 14% or less of the original kerogen at any given temperature, indicating that direct

conversion of kerogen to oil, gas, and residue products was a major pathway of conversion of this shale during pyrolysis. In contrast, significant fractions of the Colorado and Wyoming oil shale kerogens were converted to the intermediate bitumen during pyrolysis. The bitumen data indicate that the formation of soluble intermediates may depend on original kerogen structure and may be necessary for producing high yields by pyrolysis.

The H/C ratios and molecular weights of the produced oils from both shales were constant at all times and temperatures. However, the bitumen showed decreasing H/C ratios and exhibited variable molecular weights with time and temperature, demonstrating the variable composition of this material during pyrolysis.

Quenched nonisothermal pyrolysis studies were conducted on two western reference oil shales. The conversion of kerogen to bitumen and volatiles (oil and gas) was obtained for heating rates of 2 and 10 °C/min in the range of 300 to 500°C (572 to 932 °F) using a modified thermogravimetric analyzer. Particular attention was paid to the formation of the intermediate bitumen during decomposition of the shale.

The maximum amount of extractable bitumen increases with temperature and with heating rate. These observations are consistent with an oil shale decomposition model in which the activation energy for kerogen decomposition is greater than the activation energy of bitumen decomposition.

### **Related Publications and Presentations**

#### **Publications**

Chong, S.-L., F.P. Miknis, X. Zhao, and S.A. Holmes, 1989, Characteristics of Pyrobitumen and Oil Obtained from the Pyrolysis of Tipton Member, Green River Oil Shale. ACS Div. of Petrol. Chemistry Preprints, 34(1): 71-75.

Chong, S.-L., R.-Y. Wu, F.P. Miknis, and T.F. Turner, 1989, Characteristics of Pyrobitumen and Oil Obtained from Green River Oil Shale Pyrolysis. Fuel Sci. and Technol. Int., 7: 347-376.

Miknis, F.P., 1990, Oil Shale Reaction Kinetics at Low Heating Rates. Proceedings Oil Shale and Tar Sands Contractors Review Meeting, Morgantown, WV, April 18-20, 1990.

Miknis, F.P., and B.E. Thomas, 1989, Quenched Nonisothermal Decomposition Studies of Department of Energy Western Reference Oil Shales: Preliminary Results. Laramie WY, DOE/MC/11076-2886.

Miknis, F.P., and T.F. Turner, 1988, Thermal Decomposition of Tipton Member, Green River Formation Oil Shale from Wyoming. Laramie, WY, DOE/MC/11076-2702.

Miknis, F.P., T.F. Turner, and L.W. Ennen, 1987, Thermal Behavior of Bitumen Produced from Isothermal Decomposition of Colorado and Kentucky Oil Shale. 1987 Eastern Oil Shale Symposium Proceedings, Lexington, KY, 323-328.

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Miknis, F.P., T.F. Turner, L.W. Ennen, S.-L. Chong, and R. Glaser, 1988, Thermal Decomposition of Colorado and Kentucky Reference Oil Shales. Laramie, WY, DOE/MC/11076-2625.

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S.-L. Chong, F.P. Miknis, X. Zhao and S.A. Holmes, 1989, Characteristics of Pyrobitumen and Oil Obtained from the Pyrolysis of Tipton Member Green River Formation Oil Shale. ACS Symposium on Comparative Studies of Various Oil Shales, Dallas, TX.

F.P. Miknis, 1988, Thermal Decomposition of DOE Reference Shale. Third Annual Oil Shale, Tar Sand, and Mild Gasification Contractor's Review Meeting, Morgantown, WV.

F.P. Miknis, 1991, Solid State  $^{13}\text{C}$  NMR in Oil Shale and Coal Research. Government Industrial Development Laboratory, Sapporo, Japan, and National Chemical Laboratory for Industry, Tsukuba, Japan, (invited lectures).

F.P. Miknis, T.F. Turner, and L.W. Ennen, 1987, Thermal Behavior of Bitumen Produced from Isothermal Decomposition of Colorado and Kentucky Oil Shale. 1987 Eastern Oil Shale Symposium, Lexington, KY.

F.P. Miknis, T.F. Turner and R.R. Glaser, 1989, Thermal Decomposition of DOE Reference Oil Shales. ACS Symposium on Comparative Studies of Various Oil Shales, Dallas, TX.

T.F. Turner, F.P. Miknis, G.L. Berdan, and P.J. Conn, 1987, A Comparison of the Thermal Decomposition of Colorado and Kentucky Oil Shale. ACS National Meeting, Symposium on Advances in Oil Shale Chemistry, Denver, CO.



# CHARACTERIZATION OF REFERENCE OIL SHALES

Francis P. Miknis

## Background

In 1984, DOE made an assessment of its oil shale program based on information from industry, the Fossil Energy Research Working Group, a National Research Council review of safety issues related to synthetic fuels development, a review of available oil shale data, and an examination of the existing DOE oil shale program. This led to a restructuring of the DOE oil shale program. An integral part of the restructured program involved the measurement of fundamental chemical and physical properties of reference oil shales.

Under the DOE reference shale program, two oil shales per year were to have been acquired and characterized over a 5-year period. A total of ten oil shales were to have been acquired; five from the western United States deposits, and five from deposits in the eastern United States. The shales selected were to be as representative as possible of what may likely be used in future oil shale development.

Fundamental chemical and physical properties were acquired on two western and one eastern reference oil shale during the period of this Cooperative Agreement. The reference shale program was discontinued in 1990.

## Objectives

The objectives of this research activity were to define the fundamental characteristics of oil shales selected by DOE for research conducted within the oil shale program. The reference shales were to be analyzed to provide data on the chemical and physical properties of oil shales and their products. This information could then be used to better understand the reaction chemistry and transport processes in retorting and environmental systems.

## Procedures

The two western reference shales that were studied included a Mahogany zone, Parachute Creek Member, Green River Formation oil shale obtained from the Exxon Colony mine located near Parachute, Colorado and a Tipton Member, Green River Formation oil shale obtained from an outcrop near Rock Springs, Wyoming. The eastern reference shale was a Clegg Creek Member, New Albany shale obtained from the Knieriem quarry, which is located approximately 16 miles south of the Ohio River at Louisville, Kentucky.

The measurements that were made on the reference shales are listed in Table 1. The procedures are described in detail in the report by Miknis and Robertson (1987).

## Results

Material Balance Fischer Assay (MBFA) results for the reference shales are presented in Table 2. The conversion of organic carbon to oil, gas, and residue carbon is given in Table 3. The greater conversion of organic carbon to oil for the western reference shale is clearly evident from the data in Table 3. The differences in conversion of organic carbon to oil, gas, and residue products are related to the carbon structure of the original organic material.

Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) measurements were made on the reference shale and liquid-state  $^{13}\text{C}$  NMR measurement were made on the MBFA shale oils (Table 4). The carbon aromaticity values of the shales are compatible with the conversion data in Table 3.

Gross heating values were determined on the reference shales using a standard ASTM procedure (D 3286). The results are

reported in Table 4. Measurements were made on the raw shales and the spent shales from the MBFA tests. The heating value of the spent shale is greater for the eastern shale because of the greater residue carbon on the spent shale.

Eastern reference shales are dominated by silicate minerals, especially clay minerals and quartz; while western reference shales contain both carbonate and silicate minerals in moderate abundances. In the western reference shales, clay minerals constitute only a minor fraction of the total mineral assemblage, whereas clay minerals contained in the eastern reference shales are abundant and diverse in type.

The trace element data reaffirmed previous observations that all the elements of interest remain in the spent shale. Differences in the major trace element data between the shales reflected their differences in mineralogy.

ASTM D 86, D 1160, and D 2892 distillations were performed on the eastern and western shale oils. The distillation mid-point data for each cut of the ASTM D 2892 (True Boiling Point) distillations were observed to correlate quite well with the D 86 distillation end-point data over the temperature range where both the D 2892 and D 86 distillations proceeded. However, the eastern shale oil distilled at approximately 24°C (100°F) lower by the D-86 Method than by the D-2892 Method.

**Table 1. Chemical and Physical Property Measurements on Reference Shales and Products**

	Raw Shale	Retorted Shale	Shale Oil	Kerogen Concentrates
Material balance Fischer assay	X			
Carbon, hydrogen, nitrogen, sulfur	X	X	X	X
Pyritic sulfur	X			X
Mineral carbon	X	X		
Carbon aromaticity	X		X	X
Hydrogen aromaticity			X	
Oxygen	X	X	X	X
Trace metals	X	X	X	
Compound class separation			X	
Bulk mineralogy	X	X		
Clay content	X	X		
Molecular weight (average)			X	
Heat capacity	X	X	X	
Heat of retorting	X			
Heat of mineral dehydration	X			
ASTM D 86 distillation			X	
ASTM D 1160 distillation			X	
True boiling point distillation			X	
Specific gravity			X	
Viscosity			X	
Pour point			X	

**Table 2. Material Balance Fischer Assay Results for Reference Shales**

Product	wt %	Gal/ton	% Ash	Mineral Carbon wt %	C wt %	H wt %	N wt %	S wt %
<b><u>Colorado Reference Oil Shale</u></b>								
Oil	10.24	27.50	—	—	83.2	12.2	1.7	0.7
Gas	4.60	—	—	—	41.4	7.0	—	4.8
Spent shale	83.50	—	78.63	4.9	8.8	0.2	0.5	1.1
Water	1.62	3.88	—	—	—	11.1	—	—
Raw shale	100.00	—	66.90	4.2	18.0	1.9	0.6	1.3
% Recovery	99.96	—	98.14	97.42	98.8	101.4	89.7	94.1
<b><u>Kentucky Reference Oil Shale</u></b>								
Oil	5.67	14.38	—	—	84.5	10.6	1.2	1.6
Gas	3.16	—	—	—	39.5	12.4	—	40.5
Spent shale	89.54	—	87.12	0.22	8.7	0.4	0.9	4.5
Water	1.20	2.87	—	—	—	11.1	—	—
Raw shale	100.00	—	78.38	0.25	13.9	1.4	0.4	5.8
% Recovery	99.57	—	99.52	78.8	99.7	104.9	114.1	92.6
<b><u>Wyoming Reference Oil Shale</u></b>								
Oil	8.84	22.03	—	—	81.6	10.9	2.1	0.5
Gas	2.09	—	—	—	42.9	9.1	—	0.1
Spent shale	85.96	—	81.33	3.7	7.7	0.3	0.5	0.4
Water	3.15	7.56	—	—	—	11.1	—	—
Raw shale	100.00	—	71.23	3.4	14.97	1.4	0.6	0.4
% Recovery	100.04	—	98.15	93.50	98.40	129.0	102.60	97.5

**Table 3. Organic Carbon Conversion in Reference Shales**

Product	% Conversion		
	Colorado	Wyoming	Kentucky
Oil	61.7	62.4	35.1
Gas	13.8	7.8	9.1
Residue	23.7	29.8	55.8

**Table 4. Other Properties of Oil Shale and Shale Oil**

Property	Colorado	Wyoming	Kentucky
<b><u>Heating Value, Btu/lb</u></b>			
Raw shale	2,607	1,730	2,859
Spent shale	370	140	1,587
Shale oil	18,650	17,630	18,100
Molecular weight - Shale oil	295	290	275
<b>Carbon aromaticity</b>			
Raw shale	0.259	0.330	0.450
Shale oil	0.236	0.259	0.420
<b>Proton aromaticity</b>			
Shale oil	0.043	0.062	0.110

The conversion behavior of 10 oil shales from seven foreign and three domestic deposits was also studied by combining solid- and liquid-state NMR measurements with MBFA conversion data. The extent of aromatization of aliphatic carbons was determined. Between zero and 42% of the raw shale aliphatic carbon formed aromatic carbon during Fischer assay. For three of the shales, there was more aromatic carbon in the residue after Fischer assay than in the raw shale. Between 10 and 20% of the raw shale aliphatic carbons ended up as aliphatic carbons on the spent shale. Good correlations were found between the raw shale aliphatic carbon and carbon in the oil and between the raw shale aromatic carbon and aromatic carbon on the spent shale. Simulated distillations and molecular weight determinations were performed on the shale oils. Greater than 50% of the oil consisted of the atmospheric and vacuum gas oil boiling fractions.

### **Conclusions**

The properties of the reference shales are comparable to the properties of other

western and eastern oil shales. Western oil shales from the Green River Formation typically have high conversions to oil because of their low carbon aromaticities and hydrogen richness. Eastern oil shales have low conversion to oil because of their higher carbon aromaticity and low hydrogen content.

Carbon-containing minerals dominate the mineralogy of the western oil shale, while silicates and clay minerals are predominant in the eastern reference shale. These minerals are indicative of the lacustrine and near shore to shallow marine depositional environments of the western and eastern shales, respectively.

Standard API and other published correlations do not appear to be adequate for predicting properties of shale oils. Poor agreement was obtained between calculated and measured molecular weights. Consequently, calculated properties that make use of molecular weight data, such as solubility parameters, would be expected to be in disagreement with measured results.

The combination of NMR measurements with MBFA data provides a method whereby the extent of aromatization reactions can be determined. Because these reactions are precursors to coke formation, this information can be important for process optimization. Aromatization reactions were shown to be most important in those oil shales having the lowest Fischer assay conversions to oil.

## **Related Publications and Presentations**

### **Publications**

Chong, K.P., A.I. Leskinen, and F.P. Miknis, 1987, Relationships of Oil Content and Rock Density for New Albany Reference Oil Shale and Sound Velocity Measurements. 1987 Eastern Oil Shale Symposium Proceedings, Lexington, KY, 119-123.

Miknis, F.P., 1988, Characterization of DOE Reference Oil Shale: Tipton Member, Green River Formation Oil Shale from Wyoming. Laramie, WY, DOE/MC/11076-2676.

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Miknis, F.P., 1990, Conversion Characteristics of Foreign and Domestic Oil Shales. Proceedings 23rd Oil Shale Symposium, Colorado School of Mines, Golden, CO, 100-109.

Miknis, F.P., 1992, Combined NMR and Fischer Assay Study of Oil Shale Conversion. Fuel, 71, 731-738.

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Wu, R.-Y., S.-L. Chong, and F.P. Miknis, 1988, Comparison of Fischer Assay Shale Oils Produced from Different Oil Shales. 1988 International Oil Shale Symposium Proceedings, Beijing, China, 327-334.

### **Presentations**

K.P. Chong, A.I. Leokinen and F.P. Miknis, 1987, Relationships of Oil Content and Rock Density for New Albany Reference Oil Shale and Sound Velocity Measurements. 1987 Eastern Oil Shale Symposium, Lexington KY.

F.P. Miknis, 1989, Development of a Coking Indicator for Oil Shales. 1989 Eastern Oil Shale Symposium, Lexington, KY.

F.P. Miknis, 1990, Conversion Characteristics of Selected Foreign and Domestic Oil Shales. 23rd Oil Shale Symposium, Colorado School of Mines, Golden CO.

F.P. Miknis, 1991, Solid State  $^{13}\text{C}$  NMR in Oil Shale and Coal Research. Government Industrial Development Laboratory, Sapporo, Japan, and National Chemical Laboratory for Industry, Tsukuba, Japan, (invited lectures).

Wu, R.-Y., S.-L. Chong, and F.P. Miknis, 1988, Comparison of Fischer Assay Shale Oils Produced from Different Oil Shales. 1988 International Oil Shale Symposium, Beijing, China.

# SHALE OIL RESIDUA FOR PAVING APPLICATIONS

P. Michael Harnsberger

## Background

Shale oil has been used in road surfacing applications for several decades. Originally, these materials were probably used for dust control on mine roads as a way to dispose of the heavier, less-desirable fractions of shale oil similar to the way cut-back asphalts were used during the same time period. However, there has not been a great interest in using shale oil materials in paving applications (Plancher and Petersen 1984) until the last decade. During the early 1980s the work in this area resulted in a DOE patent by Plancher and Petersen (1982), licensed to Western Research Institute (WRI), using shale oil residua materials in asphalt paving applications to reduce moisture damage.

The several studies reported here investigated other uses and materials derived from shale oil residua, both eastern and western, that may be useful in the asphalt and asphalt paving industry. The studies examined using eastern and western shale oil residua as recycling agents for used pavements, the use of western shale bitumen as an additive to petroleum asphalt to reduce moisture damage susceptibility, the use of western shale oil residue as an additive to petroleum asphalt for use as a pavement crack and joint sealant material, and the energies of interaction and rheological properties of petroleum asphalt modified with western shale oil residue.

## Objectives

The objectives of these studies were to explore additional uses of western shale oil residua and to explore potential uses for eastern shale oil residua in nonfuel related areas. By focusing on nonfuel uses for these residual materials, they can be easily and inexpensively prepared for uses that are generally high-dollar specialty markets. As larger amounts of the shale oil barrel are marketed in products with relatively high

prices, the economics for producing shale oil improve.

## Procedures

The New Albany (eastern) and Green River Formation (western) shale oils used in the recycling study were produced by the WRI inclined fluidized-bed process (Merriam and Cha 1987). The petroleum asphalts and the recycled mixtures were aged using the thin-film accelerated aging test (Petersen 1989) to simulate asphalt aging with time in a pavement. Asphalt properties were measured using ASTM D 3381 tests to grade asphalt cements. Aged asphalts and recycled mixtures were analyzed using dynamic rheology and infrared spectroscopy (Petersen 1975; Petersen and Plancher 1981). Moisture damage susceptibility was assessed using the water susceptibility test (WST) (Plancher et al. 1980) using two aggregates of different mineral types. Low-temperature properties of recycled mixtures were analyzed using a tensile-elongation test to measure the stiffness modulus and the percent elongation.

The western shale bitumen used in the shale bitumen additive study was obtained by supercritical fluid extraction of oil shale using methanol and water at about 400°C (752°F). The products were recovered by extraction with organic solvent. Solvent was subsequently removed *in vacuo* (McKay et al. 1983; McKay and Chong 1983). The unrefined shale bitumen was added to a petroleum asphalt at levels of 15 and 20%. The effects of moisture damage were assessed using the WST on two aggregates of different mineral types.

The western shale oil residue used as an additive to petroleum asphalt for the crack and joint sealant evaluation, and also for the energy of interaction study was prepared by The New Paraho Corporation using a +371°C (+700°F) shale oil residue

that was further processed to produce a specification grade AC-20 asphalt. The evaluation of the shale oil-modified asphalts for use as crack and joint sealant material was accomplished using ASTM D 3407 extension testing, rheological testing of portland cement concrete-asphalt briquettes, dynamic rheological analysis of unaged and aged asphalts, and bonding energy measurements between the asphalt materials and four aggregates (including crushed concrete) using microcalorimetry (Ensley and Scholz 1972).

## **Results**

The recycling study showed that the western shale oil residue could function as an asphalt recycling agent; whereas, the eastern shale oil residue had vastly different properties. The western shale oil residue-asphalt blends had good properties with respect to moisture damage resistance, but somewhat inferior properties with respect to further aging compared with a commercial recycling agent. The results also showed that the effectiveness and the properties of petroleum asphalts recycled with western shale oil residue are dependent upon the composition of the petroleum crude source of the asphalt.

The eastern shale oil residue prepared for the recycling study had a viscosity substantially too high for use as a recycling agent; therefore, it was studied as an asphalt stiffening agent with very soft asphalts. It appeared that the chemistry of the eastern shale oil residue was appropriate for asphalt recycling because of its dispersant nature, but that its initial viscosity, and/or perhaps its average molecular weight distribution, were too high to be useful.

The results from the use of unrefined western shale bitumen as an additive to petroleum asphalt to reduce moisture damage showed that there is some advantage to using this material, but substantially less than has been shown with other shale-derived materials. Some refinement of the bitumen is needed to improve its effect on reducing moisture

damage susceptibility, perhaps because of the significant amounts of carboxylic acids present in the unrefined bitumen.

The results from the addition of western shale oil residue to petroleum asphalt for use as a crack and joint sealant material showed that some improvement was obtained with the addition of the shale oil residue compared with conventional petroleum asphalt. However, the performance of the modified materials in the ASTM extension test was substantially inferior to commercially available, but more expensive, rubber-modified sealant materials. The shale oil-modified asphalts did show better adhesive properties in the extension test. The shale oil-modified asphalts also showed improved relaxation times and larger amounts of recovery in a stress-relaxation type of test using portland cement concrete-asphalt briquettes. The dynamic rheological analysis of the shale oil-modified asphalts showed some improvement in the viscosity-temperature susceptibility properties compared with the petroleum asphalt. The shale oil-modified asphalts also showed higher energies of interaction (bonding energies) with the aggregates tested compared with the petroleum asphalt, supporting previous data that indicated shale oil-modified asphalts improve the resistance to water damage in pavements.

## **Conclusions**

The addition of western shale oil residue to petroleum asphalts showed some improved properties compared with conventional materials when used as a recycling agent and also as an additive in crack and joint sealant material. The improved properties were better resistance to moisture damage, better temperature susceptibility properties, and better bonding properties to aggregate surfaces, including crushed portland cement concrete. The addition of unrefined western oil shale bitumen only showed slight improvement in the resistance to moisture damage, indicating that some refinement is necessary.

The eastern shale oil residue did not have the necessary physical properties to be used as an asphalt recycling agent, but the material did have some dispersant characteristics that would be necessary for an asphalt recycling agent.

In summary, these studies did show that both eastern and western shale oil residua have potential for use in the asphalt and asphalt paving industry.

### **Related Publications and Presentations**

#### **Publications**

Harnsberger, P.M., and R.E. Robertson, 1990, Evaluation of Eastern and Western Shale Oil Residua As Asphalt Pavement Recycling Agents. Laramie, WY, DOE/MC/11076-2869.

Harnsberger, P.M., J.M. Wolf, and R.E. Robertson, 1992, Evaluation of Western Shale Oil Residue As An Additive to Petroleum Asphalt For Use As A Pavement Crack and Joint Sealant Material. Laramie, WY, WRI-92-R049.

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Harnsberger, P.M., 1990, Evaluation of Eastern and Western Shale Oil Residua As Asphalt Pavement Recycling Agents. Fourth Oil Shale and Tar Sand Contractors Review Meeting, Morgantown, WV.

Harnsberger, P.M., 1990, Evaluation of Eastern and Western Shale Oil Residua As Asphalt Pavement Recycling Agents. Twenty-seventh Annual Petersen Asphalt Research Conference, Laramie, WY.



# INORGANIC GEOCHEMICAL CHARACTERIZATION OF RETORTED OIL SHALE

Susan S. Sorini

## Background

Commercial production of shale oil would result in the generation of large volumes of solid oil shale processing wastes, creating a significant disposal problem. A major concern associated with disposal of spent oil shale wastes is solubilization and mobilization of environmentally harmful chemical constituents from the spent shale by ground and surface waters. As a result, methods to predict water quality from spent oil shale disposal sites are needed. To predict the fate and behavior of the elemental constituents in spent oil shale and assess the effectiveness of proposed mitigation techniques, it is important to understand the processes controlling partitioning of the elements between solid and solution phases. This requires evaluation of the mineralogy and corresponding solution chemistry of spent shale/water systems. The information obtained by studying elemental aqueous- and solid-phase distribution will provide a basis for decisions concerning disposal of spent oil shale in an environmentally sound manner.

## Objectives

Several studies were conducted on spent oil shale mineralogy and chemical and physical interactions that occur in spent oil shale/water systems to obtain a better understanding of the processes that influence the partitioning of elements between spent oil shale solid and solution phases. The objectives of this research were to (1) characterize spent oil shale and spent oil shale aqueous extracts and evaluate experimental and geochemical modeling techniques that can be used to identify processes controlling the chemical composition of oil shale leachates; (2) determine the mineralogy and leachate chemistry of spent reference oil shales, provide a preliminary assessment of spent oil shale weathering reactions, and

determine the solid and solution speciation of potentially toxic constituents in spent shale/leachate systems; (3) study processes controlling molybdenum aqueous- and solid-phase distribution in spent oil shale; (4) assess the solubility relationships of fluorine and molybdenum in spent oil shale, examine the mineralogy and leachate chemistry of combusted oil shales in laboratory weathering experiments, and examine literature on the characterization of spent oil shale; (5) examine the solution chemistry and mineralogy of spent oil shale as a function of time to determine the extent to which weathering reactions occur; (6) provide a detailed characterization of the chemistry of lysimeter leachates by subjecting the leachate concentration data to chemical equilibria model analysis; (7) evaluate trace elements in sulfide minerals from a Chattanooga shale core from central Tennessee and establish mineral residence and stratigraphic distribution of selected trace elements; (8) characterize the sulfur-bearing minerals present in raw and processed eastern and western oil shale; (9) examine the mineralogy and solubility of ettringite, a complex hydrated calcium aluminum sulfate hydroxide, in weathered spent oil shales and reexamine the ettringite equilibrium solubility characterizations of spent oil shales; (10) evaluate the applicability of existing geochemical models to predict water quality from an oil shale solid waste environment; and (11) determine the mineral phases responsible for cementation of Lurgi spent oil shale.

## Procedures

Four spent western reference oil shales, one combusted, one Paraho indirectly retorted, and two Paraho directly retorted, were subjected to detailed physical, chemical, and mineralogical characterizations. Total elemental content, calcium carbonate equivalent, specific surface area, cation

exchange capacity, clay mineralogy, exchangeable cations, and soluble cations and anions were determined in each of the spent shales. Mineralogy was determined using X-ray diffraction (XRD) following nondestructive preconcentration of mineral phases into density separates using a float-sink density fractionation technique. Selective sequential dissolution analysis was performed to partition trace and minor elements into carbonate and exchangeable, organic and manganese oxide, iron oxide, and residual combusted oil shale fractions. The influence of spent oil shale solids on leachate chemistry was examined in a batch equilibrium study. The data from this study were used as input to a geochemical model to predict elemental speciation.

In a study conducted in 1988, the solubility of calcium molybdate ( $\text{CaMoO}_4$ ) was determined, and the results were used to evaluate the occurrence of  $\text{CaMoO}_4$  in the spent western oil shale samples used in the previous study. The influence of the oil extraction process, solid-solution contact time, and recarbonation on spent oil shale leachate chemical composition was examined, along with the chemical characteristics of short-term spent western, recarbonated spent western, and spent eastern reference oil shale leachates. The mineralogy of the spent eastern and western oil shale samples was determined, along with the mineralogy of hydrated and recarbonated spent oil shale samples. The use of geochemical models to predict leachate composition was also illustrated.

A study to provide information to help in understanding the processes controlling molybdenum aqueous- and solid-phase distribution was conducted in 1990. This involved measuring the ion association constants for the formation of calcium and magnesium molybdate ion pairs by potentiometric titration at pH 7 and 25°C (77°F) in  $\text{NaNO}_3$  ionic media. The measured values were then used to examine the equilibrium solubility of powellite ( $\text{CaMoO}_4$ ) in  $\text{KNO}_3$  solutions and spent oil shale systems.

In a 1991 study, the solubility of fluorine and molybdenum in spent oil shale was examined. Combusted Green River Formation oil shale and combusted New Albany shale, both produced in a fluidized-bed reactor, and a second Green River Formation oil shale, produced by the Lurgi-Ruhrgas process (Rammler 1982) were used in the study. The spent oil shales were subjected to nonequilibrium weathering using a humidity cell technique (Caruccio 1968; Sullivan et al. 1987) involving a 7-day weathering cycle, which continued for 18 weeks. Leachates from the weathering experiments were generated weekly and were analyzed for their chemical constituents. Subsamples of the weathered spent oil shale from the humidity cells were analyzed using XRD. Fluorine and molybdenum relationships were evaluated using a modified batch leaching technique involving a solid-to-liquid ratio of 1:2 and a 28-day equilibration period. After the first equilibration period, the slurries were filtered, and a second 28-day equilibration period was started. At the completion of the second equilibration period, leachates were once again collected. The spent oil shale samples were weathered for a total of six equilibration cycles; and the resulting leachates were submitted for chemical analysis. Geochemical model analysis was performed using the model GEOCHEM (Sposito and Mattigod 1980).

In a fifth study, the changes in solution chemistry and mineralogy of spent oil shale were examined as a function of time to determine the extent of weathering reactions. The oil shale studied was a byproduct of the Lurgi-Ruhrgas processing method (Mehta et al. 1980). One hundred grams of spent shale were mixed with 50 mL of high-purity water. The mixtures were allowed to sit at room temperature for times ranging from 1 minute to 24 hours (16 time periods). After the appropriate time had elapsed, the water/spent shale mixtures were filtered, and the resulting filtrates were analyzed for pH and various cations, anions, and chemical compounds. The chemical data from analysis of the filtrates were evaluated using the chemical

equilibrium model GEOCHEM. Mineralogy of the oil shale solid waste samples was determined by XRD using an automated, computerized Scintag PAD V diffractometer.

In another study, leachates from field lysimeters containing an eastern oil shale, a retorted eastern oil shale, and an oil shale fines/retorted oil shale mixture were subjected to chemical equilibria analysis using a geochemical model. Leachates from three lysimeters were collected from sampling ports at a depth of 10 ft, and data from analysis of these leachates were studied with the chemical equilibria model GEOCHEM.

A study involving Chattanooga shale was performed to examine selected trace elements contained in sulfide minerals of the shale and to determine mineralogical residencies and stratigraphic distribution. Gravity concentration and digestion procedures were used to isolate the sulfide mineral fraction from the bulk shale. Both the bulk oil shale and the sulfide mineral fraction were analyzed for trace elements. XRD, scanning electron microscopy/energy dispersive X-ray (SEM/EDX), and analytical chemical techniques were used to evaluate the mineralogy, morphology, and elemental composition of the sulfide mineral concentrates.

In a second study to investigate sulfur-containing minerals in oil shale, raw Chattanooga shale, oil shale samples from the DOE reference shale program, and spent samples from Western Research Institute's TREE program (Mason 1984; Mones and Glaser 1986) were studied. Gravity concentration was used to concentrate the sulfide minerals; XRD analysis was used to study the mineralogy of the concentrated samples; and SEM/EDX analysis was used to study the crystal morphology, chemistry, and grain relationships to the surrounding oil shale.

In a study to investigate the composition and solubility of ettringite, a combusted oil shale, produced in a fluidized-bed reactor using air as the process gas (Merriam et al. 1987), was mixed with high-purity water in

a 1:1 solid-to-liquid ratio. The suspension was allowed to stand, with periodic shaking to precipitate ettringite from the combusted oil shale suspension. Centrifugation was used to separate a white precipitate from the other solids and liquid in the suspension. The precipitate was then washed with absolute ethanol and stored under absolute ethanol for characterization and solubility analysis. The precipitate was characterized by XRD analysis. Morphology and chemistry of the precipitate were analyzed by SEM/EDX. The precipitate was also dissolved using HNO<sub>3</sub>-HF-HCl (Bernas 1968), and the resulting solution was analyzed for metals by inductively coupled plasma analysis. Total sulfur content of the solution was also determined.

A stability diagram was constructed to determine the solution conditions under which ettringite has greater stability than gypsum and gibbsite. In equilibrium tests, the precipitate was subjected to 0.1-M and 0.05-M NaOH solutions for 7 days. After the equilibration period, the solids were analyzed by XRD. Based on this preliminary evaluation, equilibrium solubility was determined under two different ionic strength conditions. In these tests, 2-g samples of the precipitate were mixed with 150 mL of either 0.01-M or 0.005-M CO<sub>2</sub>-free NaOH for a period of 14 to 72 days. After equilibration, the solids were analyzed using XRD and SEM/EDX; and the solutions were analyzed for pH, metals, and total sulfate. Aqueous leachate data from the spent oil shale used in this study had previously been treated using the geochemical model GEOCHEM (Essington et al. 1987; Essington and Spackman 1988). As a result, information from that characterization was available for review.

Geochemical modeling research related to oil shale solid waste has involved evaluation of geochemical models and critical evaluation of thermodynamic data. To evaluate the applicability of existing geochemical codes for oil shale solid waste, the following codes were examined in detail: EQ3/EQ6 (Worley 1979), GEOCHEM (Sposito and Mattigod 1980), MINTEQ (Felmy et al. 1983), PHREEQE (Parkhurst

et al. 1980), SOLMNEQ (Kharaka and Barnes 1973), and WATEQFC (Runnells and Lindberg 1981). Based on evaluation of these models, it was decided that selection of any one of the models for application to oil shale solid waste would require the development of a more reliable thermodynamic database. This requires critical evaluation of thermodynamic data, reviewing available literature, and selecting the most reliable thermodynamic data for minerals and solution complexes that are important for oil shale solid waste studies. Critical evaluations of thermodynamic data were completed for strontium, molybdenum, fluorine, selenium, calcium, magnesium, sodium, and potassium.

A study to identify the mineral phases responsible for cementation in the byproduct resulting from the Lurgi-Ruhrgas processing of oil shale, involved preparing compacted columns of the processed oil shale and water. The columns were made using either a 20 or 30% water content, and were allowed to cure for the following periods of time: 1 day, 20% water; 1 day, 30% water; 17 days, 20% water; 14 days, 30% water; and 56 days, 30% water. The following analyses were performed: XRD analysis of unhydrated and hydrated spent shale; SEM/EDX analysis of the samples cured for 14 and 56 days; and differential thermal analysis and thermogravimetric analysis to correlate compressive strength gain with thermal alterations.

## Results

A study involving extensive characterization of four spent western reference oil shales showed that with the exception of carbon content, the elemental compositions of the spent shales examined were similar. The indirectly retorted oil shale had significantly higher concentrations of total, organic, and inorganic carbon than the directly retorted and combusted oil shales. The properties of the spent shale solids that influence the mobility of elements in a leaching environment (i.e., specific surface area and cation exchange capacity) were greatly influenced by spent oil shale type. The combusted oil shale had the greatest

specific surface area and cation exchange capacity, followed by the indirectly and directly retorted oil shale samples. The spent oil shale water extracts were highly saline, sodic, and alkaline. The major mineralogy of the spent oil shales was consistent with predictions based on process temperatures. Selective dissolution of mineral phases from the combusted oil shale indicated the following mineralogical residences: strontium-carbonates; barium-carbonates, organics, silicates, and aluminosilicates; manganese-carbonates and iron sulfides; vanadium, chromium, cobalt, molybdenum, and nickel-iron sulfides and oxides; copper-iron sulfides and oxides, and carbonates; zinc-iron sulfides and carbonates; and lead-iron sulfides, carbonates, and iron oxides. The concentrations of elements, pH, and redox potential of aqueous extracts were influenced by spent oil shale type. Leachates were dominated by sodium, potassium, sulfate, reduced sulfur species, and alkaline conditions. Adsorption isotherms showed the combusted oil shale to have the highest affinity for arsenate and selenite.

Data from the 1988 study to evaluate the occurrence of  $\text{CaMoO}_4$  in the spent western reference oil shales described above suggested that  $\text{CaMoO}_4$  does not control molybdenum concentrations in the spent oil shale equilibrium solutions and may not even occur in the spent oil shales. The chemical characteristics of short-term spent western, recarbonated spent western, and spent eastern reference oil shale leachates show that solid-solution contact times, recarbonation, oil extraction process, and oil shale resource all affect leachate chemical composition. The mineralogical study of spent eastern and western oil shales shows that spent shale mineralogy is consistent with that predicted from the process temperature history of the samples. With the exception of the combusted oil shale samples, no mineralogical differences between anhydrous and hydrated samples were observed. Gypsum and ettringite occur in hydrated-retorted and hydrated-combusted oil shale samples.

Recarbonation resulted in the precipitation of calcite. Although geochemical models have a number of shortcomings, a geochemical model was used in this study to predict the concentrations of fluoride in spent oil shale leachates.

The results of a 1990 study to help in understanding the processes controlling molybdenum aqueous- and solid-phase distribution showed that calcium and magnesium have a significant influence on the aqueous chemistry of molybdenum. Data evaluation suggested that  $\text{Ca}(\text{MoO}_4)_2^{-2}$  and  $\text{NaMoO}_4^-$  may significantly contribute to total soluble molybdenum. It was found that ion association model examination of spent oil shale solutions must include all species known to occur. However, for many important species, ion association constants are either unavailable, estimated, or not critically evaluated. In previous studies, the occurrence of powellite in spent oil shale and its control of molybdenum solubility were reported based on solubility data and ion association model analysis. However, soluble molybdenum species were not considered in the data analysis. As a result, it was believed that additional analyses were required to determine if powellite is present in spent oil shale.

During initial cycles of the equilibrium weathering study conducted in 1991 to evaluate fluorine and molybdenum in combusted oil shale, the solubility relationships for fluorine and molybdenum were similar to those found in the literature. However, as weathering progressed, the spent oil shale leachates became supersaturated with respect to fluorite ( $\text{CaF}_2$ ) and saturated with respect to powellite ( $\text{CaMoO}_4$ ), which was found to exist in the spent oil shale. These results indicate that in a weathering environment, subject to slow infiltration of water, the behavior of molybdenum in spent oil shale may be predicted on the basis of powellite solubility. However, fluorine behavior cannot be predicted due to the fact that the system becomes supersaturated over time as a result of an unknown factor. The leachate should not be supersaturated with

fluorine if  $\text{CaF}_2$  is present and equilibrium exists.

In an evaluation of spent oil shale samples subjected to weathering tests, the GEOCHEM model (Sposito and Mattigod 1980) and XRD data were used to examine changes in solution chemistry and mineralogy relative to time and weathering. Modeling results showed that gypsum is near levels of saturation in solution and may control calcium and sulfate solubilities. The modeling results also suggested that diopside ( $\text{CaMgSi}_2\text{O}_6$ ) has the potential to precipitate after 16 hours of weathering. A comparison of the 56-day hydrated sample and the 24-hour sample showed significant changes in mineral dissolutions and formations caused by hydration over time. XRD data were difficult to interpret because of the amount of amorphous material present in the samples. XRD data did show that calcite ( $\text{CaCO}_3$ ) is a major component of the system. This may be responsible for cementation characteristics of the spent oil shales.

The study involving chemical equilibria model analysis of lysimeter leachate data showed that the aqueous chemistry of the oil shales used in the field lysimeters is dominated by free ionic metal species and metal sulfate ion pairs. Leachates were predicted by GEOCHEM to approach equilibrium with respect to gypsum, goethite, melanterite, Fe-jurbanite, franklinite, molybdite, and molybdic acid.

A study examining sulfide minerals in Chattanooga shale identified pyrite (isometric  $\text{FeS}_2$ ) and marcasite (orthorhombic  $\text{FeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), sphalerite ( $\text{ZnS}$ ), millerite ( $\text{NiS}$ ), and galena ( $\text{PbS}$ ) to be present in the shale. Sulfide mineral abundance was found to be directly proportional to the abundance of organic matter, and trace element concentrations increased with sulfide mineral content. The phosphatic zone at the Maury Formation-Chattanooga shale contact was determined to contain significantly higher concentrations of some trace elements.

Three general trends in trace element abundances between bulk shale and sulfide mineral concentrates were identified: a large increase in arsenic, copper, and zinc levels; a moderate increase in cadmium, lead, and nickel concentrations; and a slight increase in the concentration of molybdenum. In all cases, the sulfide mineral concentrates had higher concentrations of trace elements than the bulk shale samples.

In a second study to investigate sulfur-containing minerals in oil shale samples, sulfur-bearing minerals determined in the raw oil shale samples included pyrite ( $\text{FeS}_2$ ) and marcasite ( $\text{FeS}_2$ ), pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), sphalerite ( $\text{ZnS}$ ), and galena ( $\text{PbS}$ ). Sulfur-bearing alteration minerals identified were gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and copiapite ( $\text{Fe}_{14}\text{O}_3(\text{SO}_4)_{18} \cdot 63\text{H}_2\text{O}$ ). Sulfur-bearing minerals identified in the processed oil shale included pyrite, hexagonal pyrrhotite, oldhamite, and the alteration product, gypsum. The temperature of thermal processing was found to be an important factor in determining the sulfur-bearing minerals that result. Other important factors include the chemical composition of the source material, pressure, and the activities of iron and sulfur.

In the study to investigate the composition and solubility of ettringite, hydration of the spent oil shale did not result in a pure, stoichiometric ettringite solid. The chemical formula of the solid that precipitated, which was calculated from energy dispersive X-ray data, was  $\text{Ca}_{6.32}\text{Al}_{1.05}(\text{SO}_4)_{2.27}(\text{SiO}_4)_{0.36}(\text{OH})_{9.83} \cdot 26\text{H}_2\text{O}$ . A calculated  $\text{pK}_{\text{sp}}$  for dissolution of this solid was -57.01; and assuming that the precipitate was homogeneous, a  $\Delta G_f^\circ$  of  $-10116.7 \pm 8.1 \text{ kJ mol}^{-1}$  was calculated. The  $\text{pK}_{\text{sp}}$  was compared to ion activity product values, calculated by applying the geochemical model GEOCHEM to the spent oil shale leachate data. The  $\text{pK}_{\text{sp}}$  and ion activity product values were comparable for leachate contact times of 28 days and less. However, at longer contact times, the spent oil shale leachates were predicted to be undersaturated with respect to ettringite, which was directly identified in the solid

matrix. These conflicting results may be due to the incongruent dissolution of ettringite. Supersaturation of the spent oil shale leachates with respect to calcite supports this and suggests that calcium released through ettringite dissolution was precipitated as calcite.

In a separate study, the geochemical models EQ3/EQ6, GEOCHEM, MINTEQ, PHREEQE, SOLMNEQ, and WATEQFC were evaluated for their applicability to oil shale solid waste. The applicability of the geochemical codes to spent oil shale was evaluated by examining the thermodynamic database and comparing ion activities in retorted shale-distilled water extracts predicted by the codes. Large differences were found in the equilibrium constants used by the models to make similar calculations. All of the models lacked data for certain relevant minerals, such as akermanite, monticellite, and rankinite, and solution species. As a result, it was concluded that selection of any one of the models for application to oil shale solid waste requires development of a reliable thermodynamic database, which in turn requires critical evaluation and compilation of thermodynamic data. This involves reviewing available literature and selecting the most reliable thermodynamic data for minerals and solution complexes that are important for oil shale solid waste studies. A compilation of thermodynamic data for calcium, magnesium, sodium, and potassium were prepared as part of this study; and in a second similar study, thermodynamic data were compiled for fluorine, molybdenum, strontium, and selenium.

Results of the study to identify the mineral phases responsible for cementation of Lurgi oil shale showed that changes occurred in the chemical properties of the hydrated spent shale that were dependent on water content and curing time. Data from XRD analysis indicated that the dissolution products of periclase, calcite, and gypsum contribute to the formation of cementitious material. SEM analysis showed that with an increase in compressive strength, there was also an increase in crystalline bridging

between particles of spent shale. EDX analysis identified magnesium, aluminum, silicon, potassium, calcium, and iron as the major elements present in all of the samples; and calcium was the major element identified in the bridging material. The initial incorporation of water into the structure of the spent shale was completed during the first 14 days of curing. Significant changes in the thermal curves of the 14- and 56-day samples were observed. This evidence suggests that a hydrated, clay-like mineral formed in the 56-day sample.

### **Conclusions**

Results of these studies provide a variety of information that is important to waste management planning for disposal of spent oil shale. Conclusions from these studies can be summarized as follows:

1. Trace elements predominantly reside in iron sulfide phases of spent western oil shale. As a result, oxidation of the reduced sulfur may solubilize these trace elements. Equilibrium solubility evaluations suggest mineral phases for strontium, barium, fluoride, molybdenum, and arsenate in spent western oil shale.
2. Environmental influences may greatly affect basic chemical, physical, and mineralogical characteristics of spent oil shale. Hydration and recarbonation of retorted oil shale significantly influence mineralogical residences of trace and major elements.
3. In a weathering environment involving slow infiltration of water, the fate and behavior of molybdenum in spent oil shale may be predicted on the basis of powellite ( $\text{CaMoO}_4$ ) solubility.
4. Fluorine chemistry in spent oil shale leachates does not appear to be controlled by fluorite ( $\text{CaF}_2$ ) solubility.
5. Solid-solution contact times, recarbonation, oil extraction process,

and oil shale resource affect spent oil shale leachate chemical composition.

6. Spent eastern and western oil shale mineralogy is predictable based on process temperature.
7. Geochemical evaluation of Lurgi-Ruhrgas processed oil shale relative to time and weathering suggests that gypsum is near levels of saturation in solution and may control the solubilities of calcium and sulfate. Significant changes occur in mineral dissolutions and formations caused by hydration reactions of the spent shale.
8. Leachates from field lysimeters containing eastern raw and spent oil shale are dominated by free ionic metal species and metal sulfate ion pairs.
9. Temperature of processing, chemical composition of the source material, pressure, and the activities of iron and sulfur are important factors in determining the sulfide minerals in spent oil shale.
10. Conclusions concerning sulfur-containing minerals in raw Chattanooga shale are that:
  - Sulfide-containing minerals in the Chattanooga shale include pyrite (isometric  $\text{FeS}_2$ ), marcasite (orthorhombic  $\text{FeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), sphalerite ( $\text{ZnS}$ ), millerite ( $\text{NiS}$ ), and galena ( $\text{PbS}$ ).
  - Sulfide mineral abundance is directly related to organic matter abundance.
  - Trace element concentrations increase with sulfide mineral content.
11. In complex chemical systems, such as aqueous spent oil shale systems, solids can undergo incongruent dissolution, where dissolution reaction products are solid species or a mixture

of aqueous and solid species. For ettringite, the solution phase is influenced by the dissolution of ettringite and precipitation of such minerals as gypsum, portlandite, and gibbsite. This type of reaction cannot be predicted using a geochemical model; and model computed ionic activities cannot be used to substantiate the presence of ettringite.

12. Conclusions concerning evaluation of the applicability of geochemical models to oil shale solid waste are that:

- There are large differences between models in the equilibrium constants used to make identical calculations.
- Geochemical models lack data for high-temperature minerals, such as silicates and both inorganic and organic solution complexes, which are important for oil shale solid waste environmental studies.
- There is a great need to develop a reliable thermodynamic database for oil shale solid waste geochemical models.

13. Identification of the cementing material in hydrated spent oil shale requires additional analyses, possibly using electron-probe microanalysis, nuclear magnetic resonance, and transmission electron microscopy.

### **Related Publications**

Brown, M., and T. Brown, 1991, Solution Chemistry and Mineralogy of Spent Oil Shale Samples Subjected to Weathering Tests. Laramie, WY, DOE/MC/11076-3018.

Brown, M., G. Huntington, and T. Brown, 1991, Identification of the Mineral Phases Responsible for Cementation of Lurgi Spent Oil Shale. Laramie, WY, DOE/MC/11076-3022.

Essington, M.E., 1989, Chemical Equilibria Model Analysis of Hope Creek Eastern Oil

Shale Lysimeter Leachate Data. Laramie, WY, DOE/MC/11076-2788.

Essington, M.E., 1989, The Composition and Solubility of Ettringite Precipitated from Combusted Oil Shale. Laramie, WY, DOE/MC/11076-2943.

Essington, M.E., and G.S. Huntington, 1990, Formation of Calcium and Magnesium Molybdate Complexes in Dilute Aqueous Solutions and Evaluation of Powellite Solubility in Spent Oil Shale. Laramie, WY, DOE/MC/11076-2851.

Essington, M.E., and L.K. Spackman, 1988, Inorganic Geochemical Investigations of Spent Oil Shales. Laramie, WY, DOE/MC/11076-2701.

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Essington, M.E., R.A. Wills, and M.A. Brown, 1991, Laboratory Weathering and Solubility Relationships of Fluorine and Molybdenum in Combusted Oil Shale. Laramie, WY, DOE/MC/11076-3020.

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# ORGANIC CHARACTERIZATION OF RETORTED OIL SHALE AND PRODUCT WATER

Susan S. Sorini

## Background

Commercial production of shale oil would result in the generation of large volumes of solid and liquid wastes. As much as 150,000 tons of spent oil shale might be produced daily by a typical oil shale facility producing 100,000 barrels of crude oil per day (Gerhart and Holtz 1981). Generation of large amounts of solid and liquid wastes would create a significant and costly disposal problem.

The solid and liquid waste products resulting from production of synthetic crude oil from oil shale contain a wide variety of organic compounds (Pellizzari et al. 1979; Stuermer et al. 1980; Leenheer et al. 1982; Poulson et al. 1985; Lane et al. 1986). Information on the nature and behavior of the organic compounds present in spent oil shale and retort water is important for assessing the environmental impact of disposal of these materials.

The potential for spent oil shale to reduce the chemical concentrations in retort waters during co-disposal has been suggested (Fox et al. 1980; George and Jackson 1985; Boardman et al. 1985). Another possible disposal option for spent oil shale may be mixing it with hazardous waste to stabilize the hazardous constituents in the waste. The high alkalinity of spent oil shale may reduce the mobility of the hazardous constituents; or the spent oil shale may sorb inorganic and/or organic constituents from the hazardous wastes and prevent their release to the environment. To develop environmentally sound and cost effective disposal techniques for spent oil shale and oil shale process waters, an understanding of the nature and behavior of organic compounds present in these wastes and their interactions with various mineral phases is needed.

## Objectives

Several studies were conducted on the nature, fate, and behavior of organic compounds associated with solid and liquid oil shale production wastes. The objectives of this research were to (1) test a sampling and analysis procedure for characterizing volatile organic components (VOCs) in spent oil shale generated by both pyrolysis and combustion processes, (2) identify volatile and semivolatile organic compounds present in water extracts of spent oil shale, (3) assess the ability of clay liner material to restrict the mobility of aromatic amines commonly found in solid and liquid oil shale production wastes, (4) investigate the sorption interactions between mineral phases and model organic compounds that either have properties similar to organic compounds present in raw or spent oil shale leachates or are actually found in raw or spent oil shale, and (5) evaluate the ability of spent oil shale to stabilize organic and inorganic constituents of hazardous waste.

## Procedures

In a study to test a sampling and analysis procedure for characterizing VOCs in spent oil shale, two spent shale samples were obtained from a two-stage, pyrolysis and combustion, process. In each stage, the oil shale was exposed to retorting temperatures of 480-510°C (900-950°F) for approximately 5 minutes. Retort recycle gas was used in the pyrolysis step and air was used in the combustion step. The retorting was performed in inclined fluidized-bed reactors built by Western Research Institute (Merriam and Cha 1987).

The spent shale sampling apparatus consisted of a Pyrex 500-mL, three-necked flask, connected through one neck to four Tenax traps in series. The second neck of

the flask was used as an inlet for the helium carrier gas; and the third neck was fitted with a thermometer for temperature monitoring. VOCs in the spent shale were sampled by heating a spent shale sample while sweeping the sample with helium. VOCs in the helium stream were collected on the Tenax traps and subsequently analyzed by gas chromatography/mass spectrometry (GC/MS).

In a second study, ten samples of spent oil shale resulting from retorting in a Paraho directly-fired retort at an average maximum bed temperature of 1022°C (1872°F) were extracted using high-purity water. A 1:4 solid-to-liquid extraction ratio was used (250 g of spent shale and 1000 mL of water). The solid and water were added to 2-L precleaned, high-density polyethylene bottles, and the bottles were placed in a temperature controlled (25°C [77°F]) shaker water bath for 28 days. At the end of 28 days, the extraction slurries were filtered using 0.6-0.8- $\mu$ m borosilicate glass fiber filters according to the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1986). Following filtration, the resulting filtrates were composited for analysis of volatile and semivolatile organic compounds.

The leachate was analyzed directly for volatile organic compounds using a purge and trap method combined with mass spectral analysis. Semivolatile organic compounds were analyzed using GC/MS. Base-neutral, acid-neutral, and acid fractions were generated for semivolatile analysis. All GC/MS analyses were performed using U.S. Environmental Protection Agency (EPA) contract laboratory protocol.

In a third study, calcium- and potassium-saturated bentonite suspensions were prepared by blending Wyoming bentonite and  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2$  and Wyoming bentonite and KCl, respectively. Aniline, o-toluidine, m-toluidine, and p-toluidine adsorption experiments were conducted in both the  $\text{Ca}^{+2}$ - and  $\text{K}^+$ -saturated bentonite systems at varying pH values. These were performed by placing 20 mL of the clay

suspension and 25 mL of an aniline or toluidine solution in 50-mL centrifuge tubes, along with a pH adjusting solution. The centrifuge tubes were placed on a wrist-action shaker for 24 hours at ambient temperatures (20-25°C, 68-77°F). After 24 hours, the adsorption systems were centrifuged. A 10-mL aliquot of the clear supernatant was then added to a 100-mL volumetric flask and brought to volume using the appropriate background electrolyte solution. The resulting solutions were analyzed for aniline or toluidines by ultraviolet (UV) spectrophotometry (Shimadzu UV-265 spectrophotometer) at a wavelength of approximately 280 nm.

In another study, adsorption of organic compounds found in spent oil shale by minerals comprising the bulk of the mineral composition of spent shale was studied. The organic compounds used were pyridine, p-cresol, phenol, and acetone; and the minerals involved were quartz, dolomite, and calcite. Three experimental procedures for contacting the chemicals and mineral phases were used: (1) vapor deposition, which involved contacting the mineral phase with the vapor of the organic compound, (2) directly adding the organic compound to the mineral samples, and (3) mixing the mineral and organic compound in an aqueous solution of pH 12 and evaporating the samples to dryness. The samples were analyzed using Fourier transform infrared (FTIR) spectroscopy. The infrared spectrometer used was a Digilab FTS-45 FTIR spectrometer. Three methods of detection were investigated for the study: FTIR/PAS (photo-acoustics), DRIFT (diffuse reflectance), and transmission through KBr pellet. The use of KBr pellets involves sintering the sample with intimately mixed KBr (the supporting substrate) under high pressure; DRIFT involves simply mixing the samples with KBr, and PAS involves running the samples without KBr.

A review of other studies performed at WRI to investigate the interactions between mineral phases in spent oil shale and model organic compounds was also conducted. Sorption mechanisms between the organic

compounds and mineral phases have been studied using FTIR, high-performance liquid chromatography, Raman spectroscopy, differential scanning calorimetry and thermogravimetric analysis techniques.

To evaluate the ability of spent oil shale to stabilize organic and inorganic constituents of hazardous waste, mixtures containing varying amounts of spent oil shale and hazardous waste were prepared, allowed to equilibrate, and then leached with deionized, distilled water. The spent shales used in this study resulted from retorting a western oil shale in an inclined fluidized-bed reactor. Two runs were performed, one at 843 °C (1550 °F) and one at 882 °C (1620 °F), resulting in two spent shales for testing. The hazardous wastes used in the study were an API separator sludge, creosote-contaminated soil, mixed metal oxide/hydroxide waste, metal-plating sludge, and smelter dust. The spent shales and hazardous wastes were mixed and allowed to equilibrate for 7 days. At the end of the equilibration period, deionized, distilled water was added to each mixture to give a 1:1 solid-to-liquid ratio, and the slurries were allowed to equilibrate for an additional day. After the second equilibration period, the mixtures were filtered, and the resulting filtrates were analyzed for the hazardous chemical constituent(s) of interest.

## **Results**

Results of the study to test a sampling and analysis procedure for characterizing VOCs in spent oil shale show that collecting the organic components on Tenax traps concentrates the organic constituents and increases the sensitivity of the analytical procedure. Problems associated with an extraction procedure were eliminated. However, other problems, such as irreversible adsorption on Tenax or sample degradation, may occur. Spent shale from a combustion process was determined to contain fewer VOCs than the spent shale from a pyrolysis process. The spent shale resulting from the pyrolysis process was determined to contain low-molecular weight

hydrocarbon compounds, aliphatic and aromatic, as well as sulfur-containing species, and some tentatively identified nitrogen- and oxygen-containing species. Benzene, toluene, and xylenes were identified. These compounds are EPA priority pollutants. In the spent oil shale resulting from the combustion process, only two alkanes in the C<sub>6</sub>-C<sub>7</sub> range were detected, and several alkenes or cyclic alkenes in the C<sub>6</sub>-C<sub>8</sub> range were identified. Benzene was the only major compound detected. A C<sub>2</sub>-substituted benzene and several possible nitrogen- or oxygen-containing compounds were also identified.

Results from the study to identify volatile and semivolatile organic compounds present in water extracts of Paraho spent oil shale show that organic acids are the predominant semivolatile compounds present in aqueous extracts of the spent shale. Basic semivolatile organic compounds are present in much lower concentrations, which approach or are below analytical detection limits. The semivolatile organic compounds tentatively identified and quantified in the base-neutral, acid, and acid-neutral fractions of the Paraho spent oil shale/water leachate are listed in Table 1. Methylene chloride and acetone were the only volatile organic compounds detected in the leachate of the Paraho spent shale. Because these are common solvents used in the laboratory, it is suggested that they are not indigenous to the leachate, but were contaminants from the laboratory atmosphere.

Results from the study to assess the ability of clay liner material to restrict the mobility of organic chemicals commonly found in oil shale processing wastes showed that the maximum amount of aniline and toluidines adsorbed on bentonite is pH dependent. Above pH 7, adsorption of the organic compounds was not detected, and as pH decreased from a value of 7, aniline and toluidine adsorption increased to a maximum when solution pH was approximately equal to the pK<sub>a</sub> of the anilinium ion deprotonation reaction: R-NH<sub>3</sub><sup>+</sup> = R-NH<sub>2</sub><sup>0</sup> + H<sup>+</sup> (pH = 4.5 to 5.1).

**Table 1. Organic Compounds Tentatively Identified in Paraho Spent Shale Aqueous Leachate**

Compound	Concentration, $\mu\text{g/L}$
<b>Base-Neutral Fraction</b>	
Toluene (Methylbenzene)	2
$\text{C}_8\text{H}_{16}$ Alkane	1
One additional compound was observed but not identified.	
<b>Acid fraction</b>	
Elemental sulfur	ND <sup>a</sup>
Benzoic acid	290
Butanoic acid or isomer	3
2,2-Dimethylpropanoic acid or isomer	0.7
Possible $\text{C}_6\text{H}_6\text{O}_3$ isomer	0.4
Possible $\text{C}_5\text{H}_{10}\text{O}_2$ carboxylic acid	2
2-Methylbenzoic acid or isomer	0.5
3-Methylbenzoic acid or isomer	0.9
$\text{C}_8\text{H}_8\text{O}_2$ Isomer	0.3
Eight additional compounds were observed but not identified.	
<b>Acid-Neutral fraction</b>	
Toluene	0.6
Butanoic acid or isomer	3
2,2-Dimethylpropanoic acid or isomer	0.6
Possible 2-Cyclohexen-1-one or isomer	0.4
Possible $\text{C}_9\text{H}_{20}$ alkane	0.6
Possible $\text{C}_6\text{H}_8\text{O}_3$ isomer	0.6
Tetrahydro-2,4-dimethylfuran or isomer	0.4
Possible $\text{C}_5\text{H}_{10}\text{O}_2$ carboxylic acid	2
Benzoic acid	18 <sup>b</sup>
The four compounds listed below were tentatively identified to be present below the detection limit of the instrument.	
2-Methylbenzoic acid or isomer	0.1
3-Methylbenzoic acid or isomer	0.2
4-Methylbenzoic acid or isomer	0.1
Possible $\text{C}_{12}\text{H}_{10}\text{O}$ phenol	0.2

<sup>a</sup> ND = Not Determined

<sup>b</sup> Determined as an inorganic salt, response factor not known.

Maximum adsorption increased with decreasing ionic strength. Adsorption of the organic compounds was inhibited in the presence of sulfate and was greater in the  $\text{Ca}^{+2}$  systems than in the  $\text{K}^{+}$  systems, regardless of ionic strength. Spectroscopic data showed that the aniline compounds are adsorbed on bentonite through direct bonding of an amine hydrogen to a surface silica oxygen.

Results from the study to investigate adsorption of organic compounds by spent oil shale mineral phases suggest that minerals in spent oil shales do not significantly contribute to the retention of spent oil shale leachate organic compounds. Very little observable sorption was detected. In most cases, no interaction was observed within the detection limits of the FTIR instrument. Indications of sorption interactions between p-cresol and calcite and dolomite, and also between phenol and quartz were detected. Physisorption, in the form of hydrogen bonding between phenolic hydroxyl hydrogen and the oxygens of calcite was the only readily identifiable sorption interaction in the study.

Preliminary investigations in this study showed DRIFT to be the best sample preparation method in terms of detection limits, sample preparation, and speed of analysis. For this study, DRIFT gave higher sensitivity and less sample preparation time than KBr pellets and had a better signal-to-noise ratio than PAS.

As with the study described above, similar studies conducted at WRI have shown little sorption of organic compounds by oil shale mineral phases. However, information on application of various analytical methods to these systems has been obtained. The newer instrumental methods of photoacoustics and diffuse reflectance have been shown to be well suited for examining organic-mineral interactions; high-performance liquid chromatography was found to be a difficult method to apply, and requires further development for this type of application; Raman spectroscopy was found to be better suited for remote, in-situ

monitoring of organic compounds in subsurface environments; and thermogravimetric and differential scanning calorimetry were determined to be too insensitive for this application.

The study to evaluate the ability of spent oil shale to stabilize hazardous constituents in wastes showed that spent oil shale can stabilize a hazardous waste by reducing the mobility of metals that precipitate as solid phases from alkaline solutions. Mixing spent shales with a smelter dust and mixed metal oxide/hydroxide waste reduced the amount of cadmium released from these wastes (on a per gram basis) during water extraction. However, mixing spent shales with a metal-plating waste, high in chromium, did not reduce the leachability of chromium from the waste. As the amount of spent shale in the metal-plating waste/spent shale mixtures was increased, which in turn increased the solution pH, the solubility of chromium also increased.

Little information on stabilization of organic compounds in the API separator sludge and creosote-contaminated soil was obtained. These wastes are complex organic wastes containing several organic compounds, and difficulties in homogenizing the materials were encountered.

## Conclusions

The conclusions that can be made from these studies are:

- A Tenax-trap sampling technique, combined with GC/MS analysis, was successful in trapping and identifying VOCs emitted from retorted oil shales.
- Volatile organic compounds are not present in concentrations above instrumental detection limits in aqueous leachate of Paraho spent oil shale.
- Organic acids are the predominant class of semivolatile compounds present in the aqueous leachate of Paraho spent shale. They are present in the parts-per-billion range.

- Aniline and toluidine adsorption by bentonite is minimal in high ionic strength saline systems and is not detected in systems having a pH greater than 7. Because spent oil shale leachates and retort waters have high alkalinity and salinity, bentonite liners will not be effective in reducing the mobility of anilines through sorption processes.
- Minerals in spent oil shales do not significantly contribute to the retention of spent oil shale leachate organic compounds.
- FTIR appears to be a useful technique for examining organic-mineral interactions.
- Spent oil shale can stabilize a hazardous waste by reducing the mobility of metals that precipitate as solid phases from alkaline solutions; however, evaluation of the long-term ability of spent oil shale to stabilize hazardous constituents based on alkalinity is needed.

### **Related Publications**

Bowen, J.M., 1988, Investigation of Sorption Interactions Between Oil Shale Principal Mineral Phases and Organic Compounds. Laramie, WY, DOE/MC/11076-2686.

Essington, M.E., J.M. Bowen, and G.M. Mason, 1988, A Summary of Research on Oil Shale Solid Waste Conducted by the Western Research Institute. Laramie, WY, DOE/MC/11076-2658.

Essington, M.E., J.M. Bowen, R.A. Wills, and B.K. Hart, 1992, Adsorption of Aniline and Toluidines on Montmorillonite: Implication for the Disposal of Shale Oil Production Wastes. Laramie, WY, WRI-92-R019.

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McKay, J.F., and D.C. Lane, 1988, Organic Compounds in the Aqueous Extract of a Retorted Green River Formation Oil Shale. Laramie, WY, DOE/MC/11076-2675.

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# ION SPECIATION OF PROCESS WATERS AND FOSSIL FUEL LEACHATES

Nancy D. Niss

## Background

The chemical form of an element in an aqueous environment greatly influences its solubility and mobility as well as its potential environmental impact. The leaching and transport of many organic and inorganic contaminants from fossil fuel leachates and retort waters is an area of environmental concern. Geochemical models are increasingly being used to predict the distribution of contaminants in leachates. These models must be validated by comparing laboratory data to model predictions before the models can be applied to a real environment. Because model validation depends on quality laboratory data, accurate and reliable methods are needed to separate and quantify the components of interest.

Hydrophilic organic solutes in oil shale retort waters are of interest because they may be indicators of aqueous contamination from retorting operations. Many inorganic species in fossil fuel-water systems are also an area of environmental concern in predicting water quality and characterizing the partitioning behavior between solid and solution phases.

In some environments, Cr(III) may be oxidized to Cr(VI), significantly increasing its toxicity. The speciation of iron in different environments is of great interest because of its importance in controlling redox and pH conditions in aqueous and solid environments.

The behavior of many inorganic sulfur, selenium, and arsenic species are of concern because many fossil fuel combustion byproducts are being considered for use in roadbed stabilization, construction materials, and other applications. Volatile sulfur species such as sulfide or sulfite may behave very differently than more stable species such as

sulfate or thiosulfate. Selenium and arsenic species are present and may be enriched in many fossil fuel byproducts. Minerals produced during the retorting of oil shales buffer the pH of spent oil shale leachates to pH 11 or higher. Under these conditions, selenium and arsenic species are anionic in nature, and hence, soluble and mobile.

## Objectives

The objectives of this research were to develop methods involving sample preparation and analysis of varied inorganic and organic species found in fossil fuel extracts. The laboratory measurements of some of these species in leachates were compared to ion speciation predictions from geochemical models.

## Procedures

To characterize hydrophilic organic species in retort waters, samples from the Western Research Institute 150-ton simulated in situ retort run 17 (R-17) were selected for study. Waters from several locations in the Rio Blanco Oil Shale Company's retort 1 on federal prototype lease tract C-a, Rio Blanco County, Colorado were also studied. In the first phase of the study, the waters were separated into total hydrophilic fractions and analyzed using total organic carbon analysis, high-resolution mass spectrometry (HRMS), reversed-phase high-performance liquid chromatography with diode array detection (RPLC/DAD), gas chromatography followed by mass spectrometry (GC/MS), gas chromatography followed by thermionic ionization detection in the nitrogen-phosphorus mode, gas chromatography followed by electron-capture detection (GC/ECD), and derivatization followed by gas chromatography with electron-capture detection. In the second phase, various hydrophilic standards were derivatized and then analyzed using gas chromatography

followed by flame ionization detection (FID) and electron-capture detection (ECD). The retort waters were then derivatized and compared to the standards.

Chromium and iron redox systems were characterized using various techniques to see if laboratory speciation data compared with predictions from geochemical models. Solutions of Cr(III), Cr(VI), Fe(II), and Fe(III) were prepared over a concentration range of 0.1  $\mu$ M to 1 mM. Solutions were then prepared with Cr(VI)/Cr(III) and Fe(III)/Fe(II) ratios ranging from 1 to  $10^{-4}$ . The solutions were analyzed using ion chromatography to determine the concentration of each ionic specie in solution. Electrode potential measurements were also made on various solutions of the metals with the oxidized and reduced forms in different ratios. The laboratory data obtained through these analyses were then compared to speciation predictions made by the geochemical model GEOCHEM and the Nernst equation.

The presence of various sulfur anions was studied in leachates from reference eastern, reference western, and Rio Blanco spent oil shales. The anions of interest were separated and quantified using a variety of ion chromatographic approaches that resulted in two sets of operating conditions. The lower sulfur anions ( $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{SCN}^-$ , and  $\text{S}_2\text{O}_3^{2-}$ ) were separated using an HPIC AG5 guard column and an AS5 high-capacity anion exchange column. Tetrathionate was chromatographed using an Ionpac NG1 guard column and NS1 separator column. Oxidation of the reduced sulfur species was inhibited by the addition of 10 vol % isopropanol to the standard solutions and eluant.

The spent oil leachates were prepared by placing them in containers and passing humidified air over them continuously. Every 7 days, deionized-distilled water was added to the container to establish a 1:1 solid-to-solution ratio. After 1 hour, the spent oil shale-water mixture was filtered through Whatman #42 filter paper. The shales were then allowed to air dry, and the 7-day cycle was repeated. The filtrates were

preserved with isopropanol and stored at 4°C (39°F) until they were analyzed for sulfur-containing anions.

The characterization of selenium and arsenic species in leachates from spent oil shales and coal fly ash involved developing techniques for the extraction of the ions from solid matrices without changing their chemical form, developing a method to extract total selenium from solid matrices with reliable results, and developing ion chromatography techniques to separate and quantify selenium and arsenic species in solution.

A NIST 1633a fly ash standard reference material (SRM) from the National Institute for Standards and Technology (NIST) in Gaithersburg, Maryland was used to develop an extraction technique for selenium and arsenic species prior to analysis by ion chromatography. Experiments were performed using an ultrasonic bath and 0.5-M, 2-M, and 4-M sodium hydroxide solutions and distilled/deionized water to extract selenite, selenate, and arsenate. Arsenite was extracted using a 1-M hydrochloric acid solution. The fly ash was extracted with each solution for different periods of time ranging from 4 to 24 hours to find the optimum extraction conditions. The fly ash samples were also spiked with selenite, selenate, arsenite, and arsenate prior to extraction to ensure that no speciation change took place during the extraction.

To develop a digestion procedure for the extraction of total selenium from solid matrices, the NIST 1633a SRM fly ash and a sodium bicarbonate blown fly ash were subjected to a number of different procedures. Both fly ash samples were digested using EPA Method 3050, followed by analysis for total selenium by atomic absorption spectroscopy (AA). The fly ash samples were extracted next using a highly alkaline solid:water (2:1) paste extract. The NIST 1633a SRM ash was also extracted using an ultrasonic alkaline paste extract procedure. Sodium peroxide fusion was tested on both ash samples to determine total selenium, with and without the



addition of sodium hydroxide to lower the fusion temperature. All results were then compared to determine an optimum digestion procedure for total selenium.

To develop methods to separate and quantify selenium and arsenic species in the presence of common anions using ion chromatography, several approaches were utilized. In the first phase of the study, an HPIC AG4A anion guard column was used in combination with an HPIC AS4A high-capacity anion exchange column. An anion eluant consisting of 1 mM  $\text{CO}_3$ /0.9 mM  $\text{HCO}_3$  was used to separate selenite and selenate. This eluant did not work because of interferences from nitrate, sulfate, and phosphate ions. In the next experiment, a 1-mM carbonate eluant was used, adjusted to pH 12 with 10 M sodium hydroxide. The elevated pH of the carbonate system was designed to eliminate interference problems from the phosphate ion. At a high pH, the phosphate ion is present in the trivalent form, and more strongly retained on the column than the selenite and selenate ions.

In the second phase of the selenium and arsenic species study, different combinations of columns and eluants were used to try and eliminate more interference problems with the selenium and arsenic species. An HPIC AG5 anion guard column was used in conjunction with an HPIC AS4A separator column. An eluant consisting of 2.0 mM  $\text{Na}_2\text{CO}_3$  and 1.0 mM NaOH at a flow rate of 2.0 mL/min was used to separate the selenium species in the presence of other common anions. All anions were detected using suppressed conductivity at 1 micro Siemen full scale. The arsenic anions were separated using the same column combination and an eluant consisting of 2.0 mM sodium carbonate and 1.5 mM sodium bicarbonate. Arsenite was detected using electrochemical detection with a platinum working electrode at a potential of 0.5 V. The electrochemical detector was installed between the column and the suppressor device. Arsenate and other common anions were detected using conductivity detection set as 1 microsiemen full-scale.

## Results

The high-resolution mass spectrometry profile of the R-17 total hydrophilic (THP) fraction showed a series of hydroxypyridines or pyridones. The presence of these compounds was confirmed with RPLC/DAD profiles. The GC/MS analysis was performed on a methylene chloride extract of the R-17 THP fraction. Benzoic acid, a compound on the U.S. Environmental Protection Agency's (EPA) Hazardous Substance List was identified at a concentration of 11 ppb. The R-17 THP fraction was derivatized with trifluoroacetic anhydride (TFAA), heptafluorobutyric anhydride (HFBA), and heptafluorobutyrylimidazole (HFBI) prior to analysis by GC/ECD. When the fraction was treated with TFAA and HFBA, no unique peaks were discovered in the GC/ECD profiles. Reaction with HFBI produced one unique peak in methanol and several unique peaks with toluene as the solvent, but none were positively identified.

The study of chromium and iron redox systems yielded valuable techniques for the separation and detection of chromium and iron species using ion chromatography. The chromium and iron species were derivatized and detected photometrically. The redox systems for chromium and iron were studied separately as they relate to the Nernst equation or GEOCHEM. The comparison of laboratory speciation data with geochemical ion speciation models showed regions of reasonable agreement for  $E_H$  for iron species above an activity ratio of  $\text{Fe(III)/Fe(II)} = 0.1$  over the concentration region studied. A similar study for the chromium redox system showed no agreement with  $E_H$  over the concentration region studied.

To develop techniques to separate and detect sulfur ions, mobile phase ion chromatography was used initially to try and separate sulfite, sulfate, thiocyanate, and tetrathionate in one run. Different combinations of ion-pairing reagents, organic modifiers, and inorganic modifiers were tried to achieve this goal. In this study, tetrabutylammonium hydroxide was

chosen first as the ion-pairing reagent. Sodium carbonate was added as an inorganic modifier, and acetonitrile was added as an organic modifier. This eluant eluted tetrathionate in a reasonable period of time, but did not separate sulfate and thiosulfate. The ion-pairing reagent was changed to tetrapropylammonium hydroxide (TPAOH) to improve the resolution between sulfate and thiosulfate. Different combinations of TPAOH, sodium carbonate, and acetonitrile were tried, but none affected the resolution between sulfate and thiosulfate.

Since the NS1 column did not separate sulfate and thiosulfate, the lower sulfur-containing anions were separated with the HPIC AS5 column. A standard bicarbonate/carbonate eluant was used with p-cyanophenol added to improve the peak shapes of strongly adsorbed ions. Tetrathionate was chromatographed with the NS1 column using a TPAOH/Na<sub>2</sub>CO<sub>3</sub>/acetonitrile eluant. The precision of the two methods was tested by ten repeat injections of standards. The standard deviations of measured concentrations using a 50- $\mu$ L sample loop ranged from 0.15 to 0.51 with the AS5 column and 0.15 to 0.29 with the NS1 column. The detection limit calculations were based on a threefold signal-to-noise ratio of the baseline. Table 1 lists the detection limits for each anion.

The leachates were analyzed using each method. The main constituent of all the leachates was sulfate with minor amounts of thiocyanate and thiosulfate. None of the leachates analyzed contained sulfite or tetrathionate.

Selecting the optimum digestion method for the determination of total selenium in fly ash samples seems to be dependent on sample type and source. When the sodium carbonate blown fly ash was digested using

EPA Method 3050 (acid digestion), the total selenium value obtained was 3.18 mg/kg. When the same sample was extracted using an alkaline paste extraction procedure, the total selenium value obtained was 6.88 mg/kg. This result confirms earlier work showing higher total selenium values from base extracts than from acid extracts.

The 3050 Method was used on the NIST 1633a SRM fly ash, and an average total selenium value of 11.6 mg/kg was obtained. An alkaline paste extraction of the NIST sample yielded a selenium value of 3.18 mg/kg, while an ultrasonic alkaline extraction procedure gave a total selenium value of 10.8 mg/kg. The certified selenium value of the NIST fly ash is 10.3 mg/kg. Sodium peroxide fusion was also tested to determine total selenium with and without the addition of sodium hydroxide to lower the fusion temperature. Fusion of the carbonate blown fly ash yielded a total selenium value of 5.54 mg/kg with sodium hydroxide, and 4.34 mg/kg without sodium hydroxide. The fusion of the NIST fly ash yielded total selenium values of 7.07 and 5.86 mg/kg with and without the sodium hydroxide, respectively.

To extract selenium and arsenic species from solid matrices without changing their chemical forms, a 0.5-M sodium hydroxide solution was added to the samples, and they were placed in an ultrasonic bath for 4 hours. This procedure effectively extracted selenite, selenate, and arsenate. A 1-M hydrochloric acid solution was used to extract arsenite. Longer extraction times did not result in any increase in the levels of selenium or arsenic detected in the leachates. The use of stronger sodium hydroxide solutions led to baseline interruption problems during chromatographic analysis. Deionized-distilled water did not extract detectable levels of the anions, even after 24 hours.

**Table 1. Detection Limits for Sulfur Anions, mg/L**

Injection Volume	SO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	SCN <sup>-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup>
50 $\mu$ L loop	0.10	0.01	0.02	0.02	0.09

Spiking experiments performed to see if there was any speciation change during extraction all showed quantitative recoveries of the anions of interest.

Preliminary attempts to separate and detect selenium species in spent oil shale leachates using ion chromatography with a bicarbonate/carbonate eluant and an anion exchange column were not successful because of interference problems from chloride, nitrate, sulfate, and phosphate. Separations using a 1-mM carbonate eluant adjusted to pH 12 with sodium hydroxide also had problems. The higher pH solved interference problems from sulfate and phosphate, but retention times and peak areas were not repeatable for selenite and selenate.

In the second phase of the study, an AG5 anion exchange guard column was used

with the AS4A analytical separation column instead of the customary AG4 guard column. This combination of columns effectively separates nitrate and sulfate from selenite and selenate due to the differences in the hydrophobicity of the functional groups in the column packings. A sodium carbonate/sodium hydroxide eluant eliminates interferences from phosphate because at an elevated pH, phosphate is present in the trivalent form, and hence retained longer on the column. Arsenite and arsenate were also separated using this column combination, using a carbonate/bicarbonate eluant. A flow rate of 1 mL/min was necessary when separating the arsenic anions because higher flow rates cause an unstable baseline with the electrochemical detector used to detect arsenite. Figure 1 shows a chromatogram of selenite and selenate with other common anions in reagent water.

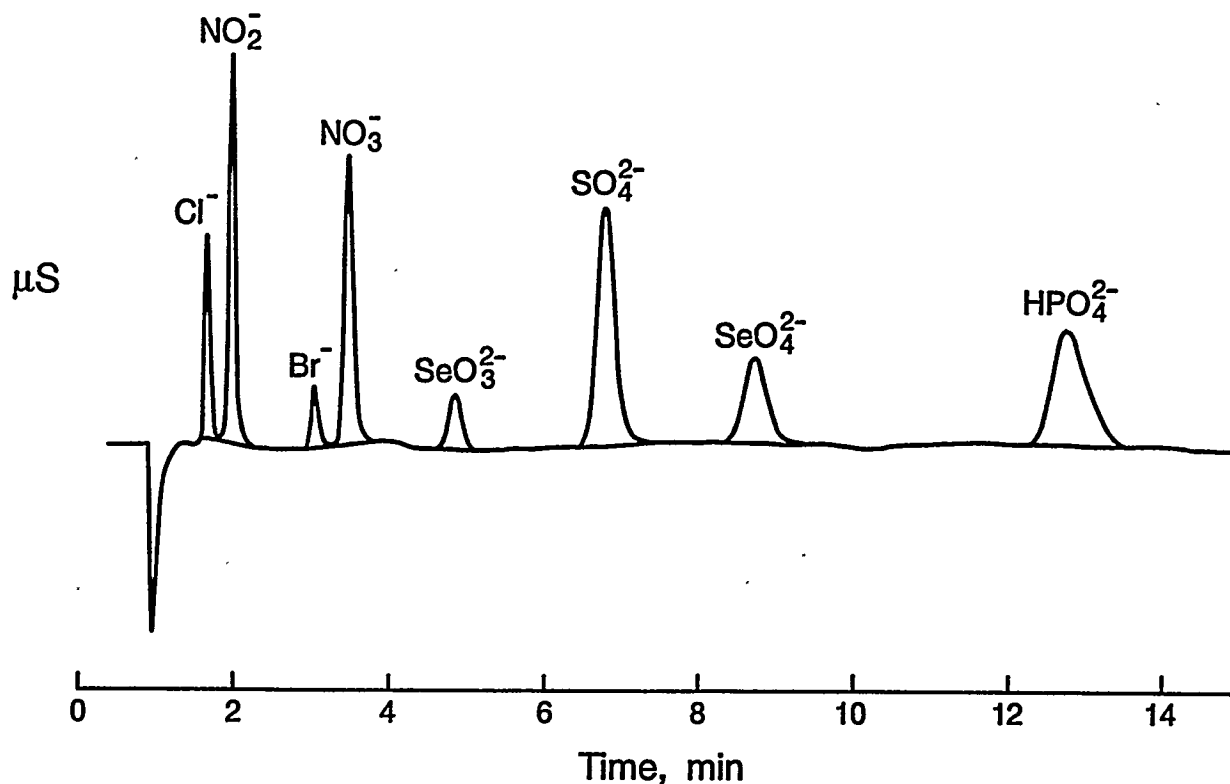
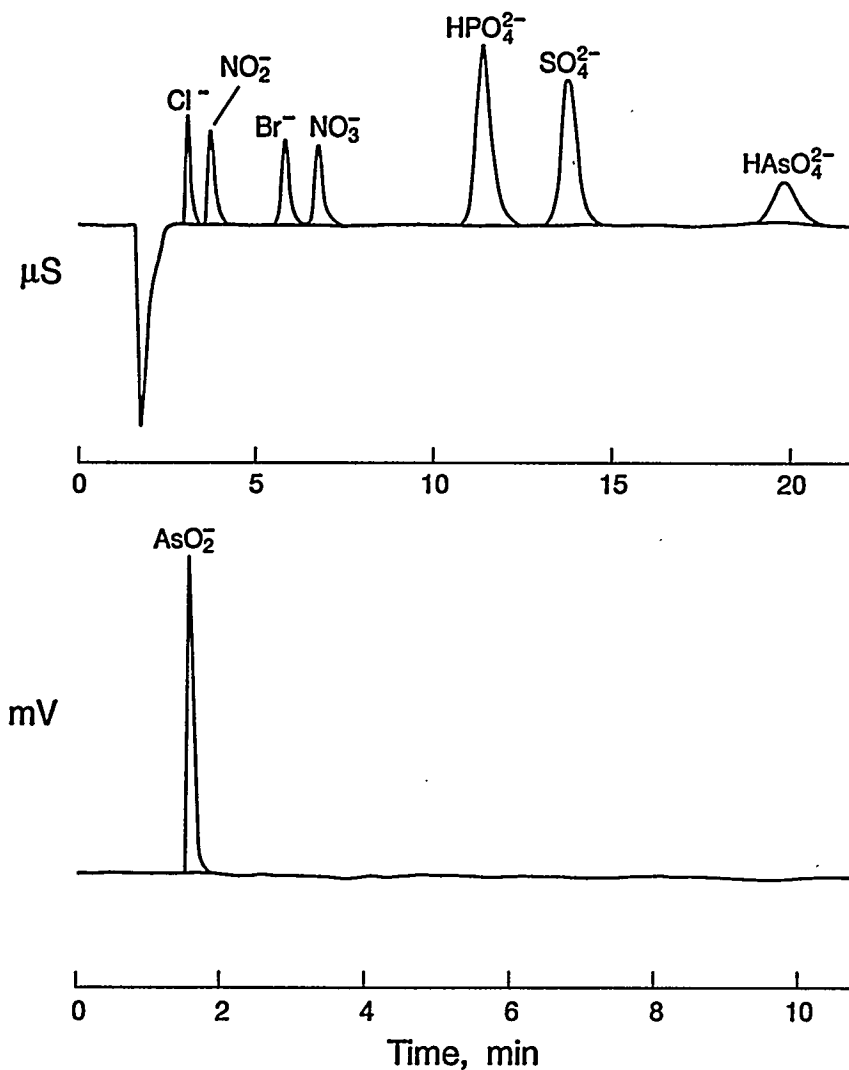


Figure 1. Ion Chromatogram of Selenite and Selenate in the Presence of Common Anions. Column, Dionex AG5 + AS4A; Eluant, 2.0 mM  $\text{Na}_2\text{CO}_3$ , 1.0 mM  $\text{NaOH}$ ; Conductivity Detection.

Figure 2 shows chromatograms of arsenite and arsenate with other anions in reagent water. Table 2 shows the method detection limits for the selenium and arsenic species.

Method detection limit calculations were based on a threefold signal-to-noise ratio of the baseline (S/N = 3).



**Figure 2. Ion Chromatogram of Arsenite and Arsenate in the Presence of Common Anions. Column, Dionex AG5 + AS4A; Eluant, 2.0 mM Na<sub>2</sub>CO<sub>3</sub>, 1.5 mM NaHCO<sub>3</sub>; Conductivity Detection with Electrochemical Detection for Arsenite.**

**Table 2. Detection Limits for Selenium and Arsenic Anions, mg/L**

Injection Volume	SeO <sub>3</sub> -Se	SeO <sub>4</sub> -Se	AsO <sub>2</sub> -As	HAsO <sub>4</sub> -As
50 μL	0.01	0.01	0.002	0.10

The NIST 1633a fly ash was extracted ultrasonically and analyzed for selenite and selenate using the ion chromatography techniques described above. The only specie detected was selenite. The value obtained for selenite as selenium was 11.2 mg/kg, which was close to the total selenium value of 10.8 mg/kg obtained by AA analysis. Three other fly ash samples were extracted and analyzed by ion chromatography. Two of the ashes contained only selenite, and one contained only selenate. The values obtained by ion chromatography compared well with the total selenium values obtained by AA analysis.

The four fly ash extracts were also analyzed for arsenic species. The NIST 1633a fly ash contained 130 mg/kg arsenate as arsenic, compared with a total arsenic value of 135 mg/kg obtained by AA analysis. Arsenic species were not detected by ion chromatography in the other extracts, although low levels were detected by AA analysis.

In general, the concentrations of selenium and arsenic species detected using ion chromatography agreed with the total selenium and arsenic values obtained by AA analysis. The alkaline ultrasonic extraction is the best sample preparation method for the determination of selenite, selenate, and arsenate by ion chromatography. The ultrasonic hydrochloric acid extraction is required for the determination of arsenite. The determination of total selenium in solid matrices may require both the ultrasonic alkaline extraction and the acid EPA Method 3050 digestion. Only the EPA 3050 digestion technique is required for total arsenic determination. Additional work is needed to establish optimized and practical analytical approaches for the determination of other species, such as selenide or organically-bound arsenic and selenium species.

## **Conclusions**

Characterization of the R-17 retort water for hydrophilic organic species resulted in the

detection of hydroxypyridines by HRMS and RPLC/DAD analyses. The R-17 THP fraction was analyzed by GC/MS, and contained benzoic acid at a concentration of 11 ppb. The R-17 fraction was subsequently treated with several different derivatizing agents prior to analysis by GC/ECD. Derivatization with HFBI produced one unique peak in methanol and several unique peaks with toluene as the solvent, but none were positively identified.

Chromium and iron species were derivatized and subsequently analyzed using ion chromatography. The speciation data obtained from these analyses, along with electrode potential data, was compared with geochemical ion speciation model predictions. The model predictions for iron species showed regions of agreement for  $E_H$  above an activity ratio of  $Fe(III)/Fe(II) = 0.1$  for the concentrations studied. Model predictions for the chromium redox system did not correlate to laboratory data over any concentration regions studied. Further work is needed to understand speciation behavior and improve model predictions.

Various sulfur-containing anions of interest in fossil fuel leachates were separated using two different methods. The more reduced sulfur anions were separated with an HPIC AS5 column and a bicarbonate/carbonate eluant. Tetrathionate was strongly adsorbed using this method, and did not elute in a reasonable period of time; so it was chromatographed using an HPIC NS1 column with a  $TPAOH/Na_2CO_3$ /acetonitrile eluant. The leachates analyzed using these methods contained sulfate with minor amounts of thiocyanate and thiosulfate.

Four methods for extraction of total selenium were studied with two coal fly ash samples. Acid digestion and sodium peroxide fusion yielded the highest recoveries for the NIST 1633a SRM, while ultrasonic extraction gave the highest recovery for the other fly ash.

Selenium and arsenic species were successfully separated using ion chromatography in the presence of other

common anions. Comparison of arsenic and selenium concentrations obtained by ion chromatography with total concentrations obtained by atomic absorption spectroscopy showed good agreement. Further work in this area could be done to develop techniques to extract and separate organically-bound arsenic and selenium species in fossil fuel materials.

### **Related Publications**

Niss, N.D., 1989, Determination of Sulfur Anions in Spent Oil Shale Leachates by Ion Chromatography. Laramie, WY, DOE/MC/11076-2956.

Niss, N.D., and R.E. Poulson, 1988, Hydrophilic Organic Solutes Associated with Oil Shale Retort Water. Laramie, WY, DOE/MC/11076-2673.

Niss, N.D., and C.R. Powers, 1988, Determination of Selenium Species in Spent Oil Shale Leachates by Ion Chromatography. Laramie, WY, DOE/MC/11076-2685.

Poulson, R.E., C.R. Powers, and M.E. Essington, 1987, Validation of Inorganic Chemical Speciation for Geochemical Models. Laramie, WY, DOE/MC/11076-2459.

Schabron, J.F., B.K. Hart, N.D. Niss, and T.H. Brown, 1991, Methods for the Speciation and Determination of Arsenic and Selenium in Coal Combustion Products. Laramie, WY, DOE/MC/11076-3073.

# STUDIES ON DEVELOPMENT OF WESTERN OIL SHALE

Verne E. Smith

## Background

Interest in oil shale development has waxed and waned a number of times in the past 150 years. The greatest level of oil shale research and development activity in the United States was precipitated by the energy crises of the 1970s. Subsequent stability of petroleum prices in the \$17-25 range and the perceived reliability of reserves have gradually curtailed most oil shale activities in the United States. It is generally considered that shale oil is not economically competitive with conventional petroleum for transportation fuel. However, alternative uses and markets for oil shale should not be precluded from consideration for this immense resource. Higher value products from oil shale and related byproducts may be economically viable in a smaller market arena.

## Objectives

Studies were undertaken to (1) evaluate the market potential for different products that can be derived from oil shale, (2) assess the economic feasibility of a small-scale production operation, (3) evaluate conventional and innovative mining techniques, (4) study the performance of propellants to enhance fracturing of oil shale, (5) study methods for economic enhancement of shale oil upgrading, (6) analyze the economics of a combined underground and surface processing system, and (7) provide technology transfer information on oil shale.

## Procedures

An extensive number of products and byproducts from oil shale were evaluated for their market potential in a study by Sinor (1989). The study examined specialty chemicals, asphalt blends, petrochemicals, special fuels, sulfur sorbent, cement, and construction materials produced from oil shale as to their value, marketability, quantities of materials present, and cost of production and delivery.

An analysis of costs of several oil shale mining alternatives, an estimate of spent shale disposal costs, and an examination of some unconventional uses for oil shale were made by McCarthy and Clayson (1989). Mining approaches considered were room and pillar, open pit, and chamber and pillar. Cost estimates were prepared based on the capital equipment and operating requirements of each mining configuration. Using oil shale with coal for cogeneration of electricity, for sulfur removal in coal-fired power plants, and for roadbed stabilization were also examined.

Innovative mining concepts were evaluated in a study done at the Colorado School of Mines (Hieta and Hustrulid 1991). Buffer blasting was studied in small field tests as a technique for improving fragmentation. A paper study was also done comparing mining features and costs of large-hole stoping, continuous loading and hauling, and mechanical miners to conventional room and pillar mining operations.

Plant construction and operating costs were estimated in a process engineering study made by Ford, Bacon and Davis Inc. (Walker et al. 1989). Capital and operating costs were developed for a 2,000 bbl/day shale oil processing system at a plus or minus 30% design level. The retorting system selected was a Paraho process combined with an inclined-fluid-bed retort to process the shale fines. The option of replacing the inclined-fluid-bed retort with a power-generation system was also evaluated.

Drawing on the results of several of these studies, an economic evaluation was made of a small-scale shale oil production facility (Smith et al. 1989). The study considered all costs from environmental compliance and permitting through plant retirement and included a sensitivity analysis of capital costs, operating costs, and production variation.

A small laboratory study was conducted by Netzel (1991) to examine increasing the amount of asphalt blending material produced from shale oil by polymerization of shale oil distillates to higher molecular weight materials. Three distillates were tested with anhydrous aluminum chloride and with sulfuric acid.

The performance of propellants to enhance fracturing of oil shale was studied in the field by Lekas et al. (1989, 1991). Propellant charges were placed in shallow oil shale deposits, detonated, and the resulting fracturing was evaluated by air injection tests and visual observation of cracks.

Methods for economic enhancement of shale oil upgrading were investigated by Bunger et al. (1989, 1992). The process system consisted of distillation of topped shale oil to three distillate fractions and residue, cracking the residue by hydrolysis, and selective hydrotreating of the fractions and residue.

The economics of larger-scale commercial production of shale oil, combining modified in situ and surface retorting with power cogeneration was evaluated in a feasibility study conducted by Bechtel (1989). Commercial, demonstration, and pilot-scale cases were considered.

To provide information on oil shale resources and their potential for development, a video tape entitled "Oil Shale: A New Light," was prepared by the Associated Governments of Northwest Colorado, and a brochure, "Oil Shale," was produced by the Department of Natural Resources of the State of Utah.

## **Results**

Sinor (1989) found that it is technically feasible to produce a wide spectrum of products from oil shale. However, the concentrations of many individual compounds are too small for separation and purification to be practical. In addition, the relationship of price to produced volume of many organic

chemicals is such that if production were significantly increased, the price would drop greatly, resulting in an uneconomic production situation. The one potentially viable market for shale oil appears to be an asphalt blending material. Laboratory and field tests indicate that the heavy fraction of shale oil mixed with petroleum asphalt results in a superior road pavement. The economic benefits derived from longer pavement life make the shale oil material worth considerably more than conventional asphalts.

Oil shale itself can serve a regional market for such things as sulfur sorber for fluidized-bed coal combustors, cement (Sinor 1989), and soil stabilization (McCarthy and Clayson 1989). The limiting factor for these uses is transportation cost. About 500 to 700 miles appears to be the economic shipping distance.

Mining constitutes a major portion of the cost of a shale oil facility. So methods to reduce mining costs significantly will improve the economics for shale oil production. Larger-scale mining operations result in lower per-ton mining costs (McCarthy and Clayson 1989), and the development of better mining techniques would also decrease mining costs (Hieta and Hustrulid 1991).

The capital and operating costs for a 2,000 bbl/day shale oil plant using a Paraho process combined with an inclined-fluid-bed retort to process the shale fines are \$82,097,600 and \$11,091,000/yr, respectively, in mid-1989 dollars (Walker et al. 1989). If the inclined-fluid-bed retort is replaced with a power-generation system, the capital cost changes to \$96,240,000 and the operating cost changes to \$9,233,000/yr, indicating that the inclined-fluid-bed retort is the more economical method for processing the raw shale fines.

An economic evaluation of a 2,000-bbl/day shale oil facility (Smith et al. 1989) indicated that the operation is potentially viable, if the price obtained for the shale oil residue is in the top range of prices projected for this product. At \$700 to



\$1,000 per ton of shale oil residue, the estimated discounted cash flow-return on investment is in the range of 18 to 26%. This return on investment results in about a 4- to 5-year return of capital. Variation in plant production capacity has a potentially greater relative impact on the economic return than does variation in the capital or operating costs. Just a 5% increase or decrease in plant throughput will increase or decrease the rate of return by over 12%.

In the study by Netzel (1991) on polymerization of shale oil distillates to heavier materials, little change in hydrocarbon composition was found using anhydrous aluminum chloride in reactions at low temperatures. However, the reaction of 85% sulfuric acid at room temperature with three distillates produced oils with higher saturate hydrogen contents and no olefins.

The initial study on using propellants for fracturing in shallow oil shale deposits determined that (1) permeability was significantly increased at distances of 5 ft from propellant charges, with increases in permeability estimated to extend up to 12 ft, (2) both horizontal and vertical fractures were created, (3) sequentially firing two propellant charges in the same hole significantly increased permeability compared to a single charge, and (4) induced fractures were more permeable in the direction of the dominant regional fracture pattern (Lekas et al. 1989). In follow-on work (Lekas et al. 1991), a propellant tool was developed that did not use blasting caps and created horizontal fractures that extended at least 20 ft.

The shale oil upgrading study by Bunger et al. (1989, 1992) found that hydrolysis of the residue portion reduced the average molecular weight from 495 to 359 at moderate severities, but high hydrotreating severities were required to remove sufficient nitrogen from the residue. Tests on the distillate cuts of molecular weight effects determined that geometric hindrance accounted for the inhibition to denitrification, indicating that molecular

weight reduction is important to improved catalytic hydroprocessing.

The feasibility study of combined modified in situ and surface processing of oil shale by Bechtel (1991) determined that a commercial plant (24,300 bbl/day) with an investment of 1.2 billion dollars and a 20% return on equity would require a syncrude price of \$23.35/bbl. A pre-commercialization program, with pilot-scale and demonstration tests that would confirm the process concepts, was estimated to require an expenditure of 213.4 million dollars over a period of 10 years.

### Conclusions

There are a number of products and byproducts that can be processed from oil shale. However, the one that appears to have the greatest potential for commercial development in today's marketplace is an additive to conventional asphalt used in pavement applications. A small-scale plant with shale oil additive as its primary product could provide an acceptable return on investment.

Methods to improve processing efficiencies, from mining through upgrading, need to be developed to make the vast oil shale resources of the United States a viable and competitive alternative to other resources that may become more costly or unavailable in the future.

### Related Publications

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