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ENVIRONMENTAL DATA FROM BENCH-SCALE PRESSURIZED FLUIDIZED-BED HYDRORETORTING OF EASTERN OIL SHALES

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Abstract

As part of a 3-year program to develop the Pressurized Fluidized-Bed Hydroretorting (PFH) Process for Eastern oil shales, IGT conducted tests in laboratory-scale batch and continuous units as well as a 45-kg/h bench-scale unit to generate a data base for 6 Eastern shales. Data were collected during PFH processing of raw Alabama and Indiana shales and a beneficiated Indiana shale for environmental mitigation analyses. The data generated include trace element analyses of the raw feeds and spent shales, product oils, and sour waters. The sulfur compounds present in the product gas and trace components in the sour water were also determined. In addition, the leaching characteristics of the feed and residue solids were determined. The data obtained were used to evaluate the environmental impact of a shale processing plant based on the PFH process. This paper presents the environmental data obtained from bench-scale tests conducted during the program.

Introduction

The Institute of Gas Technology (IGT) is developing the pressurized, fluidized-bed hydroretorting (PFH) process for producing oil from Eastern oil shales. The results to date have been encouraging. Oil yields as high as 200% or more of Fischer Assay have been achieved with shales from six states.¹ The oil yields from conventional thermal retorting are typically on the order of Fischer Assay. The overall program, funded by the U.S. Department of Energy Morgantown Energy Technology Center (DOE/METC, Laramie Project Office), is comprised of seven experimental tasks, including one that specifically addresses the environmental concerns of oil shale processing.

The overall objectives of this task are to obtain environmental data relating to PFH processing and shale beneficiation and to analyze the potential environmental impact of the integrated PFH process. Data were presented at the 1990 symposium on the physical and chemical properties of oil shales from 6 Eastern states that had been retorted by the PFH process.² The focus of that paper was on how the

physical properties of retorted shale affected subsequent stockpiling in landfills or other storage areas. The necessity for post-retorting treatment, such as agglomeration or slagging, to ensure that the spent shale could be disposed of in an environmentally innocuous manner was also discussed.

This paper presents data obtained to date on the fate and distribution of trace and minor elements in the gaseous, liquid and solid samples from shale samples that have been retorted by the PFH process. The data are compared with those presented previously and based on the HYTORT moving-bed hydroretorting process.³

Objectives

In order to mitigate the environmental impacts of the PFH process for producing oil from shales, the sources, types, and flow rates of potential pollutants that may be emitted must be quantified. Therefore, one of the objectives of the task on environmental data and mitigation analyses was to analyze process streams from the bench-scale hydroretorting unit for potential pollutants, including trace and minor ele-

ments and organic compounds. The distribution of potential pollutants in the process streams must also be quantified, including product oil, sour water, product gas, and spent shale. Finally, the leachability of the spent shale was to be determined to evaluate whether it should be considered a hazardous material for disposal. The test used to evaluate the leaching characteristics of shale samples is the TCLP (Toxicity Characteristic Leaching Procedure), promulgated by the U.S. Environmental Protection Agency (EPA).⁴ After processing, spent shale will be exposed to weather in stockpiles prior to ultimate disposal. It is during these exposures that the most significant environmental impacts could be realized by the leaching of trace metals (in addition to other components) into the water in the shale and ultimately into the ground water.

Equipment Description and Procedures

These results were obtained by IGT in bench-scale hydroretorting tests with Alabama shale (2 tests) and raw and beneficiated Indiana shale (1 test each). The shale had been beneficiated by column flotation at the University of Alabama Mineral Resources Institute. The bench-scale unit (BSU) was designed and built at IGT for conducting tests

at high-temperature and high-pressure. The BSU is based on a balanced-pressure design in which the system pressure is sustained by the outer pressure shell, while the reaction temperature is sustained by the internal reactor shell. Thus, the differential pressure across the high-temperature shell can be controlled to a minimum. The BSU can be operated at temperatures and pressures up to 7.0 MPa and 870°C (1000 psia and 1600°F). By using different reactor inserts, the inside diameter of the BSU can be varied from 15.2 to 30.5 cm (6 to 12 inches). For the current series of tests, the 15.2-cm diameter insert was used. With this insert, the nominal feed rate to the BSU can range up to 45.4 kg/h (100 lb/h). A schematic diagram of the BSU process is presented in Figure 1.

Steady-state operation in the BSU is established after about 2 to 3 bed turnovers or after about 1 to 1-1/2 hours. Test samples are collected periodically during steady-state and unsteady-state operation. These include residue solids (spent shale), product gas samples, and liquids (oil and water). After each test, the samples are submitted to IGT's Analytical Laboratory for analysis.

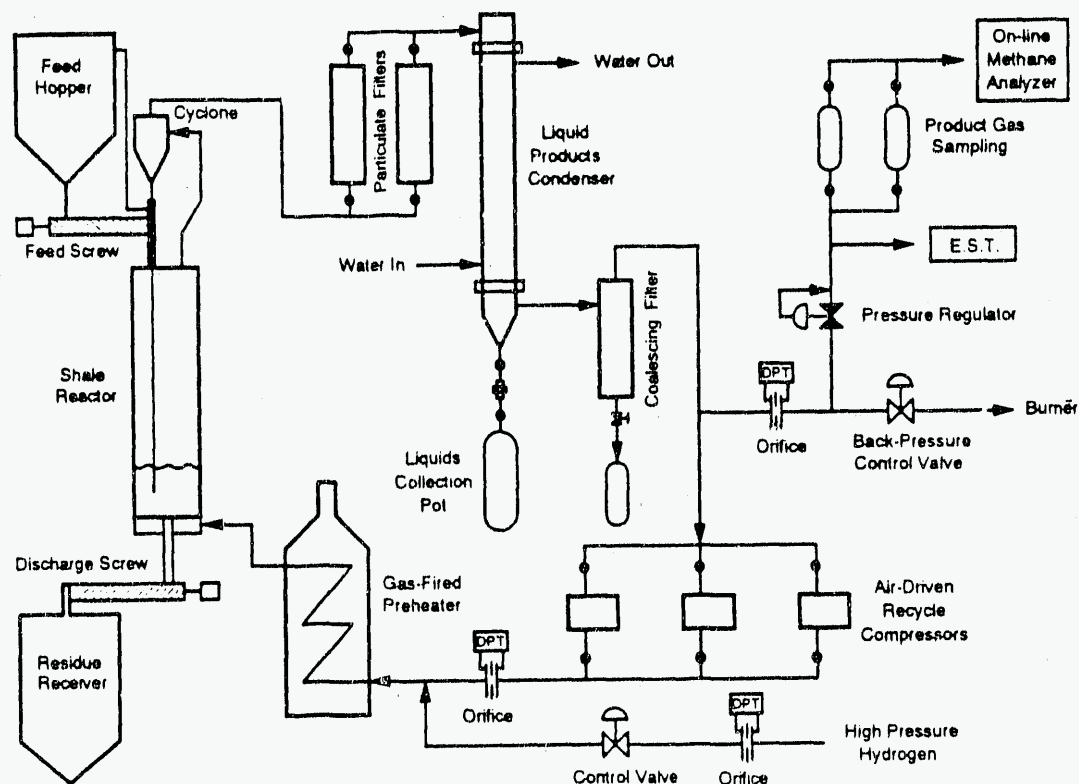


Figure 1. Schematic diagram of the bench-scale PFH test unit

Before a test is initiated, sufficient shale is charged to the feed hopper for the 5-hour duration of a typical test. At the start of the test, the feed hopper, reactor, and residue receiver are all pressurized to the targeted condition with hydrogen. Then the air-driven recycle gas compressors are started and the flow of hydrogen through the reactor is brought to the desired rate. The screw feeder is activated and shale is conveyed from the feed hopper to the reactor. Differential pressure taps located across the length of the reactor indicate the level of the fluidized bed of shale in the reactor. When the desired level of shale in the fluidized-bed level is achieved, the discharge screw is activated. The discharge screw rate is varied somewhat during the test to maintain the bed level. Fine particles elutriated from the bed are captured in a cyclone and returned to the fluidized bed via a dip leg.

Hot product gases exit the top of the BSU and pass through particulate filters in parallel. The filtered gas is then cooled (with water) in the liquid products condenser. Condensed oil and water are collected in the liquids collection pot. This pot is sampled at regular intervals during the test. The product gases next pass through a coalescing filter to remove fine droplets of oil and water. The product gas is then passed through air-driven compressors and then recycled back to the reactor. High-pressure hydrogen is added just downstream from the recycle compressors as needed for makeup. The makeup and recycled hydrogen stream is then heated to the required temperature in a gas-fired preheater.

Product gas from the BSU is passed through an orifice meter and back-pressure control valve, then burned in a flare. A fraction of the total flow (about 1 vol %) is diverted from the product gas stream through a pressure regulator. The gas flows through gas sample bombs for capture and subsequent chromatographic analysis. The hydrocarbon content of the product gas is continuously monitored via an on-line hydrocarbon analyzer.

The product gas and that being recycled through the BSU system usually contains 98% to 99% hydrogen. Thus, the organic compounds and trace elements in the product gas are present at low concentrations.

A portion of the product gas stream, typically about 1.13 m³/h (40 ft³/h), is passed through an environmental sampling train, or EST. The objective of using the EST is to concentrate the dilute organic

compounds and trace elements present in the product gas stream in different scrubbing solutions so that the amounts captured can be quantified and related back to the shale feed rate.

The EST consists of 2 parallel trains of 3 bubblers connected in series that scrub a fraction of the product gas stream. A schematic diagram of 1 train is shown in Figure 2. Each bubbler has an internal volume of 1 liter and, typically, about 400 mL of scrubbing solution are charged to each bubbler before a test. One of the EST trains is charged with an acidic solution (3 M hydrochloric); the other is charged with a basic solution (6 N sodium hydroxide). The acid scrub collects any oil and grease, phenols, phosphates, ammonia, and organic nitrogen compounds as well as nitrates and nitrites. The base scrub collects cyanide, thiocyanate, sulfides, sulfates and other sulfur-containing compounds. During sampling, the pressure in the EST is maintained at 0.24 MPa (20 psig) by a pressure regulator. After the BSU test is completed, the contents of the bubblers from each train are combined and submitted for appropriate chemical analyses.

The operating conditions and results of tests conducted in the BSU with raw Alabama and Indiana shale and beneficiated Indiana shale are presented in Table 1. Tests 4 and 5 were conducted with raw Alabama shale. These tests were conducted at temperatures of 519° and 524°C (966° and 975°F) and pressures of 4.24 and 7.0 MPa (615 and 1015 psia), respectively. The shale feed rate was about 15 kg/h (33 lb/h) for both tests. Test 9 was conducted with raw Indiana shale; Test 10 with beneficiated Indiana shale. These tests were conducted at temperatures of 513° and 519°C (955° and 966°F) and a pressure of 7.0 MPa (1015 psia). The shale feed rate was about 34.2 kg/h (75.6 lb/h) for Test 9 and 25.1 kg/h (55.3 lb/h) for Test 10. The solids residence time in the fluidized bed was about 25 minutes. The feed shale for all four tests was crushed and screened to -20+100 mesh.

The results in Table 1 show that increasing the hydroretorting pressure increased the overall carbon conversion for the Alabama shale from 64.5% to 72.9%. The fraction of feed carbon appearing in the oil increased from 44.0% to 58.1%. The Indiana shale conversions were similar to those of the Alabama shale at a pressure of 7.0 MPa (1015 psia). The beneficiated Indiana shale showed more carbon forming oil, less carbon forming gas, and an overall carbon conversion of 80.8%.

Table 1. Operating Conditions of Tests Conducted in the BSU

Run No.	4	5	9	10*
Shale	----- Alabama -----		----- Indiana -----	
Operating Conditions				
Average Fluidized-Bed Temperature, °C (°F)	519 (966)	524 (975)	513 (955)	519 (966)
Pressure, MPa (psia)	4.24 (615)	7.00 (1015)	7.00 (1015)	7.00 (1015)
Shale Particle Size, mesh	----- -20+100 -----			
Gas Flow Rate, m ³ /h (SCFH)	392.5 (13,860)	574.3 (20,280)	560.7 (19,800)	501.2 (17,700)
Superficial Gas Velocity, m/s (ft/s)	0.38 (1.26)	0.34 (1.13)	0.34 (1.10)	0.30 (0.98)
Shale Feed Rate, kg/h (lb/h)	15.1 (33.2)	14.9 (32.8)	34.2 (75.6)	25.1 (55.3)
Shale Feeding Time, h	3.2	3.6	3.1	3.3
Steady-State Period, h	2.0	2.0	1.8	1.5
Residence Time, min	26	24	26	19
Operating Results				
Carbon Conversion, % of feed carbon				
Oil	44.0	58.1	58.9	61.5
Product Gas	20.1	14.6	15.6	19.0
Residue Shale	35.5	27.1	25.3	19.2
Water (soluble HC)	0.4	0.2	0.2	0.3
Total	100.0	100.0	100.0	100.0
Oil Yield, L/t (GPT)	80.9 (19.4)	104.7 (25.1)	90.1 (21.6)	208.2 (49.9)
Oil Density, g/ml (°API)	1.016 (7.8)	1.035 (5.2)	0.996 (10.6)	0.983 (12.5)
Water Yield, L/t (GPT) ⁺	14.9 (3.6)	18.3 (4.4)	47.6 (11.4)	82.0 (19.7)
Sulfur Conversion, % of feed sulfur				
Oil	2.3	2.7	2.8	6.9
Product Gas ⁺	50.3	51.3	44.8	16.8
Residue Shale	46.4	45.0	51.9	69.4
Water	1.0	1.0	0.5	6.9
Total	100.0	100.0	100.0	100.0

* Beneficiated shale that was pelletized then crushed and screened to size.

+ Sulfur in gas includes dissolved gases in water.

The conversions of feed sulfur to gas were typically about 50% for the raw shales - resulting from pyrite conversion. With the beneficiated shale, most of the sulfur (69.4%) remained with the shale residue.

Increasing the hydrogen pressure from 4.24 to 7.0 MPa (615 to 1015 psia) increased the yield of oil during pressurized fluidized-bed hydroretorting of raw Alabama shale by about 29% from 80.9 to 104.7

liter/metric ton (19.4 to 25.1 gallon/ton [GPT]). At the same pressure (7.0 MPa) and similar temperatures, the Alabama shale yielded about 16% more oil than the Indiana shale (104.7 to 90.1 L/ton). The yield of oil from the beneficiated shale was 208.2 L/ton. Fischer Assays (FA) of the raw Alabama, raw Indiana, and beneficiated Indiana shales were 53, 54, and 108.1 L/ton (12.7, 12.9, and 25.9 GPT), respectively.

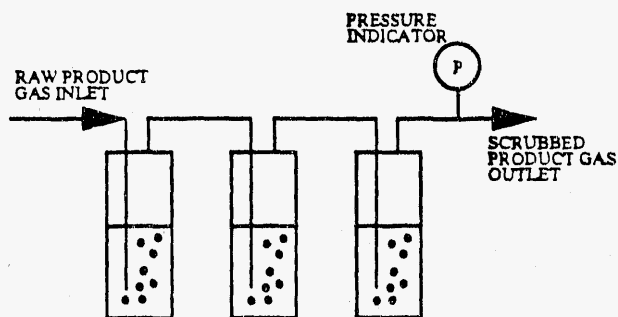


Figure 2. Schematic diagram of the environmental sampling train (1 of 2 parallel trains)

Water yields were 14.9 and 18.3 L/ton (3.6 and 4.4 GPT) for the Alabama shale. The water yield for the raw Indiana shale was 47.6 L/ton (11.4 GPT) and for the beneficiated shale was 82 L/ton (19.7 GPT).

The ultimate analyses of the feed shales that were hydroretorted in the BSU are presented in Table 2. The carbon contents were 15.94% for the Alabama shale and 12.95% for the raw Indiana shale. The beneficiated Indiana shale carbon content was 28.05%. At 9.05%, the sulfur content of the Alabama shale was significantly higher than those of the raw and beneficiated Indiana shales (2.93% and 2.77%, respectively).

The analyses of the feed shales for major and minor elements are presented in Table 3. As the data shows, the major component of the feed shales is silicon, which ranges from 18.0% to 24.8% (whole shale basis), depending upon the shale. Other elements present in significant quantities are aluminum, iron, and potassium. The analyses of the feed shales for 20 trace elements are presented in Table 4. Of the 20 elements, 8 (arsenic, barium, cadmium, chromium, mercury, lead, selenium, and silver) are analyzed as part of the TCLP test to determine if the sample exhibits a toxic characteristic. The analyses show that silver and lead were not present in the shales at concentrations greater than the analytical detection limits (<5 and <20 $\mu\text{g/g}$, respectively). Arsenic was present in the range of 67 to 110 $\mu\text{g/g}$. Barium was higher in the Indiana shale samples than the Alabama (320 and 230 $\mu\text{g/g}$ compared with 70 $\mu\text{g/g}$). Cadmium and mercury were present at 3 to 5 and 0.1 to 0.2 $\mu\text{g/g}$, respectively. Chromium contents ranged from 64 $\mu\text{g/g}$ in the Alabama shale, to 100 in the raw Indiana shale, to 220 $\mu\text{g/g}$ in the beneficiated Indiana shale. Selenium was analyzed from about 6 to 10 $\mu\text{g/g}$, depending upon the sample.

Table 5 shows the chemical analyses of the oil samples obtained from hydroretorting tests conducted in the BSU with Alabama, raw Indiana, and beneficiated Indiana shales. The carbon-to-hydrogen ratio of the oils ranged from 8.7 for beneficiated Indiana shale to 9.5 for the Alabama shale. The sulfur contents of the raw and beneficiated Indiana shale oils were significantly lower (0.91% and 0.94%) than those of the Alabama shale (2.55% and 2.24%). The nitrogen contents in the oils are comparable.

The oils were also analyzed by high-pressure liquid chromatography (HPLC) to quantify the major structural components present, including aliphatic, 1-ring, 2-ring, 3-ring, and 4-ring plus polar groups. The oils were extracted in hexane; therefore, the two major HPLC categories are hexane soluble and insoluble components. The results of the analyses (Table 5) show that the Indiana shale oils are comprised of more aliphatic compounds, less 1-ring compounds, more 2- and 3-ring compounds, and somewhat more 4-ring plus polar groups than the Alabama shale oils. The composition of the raw and beneficiated Indiana shale oils are similar, as expected.

The chromatogram obtained during the HPLC analysis of the oil from the beneficiated Indiana shale is presented in Figure 3. It is apparent from the chromatogram that the shale oil is composed of thousands of individual compounds. IGT's analytical laboratory identified and quantified some of the compounds that were present in the samples of shale oil. Table 6 shows the concentration of the compounds present at the highest quantity in the shale oils. The bulk of the oil components were not explicitly identified.

Chemical analyses were also conducted on the samples of shale oil to determine the concentrations of trace and minor elements. The results are presented in Table 7. Chlorine appears to be relatively high in the Alabama shale oil. A number of trace elements that were analyzed, including silver, arsenic, barium, cadmium, chromium, copper, mercury, potassium, lithium, magnesium, manganese, lead, and antimony, were less than 10 ppm (by weight) in the oil. The concentrations of nickel and vanadium in the shale oil are comparable to those found in vacuum resid oil.

The by-product water generated from the bench-scale tests was also analyzed for organic compo-

Table 2. Ultimate Analyses of the Feed Shales
Hydroretorted in the BSU

Shale	<u>Alabama</u>	<u>Indiana</u>	<u>Beneficiated Indiana</u>
Moisture, wt %	0.94	1.56	1.88
Ultimate Analysis, wt % (dry basis)			
Organic Carbon	15.94	12.95	28.05
Mineral Carbon	0.07	0.08	0.05
Hydrogen	1.57	1.48	2.81
Oxygen	2.90	3.16	5.41
Nitrogen	0.49	0.35	0.74
Sulfur	9.05	2.93	2.77
Ash	73.59	80.25	61.11
Gross Calorific Value, MJ/kg (Btu/lb)			
	7.60	5.81	12.52
	(3266)	(2497)	(5385)
Fischer Assay, L/t (GPT)			
	53	54	108
	(12.7)	(12.9)	(25.9)

Table 3. Elemental Analyses of Feed Shales
Hydroretorted in the BSU

Shale	<u>Alabama</u>	<u>Indiana</u>	<u>Beneficiated Indiana</u>
Element, wt % (dry basis)			
Aluminum	4.89	6.88	5.32
Calcium	0.24	0.34	0.27
Iron	7.49	3.99	3.87
Potassium	2.70	3.00	2.47
Magnesium	0.64	0.70	0.56
Sodium	0.34	0.41	0.22
Silicon	22.10	24.80	18.00
Titanium	0.36	0.41	0.36

Table 4. Trace Element Analyses of Feed Shales
Hydroretorted in the BSU

Shale	<u>Alabama</u>	<u>Indiana</u>	<u>Beneficiated Indiana</u>
Element			
		μg/g	
Antimony	95	75	68
Arsenic	110	75	67
Barium	70	320	230
Beryllium	3.6	4.6	4.9
Boron	11	23	27
Cadmium	3.4	5.7	3.4
Chlorine	330	440	530
Chromium	64	100	220
Fluorine	350	420	560
Lead	<20	<20	<20
Manganese	200	130	110
Mercury	0.20	0.11	0.21
Molybdenum	260	130	170
Nickel	250	180	220
Phosphorus	430	900	710
Selenium	5.9	10	9.7
Silver	<5.0	<5.0	<5.0
Strontium	37	56	50
Vanadium	260	600	590
Zinc	270	730	500

Table 5. Chemical Analyses of the Product Oils From Hydroretorting Tests in the BSU

Run No.	4	5	9	10*
Shale	----- Alabama -----	-----	----- Indiana -----	-----
Ultimate Analysis, wt %				
Carbon	85.74	85.91	85.80	84.94
Hydrogen	9.44	9.05	9.61	9.75
Sulfur	2.55	2.24	0.91	0.94
Nitrogen	1.41	1.52	1.84	1.94
Hexane Soluble Groups, + wt %	94	88	94	96
Aliphatics	17	13	21	22
1-Ring	35	30	23	23
2-Ring	15	14	18	17
3-Ring	<0.5	<0.5	3	3
4-Ring + Polar	27	31	29	31
Hexane Insoluble Groups	6	12	6	4

* Beneficiated shale

+ Oil:hexane dilution of 1:100.

Table 6. Component Analyses of the Product Oils From Hydroretorting Tests in the BSU

Run No.	4	5	9	10*
Shale	----- Alabama -----	-----	----- Indiana -----	-----
Component, wt %				
Acetone	0.17	0.19	BDL ⁺	BDL
Benzene	0.60	0.33	0.22	0.28
Toluene	0.27	0.37	0.24	0.38
Ethylbenzene	0.18	0.24	0.18	0.28
m, p-Xylene	0.31	0.33	0.27 ^x	0.42
Styrene	0.11	0.08	--	--
o-Xylene	0.17	0.17	0.17	0.27
Phenol	0.28	0.29	--	--
Naphthalene	0.31	0.32	0.12	0.22
2-methylnaphthalene	0.50	0.53	0.33	0.37
1-methylnaphthalene	0.44	0.42	0.25	0.26
Phenanthrene	0.14	0.18	--	--
Anthracene	0.05	0.05	--	--

* Beneficiated shale.

+ Below analytical detection limit.

x Obscured by co-eluting compounds.

Table 7. Trace Element Analyses of the Product Oils From Hydroretorting Tests in the BSU

Run No. Shale	4	5	9	10*
	Alabama		Indiana	
Trace Element	----- ppmw -----			
Aluminum	1.0	0.44	1.8	<2.0
Antimony	<4.0	<4.0	<2.0	<2.0
Arsenic	6.3	6.2	0.72	0.39
Barium	<0.20	<0.20	<0.10	<0.20
Cadmium	<0.20	<0.20	<0.50	<0.50
Calcium	1.8	0.67	1.1	0.59
Chlorine	340	920	160	71
Chromium	0.70	0.67	0.74	1.3
Copper	<0.40	0.40	<0.50	<0.50
Fluorine	11	5.5	<30	<30
Iron	7.9	11	21	10
Lead	<4.0	<4.0	<2.0	<2.0
Lithium	<0.40	<0.40	<0.40	<0.40
Magnesium	0.70	0.52	0.40	0.24
Manganese	<0.40	0.40	0.14	<0.50
Mercury	<0.50	<0.50	0.38	0.34
Nickel	36	28	16	9.2
Potassium	1.7	1.6	0.93	1.3
Selenium	7.4	11	12	1.8
Silver	<0.40	<0.40	<0.50	<0.50
Sodium	110	47	2	2
Vanadium	23	12	2.3	1.5
Zinc	3.8	17	0.7	0.2

* Beneficiated shale.

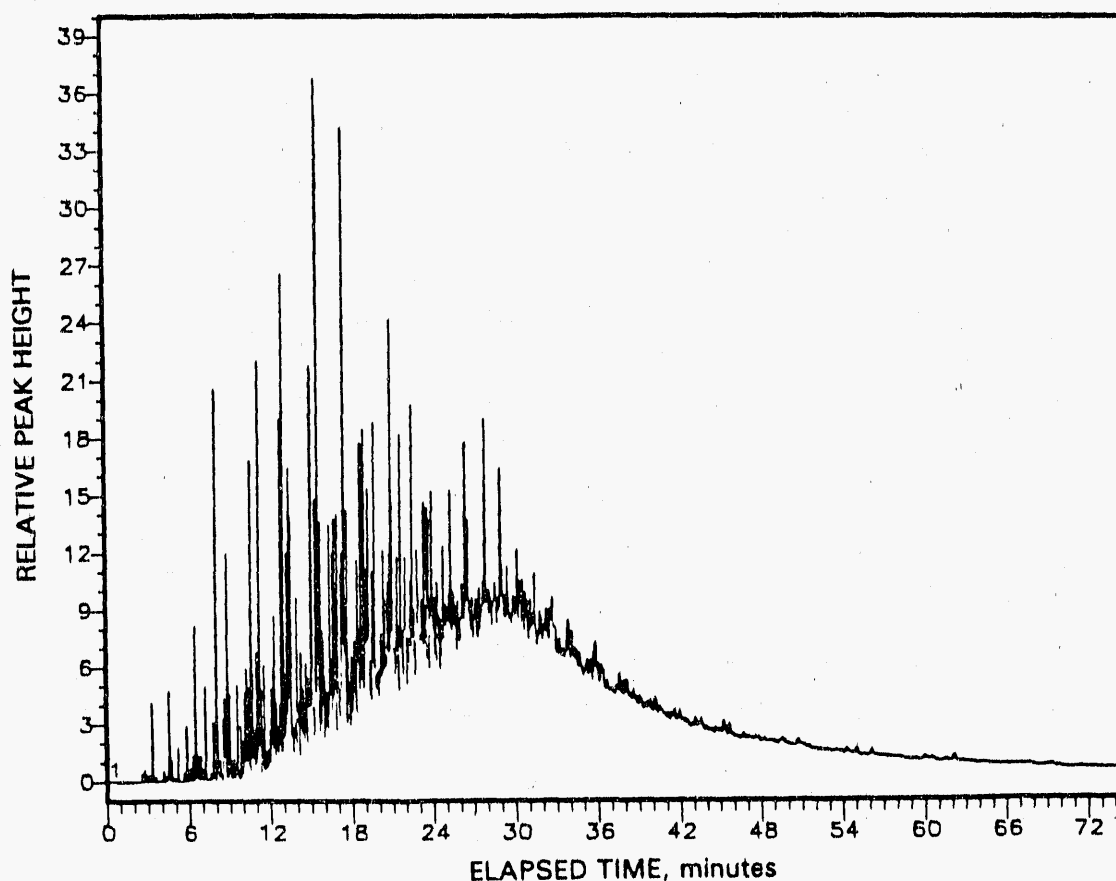


Figure 3. Chromatogram of the oil produced in the BSU with beneficiated Indiana shale

nents. The results (Table 8) show that the water produced during hydroretorting of both raw and beneficiated Indiana shale contained higher concentrations of oxygen- and nitrogen-containing compounds as well as unidentified compounds. The beneficiated shale produced relatively high levels of organic acids.

Samples of spent shale from the BSU tests were subjected to the EPA TCLP test. In the TCLP, a solid sample is mixed with 20 times its weight of an appropriate aqueous extraction fluid (depending upon alkalinity) for 18 hours. After the extraction, the concentration of metals (listed in Table 9) in the leachate (plus volatile and nonvolatile organic compounds) are determined. If the concentration of any metal (or organic compound) in the leachate exceeds the regulatory limit, the material is said to exhibit a toxic character and is classified as a hazardous waste. The solid must then be disposed in suitably constructed and monitored landfills. If the leachate is not effectively contained or collected, it could percolate down to the water table or combine with surface runoff to contaminate fresh water supplies. As this work focused on heavy metals, the leachate was not analyzed for organic compounds.

The results of the TCLP tests conducted on the spent shale samples are also presented in Table 10. None of the leachate concentrations for any of the priority metals exceed the Federal limits. In fact, most of the analyses were below the detection limit of the analytical test. This means that the spent shale will not be considered hazardous for disposal.

The analyses of the samples collected from the Environmental Sampling Train are presented in Table 10. The analyses conducted on the acid scrub solution include COD (chemical oxygen demand) as well as those mentioned previously. The analyses conducted on the base scrub comprise cyanides, thiocyanates, and sulfur species.

The COD was about 15,000 mg/L for the test conducted with Alabama shale at 4.24 MPa and 15,100 mg/L for the test conducted with the same shale at 7.0 MPa. Assuming comparable EST capture efficiencies, increasing the pressure decreased the quantity of material present in the acid scrub. In the tests conducted with the Indiana shale, the COD was about 10,000 mg/L, whether the sample was raw or beneficiated. In general, the analyses of the EST acid scrub for the raw and beneficiated Indiana

Table 8. Component Analyses of the By-Product Water From Hydroretorting Tests in the BSU

Run No.	4	5	9	10*
Shale	----- Alabama -----	-----	----- Indiana -----	-----
Oxygen-Containing Compounds, mg/L				
Methyl Ethyl Ketone	42	30	120	180
Acetic Acid	17	260	--+	5000
Propionic Acid	1	100	--	1600
Butanoic Acid	12	65	--	680
Pentanoic Acid	29	210	--	--
Phenol	27	45	230	275
Methyl Phenols	37	29	130	210
Nitrogen-Containing Compounds, mg/L				
Propionitrile	4	3	125	190
Aniline	18	67	320	270
Methyl Aniline	3	9	120	80
Pyrrrole	31	36	680	720
Methyl Pyrroles	10	2	890	830
Pyrrrolidinone	30	37	--	--
Unidentified Compounds	440	470	1360	3130

* Beneficiated shale.

+ Below detection limit.

Table 9. Results of TCLP Tests Conducted on Shales Hydroretorted in the BSU

Run No.	4	5	9	10*
Shale	----- Alabama -----	-----	----- Indiana -----	-----
Element	TCLP Leachate Limit			
	----- mg/L -----			
Silver	5.0	<0.020	<0.020	<0.050
Arsenic	5.0	0.35	0.61	0.038
Barium	100.0	0.097	0.13	0.28
Cadmium	1.0	0.012	<0.020	0.039
Chromium	5.0	0.043	0.034	<0.020
Mercury	0.2	<0.003	<0.0015	<0.0015
Lead	5.0	<0.20	<0.20	<0.20
Selenium	1.0	<0.001	<0.010	0.0071

* Beneficiated shale.

Table 10. Analysis of Components Collected in the Acid and Base Scrubbers From the EST

Run No.	4	5	9	10*
Shale	----- Alabama -----	-----	----- Indiana -----	-----
Acid Scrub, mg/L				
COD	15100	4900	11000	10200
Oil and Grease	16.9	4.0	10.6	6.7
Total Nitrogen	254	75	30	60
NO ₂	1.7	0.7	<0.3	<0.3
NO ₃	6.8	5.0	0.5	0.65
Ammonia Nitrogen	254	71	30	60
Phosphorous	1.1	0.5	<0.3	<0.3
Phenols	3.5	0.33	0.19	0.15
Organic Carbon	180	1168	78	83
Base Scrub, mg/L				
Cyanide	0.64	0.89	<0.03	<0.03
Thiocyanates	200	390	<1	<1
Total Sulfur	1500	3600	1200	460
Sulfate Sulfur	92	310	33.6	17.2
Sulfide Sulfur	1470	3280	690	380

* Beneficiated shale.

shale were not significantly different. The analyses of the base scrub showed that increasing the pressure increased the concentration of sulfur species from Alabama shale. For the Indiana shale, beneficiation decreased the quantities of sulfur species in the base scrub by about 45% to 60%.

Conclusions

- Most of the trace elements in the feed shale remained with the spent shale.
- Some elements, such as Cl, F, Hg, Li, Se, and V, were volatilized at least to some extent during hydroretorting in the BSU.
- Leaching tests conducted with hydroretorted raw and beneficiated shales show that none exceed the TCLP limits for toxicity.
- Overall, the compounds collected in the EST were qualitatively similar to those collected previously in the smaller mini-bench-scale unit.³
- The acid and base scrubs of the EST were effective in collecting various categories of compounds from the BSU product gas stream.
- The base scrub absorbed most of the sulfur compounds in the gas stream.
 - Sulfur ranged from 460 to 3600 mg/L, depending upon the shale.
 - Thiocyanates were 200 and 390 mg/L for the Alabama shale and below the analytical detection limit for the Indiana shale.
- The acid scrub contained very low concentrations of nitrates and nitrites.
 - Nitrates ranged from 18 to 545 ng/g shale feed
 - Nitrites ranged from 10 to 140 ng/g shale feed

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