Characterization of Mercury, Arsenic, and Selenium in the Product Streams of the Pacific Northwest Laboratory 6-kg Retort

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SUMMARY

The objective of this program is to determine how retorting process parameters affect the partitioning of Hg, As, Se, and Cd from raw oil shale to spent shale, shale oil, retort water, and offgas.

For each of the elements, the objective of this study is to 1) determine the distribution coefficients for each product stream; 2) identify the chemical forms in water, gas, and oil streams, with particular emphasis on inorganic or organometallic species known to be or suspected of being carcinogenic, toxic, or otherwise harmful; 3) investigate the mechanism(s) responsible for mobilization into each product stream for toxic or labile chemical forms identified in item 2 are mobilized into each product stream; and 4) the effect of retorting rate, maximum retorting temperature, and retorting atmosphere on items 1 and 3.

A Green River shale from Colorado and a New Albany shale from Kentucky were heated at 1 to 2°C/min and at 10°C/min to maximum temperatures of 500 and 750°C under a nitrogen sweep gas. The product streams were analyzed using a variety of methods including Zeeman atomic absorption spectroscopy, microwave-induced helium plasma spectroscopy, x-ray fluorescence, instrumental neutron activation analysis, high-pressure liquid and silica gel column chromatography, and mercury cold vapor atomic absorption. The results obtained using these analytical methods indicate that the distribution of mercury, arsenic, and selenium in the product stream is a function of oil shale type, heating rates, and maximum retorting temperatures.

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INTRODUCTION

The volatile nature of mercury, arsenic and selenium result in a fraction of these elements being released from the raw oil shale matrix during retorting and subsequently migrates to the product oil, retort water, or offgas streams. Thus, depending upon the stability of the chemical form in each product stream, the elements may be mobilized into the environment unless removed from these streams before their disposal.

Pacific Northwest Laboratory (PNL) is conducting a program entitled "Partitioning and Chemical Speciation Studies of Volatile Trace Elements" for the Office of Fossil Energy of the U.S. Department of Energy (DOE). The program goals are to determine the distribution of mercury (Hg), arsenic (As), selenium (Se), and cadmium (Cd) in the offgas, retort water, and shale oil, and to determine the chemical species of these elements in the product streams. These elements were chosen because of their potential for volatilization out of the oil shale rock matrix and subsequent redistribution into the product streams of a commercial retort. In this study, a fully instrumented 6-kg retort was used to carefully control retorting parameters. The information resulting from the studies will be helpful in minimizing environmental concerns while maximizing the quality of the liquid fuel produced in the retorting process.

This report, the second in a series of three, describes the analytical methods used to determine the partitioning of Hg, As, and Se under various retorting parameters in the 6-kg PNL retort. Further topics include a comparison of the partitioning of Hg, As, and Se in the product streams for various heating rates and maximum temperatures, and the identification of the organomercury compounds isolated in the offgas.

ANALYTICAL METHODS FOR DETERMINING MERCURY, ARSENIC,
AND SELENIUM IN OIL SHALE RETORTING

SAMPLE COLLECTION

Shale oil and retort water samples were collected immediately after the maximum programmed temperature of the retort was reached. The shale oil and retort water were separated, placed in Teflon® bottles, and stored at 4°C. Following the retort run, the vessel was allowed to cool to room temperature for 24 to 48 h under a continuous nitrogen sweep gas. The vessel was machined open and the contents were transferred into a 4-mil plastic bag and place in a sealed 19-L steel container (5 gal) for temporary storage. The spent shale was then passed through a Gibson splitter to produce a 100-g aliquot for further analysis.

The sampling point for the noncondensable species of Hg, As, and Se was located immediately after the outlet of the second condenser (Figure 1). This location was also the sampling point for Zeeman atomic absorption (ZAA) spectroscopy and microwave plasma detector (MPD).

Noncondensable Hg species in the offgas from retort run PNL-2 were sampled by a combination of a cold trap followed by silver and gold traps. The cold trap consisted of a 6-mm-ID quartz U-tube with a path length of 30 cm. The U-tube was immersed in an acetone/dry-ice (-78°C) bath. Upon leaving the cold trap, the offgas passed first through a trap containing silver-coated quartz beads and then through a trap containing gold-coated quartz beads. The intent of the cold trap was to condense the organomercury compounds; the silver trap collected elemental mercury, and the gold trap was sensitive to all remaining forms of gaseous mercury and functioned as a system backup. This trapping arrangement allowed a determination of the trapping efficiency of the collection system for organically bound and elemental mercury. Sampling periods with this system ranged from 1D to 30 min with a flow rate of 375 mL/min for the offgas. Four cold trap samples were collected during the period of mercury evolution as determined by the ZAA monitor. Following each sample run, the U-tube was rinsed three times with "distilled-in-glass" quality methylene chloride. The methylene chloride solution was stored in sealed volumetric

FIGURE 1. Schematic Diagram of PNL 6-kg Retort

flasks on dry ice. The samples were analyzed the following day using gas chromatography-microwave plasma detector (GC-MPD).

Noncondensable species of Hg, As, and Se in subsequent retort runs were collected using a modified cold trap system. Two 19-mm-ID by 22-cm glass impingers with Teflon® stopcocks were connected in series by 6.2-mm-OD Teflon® tubing. The impingers were immersed in a CH₂Cl₂/dry-ice bath. After leaving the impingers, the offgas passed through a rotometer and was returned into the offgas system. Typical sampling periods for this system spanned the entire retort run. The flow rate through the impinger system was maintained at 60 cm³/min. Following the completion of the retort run, the samples were transferred immediately into 125-mL volatile organic septum bottles sealed with Teflon® caps and stored at -17°C until analyzed by GC-MPD for species containing Hg, As, and Se. In addition, 5-mL aliquots (one from each impinger from each retort run) were transferred into quartz ampoules, sealed by glassblowing, and stored in liquid nitrogen.

OFFGAS ANALYSIS

Six low molecular-weight gases were quantitated during retort run PNL-2: O₂, CO, CO₂, CH₄, C₂H₆, and C₂H₄. The gases were separated from each other and from N₂, H₂O, C₃, and higher molecular weight hydrocarbons using a Carle GC specifically designed for this purpose. The Carle GC employs a combination of Porapak and molecular sieve columns with automatic switching valves to facilitate bypass and backflushing functions. The column temperature was isothermal at 75°C. Samples were injected from a 1-mL sample loop every 25 min through the course of the retort run. Samples were calibrated against a mixture of CO, CO₂, CH₄, C₂H₆, and C₂H₄ (1% each in N₂) or a mixture of CO, CO₂, O₂, and CH₄ (1% each in N₂). The linearity of the thermal-conductivity detector was confirmed over the range of compositions observed.

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ZEEMAN ATOMIC ABSORPTION SPECTROSCOPY

Mercury in the offgas was monitored by ZAA during retort run PNL-2, but ZAA was abandoned on later runs in favor of the more sensitive plasma emission technique described below. Zeeman atomic absorption spectroscopy is similar to conventional atomic absorption spectroscopy; it differs principally in that the light source is placed in a magnetic field, which splits the 257.3-nm mercury resonance line into a linearly polarized (π) component and a two circularly polarized (σ) components. The π component is used to detect the presence of mercury, and the two σ components, which are shifted in wavelength, are used to monitor light scattering by smoke or nonspecific absorption by molecular species. This technique was originally developed at Lawrence Berkeley Laboratory (LBL) by Tetsuo Hadeishi (Hadeishi and McLaughlin 1971) and was used successfully to detect mercury in oil shale retort offgas in an earlier version of a related research effort at LBL (Fox et al. 1978; Girvin and Fox 1980). The ZAA system used in this work was custom built by Hadeishi for our program. A description of an earlier version of the instrument is given by Girvin and Fox (1980). Our system differed from the earlier model primarily in the addition of a dual channel mode to correct for drift in lamp intensity.

Offgas from the retort was diverted through the ZAA system from the sampling point shown in Figure 1 through a 6.2-mm-OD Teflon® tube. The gas passed into a 30-cm length of quartz tube filled with loosely packed quartz wool and then into a 10-cm-long absorption cell. The quartz tube and absorption cell were heated with ceramic-insulated nichrome wire. The entire quartz assembly was maintained at 800° to 900°C during the run to pyrolyze organically associated mercury compounds in the offgas and atomize the mercury. Unfortunately, this temperature also thermally polymerized volatile offgas compounds, resulting in a tar deposit on the windows of the cell. This polymerization eventually caused the termination of the run during the period of oil production. The exhaust flow leaving the absorption cell was diverted through a mass flow controller to maintain a constant flow of 500 cm³/min. The system was calibrated using a mercury vapor generator constructed according to the description of Nelson (1970). The mercury generator was operated with

nitrogen gas flowing at a rate of $184 \text{ cm}^3/\text{min}$. The nitrogen flow was added to the retort flow of $500 \text{ cm}^3/\text{min}$ using the mass flow controller, to produce a constant total flow of $684 \text{ cm}^3/\text{min}$. Under these conditions, the concentration of mercury in the cell was $4.85 \text{ } \mu\text{g/L}$. The system was calibrated six times over the observed mercury peak with an observed relative standard deviation of 8%. The retort gas did not cause any measurable suppression of signal during the period of mercury evolution from the retort.

MICROWAVE INDUCED HELIUM PLASMA DETECTOR

Gas Chromatography-Microwave Plasma Detector of Organomercury Compounds in Offgas

The atmospheric-pressure microwave plasma detector (Figure 2) used for speciating the organomercury compounds in the offgas employs a Beenakker cavity constructed by J&D Industries (Lexington, Massachusetts) following the description of Beenakker (1976). The microwave generator (Kiva Instrument Corporation, Rockville, Maryland) has a resonant frequency of 2450 MHz. The Beenakker cavity was normally operated at a forward power level of 60 to 65 W. A Hewlett-Packard 5840 A GC was used with splitless injection onto a 30-m-long fused-silica capillary column coated with $1.0\text{-}\mu\text{m}$ -thick DB-5 (J&W Scientific, Rancho Cordova, California). The fused-silica column was connected to a heated zero-dead-volume four-port valve (Valco Instruments, Houston, Texas). A second length of DB-5-coated fused-silica capillary column (about 20 cm long) enclosed in a 1.6-mm heated nickel tube and passing through a heated tee was used to connect the valve outlet to the plasma tube. The fused-silica capillary extended 2 to 3 mm beyond the end of the nickel tubing, placing it very close to the plasma excitation region. This configuration allowed a controlled flow of helium make-up gas containing 0.2% v/v of a scavenge gas (oxygen) to be added through the heated tee into the nickel tubing surrounding the fused silica and from there into the plasma. The four-port valve was used for the column effluent to bypass the plasma (e.g., during elution of the solvent peak). The four-port valve also allowed continuous helium flow through both portions of the capillary column at all times. The

FIGURE 2. Schematic Diagram of the Atmospheric-Pressure Microwave Plasma Detector System

valve was electronically connected to the valve driver board of the GC controller and was controlled by the GC microprocessor. The entire transfer line was heated by nichrome wire to the maximum column temperature. This interface arrangement satisfied the criteria for interfacing a capillary column GC to an MPD without loss of sensitivity or resolution. The arrangement was a modification of the system developed by Quimby et al. (1980).

The spectrometer used for the atmospheric-pressure GC-MPD system was the ultra-high-resolution Spectraspan IIB 0.75-m echelle spectrometer from Beckman Instruments (Irvine, California). This spectrometer has a reciprocal linear dispersion of 0.122 nm/mm at 400 nm, which results in greatly improved selectivity and an improved signal-to-noise ratio because of the narrower peak widths. The system was operated exclusively in the single-element mode, with the output of the phototube connected to the GC electrometer board. The signal was thus acquired and integrated by the GC microprocessor.

Ethylmercury, methylmercury chloride, and di-n-propyl, di-n-butyl, di-n-hexyl, and di-benzyl mercury calibration standards were obtained from Organometallic Inc., East Hampstead, New Hampshire. Dimethyl and diethyl mercury standards were obtained from Strem Chemical Inc., Newburyport, Massachusetts. All solvents used to dilute and inject samples onto the GC were "distilled in glass" quality from Burdick and Jackson Laboratories, Muskegon, Michigan.

Real-Time Monitoring for Mercury and Arsenic in Offgas by Microwave-Induced Helium Plasma Detector

The detection of gas phase mercury and arsenic was monitored in real time by microwave-induced helium plasma sources mounted on either an MPD-850 spectrometer (Applied Chromatography Systems, Luton, Bedfordshire, England) or the Spectraspan IIB 0.75-m echelle spectrometer discussed previously. The microwave generator used with both systems includes a high-voltage power supply and a Mullard-type 7090 200-W magnetron oscillator resonant at 2450 MHz. The microwave cavities were obtained from Applied Chromatography Systems (ACS) and J&D Industries (Lexington, Massachusetts) and were constructed in accordance with the description of Beenakker (1976). The ACS system was modified somewhat using a tuning arrangement adapted from their low-pressure Evenson source. It

was found to have very favorable operational characteristics. All retort runs subsequent to PNL-3 were done with the ACS source. The helium plasma was initiated with a Tesla coil and was then self-sustained in a capillary quartz plasma tube of 1-mm ID. A reactive scavenge gas (oxygen) was added to the helium in concentrations of 0.2% v/v to prevent the formation and consequent deposition of analyte elements on the walls of the plasma tube.

The MPD-850 spectrometer consisted of an 0.75-m Rowland circle direct reader with phototubes and associated slits distributed on the arc of the Rowland circle. A reciprocal linear dispersion of 1.39 nm/mm in the first order or 0.695 nm/mm in the second order is achieved using a 960-groove/mm ruled grating fitted into a Paschen-Runge mounting. Separate amplifiers provide 0 to 10-V output for each of the eight phototubes.

Offgas was sampled from a point immediately after the second and last condenser in the offgas stream (Figure 1). At this sampling point, most of the matter present in the gas phase could be considered noncondensable species. The offgas sample stream was routed through a 1.6-mm Teflon® tubing to an all-glass-and-Teflon® low-flow (0 to 10-mL/min) rotometer followed by a 7-cm-long by 50- μ m-dia uncoated fused-silica capillary tube used as a critical orifice. The flow of offgas into the plasma was accurately measured at 3.3 mL/min for both plasma systems. At the point where the capillary tube terminated, a four-way cross was present to allow the addition of a helium make-up gas containing oxygen as a scavenge gas, and/or a calibration gas, when needed.

Mercury concentration in the offgas was monitored on both the MPD-850 and the Spectraspan IIIB spectrometer systems on subsequent retort runs. The mercury 253.7-nm emission line was monitored on each system. An attempt was made to measure the concentration of volatile arsenic in the offgas using the MPD-850 spectrometer; however, it was found that the 200.3-nm emission line in this unit had insufficient sensitivity for our needs (Olsen, Sklarew and Evans 1985). Unlike the MPD-850 instrument, which has fixed locations for the phototubes, the Spectraspan IIIB spectrometer allows the selection of any emission line between 190 and 800 nm. In this case, the 234.9-nm line was initially selected to monitor arsenic concentration in the offgas. This line was found

to be the most sensitive emission line for arsenic in the helium source; however, it also proved to exhibit a large spectral interference of unknown origin, rendering it unusable for our purposes. Subsequent runs were then done using the 228.8-nm line, which is about 50% less sensitive but is relatively free of interference.

X-RAY FLUORESCENCE

The x-ray fluorescence (XRF) procedure utilized in this program is a highly automated multielement technique capable of producing a large amount of high-quality data in a very short time. The system is capable of analyzing a wide range of sample types (including raw shale, spent shale, shale oil, and retort water) for total As and Se, in addition to numerous other elements. However, its detection limit for Hg was well above the concentrations actually observed in the raw shales, spent shales, shale oils, and retort waters.

Preparation the raw shale and spent shale samples entailed aliquoting a subset of the bulk shales obtained using a Gibson splitter, and pulverizing and grinding the material using a Spex shatterbox. The prepared samples were stored in amber glass containers, from which aliquots were taken for analysis by instrumental neutron activation, cold vapor atomic absorption, and XRF analysis. Five-hundred-mg aliquots of the shale samples were pressed into wafers and analyzed by XRF. Shale oil samples from each run were warmed to room temperature. A 1-mL aliquot was removed from near the surface of the oil. The oil sample was subsequently deposited into a polyethylene snap cell for XRF analysis. X-ray fluorescence analysis of retort water required the room temperature evaporation of 10 to 15-mL aliquots into a cellulose matrix. The cellulose was then pressed into a wafer, inserted into a 35-mm slide mount, and analyzed.

An energy-dispersive x-ray fluorescence system was used for determining As and Se concentrations in the various product streams of the PNL 6-kg retort. The XRF system uses an 80-kV tungsten x-ray tube to excite a Zr secondary source producing characteristic radiation to fluoresce the sample. Data acquisition utilizes a Canberra System 80 multichannel analyzer with multiple analog-to-digital converters interfaced to a DEC PDP 11/34 computer. All data

reduction is done on line by the PDP 11/34. A fundamental-parameter method is used that utilizes coherent-to-incoherent peak-scattering ratios to calculate the absorption properties of the matrix. The program (SAP3) makes peak overlap, grain size, and self-absorption corrections. These results are then compared with a library of thin-film standards to calculate a final concentration. A complete discussion of the most recent version of the programs is given by Nielson and Sanders (1982).

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Selected samples of raw shale and spent shale were analyzed for total arsenic and selenium. Selected samples of shale oil and retort water were analyzed for total mercury, arsenic, and selenium using standard instrumental neutron activation analysis (INAA) techniques. In addition, a separate irradiation was carried out on some selected shale oil samples specifically for selenium analysis using a neutron multiplier system.

Approximately 1 mL of each shale oil was transferred to acid-cleaned quartz ampoules and sealed. Aliquots of raw and spent shale were transferred to acid-cleaned 2/27-dram polyethylene vials and sealed. Column fractions were analyzed as received in 2/5-dram polyethylene vials. Additionally, numerous standards were prepared, including mixed As and Se liquid standards sealed in 2/5- and 2/27-dram polyethylene vials and quartz ampoules, National Bureau of Standards (NBS) Standard Reference Material (SRM) 1632A coal and NBS SRM 1633A fly ash in 2/27-dram polyethylene vials, and NBS 1641B (Hg in water) and Hg atomic absorption standards sealed in quartz ampoules.

The samples and standards were irradiated in a 1-MW TRIGA reactor operated by Oregon State University. Samples and standards were irradiated for 7 h at a flux of 2.2×10^{12} n/cm² • sec in a rotating specimen rack. The samples and standards were returned to the laboratory and transferred to clean polyethylene vials, with the exception of the column fractions, for counting on two high-efficiency germanium diodes. The activated samples were counted twice. The first count determined As in the samples and standards and was done 3 to 5 days after irradiation. The second count determined Hg and Se in the samples and standards and began 20 days after irradiation. Counting times per sample

ranged from a few hours for As determination to 24 h for Se determination in the fractionated shale oil samples.

The spectral data were acquired from the germanium diodes by a Canberra Systems 80 multichannel analyzer with multiple analog-to-digital converters interfaced to a PDP 11/44 computer for data analysis. The spectral data were reduced using CANGAS (Laul, Wilkerson and Crowe 1979). This program uses an operator-created library with the parametric information necessary for each radionuclide sought (see Table 1). The specific activity of the sample was then compared to the specific activity of the standard to obtain concentration in $\mu\text{g/g}$. The spectral interference corrections for Se on Hg were also made using the CANGAS program.

To verify the accuracy of the method, standard reference materials were analyzed in addition to the oil shale samples. Table 2 shows a comparison of the observed and reported values for NBS 1632A coal, NBS 1633A fly ash, and NBS 1641B Hg in water standards. In general, agreement was excellent. As a check

TABLE 1. Parametric Information for Selected Radionuclides

Element	Nuclide	Half-Life (days)	Gamma-ray (keV)
As	^{76}As	1.097	559.1, 657.0, 1216.0
Se	^{75}Se	118.4	136.0, 264.7, 279.5
Hg	^{203}Hg	46.76	279.2

TABLE 2. Comparison of Observed and Reported Element Concentrations for Standard Reference Materials

Standard Reference Material	Element	Concentration (ppm)	
		Observed	Reported
NBS 1632A coal	As	9.16 ± 0.37	9.3 ± 0.4
	Se	2.50 ± 0.12	2.6 ± 0.2
NBS 1633A fly ash	As	130 ± 11	145 ± 15
	Se	10.1 ± 0.4	9.5 ± 1.0
NBS 1641B Hg	Hg	1.52 ± 0.02	1.52 ± 0.04

on the accuracy of the selenium results in the oils, a separate set of irradiations was carried out using the PNL californium-252 subcritical neutron multiplier assembly at a neutron flux of $5 \times 10^9 \text{ n/cm}^2 \cdot \text{sec}$. Sample preparation consisted simply of weighing 4 g of oil into 2/5-dram acid-cleaned polyethylene vials. The irradiation and counting system is fully automated, with a pneumatic rabbit transferring the sample directly to the counting system with no significant decay interval. The sample transfer system, counting system, and data reduction are controlled with a Tracor Northern TN-11 computer-based multichannel analyser system. Each sample was irradiated for 30 sec, then counted for 1 min with a pair of high-efficiency Ge(Li) detectors in an opposed geometry. The 162-keV line of selenium-77m was used for quantitation. Counter background was essentially zero for the short counting period used. Each sample was irradiated and counted seven times and the spectra were summed. The detection limit for selenium in oil by this method is estimated to be 80 μg (20 ppb) for a 4-g sample.

SILICA GEL COLUMN CHROMATOGRAPHY

Two oils representing eastern and western shales retorted at 2°C/min to a maximum temperature of 750°C were fractionated on silica gel. The eastern shale oil was allowed to warm to room temperature before a 1-g aliquot was removed. The western shale oil required heating to 37°C because of its high pour point before a 1-g aliquot was obtained. A 19-mm-ID by 450-mm column was loaded with activated silica gel (heated for 4 h at 120°C) in hexane. The 1-g shale oil aliquots were dissolved in a minimal amount of hexane and loaded onto the column. The complete elution scheme is shown in Table 3. One 150-mL fraction of hexane was collected initially, followed by 13- to 75-mL fractions through the column elution. Each fraction was evaporated to dryness, weighed, and redissolved in a minimal amount of hexane, toluene, or methanol. These solutions were evaporated into acid-cleaned 2/5-dram polyethylene vials, dried, sealed, irradiated, and analyzed for total arsenic and selenium.

TABLE 3. Elution Scheme Used to Fractionate As and Se in Shale Oil

<u>Fraction</u>	<u>Vol/mL</u>	<u>Solvent</u>
1	150	Hexane
2	75	Hexane
3	75	5% toluene/hexane
4	75	15% toluene/hexane
5	75	Toluene
6	75	5% dichloromethane/toluene
7	75	15% dichloromethane/toluene
8	75	Dichloromethane
9	75	5% ethyl acetate/dichloromethane
10	75	15% ethyl acetate/dichloromethane
11	75	Ethyl acetate
12	75	5% methanol/ethyl acetate
13	75	15% methanol/ethyl acetate
14	75	Methanol

MERCURY COLD VAPOR ATOMIC ABSORPTION

This analytical method is based on the cold vapor, ultraviolet absorptiometric detection of vaporized elemental Hg. Very high sensitivities are achieved by sweeping the generated Hg vapor through a long, focusing absorption cell in a dual-beam Laboratory Data Control (LDC) mercury analyzer.

The method, which measures total mercury, consists of adding 0.1 to 0.5 g of oil shale, 0.5 to 2 g of spent shale, 0.5 to 1 mL of shale oil, or 5 to 20 mL of retort water to precleaned 250 mL flat-bottom Pyrex® glass flasks. To the flasks are added 15 mL of 16 N ultrex HNO₃ and 5 mL each of reagent grade 10% solution of K₂S₂O₈ and KMnO₄. The flasks are connected to reflux condensers, and the samples are refluxed under medium heat on a hot plate for 2 h. The samples are cooled and the whole samples or appropriate aliquots are transferred to a purging flask connected to the Hg analyzer and diluted to 100 mL with mercury-free tap water. The flask is purged with air to remove any

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organic vapors, 10 mL of a 10% solution of SnCl_2 (prepared in 0.7 N H_2SO_4) are added, and the flask is quickly stoppered. After a 30-sec waiting period, the reduced, vaporized elemental Hg is swept from the flask in a stream of N_2 gas into the absorption cell of the LDC mercury analyzer. The absorption of the ultraviolet beam by the vaporized Hg atoms is directly proportional to the Hg concentration. Quantification is made by comparing the peak height response of the sample with standard curves obtained by spiking reagent blanks prepared in mercury-free tap water with known quantities of standard Hg solutions. Reagent blanks and sample blanks are analyzed and the blank value is subtracted from the sample peak height.

DISTRIBUTION OF MERCURY, ARSENIC, AND SELENIUM DURING OIL SHALE RETORTING

RETORT CONDITIONS

Variations in retorting parameters affect the mobilization and relative partitioning of Hg, As, and Se from the raw oil shale matrix into product streams. To determine the effect of heating rate and maximum retorting temperature on the mobilization of these elements, a Green River shale from Colorado and a New Albany shale from Kentucky were heated at 1° to 2°C/min to a maximum temperature of 500°C. Subsequently, the eastern and western shales were heated at 2°C/min to 750°C and 10°C/min to 750°C. Using this type of analytical approach, we were able to determine the individual effect of heating rates and maximum temperatures on the redistribution of Hg, As, and Se into the spent shale, shale oil, retort water, and offgas.

The results of seven retort runs are included in this report. Table 4 is a list of the retorting parameters and shales used in retort runs PNL-2 through PNL-8. An in-depth discussion of the design and operation of the PNL 6-kg retort (Figure 1) was published earlier (Olsen et al. 1984).

PNL-2

Figure 3 is a plot of retorting temperatures versus time through the retort run. The top line is the temperature measured at the external surface of the retort vessel, and the lower line is the internal temperature measured

TABLE 4. Retorting Parameters for Retort Run PNL-3 through PNL-8

<u>Retort Run</u>	<u>Shale</u>	<u>T_{max} (°C)</u>	<u>Heating Rate (°C/min)</u>	<u>Comments</u>
PNL-2	Western	500	1	
PNL-3	Western	750	2	
PNL-4	Western	750	10	Terminated early
PNL-5	Eastern	500	2	
PNL-6	Eastern	750	2	
PNL-7	Western	750	10	
PNL-8	Eastern	750	10

FIGURE 3. Furnace and Retort Temperatures Versus Time During Retort Run PNL-2

in the center of the retort. This plot clearly demonstrates the 50° to 100°C radial thermal gradient that occurs during the retort run. The axial gradient in the retort is negligible.

Figure 4 is a plot of outlet gas temperature measured just below the retort versus the centerline temperature of the retort vessel. The peak corresponds to the oil production during the retort run. The peak begins at 300°C, maximizes at 380°C, and approaches base line somewhere between 450° and 500°C.

Figure 5 is a plot of the flow rate of gas through the retort versus the centerline temperature of the retort. Again we see the flow rate beginning to rise at 300°C, maximizing between 380° and 400°C, and returning to base line between 450° and 500°C. If we superimposed Figure 4 and 5, we would see excellent correlation between maximum gas outlet temperatures and offgas flow rate.

FIGURE 4. Retort Outlet Gas Temperature Versus Retort Temperature During Retort Run PNL-2

Figure 6 is a plot of the concentration in volume percent of CO_2 , CH_4 , C_2H_4 , C_2H_6 , and CO in the offgas as a function of temperature in the center of the retort vessel. All the measured components peak during oil production (320° to 450°C) and decline rapidly toward baseline by 500°C. The concentration of CO_2 increases slowly between 50° to 350°C.

PNL-3

Figure 7 shows plots of the middle temperature within the retort vessel and the retort gas flow rate versus time. The plot of the retort gas flow rate has two peaks, and a third begins near the end of the run. The first peak, caused by oil production, starts at 320°C and maximizes at 400°C. The second peak, presumably caused by the decomposition of dolomite, reaches a maximum at

FIGURE 5. Retort Gas Flow Rate Versus Retort Temperature During Retort Run PNL-2

600°C. The third peak is believed to be caused by the decomposition of calcium carbonate. It begins to appear in the range of 650° to 700°C.

Figure 8 shows plots of the middle temperature of the retort vessel and the outlet gas temperature versus time. We see two distinct peaks and the beginning of a third in the gas temperature plot, as was found in the plot of gas flow rate in Figure 7. The first peak shows a higher outlet gas temperature than the second peak, even though the gas flow rate is 30% higher in the second peak of Figure 7 than in the first. This result indicates that the offgas laden with oil has a greater heat capacity than CO₂ laden offgas.

Figure 9 shows plots of the relative concentration of carbon- and hydrogen-containing compounds in the offgas of retort run PNL-3 as measured by the microwave-induced helium plasma detector. The carbon plot contains two peaks, the first caused by the oil production and the second by the carbonate decomposition. The peaks for the maximum concentration of carbon-containing compounds in the offgas correspond well with the peaks for maximum gas flow rates and outlet gas temperatures shown in Figures 7 and 8. The plot of

FIGURE 6. Concentration of Selected Gases Versus Retort Temperature During Retort Run PNL-2

hydrogen-containing compounds in the offgas exhibits only a single peak that maximizes between 425° and 450°C, a slightly higher temperature than the first peak on the carbon plot.

PNL-4

Retort run PNL-4 was terminated 2 h into the run because of a rupture in the transfer line between the oil/water collector at the base of the retort and the first condenser.

PNL-5

This retort run was the first one using eastern shale. Figure 10 shows the temperature in the center of the retort vessel, the outlet gas temperature below the retort, and the retort gas flow rate versus time.

FIGURE 7. Retort Temperature and Retort Gas Flow Rate Versus Time During Retort Run PNL-3

PNL-6

Figure 11 is a plot of the external temperature of the furnace, centerline temperature within the retort vessel, outlet gas temperature, and retort gas flow rate versus time. A comparison of the external and internal temperatures of the retort vessel shows a thermal gradient of approximately 100°C across the furnace at the beginning of the run, which decreases to 50°C by the end of the run. In addition, there is a notable negative inflection in the internal heating curve corresponding to the oil production (320° to 450°C). In response to this internal absorption of heat, the furnace overcompensates in the positive direction, resulting in an elevated heating rate at the surface of the retort.

The outlet gas temperature exhibits a small peak when the center of the retort reaches 100°C. This effect, which can be seen more clearly in Figure 12, appears to be caused by the volatilization of absorbed water from the

FIGURE 8. Retort Temperature and Outlet Gas Temperature Versus Time During Retort Run PNL-3

shale. The second peak in the outlet gas temperature occurs during oil production, beginning between 300° and 320°C and reaching a maximum at 400°C. Notably absent from this plot is a second major peak, caused by carbonate decomposition, that was observed during the retorting western shale.

PNL-7

Figure 13 shows plots of the furnace temperature, the centerline temperature in the retort vessel, the outlet gas temperature, and the retort gas flow rate versus time. A comparison of the external and internal temperatures shows a thermal gradient across the retort vessel of almost 400°C. Additionally, the outlet gas temperature is higher than the centerline temperature by 200°C at approximately 1 h into the run. It appears that the thermal equilibrium across the retort vessel at a heating rate of 10°C/min is much worse than at the lower heating rates described above. Since the heating rate is very rapid compared

FIGURE 9. Relative Concentration of Carbon- and Hydrogen-Containing Species in the Offgas Versus Time During Retort Run PNL-3

to that of earlier runs, the gas flow rate out of the retort is extremely high compared to that of other runs. The maximum flow rate during the retort run exceeded 6 L/min during peak oil production. The profile of the oil production region is also very broad because of the large radial thermal gradient in the retort vessel.

PNL-8

Figure 14 shows plots of the external temperature of the retort vessel, the centerline temperature in the retort vessel, and the outlet gas temperature versus time. A comparison of the external and centerline temperatures of the retort vessel again shows a radial thermal gradient of almost 400°C. Again the outlet temperature of the offgas exceeds that of the centerline temperature in the furnace by 200°C at approximately 1 h into the run, as previously reported for retort run PNL-7. Additionally, the heating-rate curve for the centerline

FIGURE 10. Retort and Outlet Gas Temperatures and Retort Gas Flow Rate Versus Time During Retort Run PNL-5

of the retort vessel levels off briefly at 100°C, because of the volatilization of water out of the oil shale matrix during heating. This effect was not noted in the western shale, apparently because of its lower moisture content.

COMPARISON OF EASTERN AND WESTERN SHALE RETORTING

A comparison of three retort runs on western oil shale retorted at different heating rates and to different maximum temperatures reveals a number of interesting trends (Table 5). When the shale is heated at a slow heating rate to a maximum temperature of 500°C (PNL-2), the oil and water yields are approximately 95% and 68% of the Fischer Assay results, respectively. When the maximum temperature is 750°C (PNL-3), the oil yield remains at 95%; however, the water yield increases to approximately the Fischer Assay value. At the faster heating rate (10°C/min--PNL-7), the oil yield is reduced slightly to 87% of the Fischer Assay yield, while the water yield remains close to the Fischer

FIGURE 11. Furnace, Retort, and Outlet Gas Temperatures and Retort Gas Flow Rate Versus Time During Retort Run PNL-6

Assay number. Apparently, the significant increase in water yield at the 750°C maximum temperature is due to the increased loss of water of hydration in the shale.

Similar though more pronounced trends are evident with the eastern shale (Table 5). When the shale is heated to a maximum temperature of 500°C (PNL-5), the oil and water yields are approximately 86% and 98% of the Fischer Assay values, respectively. When the maximum temperature is increased to 750°C, the oil yield remains at 87% of the Fischer Assay value; however, the water yield increases dramatically to 169% of the Fischer Assay yield. After heating at the faster rate of 10°C/min, the oil and water yields noticeably decrease to 78% and 152% of the Fischer Assay values, respectively. As with the western shale, the significant increase in water yield at a maximum retorting temperature of 750°C, compared with 500°C, is due to the increased loss of water of hydration in the shale.

FIGURE 12. Retort Gas Temperature Versus Retort Temperature During Retort Run PNL-6

In summary, our samples of western shale produced significantly more oil and considerably less water than our eastern shale samples. Oil yield appeared to somewhat decrease at the faster rates for both types of shale. At a final temperature of 750°C, the eastern shale produced almost as much water as oil.

MERCURY

Mercury was monitored in the offgas during retort runs PNL-2, -3, -6, -7, and -8. During retort run PNL-2, mercury in the offgas was monitored and quantified by ZAA. On subsequent retort runs, mercury evolution was monitored by either the Spectraspan MPD or the MPD-850. The mercury concentration in the offgas, monitored using the MPD, was only calculated for retort run PNL-6 (eastern shale); however, qualitative data on time-dependent release patterns

FIGURE 13. Furnace, Retort, and Outlet Gas Temperatures and Retort Gas Flow Rate Versus Time During Retort Run PNL-7

for the volatilization of mercury from the shale were determined for retort run PNL-3. The amount of information obtained from retort runs PNL-7 and -8 (10°C/min heating rate) was limited because mercury volatilization overlapped oil production at these higher heating rates.

PNL-2

The ZAA output from retort run PNL-2 showed that mercury first appeared in the offgas by 160°C, peaked at 220°C, and approached baseline by 260°C (Figure 15). The mercury signal never returned to the original baseline because of interference from hydrocarbons in the offgas. However, the mercury was released well before oil production began in the retort. The total amount of Hg in the offgas, measured by the ZAA, was 220 µg with a large uncertainty. This number, when compared with 204 µg in the raw shale, accounted for a 108% recovery in the offgas. Using the ZAA as an indicator, four cold trap samples

FIGURE 14. Furnace, Retort, and Outlet Gas Temperatures and Retort Gas Flow Rate Versus Time During Retort Run PNL-8

TABLE 5. Comparison of Oil and Water Yields from PNL Retort Runs

Retort Run	T _{max} (°C)	Heating Rate (°C/min)	Oil Yield		Water Yield		
			gal/ton	% of Fischer Assay	gal/ton	% of Fischer Assay	
Western Shale							
Fischer Assay			25.6		3.4		
PNL-2	500	1	24.2	95	2.3	68	
PNL-3	750	2	24.1	95	3.8	112	
PNL-7	750	10	22.2	87	3.9	115	
Eastern Shale							
Fischer Assay			12.4		5.4		
PNL-5	500	2	10.6	86	5.3	48	
PNL-6	750	2	10.8	87	9.1	169	
PNL-8	750	10	9.7	78	8.2	152

FIGURE 15. Relative Concentration of Mercury in the Offgas of Retort Run PNL-2 as Determined by ZAA

were collected and analyzed for Hg species. The results from the first sampling period (onset of mercury in the offgas) show only traces of dimethylmercury (23 ng/L offgas), the majority being elemental Hg (183.0 ng/L). The second sample was collected at the peak of Hg evolution in the offgas, as indicated by ZAA. However, only traces of any mercury species were measured (1.7 ng/L), of which 40% was elemental. The third sample was taken on the downside of the ZAA peak. This sample contained the majority of the mercury collected, including the equivalent of 3350 ng/L dimethylmercury, 45.2 ng/L diethylmercury, 11.4 ng/L di-n-propylmercury, 11.4 ng/L methylethylmercury (tentatively identified), and only 0.62 ng/L elemental Hg. Sample 4, collected at the end of Hg evolution (as measured by ZAA), contained 24.5 ng/L dimethylmercury and 12.7 ng/L diethylmercury. No elemental Hg was found in this sample. Overall, 134 μ g of mercury were accounted for in the cold traps. This finding is in good agreement with the ZAA results and elemental mass balance

for total mercury in the raw shale. Note that for approximately 30 min of the 100-min mercury peak, the offgas was not sampled by the cold trap system.

The different times at which peak concentrations of mercury were measured by the ZAA and the cold-trapping technique may be a result of differences in the relative response of the ZAA to elemental Hg versus organic complexes of mercury. The trapping results definitively determined that the initial appearance of Hg in the offgas was in its elemental form. In Sample 2, the Hg species decreased significantly to barely detectable quantities. The highest concentration of Hg species in the cold trap was measured in Sample 3, which was essentially 100% organomercury.

PNL-3

Mercury evolution into the offgas was monitored with the MPD-850. The retorting conditions were similar to those for retort run PNL-2 except for an increase in the heating rate from 1° to 2°C/min. The Hg began evolving from the retort at 160°C, peaked at 190°C, and returned to base line between 250 and 260°C (Figure 16). These results are similar to those for retort run PNL-2.

PNL-6

This retort run was the first one to monitor Hg evolution in the offgas from eastern shale. The behavior of Hg in the eastern shale was significantly different from its behavior in the western shale. Mercury first appeared at 220°C, 50° to 60°C higher than in a similar run using western shale. The peak concentration of Hg in the offgas was observed at 280°C, with the approach toward the baseline by 360° to 380°C (Figure 17). At this time the plasma was overwhelmed by hydrocarbons from oil production, which obscured the tail of the Hg peak. An integration of the area under the curve accounted for 180 µg, or 35% of a total of 510 µg in the raw shale. However, this concentration can be considered a lower limit since there was considerable quenching of the plasma by the hydrocarbons in the offgas.

PNL-7 and PNL-8

Few useful mercury data were obtained from these retort runs because the Hg evolution into the offgas coincided with oil production.

FIGURE 16. Relative Concentration of Mercury in the Offgas During the Retorting of Western Shale at 2°C/min to 750°C

Distribution of Mercury Distribution in the Product Streams as a Function of Retorting Parameters

The eastern shale had a mercury concentration of 95.1 ppb, compared with 40.4 ppb in the western shale. Upon retorting, 80 to 98% (determined by difference) of the mercury in the raw shale was volatilized into the offgas and not recovered in either the shale oil or retort water. For eastern shale, in retorting to maximum temperatures of 500°C and then 750°C resulted in the amount of Hg in the spent shale dropping from 15.6 to 0.6% of the total Hg in the raw shale (Figure 18). In general, it can be demonstrated from Figure 19 that Hg in eastern shale preferentially migrates to the retort water rather than the shale oil. For western shale, the reverse behavior was evident: the

FIGURE 17. Relative Concentration of Mercury in the Offgas During the Retorting of Eastern Shale at 2°C/min to 750°C

Hg in the liquid products preferentially migrated to the shale oil except at a maximum temperature of 500°C.

ARSENIC

Arsenic in the offgas was monitored by the Spectraspan MPD during retort run PNL-5, -6, and -7; however, no arsenic was detected during any of these runs.

Distribution of Arsenic in the Product Streams as a Function of Retorting Parameters

The eastern and western shales contained similar levels of arsenic, at 51.0 and 43.4 ppm, respectively. Most of the arsenic remained in both the eastern and western shales following retorting, with spent shale concentrations

FIGURE 18. Comparison of Mercury Distribution for Eastern and Western Shales as a Function of Retorting Parameters (% of Total in Raw Shale)

FIGURE 19. Concentration of Mercury in Retort Products as a Function of Retorting Parameters

accounting for 89 to 105% of the As in the raw shale. Comparing the eastern and western shales under identical retorting conditions demonstrates that the As in the western shale is considerably more mobile (Figure 20): the As distribution in shale oil ranged from 0.2 to 1.7% of the amount in the raw shale for eastern shale oil and from 2.4 to 4.7% for western shale oil. Arsenic redistribution into retort water was less than 0.1% for eastern shale compared with a range of less than 0.1 to 0.5% for western shale. The As preferentially redistributed into the shale oil of the liquid products during the retorting of both eastern and western shales. A comparison of how maximum temperatures and

FIGURE 20. Comparison of Arsenic Distribution for Eastern and Western Shale as a Function of Retorting Parameters (% of Total in Raw Shale)

heating rates affect the redistribution of As shows a generally increasing trend when the shale is heated to higher temperatures and at more rapid heating rates.

The concentrations of As in the spent shale, shale oil, and retort water for eastern and western spent shales can be seen in Figure 21. The concentrations do not appear to be dependent on retorting parameters. In general, the arsenic concentration in the shale oils increased as higher retorting temperatures and faster heating rates were achieved. Arsenic concentrations in eastern retort water ranged from 0.18 to 2.1 ppm, with increasing concentrations at higher retorting temperatures and faster heating rates were employed.

Separation of Arsenic by Silica Gel Chromatography

Two shale oils, an eastern and a western, retorted at a 2°C/min heating rate to a maximum of 750°C were fractionated on silica gel. Approximately 1 g of shale oil was loaded onto the column. The quantity of shale oil contained 10.8 and 14.6 µg of As for the eastern and western shale oils, respectively. Total As recovery in the 14 fractions amounted to 16.5% for the eastern shale oil and 23.7% for the western shale oil. Figure 22 shows the arsenic metalgram generated by the silica gel separation. This metalgram demonstrated distinct differences in the behavior of As in each oil using this separation technique. A significant portion of the As in the eastern shale oil was eluted in the

FIGURE 21. Concentration of Arsenic in Retort Products as a Function of Retorting Parameters

FIGURE 22. Silica Gel Fractionation of Arsenic in Shale Oil from Eastern and Western Shale Retorted at 2°C/min to 750°C

nonpolar portion of the chromatogram; in the western shale oil, little As appears in this portion of the chromatogram. The western shale oil had a more polar As constituent, with 10.9% beginning to appear in fraction 8 and a maximum of 65.6% in fraction 14. Fraction 14 in the eastern shale oil chromatograph also contained the most As, at 55.8%. As part of future work, these fractions will be further characterized to identify the As-containing compounds in the eastern and western shale oils.

Mass Balance for Arsenic

The average recovery for arsenic in eastern and western shales was 103.4% with a one-sigma standard deviation of 9.0%. The average range of uncertainty for each individual run was $\pm 6.9\%$ (Figure 23). Only the western shale heated at $2^\circ\text{C}/\text{min}$ to 750°C demonstrated a significant discrepancy compared with other retort runs. However, this discrepancy was in the direction of positive recovery of arsenic. Analytical error may be the cause of this discrepancy. The data strongly suggest that when these shales are retorted under the conditions of this study, little As is lost to the offgas.

SELENIUM

Dedicated monitoring for Se in the offgas has not been implemented to date; however, periodic checks for Se in the offgas of retort run PNL-6 using the MPD have not resulted in the detection of any gaseous Se component. Analysis for Se in the offgas is a challenge because Se is not sensitively detected by emission spectroscopy. A more sensitive method would utilize ZAA, since detection of Se by absorption has much greater sensitivity. The analytical results from the spent shale, oil, and water account for essentially all of the selenium in the raw shale.

Distribution of Selenium in the Product Streams as a Function of Retorting Parameters

The relative distribution of selenium into the various product streams is shown in Figure 24, with the concentrations shown in Figure 25. After retorting, most of the Se remains in the spent shale (78.2 to 110.2% of the original amount in the raw shale). The redistribution of Se into the retort water

FIGURE 23. Mass Balance for Arsenic in Eastern and Western Shales Under Various Retorting Conditions

FIGURE 24. Comparison of Selenium Distribution for Eastern and Western Shales as a Function of Retorting Parameters (% of Total in Raw Shale)

FIGURE 25. Concentration of Selenium in Retort Products as a Function of Retorting Parameters

ranged from 0.5 to 2.0% for eastern retort water and 0.5 to 0.8% for western retort water. The redistribution of Se into the liquid products appeared to be independent of the retorting parameters used. Selenium in the eastern liquid products slightly favors partitioning into retort water. Selenium in the western liquid products is preferentially distributed into shale oil.

Separation of Selenium by Silica Gel Chromatograph

Two shale oils, an eastern and a western, retorted at 2°C/min heating rate to a maximum of 750°C were fractionated on silica gel. Approximately 1 g of shale oil was loaded onto the column. The quantity of shale oil contained 0.636 and 0.396 µg of Se for the eastern and western shale oils, respectively. Total Se recovery in the 14 fractions amounted to 99% for the eastern shale oil and 87% for the western shale oil. Figure 26 shows the selenium metalgram generated by the silica gel separation. This metalgram demonstrated distinct differences in the behavior of Se in each oil using this separation technique. In general Se behaved similarly in fractions 1 through 10 for the eastern and western shale oil. However, significantly more Se eluted in fractions 11, 12, and 13 for the eastern shale oil. Fraction 14 in both the eastern and western shale oil chromatogram contained most of the Se recovered, ranging from 31.6% and 51.9%, respectively.

Mass Balance for Selenium

The average recovery for Se in both eastern and western retort runs was 101.4% with a one-sigma standard deviation of 11.7% for all the retort runs (Figure 27). The average uncertainty for each individual runs was ±8.7%. Only the eastern shale heated at 2°C/min to 750°C demonstrated a marked discrepancy for selenium mass balance from other retort runs. These data strongly suggest that our Green River and New Albany shale retort under our retorting conditions, have little, if any gas phase component.

FIGURE 26. Silica Gel Fractionation of Selenium in Shale Oil from Eastern and Western Shale Retorted at 2°C/min to 750°C

FIGURE 27. Mass Balance for Selenium in Eastern and Western Shales Under Various Retorting Conditions

CONCLUSIONS

Our Green River shale (western) produced more than twice as much shale oil and less than half as much retort water as our New Albany shale (eastern) retorted under similar conditions.

When the shale is heated to 750°C, retort water production increases 165% and 172% for western and eastern shales, respectively, as compared with the quantity of water produced at 500°C maximum temperatures. This increase in water production is due to the loss of water of hydration from the oil shale matrix.

For western shale, mercury first appeared in the offgas at 160°C, peaked at 220°C, and approached baseline by 260°C, all well before oil production. During the retorting of eastern shale, Hg first appeared in the offgas at 220°C, peaked at 280°C, and approached baseline by 360° to 380°C. This release pattern has a slight overlap with the beginning of oil production.

The amount of Hg quantified by ZAA in the offgas of retort run PNL-2 corresponded to essentially 100% of the mercury in the raw shale. During this retort run, 134 µg of Hg species were identified in the offgas by trapping. Of this amount, 130 µg consisted of dimethylmercury, diethylmercury, and di-n-propylmercury (in order of descending concentration), with only 4 µg of elemental mercury detected. This conclusion supports earlier findings by Fox et al. (1982) suggesting that the majority of the mercury in the offgas is organically bound.

The evolution of Hg in the offgas during retort run PNL-2 occurred in two clearly defined stages, with elemental Hg appearing first followed by the organomercury. During the initial stage of Hg release into the offgas, 87% (4 µg) was identified as elemental. The organomercury appeared at the later stage of Hg evolution in the retort run, accounting for more than 99% (126 µg) of the mercury in that sample.

In general more than 90% of the As remained in the shale after retorting. The As in the western shale demonstrated a slightly greater tendency to mobilize into the liquid products than did the As in the eastern shale retorted

under similar conditions. The arsenic that mobilized preferentially redistributed into the shale oil rather than the retort water in both eastern and western shales, and the redistribution into the liquid products appeared to increase with higher heating rates and maximum temperatures. No As was observed in the offgas during any of the three retort runs monitored.

In general, more than 80% of the Se remained in the shale after retorting. The selenium in the eastern liquid products slightly favored partitioning into the retort water. Selenium in the western liquid products was clearly preferentially redistributed into the shale oil.

FUTURE WORK

The goal of the national shale oil program is to investigate 10 reference shales under different retorting parameters. As this work clearly demonstrates, particularly for mercury, the behavior of volatile trace elements during retorting can be substantially different for each shale type. It is important to systematically study the redistribution of Hg, As, and Se in the various product streams of the 10 reference shales retorted under similar conditions. This information will aid in assessing possible environmental or process-associated problems if any of these shales are used commercially in the future.

REFERENCES

- Beenakker, C. I. M. 1976. "A Cavity for Microwave Induced Plasma Operated in Helium and Argon at Atmospheric Pressure." Spectrochim. Acta 31B, 483.
- Fox, J. P., J. J. Duvall, K. K. Mason, R. D. McLaughlin, T. C. Bartke and R. E. Poulson. 1978. "Mercury Emissions from a Simulated In-Situ Oil Shale Retort." In Proceedings of the 11th Oil Shale Symposium, Colorado School of Mines, Golden, Colorado.
- Fox, J. P., A. T. Hodgson and D. C. Girvin. 1982. "Trace Elements in Oil Shale Materials." In Energy and Environmental Chemistry - Fossil Fuels, L. H. Keith (ed.), Vol. 4, Chapter 4, Ann Arbor Science Publishers, Ann Arbor, Michigan.
- Girvin, D. C., and J. P. Fox. 1980. On-Line Zeeman Atomic Absorption Spectroscopy for Mercury Analysis in Oil Shale Gases. EPA-600/7-80-130, U.S. Environmental Protection Agency, Washington, D.C.
- Hadeishi, T., and R. D. McLaughlin. 1971. "Hyperbolic Zeeman Effect Atomic Absorption Spectrometer for Mercury." Science, 174, 404.
- Laul, J. C., C. L. Wilkerson and V. L. Crowe. 1979. "Computer Methodology and its Application to Geological and Environmental Matrices." In Proceeding of Computers in Activation Analysis and Gamma Ray Spectroscopy. DOE Symposium Series #49:840, U.S. Department of Energy, Washington, D.C.
- Nelson, G. O. 1970. "Simplified Method for Generation Known Concentration of Mercury Vapor in Air." Rev. Sci. Instr. 41:776.
- Nielson, K. K., and R. W. Sanders. 1982. SAP3 Computer Program for Quantitative Multielement Analysis by Energy Dispersive X-Ray Fluorescence. PNL-4173, Pacific Northwest Laboratory, Richland, Washington.
- Olsen, K. B., D. S. Sklarew, and J. C. Evans. 1985. "Detection of Organomercury, Selenium and Arsenic Compounds by a Capillary column Gas Chromatograph-Microwave Plasma Detector System." Spectrochim. Acta. 40B:357.
- Olsen, K. B., J. C. Evans, D. C. Girvin, D. S. Sklarew and C. L. Nelson. 1984. Testing and Performance of the Pacific Northwest Laboratory 6-kg Retort. PNL-5055, Pacific Northwest Laboratory, Richland, Washington.
- Quimby, B. D., M. F. Delaney, P. C. Uden and R. M. Barnes. 1980. "Determination of the Aqueous Chlorination Products of Humic Substances by the Gas Chromatography with Microwave Emission Detection." Anal. Chem. 52:259.

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