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MERCURY MASS DISTRIBUTION DURING LABORATORY AND SIMULATED IN-SITU OIL SHALE RETORTING

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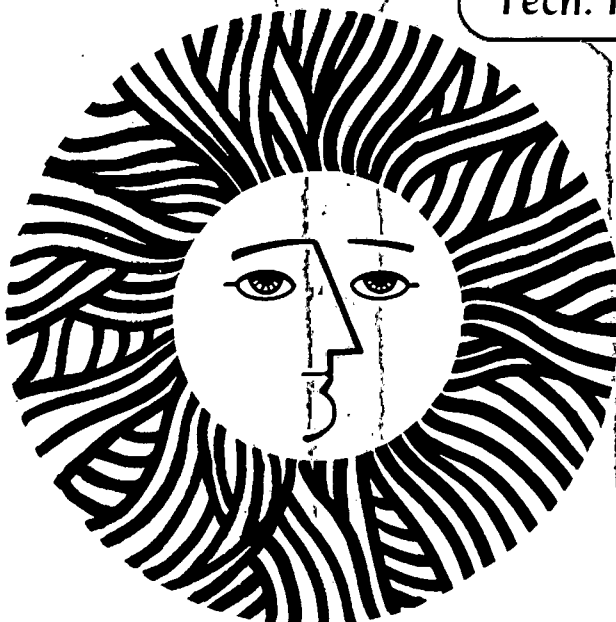
Alfred T. Hodgson, Martin J. Pollard,  
Gloria J. Harris, Donald C. Girvin,  
J. Phyllis Fox and Nancy J. Brown

February 1982

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MERCURY MASS DISTRIBUTION DURING LABORATORY AND  
SIMULATED IN-SITU OIL SHALE RETORTING

by

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February 1982

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This work was supported by the Assistant Secretary for Fossil Energy; Office of Oil Shale; Oil, Gas and Shale Technology Division and by the Assistant Secretary for Environment, Office of Environmental Compliance and Overview, Environmental Control Technology Division of the United States Department of Energy under Contract No. W-7405-ENG-48. This work was also supported by the Office of Research and Development, Industrial Environmental Research Laboratory, Energy Pollution Control Division of the United States Environmental Protection Agency under Contract No. AD-89-F-0-062-0.

## FOREWARD

When energy and material resources are extracted, processed, converted, and used, the related polluttional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes the partitioning of mercury during simulated in-situ oil shale retorting. The study was conducted to assess the potential for release of mercury into the environment as a result of in-situ oil shale retorting. Further information on this subject may be obtained from the Oil Shale and Energy Mining Branch, Energy Pollution Control Division.

David G. Stephan  
Director  
Industrial Environmental Research Laboratory  
Cincinnati

## ABSTRACT

Total mercury mass in oil shale retort offgas was quantified in a series of laboratory retorting experiments and in a simulated modified in-situ (MIS) retorting experiment. Accurate quantitative determinations of offgas Hg mass were made possible by the use of a continuous on-line Hg monitor. Total Hg mass in the raw shale feedstock and in the processed shale was quantified for all experiments. In addition, total Hg mass in the product oil and water was quantified for the laboratory experiments.

When Hg losses to the physical components of the laboratory retort were minimized, approximately 80 to 100% of the Hg originally present in the raw shale partitioned to the untreated offgas. Seven percent or less of the Hg partitioned to the oil. Approximately 2% of the Hg remained in the processed shale which had been heated to 500°C in N<sub>2</sub>. Distribution to the water was negligible. Gaseous Hg evolved from the shale as a single pulse over a temperature range of 160 to 320°C.

The results of the laboratory and simulated in-situ retorting experiments provided evidence which suggest that adsorption of Hg on unretorted or partially retorted shale ultimately controls the movement and final release of Hg to the offgas during MIS retorting. The laboratory experiments also demonstrated that adsorption and condensation losses of gaseous Hg to the retorting system can be substantial.

Invoking a number of assumptions it was possible to estimate atmospheric Hg emissions for underground retorting at a MIS oil shale facility producing 8x10<sup>6</sup> liters (50,000 barrels) of oil per day. Within the bounds imposed by invoking the assumptions, Hg emissions from a MIS facility could exceed emissions limitations which have been established for other industries. It is possible that retort design parameters and retort operating procedures can be used to control Hg emissions from MIS retorting.

This report was submitted in fulfillment of Contract No. AD-89-F-0-062-0 by Lawrence Berkeley Laboratory under the sponsorship of the United States Environmental Protection Agency. This report covers the period from August 1, 1978 to July 31, 1981, and work was completed as of September 30, 1981.

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## SECTION 1

### INTRODUCTION

Shale oil derived from Green River Formation shale in Colorado, Utah, and Wyoming is a relatively dilute hydrocarbon resource which requires the processing of approximately 8 to 16 kilograms of shale for each liter of product oil. The possible public health and environmental impacts directly associated with extensive oil shale development largely result from the vast quantity of rock which must be heated to a minimum temperature of 500°C to produce a significant quantity of oil. One of the primary concerns about oil shale development centers around atmospheric emissions of potential pollutants such as sulfur dioxide, hydrogen sulfide, oxides of nitrogen, hydrocarbons, carbon monoxide, carbon dioxide, particulates, and trace elements (e.g. Hg and As) as the result of retorting. The case of sulfur illustrates the magnitude of the anticipated problem. A typical shale in the Green River Formation contains about 0.7% sulfur by weight which is not considered to be a high concentration (Thurnau 1981). However, up to 68 tonnes (metric tons) of sulfur in the form of H<sub>2</sub>S could be generated each day when shale is processed by an 8x10<sup>6</sup> liter (50,000 barrel) per day facility (Crawford et al. 1977, Thurnau 1981). As a result, sulfur emissions controls are required for oil shale facilities in Piceance Basin, Colorado.

Several investigators have examined the partitioning of trace elements among the products of oil shale retorting (Wildeman and Meglen 1978; Shendrikar and Faudel 1978; Fruchter et al. 1978, 1979, 1980; Fox et al. 1978; Fox 1980). These investigators have determined that a portion of the mercury and arsenic contained in shale is released to the offgas during retorting. However, additional information is required to assess the potential magnitude of trace element emissions to the atmosphere from large-scale oil shale development.

Mercury occurs in Green River Formation shale in concentrations that are typical for sedimentary materials, on the order of one hundred to several hundred nanograms per gram (ppb) (Turekian and Wedepohl 1961; Giaque et al. 1980). Although these concentrations are seemingly low, there is a potential for the evolution of almost all of this mercury into the offgas during retorting due to the volatility of mercury and its compounds. In the absence of significant control mechanisms, atmospheric emissions of mercury could exceed air pollution standards established for other industries (Federal Register 1973). To determine if the requirements for mercury emissions monitoring and controls should be extended to the oil shale industry, it is necessary to examine mercury mass distributions for the major retorting options with particular emphasis on offgas emissions.

This investigation was established primarily for the purpose of evaluating the potential mass distribution of mercury from shale to offgas during modified in-situ (MIS) oil shale retorting. In order to meet this objective, mercury mass distributions were determined for several small-scale laboratory retorting experiments and a single large-scale simulated in-situ retorting experiment. Accurate determinations of mercury mass distribution to retort offgas were made possible by the use of a continuous on-line mercury monitor. This instrument, which is based upon Zeeman atomic absorption (ZAA) spectroscopy, was developed as a continuous monitor under a previous United States Environmental Protection Agency contract (Girvin and Fox 1980).

## SECTION 2

### SUMMARY AND CONCLUSIONS

Total gaseous Hg evolved during four laboratory oil shale retorting experiments was measured, and the mass distribution of Hg among offgas, spent shale, product oil, and water was accurately determined. When Hg losses to the physical components of the laboratory retort were minimized, approximately 80 to 100% of the Hg originally present in the raw shale partitioned to the offgas. Approximately 2% of the Hg remained in the spent shale which had been heated to a maximum temperature of 500°C. Seven percent or less of the Hg partitioned to the oil. Distribution to the water was negligible (<1%).

The temperature range for the evolution of Hg during laboratory retorting experiments was found to be 160 to 320°C. Mercury in shale volatilized almost entirely in advance of oil formation which was initiated at about 275°C and achieved a maximum value at 400°C at the 1°C/min heating rate. Preliminary results indicate that organomercurials were the dominant chemical species of Hg in the offgas of the laboratory retort. Additional work is required to substantiate this observation.

Mercury mass distribution resulting from the burn of a 6000-kg simulated in-situ retort was also investigated. Total offgas Hg was quantified throughout most of the burn, and the vertical distribution of Hg in the spent shale column was determined.

The laboratory and simulated in-situ retorting experiments produced evidence which suggests that adsorption of Hg on unretorted or partially retorted shale will control the movement and final release of Hg to the offgas during MIS retorting. According to this hypothesis, Hg is volatilized and swept ahead of the reaction front by the gas stream as the front moves down through the rubblized bed. The Hg adsorbs on cool shale and only appears in the offgas in significant quantities near the end of the burn when the bottom of the retort reaches the volatilization temperature for Hg or when the adsorptive capacity of the remaining unretorted shale is exceeded.

Not all of the Hg released to the offgas will enter the atmosphere. The laboratory experiments demonstrated that adsorption and condensation losses of gaseous Hg to the physical retorting system can be substantial. Consequently, the quantity of Hg reaching the atmosphere during MIS retorting will probably be extensively limited by these losses.

Atmospheric Hg emissions were estimated for underground retorting at a MIS oil shale facility. Production of  $8 \times 10^6$  liters of oil per day could result in an average release of 4000 grams of Hg per day assuming: (1) an average Hg concentration in shale of 100 ng/g, (2) processing of 2000 kg of

shale per barrel of oil produced, (3) an 80% distribution of Hg from shale to noncondensable gas (5°C), (4) loss of one-half of the offgas Hg to the retorting system by condensation and adsorption, (5) no temporal variation in Hg emissions, and (6) no emissions controls.

Retort facility design and operational procedures could result in lower mass emission rates of Hg than estimated. The major unknown factor in the mass emissions estimate is the magnitude of the potential condensation and adsorption losses of Hg to components of the retorting system. These losses will depend upon the design and materials of the offgas handling and scrubbing systems and could exceed the estimated 50%. Another inherent control mechanism for Hg emissions is the practical limit to which a MIS retort can be burned. The complete burn of a retort may be prevented by channeling of the reaction front, the need to maintain the physical structure of the exit of the retort, and safety considerations. Unretorted shale left in the bottom of a MIS retort may act as a sink for Hg and, thus, reduce Hg emissions.

Further investigations during burns of several large-scale MIS retorts are required before recommendations can be made concerning the future necessity for offgas Hg emissions monitoring or controls at MIS oil shale facilities.

## SECTION 3

### RECOMMENDATIONS

1. Monitoring of total offgas Hg should be conducted during burns of several large-scale MIS oil shale retorts to establish the level and temporal variability of offgas Hg emissions. It is essential that Hg emissions be fully characterized near the termination of the MIS retorting process since the mass emission rate of Hg is expected to be higher during this period.
2. Monitoring of total offgas Hg should be conducted during testing of various surface retorts which are currently under development. The levels of offgas Hg emissions for these retorts cannot be estimated with confidence from existing data since retorting parameters and operating conditions will be substantially different from those employed for MIS retorts.
3. Additional chemical speciation work is warranted to determine the chemical form of Hg in untreated offgas. The possible predominance of organomercurials has several implications. The accurate determination of Hg emissions in untreated offgas would require the use of analytical techniques which quantify total Hg. In addition, accumulation of organomercurials in components of the retorting system might constitute a potential industrial health hazard if workers came into contact with these components.
4. The various techniques for monitoring of Hg in retort offgas should be subjected to rigorous intercomparisons during burns of large-scale retorts. Selection of an appropriate technique(s) should be based upon measures of accuracy, precision, reliability, and ease of use.

## SECTION 4

### EXPERIMENTAL

#### RETORTS

A series of experiments was conducted using a small-scale laboratory retort. Raw shale and all products of these experiments, including retort offgas, were sampled and analyzed for Hg. The analytical data were used to calculate the mass distribution of Hg among the products of retorting. Experimental apparatus and procedures were modified throughout the course of the investigation in an attempt to obtain closure of an elemental balance equation for Hg. The progressive modification of the retort and the retort operating parameters is documented in Table 1. The first three laboratory experiments (E1-E3) were used to gain familiarity with retort operation and to develop analytical techniques. Descriptions and results of these experiments are omitted from this report. A switch from a ceramic retort vessel (5.5-kg capacity) to a stainless steel retort vessel (4.0-kg capacity) was made between experiments E4 and E5 when it was discovered that Hg losses to the ceramic vessel were substantial. A heated sample line ( $>100^{\circ}\text{C}$ ) was employed beginning with experiment E6 when it was discovered that Hg also was being lost to the unheated stainless steel line.

The laboratory experiments were augmented by a single experiment conducted during the burn of a large simulated in-situ retort. Offgas produced during this burn was monitored for Hg, and Hg concentrations in raw and spent shale samples were determined.

#### Laboratory Retort

##### Retort Description --

The laboratory retort was designed specifically for this investigation. It is a batch process retort in which heat is supplied to the shale through the walls of the containing vessel (Atwood 1977). Although larger in size, it is closely related to the Fischer assay retort in both design and operation. The laboratory retort is shown schematically in Figure 1.

The retort vessel for experiment E4 is a mullite (ceramic) tube, 10.2 cm O.D. by 8.9 cm I.D. by 162 cm long. The ends are sealed with removable stainless steel flanges. A 5.5-kg shale charge is supported in the heated zone of the furnace by a 40.6 cm high ceramic pedestal. For experiments E5 through E7, the retort vessel is a 304 stainless steel tube, 10.2 cm O.D. by 8.9 cm I.D. by 90.5 cm long with welded ends. This vessel, which holds 4.0 kg of shale, fits entirely within the heated zone of the furnace. In both vessels, a small diameter ceramic tube, closed on one end, serves as a thermocouple well. Thermocouple junctions (type K) are positioned along the radial axis of

TABLE 1. MAJOR VARIABLE RETORT AND RETORT OPERATING PARAMETERS FOR LABORATORY EXPERIMENTS. ALL OTHER PARAMETERS WERE HELD CONSTANT.

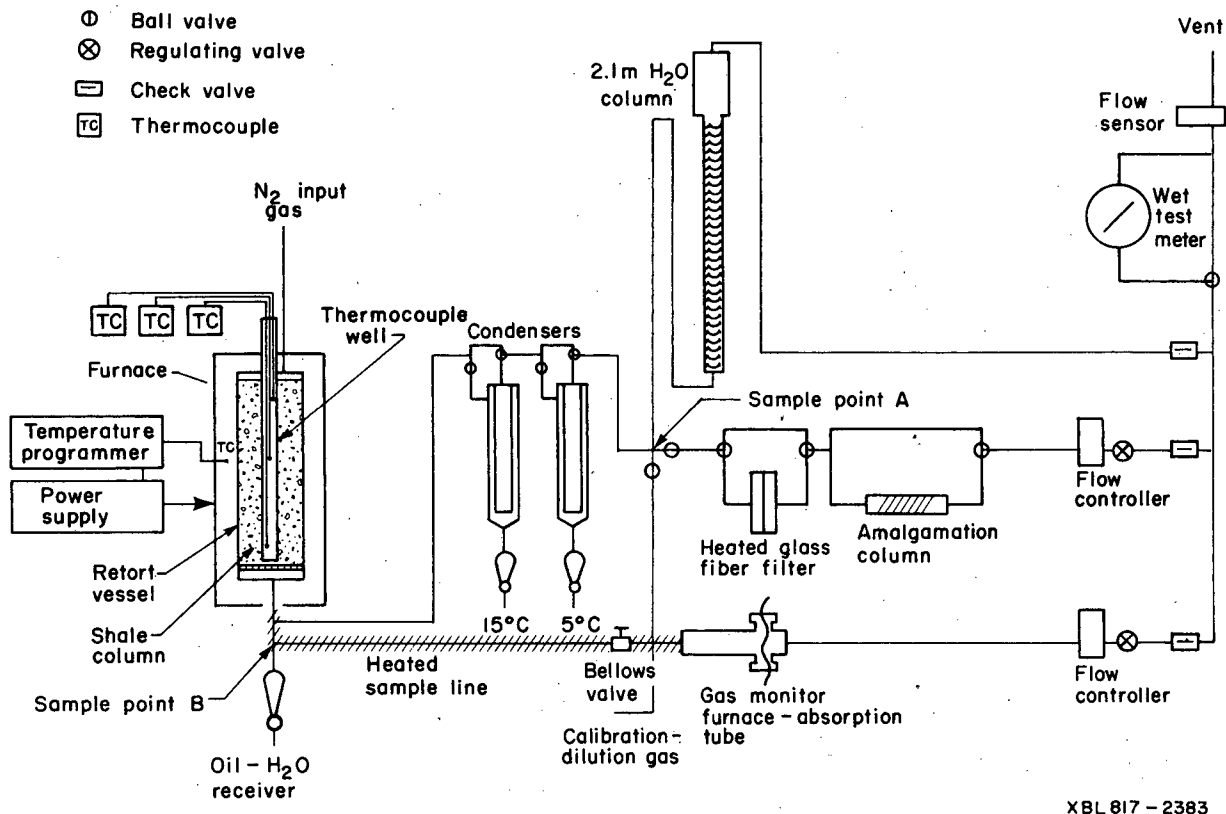
Experiment	Retort Capacity (kg)	Vessel Material	Gas Monitor Sample Point (see Fig. 1)	Sample Line Temperature (°C)	Vertical Shale Temp. Variation <sup>b</sup> (°C)	GC <sup>c</sup> Offgas Analysis
E1-E3	5.5	mullite	A	unheated	--	no
E4	5.5	mullite	A	unheated	20	no
E5	4.0	304 SS <sup>a</sup>	A	unheated	160	no
E6	4.0	304 SS	B	120-215	<20	yes
E7	4.0	304 SS	B	175-300	<20	yes

<sup>a</sup>Stainless Steel

<sup>b</sup>Maximum Temperature Differential

<sup>c</sup>Gas Chromatograph





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Figure 1 Schematic of laboratory retort showing installations of on-line Hg monitor and discrete gas sample apparatus.

the retort at the center and 5 cm from both ends of the shale column.

The retort vessel is heated by a vertically mounted, single-zone, 1200°C, tube furnace (Lindberg model 54572). Two 2-ohm, 225-watt variable resistors are used to reduce power to the upper heating elements to achieve uniform temperatures throughout the length of the shale column. The heating rate is controlled by a temperature-controller programmer with 0.1°C/min accuracy.

#### Retort Operation --

Equivalent batches of raw shale for the retorting experiments were simultaneously prepared using Mahogany Zone shale originating from Anvil Points, Colorado. Chunks of shale were crushed, ground, and sieved. Particle sizes retained for use ranged between 6.4 mm and 0.6 mm. A Fischer assay (Goodfellow and Atwood 1974) of this sample yielded a shale grade of 145 L/tonne (34.8 gallons per ton).

The shale grade, shale particle size distribution, and heating rates are the same for all of the retorting experiments. The shale column is heated to a center-line temperature of 150°C with the furnace in full power mode and then ramped to a maximum temperature of 500°C at 1°C/min.

In operation, the retort is swept with N<sub>2</sub> at a flow rate of 2 standard

L/min. Back pressure in the retort is maintained at 21 kpa (3 psig). A portion of the product oil and water is collected in a glass separatory funnel at the exit of the retort. Offgas is routed either through or past two stainless steel condensers, the first at 15°C and the second at 5°C. The remainder of the liquid products collect in separatory funnels fitted to the condensers. Offgas flowrate is monitored downstream of the condensers with a mass flow sensor. All offgas plumbing components are stainless steel.

Offgas flow rates and temperatures at 26 points throughout the retort system are monitored and displayed with a Doric model 230A data logger. Flowrates are logged at 7-second intervals, and temperatures are logged at 5-minute intervals. The data logger is interfaced with a Digital Microsystems model DSC-2 microcomputer. Data are stored and formatted on a double-density 20-cm (8-in) floppy disk.

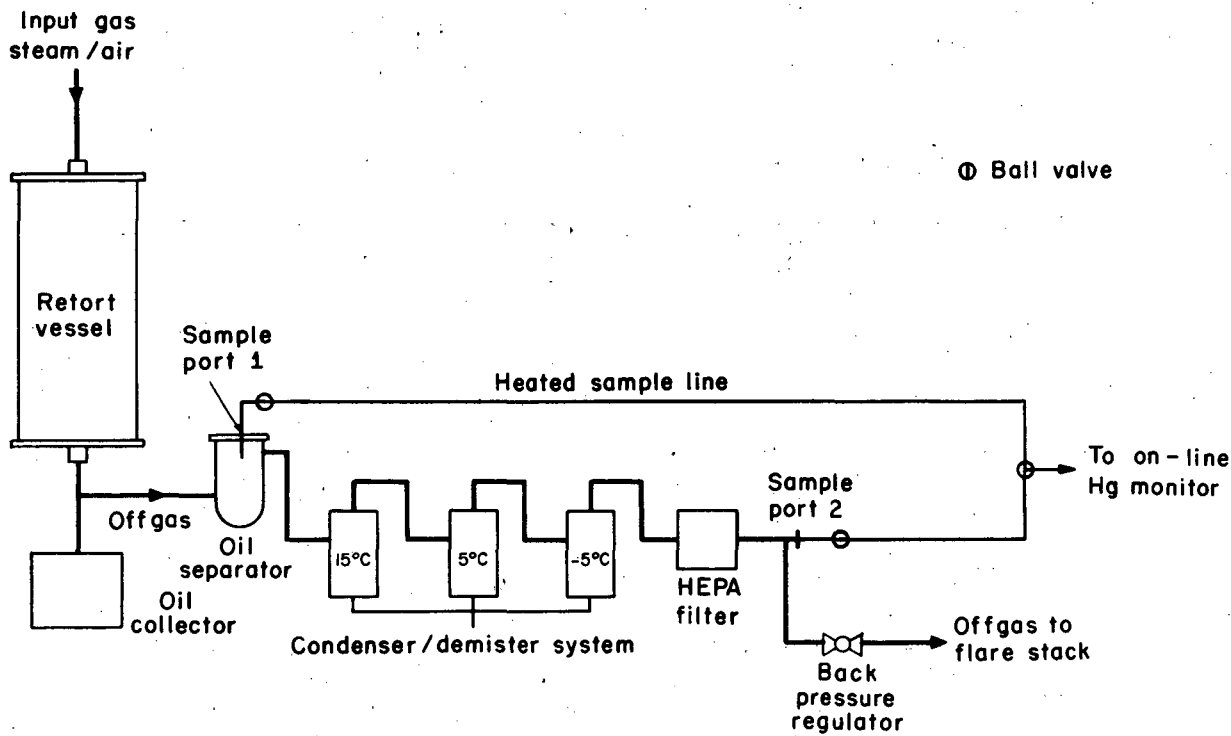
Offgas composition is determined throughout an experiment with a Hewlett-Packard model 5880A gas chromatograph equipped with an automatic gas sampler, thermal conductivity detector, and four analytical columns (6 ft 35% DC-200 on 80/100 mesh Chromosorb PAW, 24 ft 20% bis (2-methoxyethyl) adipate on 80/100 mesh Chromosorb PAW, 6 ft 80/100 mesh Porapak Q, 10 ft 60/80 mesh Molecular Sieve 13x). This system automatically determines the relative weight percents of N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, ethane, ethylene, propane, propylene, n-butane, i-butane, n-pentane, and i-pentane at 30-minute intervals. The gas chromatograph sampling port is located immediately downstream from the condensers (sample point B, Figure 1).

#### LLNL 6000-kg Retort

Lawrence Livermore National Laboratory's (LLNL) 6000-kg capacity oil shale retort is designed to simulate in-situ retorting conditions. It has been used to investigate the in-situ retorting process and to develop process controls for commercial-scale MIS retort operations. Descriptions of the retort have appeared in several publications (e.g., Sandholtz and Ackerman 1977, Raley et al. 1978).

The stainless steel process vessel is 6.1 m high by 0.91 m in diameter and holds approximately 6000 kg of raw shale. A schematic of the retort is presented in Figure 2. Retorting is initiated by igniting the shale at the top of the packed bed. The reaction front is driven downward by injecting a gas from the top. The hot offgas exits the bottom of the retort. The liquid product collection system consists of a collector, an oil separator, three condenser-demisters, and a high efficiency filter (HEPA). Temperatures, pressures, gas flowrates, and gas compositions are measured throughout an experiment.

On-line measurements of Hg in the offgas were made during LLNL's retort experiment L-3 conducted in May 1979 (Ackerman et al. 1980). The lower 3 m of the process vessel was packed with shale having a Fischer assay yield of 150 L/tonne (36 gal/ton). The upper 3 m was packed with shale having a Fischer assay yield of 75 L/tonne (18 gal/ton). Both shales originated from Federal Lease Tract C-a, Colorado. Input gas was an equimolar mixture of air and steam. The isothermal advance rate was 1.8 m/day, and the average maximum centerline temperature was 850°C. The experiment was terminated 100 hours



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Figure 2 Schematic of LLNL, 6000-kg, simulated in-situ retort showing sample ports for on-line Hg monitor.

after ignition with approximately the lower 0.5 m of the shale column incompletely retorted. Following the retort experiment, the column was carefully removed. Each of 40, 15-cm thick, vertical layers was weighed and sampled for analysis.

#### ON-LINE MERCURY GAS MONITOR

An on-line Hg gas monitor was used to make continuous measurements of Hg in offgas produced by both the laboratory retort and the LLNL simulated in-situ retort. This instrument, which is uniquely suited for use in complex gas streams because of its background correction capability, quantifies total off-gas Hg (inorganic + organic + particulate). The continuous on-line feature of the instrument allowed us to determine the temporal variability of Hg emissions and to make accurate estimates of the total mass of offgas Hg emitted during an experiment.

#### Gas Monitor Description

The on-line Hg gas monitor is a modified Zeeman Atomic Absorption (ZAA) Spectrometer (Hadeishi 1972, Girvin and Fox 1980). The background correction ability of ZAA spectrometry allows the instrument to measure Hg in retort off-gas with up to 90% extinction of the analytical and reference beams due to

broadband absorption phenomena. The instrument is source shifted and uses a Pen Ray Hg lamp immersed in a 15 kilogauss magnetic field. This Hg lamp must be maintained at a constant temperature to eliminate temperature induced changes in the relative intensities of the analytical and reference beams. The temperature controlled water bath which was developed for this purpose is capable of maintaining the lamp at  $25 \pm 0.2^\circ\text{C}$  over an ambient temperature range of  $6^\circ\text{C}$  to  $35^\circ\text{C}$ . The components of the ZAA spectrometer based gas monitor are shown schematically in Figure 3.

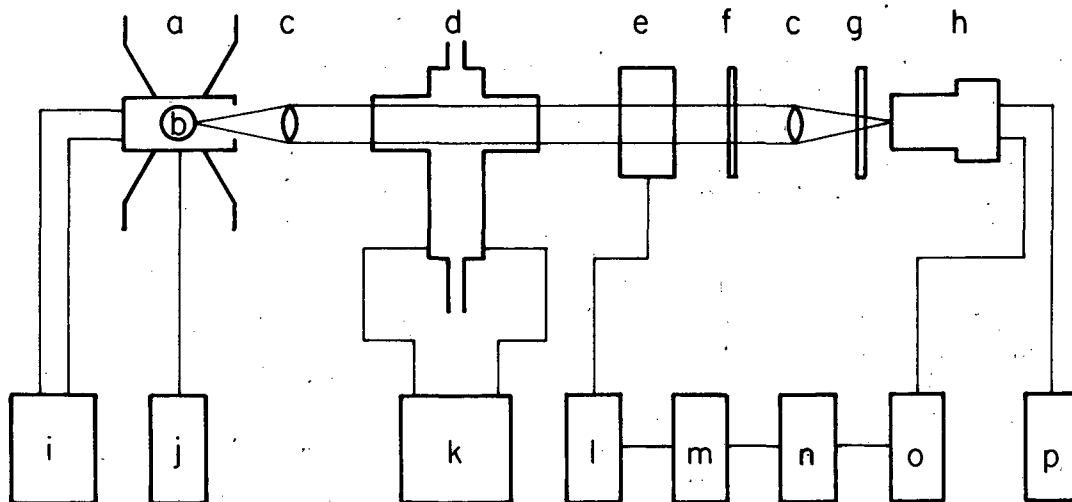
The gas monitor is equipped with a gas-tight furnace-absorption tube designed for continuous operation (Girvin and Fox 1980). This furnace-absorption tube is a 1.25-cm O.D., 29.0-cm long, 321 stainless steel tube welded perpendicularly to a 5-cm long absorption chamber fitted with sealed quartz windows. The device is heated, by joule heating, to  $900^\circ\text{C}$  at the center of the furnace and approximately  $470^\circ\text{C}$  in the absorption chamber. Aluminum is diffused into the surfaces of the furnace-absorption tube by a process termed alonization. The resulting microlayer of alumina effectively reduces corrosion.

Calibration gas is produced with an apparatus similar to the dynamic Hg vapor generator described by Nelson (1970). This apparatus consists of a flask of Hg with a heated stream of  $\text{N}_2$  gas impinging on the surface of the Hg. The saturated Hg vapor in the flask is passed through two equilibrium vessels and then injected into the inlet of the furnace-absorption tube of the gas monitor. The concentration of the generated Hg vapor is determined from its temperature as it leaves the calibration device (CRC 1981). Calibration gas with Hg concentrations ranging from 0-20  $\text{mg}/\text{m}^3$  may be obtained by varying the calibration and dilution gas flowrates.

#### Gas Monitor Sampling and Analysis

Laboratory retort offgas was sampled at two different locations with the on-line Hg monitor. During experiments E4 and E5, the sampling point was located immediately after the condensers (sample point A, Figure 1). Sampling for experiments E6 and E7 was through a heated stainless steel line connected directly between the exit of the retort and the furnace-absorption tube (sample point B, Figure 1). This line is maintained at a temperature of  $>120^\circ\text{C}$  to minimize Hg loss to the stainless steel. During experiment E7, intermittent samples were taken from the location after the condensers (sample point A). Retort offgas is continuously monitored for Hg with the gas monitor. Instrumental baseline is established by periodically switching from offgas to pure  $\text{N}_2$ . Any deviation from this baseline during on-line monitoring is attributed to Hg. Additions of known concentrations of Hg are made to the offgas throughout an experiment with the dynamic calibration apparatus. Calibration curves are constructed from the peak height responses to these additions. A number of calibrations are made to compensate for varying chemical interferences during Hg evolution.

The gas flowrate downstream of the gas monitor is maintained at 1 standard L/min by an electronic flow controller (Brooks model 5810). The remainder of the gas exits via the water column (Figure 1) which maintains the pressure upstream of the gas monitor at 21 kpa (3 psig). A 0-10 standard L/min flow sensor (Brooks model 5811) monitors the total gas flowrate of the



XBL 817-2384

Figure 3 Schematic of Zeeman atomic absorption spectrometer used for continuous on-line monitoring of total Hg in retort offgas a) magnet, b) Hg lamp and housing, c) focusing lens, d) furnace-absorption tube, e) variable phase retardation plate (VPRP), f) linear polarizer, g) 253.7 nm band-pass filter, h) multiplier phototube (MP), i) temperature controlled water bath, j) lamp power supply, k) furnace power supply, l) VPRP power supply, m) audio-frequency generator, n) lock-in amplifier, o) log-amplifier, p) MP power supply.

system. The electronic flow devices are periodically calibrated against a 3-liter wet test meter to compensate for changing gas composition. All gas flow measurements are corrected to standard temperature and pressure (0°C and 1 atm).

Offgas from the 6000-kg retort was sampled at two locations (Figure 2). Sample port 1 was located at the top of the oil separator and sample port 2 was located downstream of the high efficiency filter. The stainless steel transport lines connecting the sample ports to the gas monitor were heated to a minimum temperature of 200°C.

#### DISCRETE GAS SAMPLES

An independent method for the analysis of Hg in retort offgas was needed to determine the relative accuracy of the on-line Hg monitor. The U.S. Environmental Protection Agency reference method 101 for the determination of gaseous Hg emissions (Federal Register 1973) was tested during the LLNL simulated in-situ retort experiment. This method was found to be inadequate for use in retort offgas because the acid-iodine monochloride solution was exhausted before a sufficient sample was collected. In addition, the method is too laborious for the rapid analysis of samples. Following the LLNL experiment, other previously described techniques for the collection and analysis

of inorganic, organic, and particulate Hg in ambient air (Chase et al. 1972, Braman and Johnson 1974, Trujillo and Campbell 1975, and Fitzgerald and Gill 1979) were tested. These proved to be superior to the reference method, and they were subsequently adapted and used as an alternate method for the collection and analysis of total Hg in retort offgas.

### Sample Collection

The collection of gaseous Hg is accomplished by amalgamation and/or activated carbon adsorption in packed columns. All columns are either borosilicate glass or quartz tubes (125 mm long, 5 mm I.D. with 12/5 ball joints) wrapped with 80 turns of 22 gauge Nichrome heating wire. Three different types of columns are used depending upon the sample being collected. The first column type is loaded with a 25-mm section of borosilicate glass beads (80 mesh) which are plated with Au by vapor deposition. The beads are held in place with quartz wool plugs. The second type is loaded with a 15-mm section of a proprietary activated carbon, Carbosieve B (Supelco Inc., 45-60 mesh), on the inlet side followed by a quartz wool plug and then a 15-mm section of Au-plated beads. The third type of column is packed with a 5-mm section of Carbosieve B. Prior to use, columns are blanked at 400°C in a stream of N<sub>2</sub> or He by controlled heating of the Nichrome wire with a variable transformer.

Samples for total gaseous Hg are collected either with the Au-plated bead columns or with the combination columns of Carbosieve-B and Au-plated beads. The Carbosieve-B columns are used specifically for the collection of organomercurials.

The separation of gaseous Hg between inorganic and organic forms is accomplished with a close adaptation of the method of Trujillo and Campbell (1975). They found that Carbosieve-B retains metallic Hg only slightly but efficiently collects methylmercury chloride, ethylmercury chloride, dimethylmercury, diethylmercury, and diphenylmercury vapors. By purging their two-stage sampling tubes with pure, dry N<sub>2</sub>, they were able to selectively remove metallic Hg from the first Carbosieve-B stage and thus, effect a separation of metallic Hg from organomercurials. The method employed in this study utilizes two columns arranged in series for the collection of Hg speciation samples; offgas first enters a Carbosieve-B column and then passes through a Au-plated bead column to collect metallic Hg. After collection, the serially arranged columns are purged with 12 liters of N<sub>2</sub> introduced from the inlet end at 800 scm<sup>3</sup>/min. This volume of N<sub>2</sub> effectively transfers any residual metallic Hg adsorbed on the Carbosieve-B to the second column. The columns are analyzed separately using the procedures described below.

Samples for particulate Hg analysis are collected on 47-mm glass fiber filters (Gelman, Spectro Grade, 99.9% retention of 0.3 μm particles). These filters are blanked for Hg by heating to 400°C for 1 hour. Filters are supported in stainless steel holders. During sampling, filter holders are maintained at 100°C in a laboratory oven to prevent condensation of oil and water.

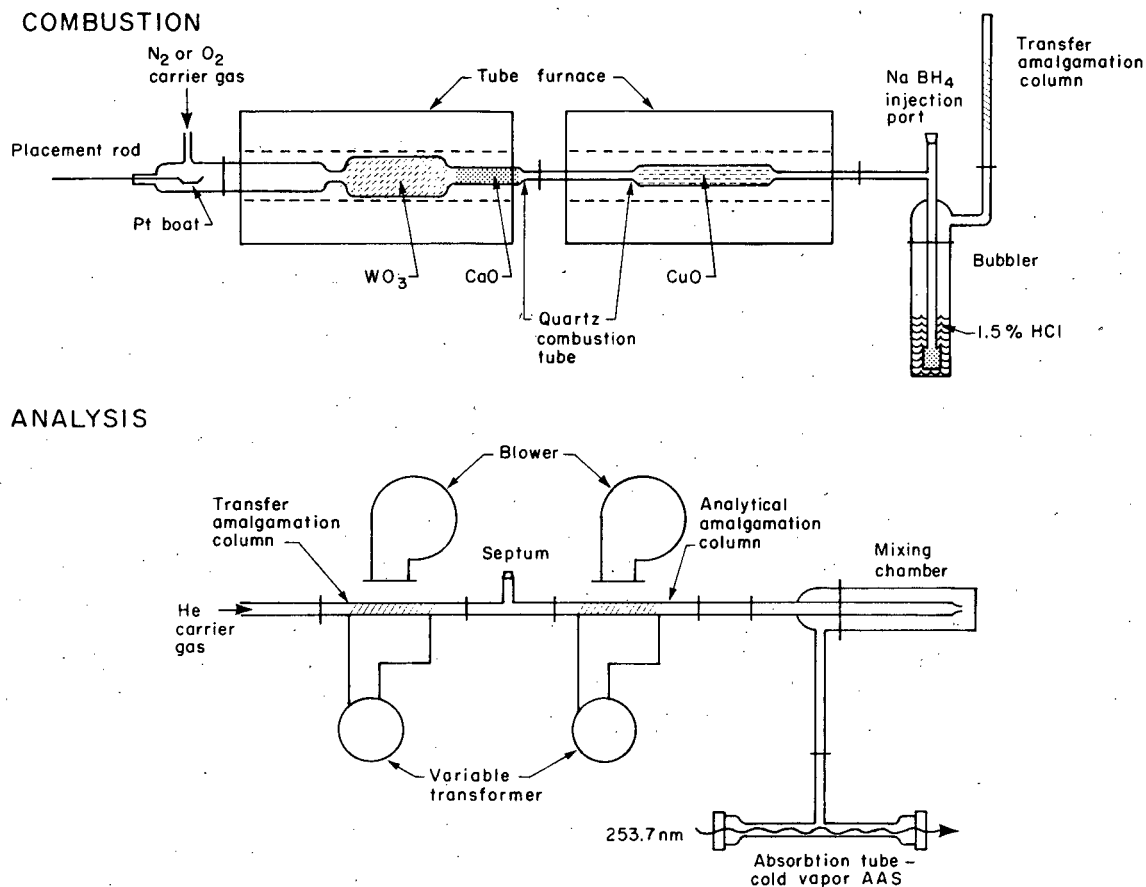
A schematic diagram of the gas flow system used for the collection of particulate and gaseous Hg is included in Figure 1. Valves are positioned so that flow is established in the bypass lines which circumvent the filter holder and column. The flow rate is adjusted to 100 scm<sup>3</sup>/min with the

calibrated electronic flow controller located downstream from the collection apparatus. Sampling is accomplished by switching in either the filter or the column for a carefully measured time period. Particulate and gaseous Hg samples are not collected concurrently since particulate samples require longer sampling intervals.

Particulate samples are collected immediately downstream of the condensers as shown in Figure 1. This location is adjacent to sample point A for the on-line gas monitor. Gaseous Hg samples are collected from two locations. The first immediately follows the particulate sampling location. The second is situated at the bottom of the retort vessel adjacent to sample point B.

### Sample Analysis

A schematic diagram of the two components used for the analysis of Hg in discrete gas samples and particulate samples is presented in Figure 4.



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Figure 4 Schematic of two-stage system for combustion and analysis of Hg in discrete gas samples and in solid and liquid samples.

## Combustion --

The first step in the analysis of both gaseous and particulate Hg samples is oxidation. Oxidation is accomplished with a quartz combustion tube, the main body of which is packed with approximately 3 grams of powdered tungsten trioxide ( $WO_3$ ) mixed with asbestos fibers and ceramic beads to achieve permeability. The  $WO_3$  serves as a renewable oxygen source. The smaller exit chamber is packed with 0.1 grams of powdered CaO which is also mixed with asbestos fibers. The CaO removes  $SO_2$  from the gas stream. The center of the combustion tube, containing the  $WO_3$ , is heated to  $1000^\circ C$  with a tube furnace. At this setting, the temperature of the CaO is approximately  $700^\circ C$ . If additional oxidation is required, the  $WO_3$  combustion tube is followed by a second quartz combustion tube containing 8 grams of CuO in wire form. The CuO combustion tube is heated to  $600^\circ C$ . Nitrogen carrier gas is routed through the combustion tube(s) to a miniature bubbler and exits the system through an amalgamation column containing Au-plated glass beads. This column is termed the transfer column.

## Analysis --

Analysis of particulate Hg samples is initiated by inserting the glass fiber filter into the combustion tube in a stream of  $N_2$  flowing at 500  $scm^3/min$ . After 3 min, the gas is switched to  $O_2$  at 500  $scm^3/min$  for an additional 3 min to regenerate the  $WO_3$ . The gas exiting the combustion tube bubbles through 10 ml of 1.5% (v/v) HCl and exits through the amalgamation column. Gas flow is stopped and 1 ml of a solution of 3% sodium borohydride ( $NaBH_4$ ) with 1% NaOH is added to the bubbler. Mercury in the solution is reduced to the metallic state by the  $NaBH_4$ . Nitrogen flow is re-established for 3 min, and the metallic Hg is driven out of solution and collected on the amalgamation column.

Analysis of discrete gas samples is initiated by attaching the collection column to the inlet of the combustion tube and establishing a  $N_2$  flow rate of 500  $scm^3/min$  through the column. Collected vapors are volatilized by heating the column to  $400^\circ C$ . Subsequent steps are identical to those used for particulate samples.

Following combustion, Hg collected on the transfer column is analyzed using a two-stage amalgamation and cold vapor detection system similar to the one described by Fitzgerald and Gill (1979). The two-stage amalgamation technique further separates interfering substances from Hg vapor and enhances analytical precision. Helium is used as the carrier gas. With the He flowing at 850  $scm^3/min$ , the transfer column is heated to  $400^\circ C$  in 45 seconds. The Hg collected on the transfer column, thus, passes to a room temperature, blanked, analytical column. When the transfer column cools to room temperature, the analytical column is similarly heated. The analytical column is followed by a 30-ml mixing chamber. Detection is performed with a Perkin Elmer model 306 atomic absorption spectrometer fitted with a quartz absorption chamber for cold vapor Hg analysis. The spectrometer is operated with  $D_2$  background correction.

Additions of Hg saturated air are used to construct calibration curves. The standard is prepared by allowing elemental Hg come to equilibrium with air in a closed 2-liter glass container. Measured volumes of standard are withdrawn with a gas-tight syringe and are injected into the analytical system



through the septum located between the transfer and analytical columns.

## OIL, WATER, AND SHALE SAMPLES

### Oil Sample Collection and Analysis

Oil and water produced during retorting are collected in the separatory funnel below the retort and in the separatory funnels attached to the condensers. The organic and aqueous layers are clearly differentiated. Immediately following the completion of a retorting experiment, the oil and water are separated. The small quantity of oil which does not drain from the line connecting the retort and the separatory funnel is recovered after retorting. All of the oil fractions are combined in a glass container and are stored in a refrigerator at 4°C. Separatory funnels and collection containers are acid washed prior to use.

The oil is analyzed for Hg by two methods. The primary method is instrumental neutron activation analysis (INAA). The oil is briefly heated to 80°C and thoroughly stirred. Then an aliquot of approximately 4 grams is pipetted into a quartz ampule. The sample is frozen in liquid nitrogen and quickly heat sealed under vacuum. The TRIGA reactor at the University of California, Berkeley, is used for irradiation. Following irradiation, the oil is removed from the ampule and transferred to a second container for counting. Details of the irradiation and counting procedures are described elsewhere (Heft 1979).

The combustion-amalgamation-spectroscopy technique described above for particulate gas samples is used as an alternate method for the analysis of Hg in oil samples since INAA of oil samples requires in excess of one month for completion. A small quantity of oil (30-50 mg) is weighed into a platinum boat. Subsequent analysis procedures are the same as for particulate samples. A second quartz combustion tube containing 8 grams of CuO in wire form is added to the gas train between the WO<sub>3</sub> combustion tube and the bubbler (Figure 4). INAA Hg concentrations in oil are reported in Table 2. Results obtained by the alternate method are in general agreement.

### Water Sample Collection and Analysis

Immediately following the completion of a retort experiment, all of the product water collected in the separatory funnels is combined in an acid washed glass container. This water is preserved by acidification to pH 1 with concentrated, high-purity HNO<sub>3</sub> and by addition of 0.05% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Feldman 1974, Lo and Wai 1975). Due to the high carbonate content of the water, approximately 15% (v/v) HNO<sub>3</sub> is required.

The water is analyzed for Hg by adding a 100 to 250 µl aliquot to 10-ml of 1.5% (v/v) HCl in a miniature bubbler. A Au-plated bead amalgamation column is attached to the exit of the bubbler, and 1 ml of a solution of 3% NaBH<sub>4</sub> with 1% NaOH is added. A N<sub>2</sub> flow rate of 500 scm<sup>3</sup>/min is gradually established, and the evolved Hg is collected on the amalgamation column. After 3 min, gas flow is stopped, and the amalgamation column is transferred to the second component of the analytical system. Analysis proceeds as for gas samples.

## Shale Sample Collection and Analysis

One of the equivalent batches of raw shale prepared for the retorting experiments was mechanically split at the time of preparation to produce a one-quarter fraction for analysis. Processed (spent) shale is removed after an experiment upon cooling of the retort. This material is then manually split to produce a one-eighth fraction for analysis. Both raw and spent shale samples are ground to <0.3 mm in an alumina planetary ball mill. Samples are stored in clean polyethylene bags.

Raw shale samples are analyzed for Hg using a batch sample ZAA spectrometer. With this instrument, Hg concentrations are determined directly without prior sample decomposition (Hadeishi 1972, Hadeishi and McLaughlin 1975). This is accomplished by introducing a weighed sample (10-50 mg) into a heated combustion-absorption chamber ( $T = 900^{\circ}\text{C}$ ) which is swept with  $\text{O}_2$ . Peak sample absorbance is measured and compared with calibration curves similarly produced using aqueous standards.

Spent shale samples, which typically have much lower Hg concentrations than raw shale samples, are analyzed using the method described for oil samples and particulate gas samples. The advantage of this method over the batch sample ZAA spectroscopy technique is that it can accommodate larger sample sizes.

## SECTION 5

### RESULTS

#### LABORATORY EXPERIMENTS

As previously noted, the progressive modification of the retort and the retort operating parameters throughout the course of the laboratory investigation is documented in Table 1. Referral to this table will help clarify the following presentation of results.

For simplicity, experiment E7, and to a lesser extent E5, have been emphasized throughout the results section. This emphasis is justified by several general observations. Retort operation results (temperature profiles, product evolution, and material balances) for experimental E7 are representative of retort operation results for experiments E4 and E6 despite the major parameter differences shown in Table 1. Measurements of Hg in offgas for experiments E7 and E6 are similar. Experiment E4 has reduced significance due to subsequent improvements in techniques. Exceptions to these generalizations are noted. Finally, experiment E5 warrants separate treatment because it is unique in that the shale column was heated unevenly.

#### Retort Operations

##### Temperature Profiles --

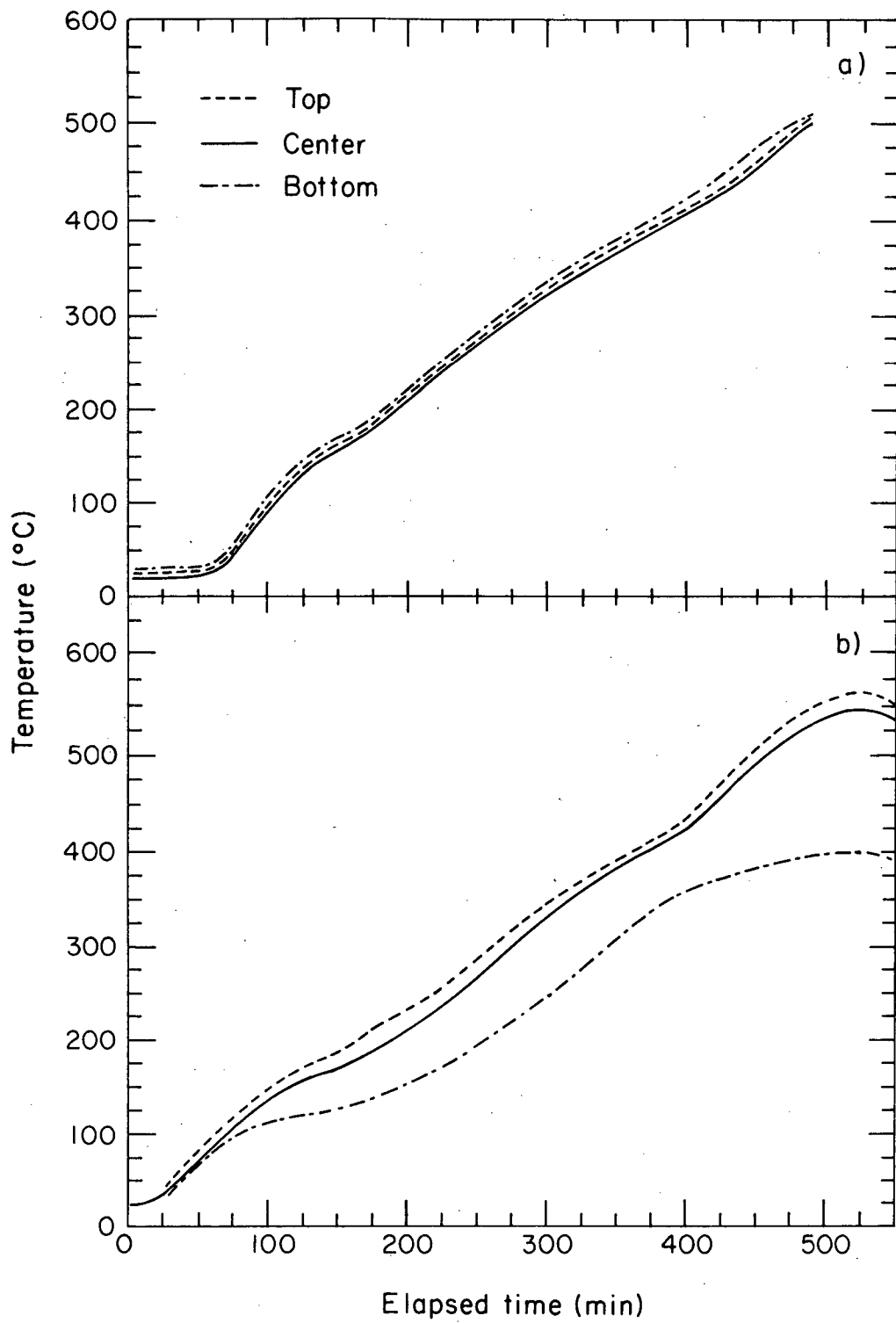
Shale column temperatures versus elapsed time (time into the experiment) for laboratory retort experiment E7 are shown in Figure 5a. During experiment E7, vertical temperature variations at a specific time did not exceed 20°C. Similar temperature profiles were achieved for experiments E4 and E6.

The shale column was heated unevenly during experiment E5 due to improper balance of the heating elements in the vertical furnace and inadequate insulation at the bottom of the furnace. Shale column temperatures for this experiment are shown in Figure 5b. The bottom retort temperature lagged substantially behind the center and top retort temperatures. When the shale column was unloaded from the retort vessel, the bottom 10 cm of the column was wet with oil.

##### Product Evolution --

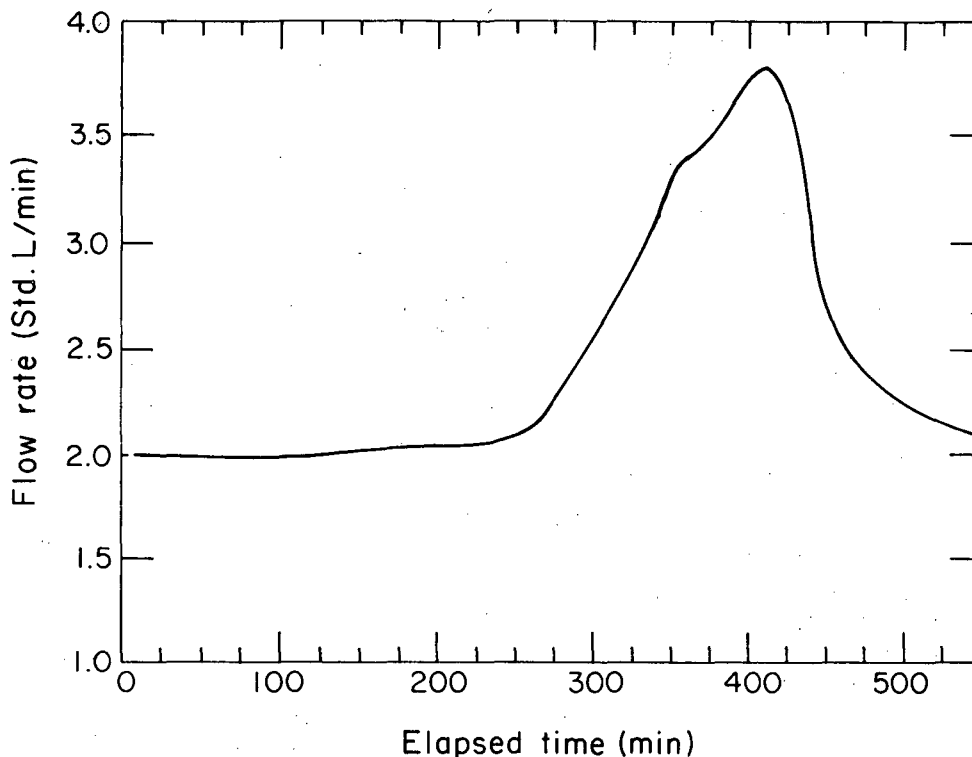
Figure 6 shows the total offgas flowrate versus elapsed time for experiment E7. All of the retort runs have similar total flowrate profiles. The volume of gas produced during an experiment was found by integrating the area under the curve and subtracting the volume of input N<sub>2</sub>.

The volume percents of N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, ethane, ethylene, propane, propylene, n-butane, i-butane, n-pentane, and i-pentane were determined by gas



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Figure 5 Shale column temperatures versus elapsed retorting time.  
 a) Experiment E7. b) Experiment E5.



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Figure 6 Flowrates of combined input gas and offgas versus elapsed retorting time--Experiment E7.

chromatography. Figure 7 shows the volume percents of  $H_2$ ,  $CO$ ,  $CO_2$ , and  $C_1-C_5$  hydrocarbons throughout experiment E7 (profiles for experiment E6 were almost identical). The remainder of the offgas is input  $N_2$ . The initiation of gaseous hydrocarbon evolution at  $275^\circ C$  closely corresponds ( $\pm 25^\circ C$ ) to the beginning of oil production at the  $1^\circ C/min$  heating rate.

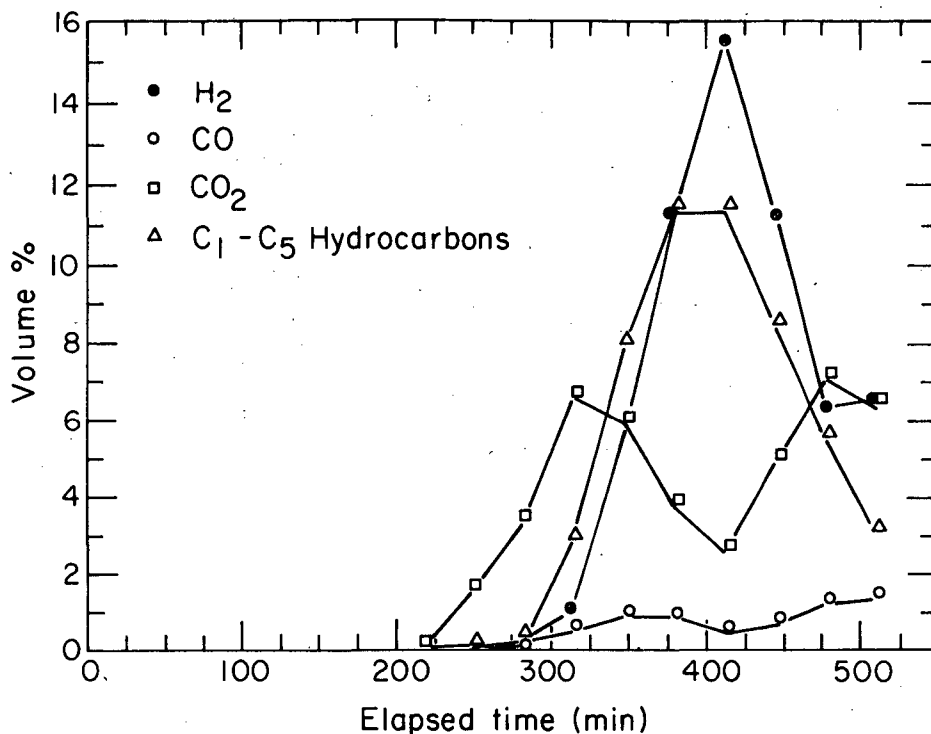
#### Material Balances --

Product distributions for retort experiments E4-E7 and for a Fischer assay of the raw shale used for these experiments are included in Table 2. The mass of product gas was calculated for Experiments E6 and E7 by integrating product gas volume and gas density determined from gas composition (Figure 7) over time. The average density of product gas for experiments E6 and E7 was approximately 0.65 g/standard liter. This value was used to calculate the mass of experimental gas for experiments E4 and E5. The average loss of material for the four experiments was 3.8% of the raw shale mass. Experimental distribution of retorting products is in good agreement with Fischer assay partitioning.

#### Mercury in Offgas

##### On-line Hg Gas Monitor --

The Hg gas monitor, lock-in-amplifier (LIA) signal, in D.C. volts, versus



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Figure 7 Volume percentages of H<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>5</sub> hydrocarbons in total offgas versus elapsed retorting time--Experiment E7.

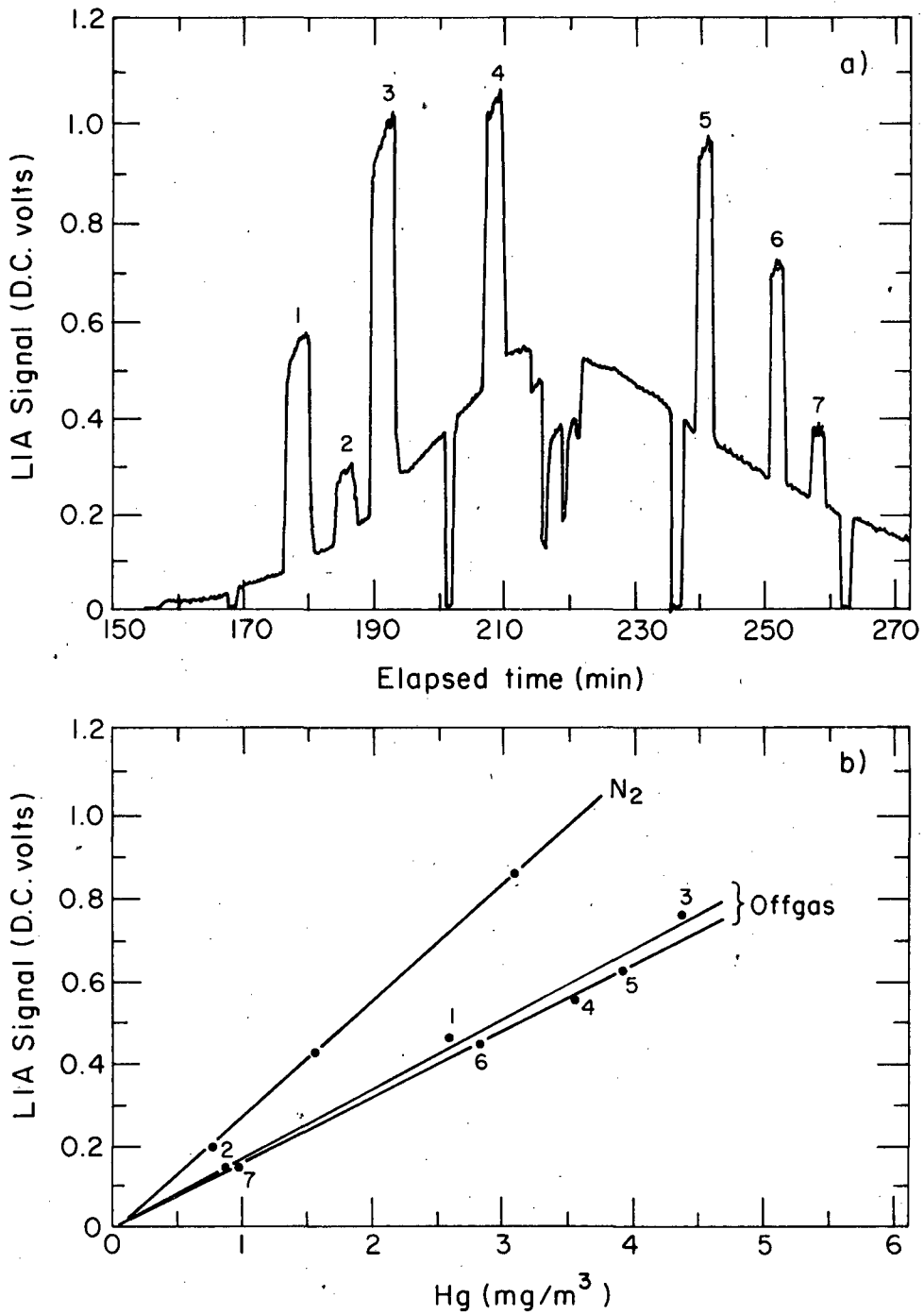
elapsed time is shown in Figure 8a for a portion of experiment E7. The LIA signal, which is the background corrected Hg signal, is converted to Hg concentration in mg/m<sup>3</sup> with calibration curves. Three calibration curves for experiment E7 are shown in Figure 8b. The curve with the greatest slope was constructed before the appearance of offgas Hg when the offgas stream consisted solely of N<sub>2</sub> input gas. A second curve was made as offgas Hg was increasing in concentration. The curve is linear, but instrumental sensitivity is substantially lower. A third calibration curve was made as offgas Hg was decreasing. Sensitivity in this region of the Hg peak is only slightly suppressed relative to sensitivity for the first half of the peak even though gas composition is starting to change measurably (Figure 7). Offgas Hg concentrations were calculated using the appropriate, temporally corresponding, calibration curve. The decreases in LIA signal to zero volts in Figure 8a are the result of switching the gas monitor from offgas to N<sub>2</sub> to establish instrumental baseline.

A heated sample line was used between the bottom of the retort vessel and the furnace-absorption tube for experiments E6 and E7. The line was maintained at 120-215°C for experiment E6 and 175-300°C for experiment E7. This temperature difference was judged to be insignificant based upon laboratory tests with calibration gas (see Loss Mechanisms). Total offgas Hg concentration for experiment E7, as determined by the gas monitor, is shown versus

TABLE 2. PRODUCT DISTRIBUTION AND MERCURY MASS DISTRIBUTION PATTERNS  
FOR LABORATORY RETORT EXPERIMENTS E4-E7

	Material Distribution		Mercury Mass Distribution		
	Mass (g)	Distribution (%)	Hg Conc. ( $\mu\text{g/g}$ )	Hg Mass ( $\mu\text{g}$ )	Distribution (%)
<u>Experiment E4</u>					
Raw Shale	5465		0.155+0.007	847.1+38.3	
Spent Shale	4496	82.3	0.008+0.003	36.0+13.5	4.2+1.6
Oil	641	11.7	0.077+0.011	49.4+ 7.0	5.8+0.8
Water	58	1.1	0.156+0.021	9.0+ 1.2	1.1+0.1
Gas	117	2.1		333.7+21.9 <sup>a</sup>	39.4+2.6
Total		97.2			50.5+3.3
Imbalance		-2.8			-49.5
<u>Experiment E5</u>					
Raw Shale	5392		0.155+0.007	835.8+37.7	
Spent Shale	4377	81.2	0.015+0.007	65.7+30.6	7.9+3.7
Oil	573	10.6	0.016+0.010	9.2+ 5.7	1.1+0.7
Water	82	1.5	0.174+0.005	14.3+ 0.4	1.7+0.01
Gas	116	2.2		147.5+ 6.2 <sup>a</sup>	17.6+0.7
Total		95.5			28.3+3.9
Imbalance		-4.5			-71.7
<u>Experiment E6</u>					
Raw Shale	4011		0.155+0.007	621.7+28.1	
Spent Shale	3255	81.2	0.003+0.001	9.8+ 3.3	1.6+0.5
Oil	461	11.5	0.095+0.011	43.8+ 5.1	7.0+0.8
Water	20	0.5	0.014+0.002	0.3+ 0.04	0.1
Gas	112	2.8		495.3+17.9 <sup>a</sup>	79.7+2.9
Total		96.0			88.4+ 4.7
Imbalance		-4.0			-11.6
<u>Experiment E7</u>					
Raw Shale	4081		0.155+0.007	632.6+28.6	
Spent Shale	3297	80.8	0.004+0.0002	13.2+ 0.7	2.1+0.1
Oil	488	12.0	0.058+0.011	28.3+ 5.4	4.5+0.9
Water	36	0.9	0.028+0.005	1.0+ 0.2	0.2+0.03
Gas	105	2.6		660.8+39.6 <sup>a</sup>	104.5+6.3
Total		96.3			111.3+ 8.2
Imbalance		-3.7			+11.3
<u>Fischer Assay</u>					
Spent Shale		81.5			
Oil		13.3			
Water		1.5			
Gas		3.7			
Total		100.0			

<sup>a</sup> Determined by integrating the product of offgas Hg concentration and offgas flow rate over time.



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Figure 8

Determination of Hg concentrations in retort offgas with the on-line Hg monitor--Experiment E7. a) Lock-in-amplifier (LIA) signal versus elapsed retorting time. Numbered peaks are additions of gaseous standards. b) Calibration curves in N<sub>2</sub> and offgas. Numbered points correspond to numbered peaks above.



elapsed time in Figure 9a. Mercury was first detected in the offgas at 160 minutes after initiation of experiment E7. This corresponds to a bottom shale column temperature of 166°C. Mercury concentration in the large, initial peak reached a maximum of 4.0 mg/m<sup>3</sup> at 220 min and a bottom shale temperature of 240°C. At 285 min and 314°C, the concentration had declined to 1.0 mg/m<sup>3</sup>. From the Hg concentration data and the total offgas flow rate data, it was determined that 554 µg of Hg had evolved from the shale during this period.

At 285 min elapsed time in experiment E7, O<sub>2</sub> was added to the furnace-absorption tube at a rate of 350 scm<sup>3</sup>/min. The addition of O<sub>2</sub> was necessary to combust offgas organics which were beginning to result in broadband extinction of the 253.7 nm analytical line. Additional offgas Hg evolved in irregular peaks concurrently with the addition of O<sub>2</sub>. Integration of these peaks resulted in a Hg mass of 107 µg. The reason for this anomalous evolution of Hg was not investigated. However, the O<sub>2</sub> addition resulted in the heating of the short inlet section of the furnace-absorption tube which was previously <100°C. Any Hg trapped on this tubing could have evolved at this time.

Oil collection in the separatory funnels commenced at 320 minutes during experiment E7. At this time, the heated sample line was turned off and the sampling location for the Hg monitor was changed to the sample point A with the condensers switched in. No Hg was detected at this location.

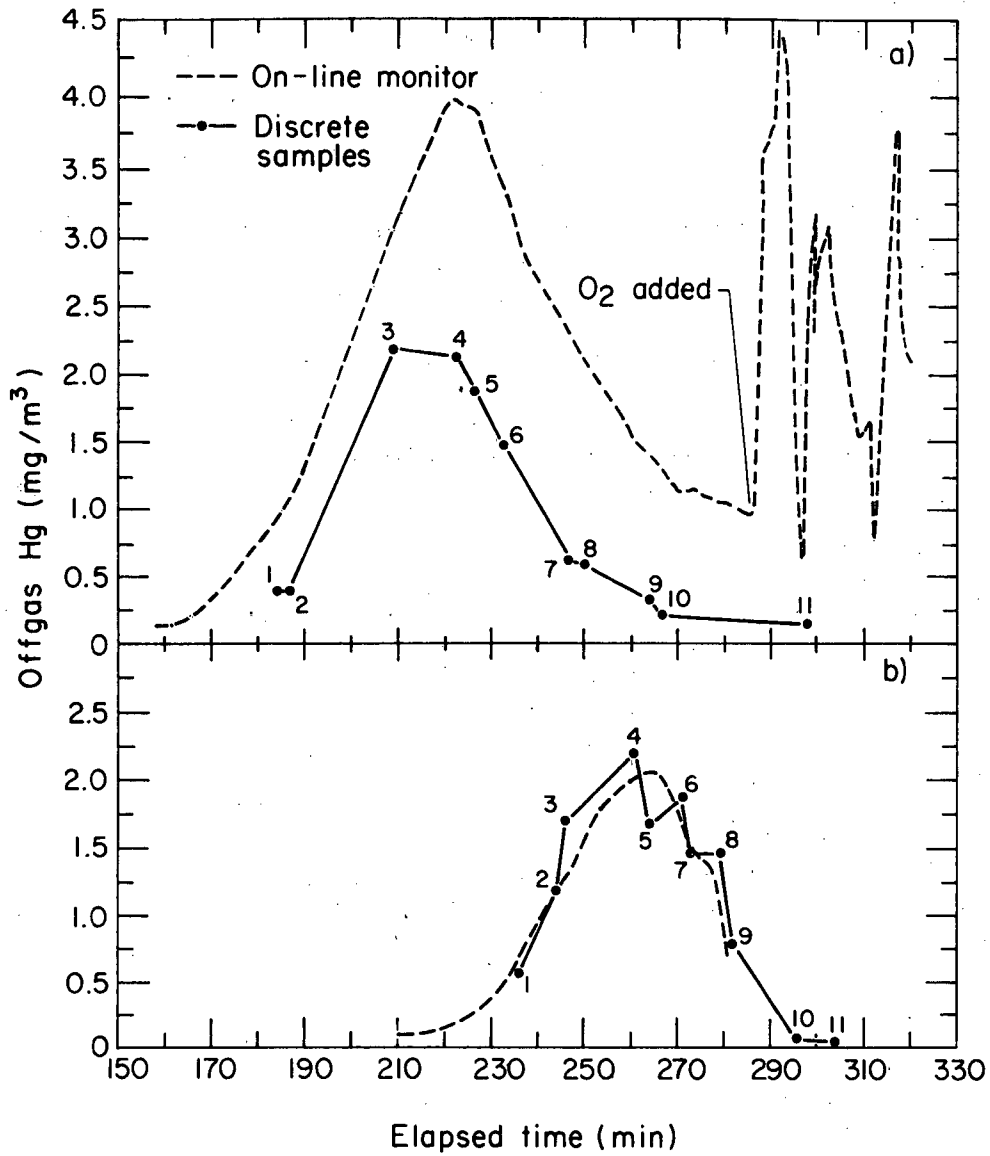
The total mass of offgas Hg evolved during experiment E7 from 4081 µg of raw shale was 661 µg (Table 2).

The decrease in the LIA signal shown in Figure 8a near the peak in voltage output (220 min elapsed time) for experiment E7 was due to switching the gas monitor from the heated sample line (sample point B) to the unheated offgas line (sample point A). Since the LIA voltage is directly proportional to background-corrected Hg concentration, the voltage decrease represents a decrease in Hg concentration. The initial decrease of 14% resulted from changing to the unheated line with the condensers switched out. Switching in the first condenser (15°C) dropped the voltage an additional 18%. No further decrease occurred when the second condenser (5°C) was switched in.

Total offgas Hg concentration for experiment E5, as determined by the gas monitor, is shown versus elapsed time in Figure 9b. The condensers were switched into the offgas line at 280 min elapsed time. Comparison of offgas Hg concentrations in Figures 9a and 9b shows that the maximum Hg level for experiment E5 was one-half of the maximum level for experiment E7. The Hg concentration curve for experiment E5 represents a total mass of Hg of 148 µg which is 22% of the total mass of offgas Hg evolved during experiment E7.

The heated sample line between the bottom of the retort and the furnace-absorption tube was not used for experiment E5. Instead, the gas monitor was connected to the sample point A on the unheated offgas line downstream from the condensers. The temperature of the offgas line averaged 25°C.

Another important difference between experiments E5 and E7 is apparent from Figures 5a and 5b which demonstrate the poor vertical temperature control achieved during experiment E5. As shown in Figure 5b, the bottom shale column temperature lagged substantially behind the center temperature. Evolution of



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Figure 9 Concentrations of total offgas Hg determined by the on-line monitoring system and from discrete samples versus elapsed retorting time. a) Experiment E7. b) Experiment E5.

Hg did not begin until 210 min elapsed time during experiment E5. This 210 min elapsed time corresponds to a bottom temperature of 160°C, which was close to the bottom shale column temperature at the beginning of Hg evolution in experiment E7. In experiments E4 and E6 with vertically uniform shale column temperatures, Hg evolution also started at a bottom temperature of around 160°C.

Total offgas Hg concentrations for experiments E6 and E4, as determined by the gas monitor, are shown versus elapsed time in Figures 10a and 10b, respectively. Monitoring for Hg was terminated at 305 min elapsed time during experiment E6, and no O<sub>2</sub> was added to the furnace-absorption tube. The Hg concentration profile for this experiment closely matches the portion of the profile for experiment E7 before the addition of O<sub>2</sub> (Figure 9a). Comparison of the Hg concentration profiles for experiments E4 and E6 demonstrates that the duration of the peak is shorter and that the maximum concentration is 25% lower for experiment E4. Loss mechanisms, as discussed below, presumably account for these differences.

#### Discrete Gas Samples --

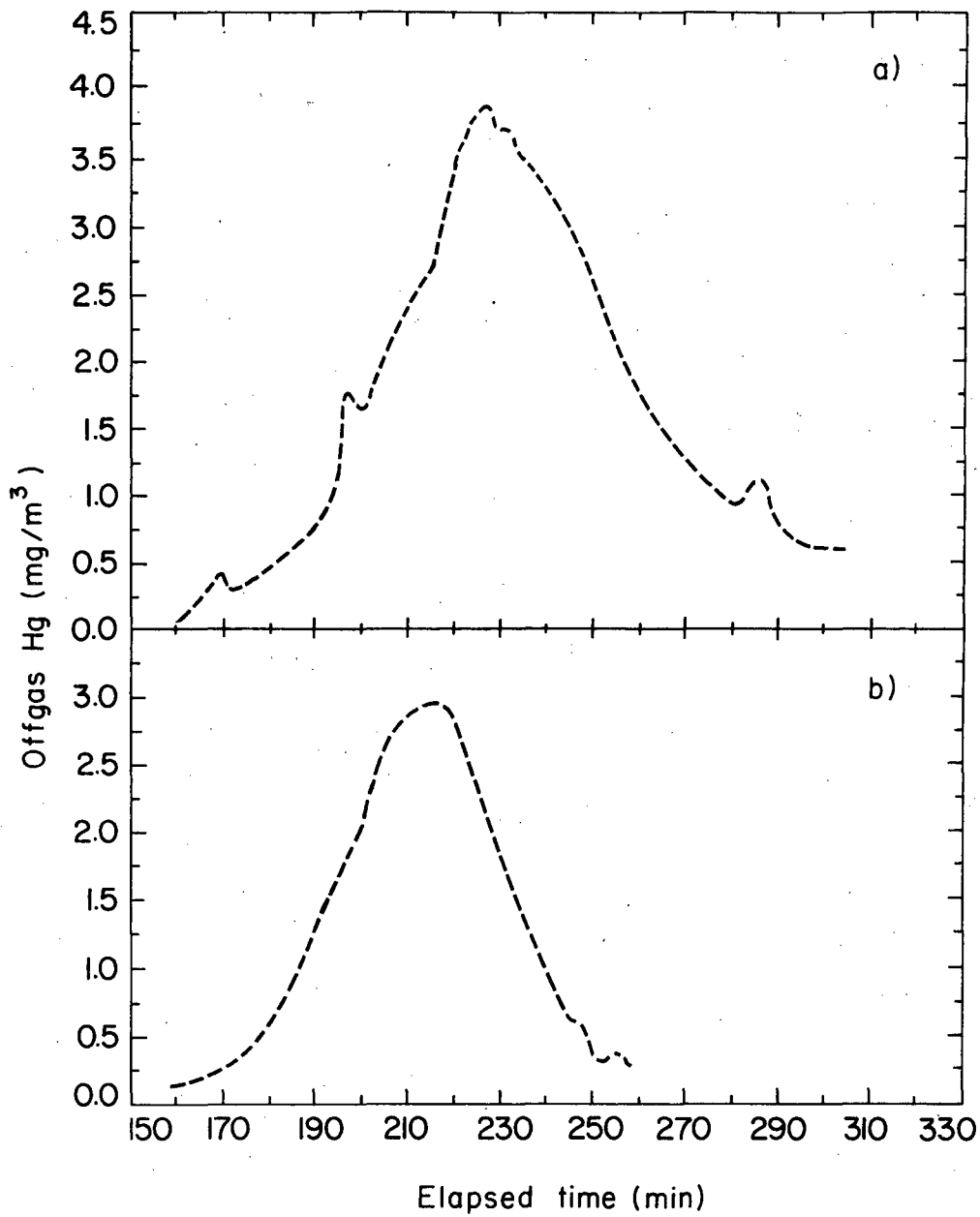
Concentrations of total Hg in discrete gas samples collected either on Au-plated glass bead columns or on combination columns of Carbosieve-B and Au-plated beads are shown in Figures 9a and 9b.

For experiment E5, adjacent sampling locations on the unheated offgas line (sample point A) were used for both the gas monitor and the discrete gas samples. Nine discrete samples were obtained during the E5 Hg peak. Of these, samples 8 and 9 were collected on the Carbosieve-B and Au-plated bead combination columns. There is good agreement between Hg concentrations determined by the gas monitor and the discrete gas sample methods; no significant difference was found between the set of nine discrete sample concentrations and the set of nine temporally corresponding gas monitor concentrations using a paired Student's t statistical test ( $t = 1.34$ ,  $p = 0.22$ ,  $df = 8$ ).

For experiment E7, discrete gas samples were collected adjacent to sample point B using 0.5 m of polyethylene tubing. Eleven samples were obtained during the period of Hg evolution. Of these, samples 6, 9, and 11 were collected on a combination of Carbosieve-B and Au-plated beads. In contrast to experiment E5, all of the discrete sample Hg concentrations for experiment E7 are substantially lower than the corresponding concentrations determined by the gas monitor. This difference is undoubtedly due to the loss of Hg to the cool polyethylene tubing.

One gaseous Hg speciation sample was collected during experiment E7. This sample is shown on Figure 9a as discrete gas sample number 6. All of the Hg was retained on the Carbosieve-B column; no Hg was transferred to the Au-plated bead column by purging. This suggests that all of the offgas Hg was organically bound.

Two particulate Hg samples were obtained from the offgas at sample point A during retort experiment E6. One was collected immediately preceding the peak in offgas Hg concentration and the other immediately after the peak. Calculated concentrations of particulate phase Hg were 0.005 and 0.014 mg/m<sup>3</sup>, respectively. These concentrations were 1.1% and 1.7%, respectively, of total



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Figure 10 Concentrations of total offgas Hg determined by the on-line monitoring system versus elapsed reporting time. a) Experiment E6. b) Experiment E4.

Hg concentrations for temporally corresponding discrete gas samples. In retrospect, it would have been preferable to sample for particulates closer to the exit of the retort. However, particulate levels in retort offgas were exceedingly low, and particulates, therefore, are probably not a significant sink for Hg.

#### Loss Mechanisms --

The total Hg recovery of 50% for experiment E4 (Table 1) was typical of recoveries obtained for unreported experiments E2 and E3 which also utilized a mullite retort vessel. Following experiment E4, the mullite pedestal used to support the shale column was suspended in the center of the retort vessel and reheated to 500°C. A substantial amount of Hg was evolved into the gas by this procedure. The degree of Hg adsorption on cool mullite surfaces was further evaluated by passing Hg calibration gas at 3 mg/m<sup>3</sup> through a stainless steel canister containing mullite chips at room temperature. The chips had an estimated surface area of 1350 cm<sup>2</sup>. An 18% decrease in LIA signal was immediately observed. The decrease gradually diminished to 4% over a period of 100 min. Heating the mullite chips to 450°C resulted in the release of 70% of the lost Hg to the gas phase.

In experiment E5, cool mullite surfaces were eliminated by the use of the stainless steel retort vessel. The percentages of Hg recovered in the spent shale, oil, and water are close to the respective percentages for experiment E4 (Table 2); however, only 18% of the original Hg entered the offgas leaving 72% of the Hg unaccounted for. As described above, the bottom 10 cm of shale were incompletely retorted and wet with oil due to uneven heating of the shale column. This oily shale was not included in the spent shale Hg analysis.

Subsequent to experiment E5, tests similar to the mullite chip experiment were conducted using different lengths of stainless steel tubing. These tests demonstrated that cool stainless steel surfaces could also be a significant Hg sink. For example, switching calibration gas at 3 mg/m<sup>3</sup> from a 0.3 m to a 12 m length of tubing resulted in an initial 24% decrease in measured Hg concentration and no noticeable Hg saturation during the 100 min of the experiment. The lost Hg was entirely recovered by heating the tubing to 150°C. No Hg was lost to tubing maintained at temperatures in excess of 100°C. Loss to the cool stainless steel offgas line probably accounts for a significant portion of the low recoveries in experiments E4 and E5.

#### Mercury Mass Distributions

The distribution of Hg among spent shale, oil, water, and offgas is shown in Table 2 for each of the four reported laboratory experiments. Product masses and Hg concentrations were used to compute the percent of total Hg in solid and liquid products. The Hg mass distribution values for offgas were calculated by integrating offgas Hg concentration (gas monitor data) and total offgas flow rate. Errors were determined using error propagation theory (Bevington 1969).

The low recoveries of total Hg for experiments E4 and E5 (50% and 28%, respectively) can be attributed to adsorption and condensation losses of offgas Hg. Mass distribution of Hg to the other products of E4 and E5 is similar to mass distribution in E6 and E7 with the exception of higher percentages of

total Hg occurring in the spent shale of the former two experiments.

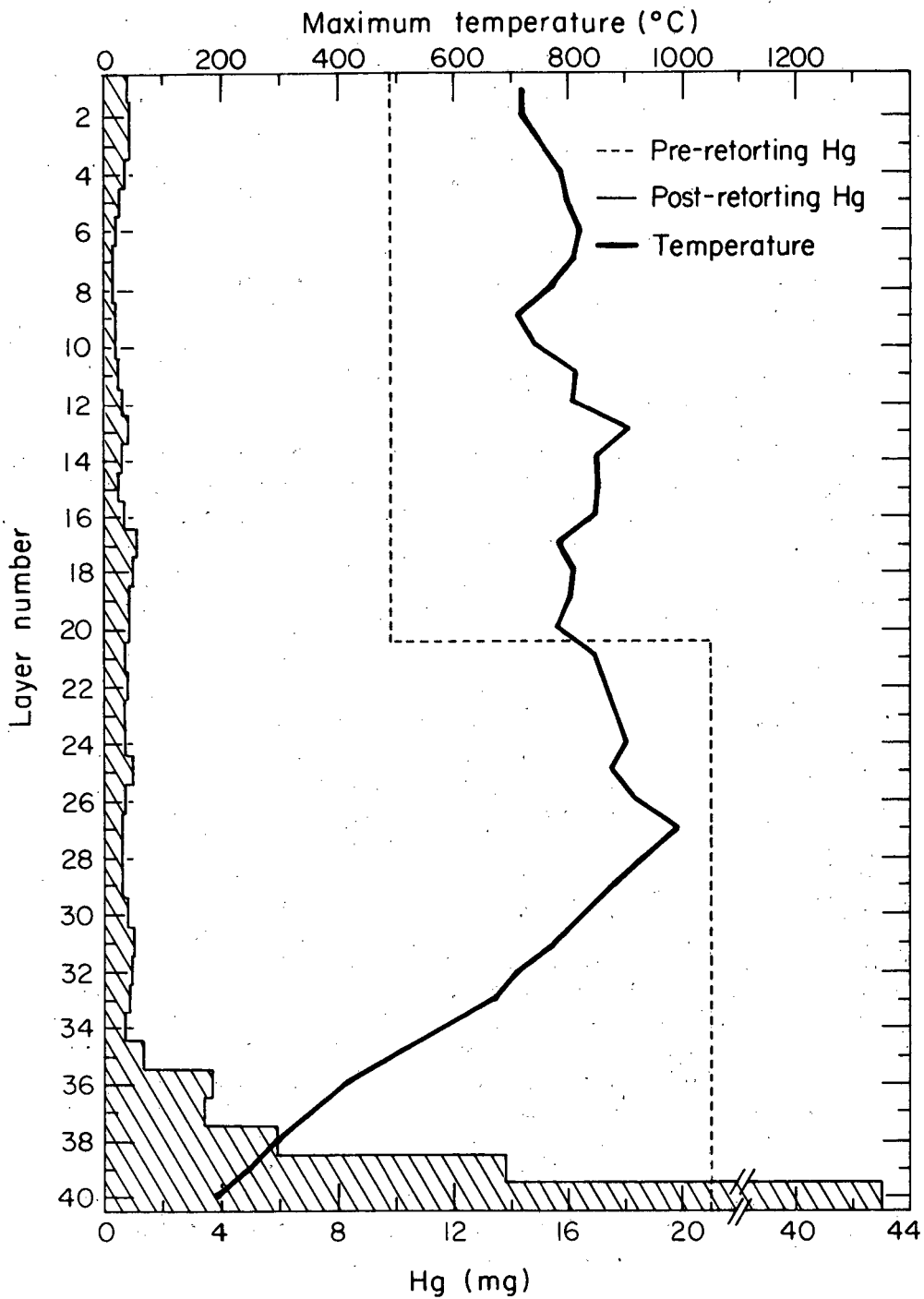
Uniform retort heating was achieved for experiment E6, and all cool tubing surfaces between the retort and the furnace-absorption tube were eliminated by the use of the heated sample line. Eighty percent of the original Hg was detected in the offgas, and quantitative recovery of Hg was achieved within the limits of error established for the experiment.

The only difference between experiments E6 and E7 was the use of O<sub>2</sub> in experiment E7 which allowed the gas monitor to be kept on-line longer before being switched from the heated sample line to the cool offgas line and condensers. In experiment E7, 104% of the original Hg was detected in the offgas yielding an overall recovery of 111% which is narrowly outside the limits of error for quantitative recovery.

Very small quantities of water were recovered from the laboratory retort. These small quantities combined with relatively low Hg concentrations resulted in low mass distributions of Hg to water (<2%) for all experiments. The mass of Hg remaining in spent shale was also very low (approximately 2% of total Hg for E6 and E7). The mass distribution of Hg to product oil was 7% or less for the four laboratory experiments.

#### SIMULATED IN-SITU EXPERIMENT

Data from LLNL's 6000-kg retort experiment, L-3, are summarized in Figure 11. This figure shows the pre- and post-retorting Hg contents in milligrams for each of the 40, 15-cm thick, vertical, shale column layers along with the average maximum retorting temperature for each layer. The initial mass of Hg was determined by the analysis of two representative shale samples, one from each of the two shale grades (upper and lower halves of the shale bed). The Hg content of the entire shale column was estimated to be 618 mg before retorting. After retorting, 95 mg of Hg, or 15% of the original Hg, remained in the column. The majority of the remaining Hg was present in the bottom 45 cm of the column which was mostly unretorted due to early termination of the experiment 100 hr after ignition. Accumulation of Hg only occurred in the last 15-cm layer. Offgas Hg concentrations at sample port 2 (Figure 2), downstream from the retort's condenser-demister system, were determined periodically throughout the experiment with the gas monitor. Concentrations at this location ranged between 0.09 and 0.55 mg/m<sup>3</sup>. Eight hours before termination of retorting, the sampling location for the Hg monitor was moved to sample port 1 on the oil separator where similar concentrations were measured. The gas monitor was shut down 96 hrs after retort ignition due to instrumental problems associated with a high (>40°C) ambient temperature.



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Figure 11 LLNL retort experiment L-3--pre- and post-retorting Hg contents and average, maximum, retorting temperatures for each of the 40, 15-cm thick vertical shale column layers.

## SECTION 6

### DISCUSSION

The behavior of Hg during oil shale retorting can be partially elucidated by a comparison of observed Hg distribution patterns for various retorts and retorting processes. Data from previous investigations of Hg distribution during retorting (Donnell and Shaw 1977, Fruchter et al. 1980, Fox et al. 1978, Fox 1980) are summarized in Table 3.

Fox (1980) determined Hg mass distributions for six combustion runs (S-10, S-11, S-13, S-14, S-15, L-1) of LLNL's two simulated in-situ retorts. The previous description of the 6000-kg retort suffices for both retorts. All of the six runs used 84 to 108 L/tonne Anvil Points, Colorado shale. Maximum average centerline temperatures ranged between 868 and 1025°C.

Mercury mass distributions for a number of runs of Laramie Energy Technology Center's (LETC) controlled-state retort also were determined (Fox et al. 1978, Fox 1980). This retort, which is designed to partially simulate in-situ retorting, is indirectly heated by a contiguous series of 24 external heaters. Peak temperature is propagated down the bed by successively activating the heaters. The retort and its operation have been described by Duvall and Jensen (1975). We have selected the 10 completed runs which had data for all retorting components (CS-62 - CS-70, CS-73) and have summarized the results in Table 3. Shales from Colorado, Utah, Michigan, and Morocco with Fischer assay grades varying between 40 and 248 L/tonne were used. Maximum retorting temperatures ranged between 540 and 760°C. One of the 10 runs is shown separately. This run, CS-69, with Colorado shale is unique in that off-gas Hg was quantified with a prototype of the on-line Hg monitor used in this investigation.

The distribution of Hg in the products of a single Fischer oil shale assay was reported by Donnell and Shaw (1977). This distribution has been included in the summary with some reservation since the supporting experimental description is insufficient to assign an uncertainty to the data.

Fruchter et al. (1980) investigated elemental partitioning for the Paraho semi-works, directly heated (combustion) surface retort. Recycle gas Hg concentration was determined with an amalgamation method (Fruchter et al. 1979) similar to the one used in this investigation. The Paraho retorting process has been described by Jones (1976).

Less than 5% of the Hg originally present remained in the spent shale following our retort experiments E4, E6, and E7. The spent shale from the LLNL retorts and the Fischer assay retort also contained a small percentage, <4%, of the original Hg. Higher percent distributions, 12-33%, were reported



TABLE 3. SUMMARY OF MERCURY MASS DISTRIBUTION PATTERNS FOR PREVIOUSLY  
REPORTED RETORTING EXPERIMENTS

	Percent Distribution				
	LLNL Simulated In-Situ 6 Combustion Runs <sup>a</sup>	LETC Controlled State 10 Runs <sup>a,b</sup>	LETC Controlled State CS-69 <sup>a,b</sup>	Fischer Assay <sup>c</sup>	Paraho Direct <sup>d</sup>
Spent Shale	3.3	21.5	12.4	1.9	32.8
Oil	21.7	6.6	8.3	24.9	28.2
Water	3.4	4.7	2.5	15.5	0.01
Gas	--	--	72.2	--	23.0
Total	28.4	32.8	95.4	42.3	84.0
Imbalance	-71.6	-67.2	-4.6	-57.7	-16.0

<sup>a</sup> Fox 1980.

<sup>b</sup> Fox et al. 1978.

<sup>c</sup> Donnell and Shaw 1977.

<sup>d</sup> Fruchter et al. 1980.

for the LETC and Paraho retorts.

The relatively high distribution of Hg to the spent shale from the LETC retort can be explained by the adsorption of Hg by unretorted or partially retorted shale. Fox (1980) noted that retorting is often incomplete in the bottom of the LETC retort. Adsorption of Hg, volatilized from the upper sections, by unretorted or partially retorted shale at the exit of the retort would result in relatively high spent shale Hg concentrations. An examination of the experimental data shows that post retorting Hg levels in the bottom of the shale column were, in fact, higher than raw shale Hg concentrations and considerably higher than Hg levels in the upper portion of the column for six of the 10 runs (CS-63, CS-65, CS-67, CS-68, CS-70, CS-73). Organic extraction of oil wetted, unretorted and partially retorted shale from the bottom of the columns of interrupted runs demonstrated that the Hg was not associated with oil or bitumen (Fox 1980).

A hypothesis based upon the adsorption of Hg by shale may also account for the high percentage of Hg remaining in the spent shale produced by the Paraho direct process. This process is continuous with flows of shale and gas moving countercurrently to each other. Shale is introduced from the top, and air and recycled offgas are injected at the bottom. The combustion temperature of 750°C should be sufficient to volatilize most, if not all, of the Hg in the shale. This Hg would enter the offgas and be swept upwards from the retort. The offgas passes through a condenser system and a portion is reinjected at the bottom of the retort to cool the exiting shale. Adsorption of remaining offgas Hg on this spent shale, which has a temperature of approximately 150°C, could result in a relatively high spent shale Hg concentration. Experiments to determine the Hg adsorptive capacity of processed shale are necessary to evaluate the validity of this hypothesis.

In our retorting experiments E6 and E7, 80% and 104% of the original Hg partitioned to the offgas phase (Table 2). Imbalances in the Hg distribution equations for these experiments were -12% and +11%, respectively. Thus, most of the Hg contained in the shale partitioned to the offgas phase at the 500°C maximum retorting temperature.

Offgas Hg measurements were made for only one of the simulated in-situ experiments summarized in Table 3. In that experiment, LETC run CS-69, 72% of the total Hg partitioned to the offgas with 5% of the total Hg unaccounted for. If it is assumed that the imbalances shown for the other simulated in-situ experiments can be primarily attributed to the offgas phase, then the data suggest that Hg partitioning to this phase was approximately 67% or more for these experiments. However, as discussed below, Hg losses to retorting components can reduce the mass and percentage of Hg detected in retort offgas.

Only 23% of the total Hg was detected in the gas phase of the Paraho direct process. This relatively low percent distribution is offset by relatively high percent distributions to spent shale and oil.

The percentage of Hg redistributed to product oil varies from 5% to 28% for the different retorts and processes (Tables 2 and 3). The causes of this variation are unknown.

Partitioning to water is relatively unimportant. Percent distributions to water ranged between 0.01% and 4.7% excluding the uncertain Fischer assay value. (Tables 2 and 3).

The partitioning experiments summarized in Tables 2 and 3 indicate that the majority of the Hg in raw shale can be expected to be emitted to the off-gas during retorting. Gaseous Hg emissions are not, however, expected to be uniform throughout a MIS retort burn.

From our experiments using a heating rate of  $1^{\circ}\text{C}/\text{min}$ , the temperature range for the evolution of Hg from shale during retorting was found to be  $160\text{--}320^{\circ}\text{C}$  with the peak in Hg evolution occurring at approximately  $240^{\circ}\text{C}$ . The evolution of low molecular weight hydrocarbon gases corresponds closely (within  $25^{\circ}\text{C}$ ) to the production of oil (Campbell et al. 1980). Using this relationship and the  $\text{C}_1 - \text{C}_5$  hydrocarbon evolution profile in Figure 9, oil production was estimated to start at about  $275^{\circ}\text{C}$  and peak at  $400^{\circ}\text{C}$ . Thus, the Hg in raw shale was volatilized almost entirely in advance of oil formation.

In a MIS retort, Hg would be volatilized and swept ahead of the reaction front by the gas stream as the front moves down through the rubblized bed. Fox (1980) presented evidence which indicates that the timing of the appearance of elevated Hg concentrations in the offgas from a MIS retort would be controlled by the adsorption of Hg on unretorted or partially retorted shale. Additional evidence for this control mechanism was obtained from two of our experiments.

Uniformly heated laboratory retort runs demonstrated that Hg volatilization begins at a shale temperature of  $160^{\circ}\text{C}$  with a heating rate of  $1^{\circ}\text{C}/\text{min}$ . During run E5, the bottom retort temperature lagged substantially behind the center temperature. Mercury was not detected in the offgas until the bottom temperature reached  $160^{\circ}\text{C}$  even though the center of the shale column was at the temperature of maximum Hg volatilization. Adsorption of Hg volatilized from the center of the column on shale at the bottom of the retort and subsequent volatilization of this Hg would account for the observed emissions behavior.

The LLNL 6000-kg retort experiment also indirectly indicates that the timing of Hg emissions during in-situ retorting may be controlled by the adsorption of offgas Hg on unretorted or partially retorted shale. An average weighted offgas Hg concentration of  $0.22\text{ mg}/\text{m}^3$  was assumed for the first 96 hrs of the L-3 retort burn. The total volume of input gas plus produced gas during this period was calculated to be approximately 2250 standard  $\text{m}^3$  from Ackerman et al. (1980). Thus, an estimated 68 mg, or 11% of the original Hg content of the shale, partitioned to the offgas during the 96 hr period. Post burn analysis of the shale column revealed that 95 mg, or 15% of the original Hg, remained in the column. One-half of this remaining Hg was in the bottom 15 cm which was the only layer which contained Hg in excess of its original Hg content. Since the reaction front was moving at a rate of  $7.5\text{ cm}/\text{hr}$ , much of the 74% unaccounted for Hg may have evolved from the bottom of the shale column during the final 4 hrs between shut down of the ZAA Hg monitor and termination of the retort experiment. It is certain also that a portion of the unaccounted for Hg was lost to the bottom of the retort vessel and to the off-gas plumbing system.

Mercury released to the offgas during the laboratory retorting experiments was almost entirely in gaseous and not in particulate form. Preliminary results indicate that organomercurials were the dominant chemical species of Hg as the offgas left the retort. Additional work is required to substantiate this observation. Our measurements of offgas Hg were not, however, effected by speciation since both analytical techniques quantify total Hg.

The difficulties encountered in obtaining closure of the Hg mass distribution equation in laboratory retorting experiments demonstrated that adsorption and condensation losses of gaseous Hg to the physical retorting system can be substantial. Even though the losses observed in the laboratory cannot be extrapolated to actual MIS retorts, it is probable that the quantity of Hg reaching the atmosphere will be determined to a large extent by these losses.

Based on the information generated by this and other investigations, an approximate estimate can be made for atmospheric Hg emissions from underground retorting at a MIS oil shale facility. Production of  $8 \times 10^6$  liters (50,000 barrels) of oil per day could result in an average release of 4000 grams of Hg per day or 1500 kg/yr assuming: (1) an average Hg concentration in shale of 100 ng/g (Mahogany Bed concentration from Giaouque et al. 1980), (2) processing of 2000 kg of shale per barrel of oil produced (104 L/tonne shale and 75% of Fischer assay oil yield), (3) an 80% distribution of Hg from shale to noncondensable offgas (5°C), (4) loss of one-half of the offgas Hg to the retorting system by condensation and adsorption, (5) no temporal variation in Hg emissions, and (6) no emissions controls.

The National Emission Standards for Hazardous Air Pollutants limit Hg emissions to the atmosphere from Hg ore processing facilities and Hg cell chlor-alkali plants to 2300 grams of Hg per 24-hour period (Federal Register 1973). Emissions to the atmosphere from wastewater sludge drying and incineration plants are not to exceed 3200 grams of Hg per 24-hr period (Federal Register 1973). If similar regulations are extended to the oil shale industry, control of gaseous Hg emissions might be required.

Retort facility design and operational procedures could result in lower mass emission rates of Hg from MIS retorting than the above estimate.

The major unknown factor in the mass emissions estimate is the magnitude of the potential condensation and adsorption losses of Hg to components of the retorting system. We do, however, have good reason to expect the losses to be large and to play a major roll in controlling mass emission rates of Hg. The actual losses, which could be greater than the estimated 50%, will depend upon a number of factors. These factors include offgas temperature and composition, the type of materials and amount of surface area coming into contact with the offgas, as well as, the extent of turbulent mixing and the duration of contact. Specific components of the retorting system, such as desulfurization units, may also serve to reduce the mass of offgas Hg by chemical and/or physical means. For example, Hg has been detected in a flue gas, sulfur dioxide scrubber, effluent liquid from a coal fired power plant (Billings et al. 1973).

Operational considerations may also serve to limit Hg emissions from MIS retorting. Most importantly, there appears to be a practical limit on how

completely an MIS retort can be burned due to channeling of the reaction front that develops as the result of large scale variations in permeability (Gregg and Campbell 1980). Once any portion of the reaction front reaches the floor of the retort, air input is stopped to prevent fires and explosions due to oxygen breakthrough, and retorting ceases. The need to maintain the physical structure of the exit of the retort so that gas and liquid flows can be maintained may also preclude the complete burning of a retort. Any unretorted or partially retorted shale left in the bottom of a MIS retort may act as a sink for Hg and, thus, effectively reduce the amount of Hg emissions.

Because of the uncertainties about the magnitude of inherent control mechanisms for Hg emissions from MIS retorts, no recommendations can currently be made concerning the necessity for offgas Hg emissions monitoring or controls at MIS retorting facilities. However, this investigation has clearly demonstrated that Hg emissions from MIS retorts have the potential to be substantial, relative to other industries. Evaluation of Hg emissions from MIS retorts should now progress to the monitoring of total offgas Hg during the burns of several large-scale MIS retorts.

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