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MERCURY EMISSIONS FROM A SIMULATED IN-SITU OIL SHALE RETORT

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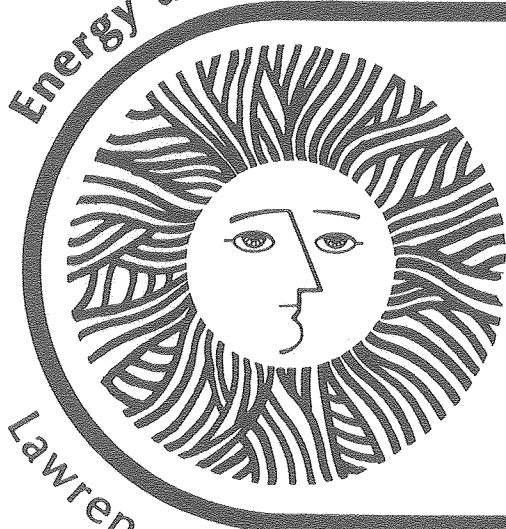
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IN-SITU OIL SHALE RETORT

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INTRODUCTION

Mercury emissions from fossil-fuel processes have received considerable attention in the past several years. They have been studied by Bertine and others (1971), Diehl and others (1972), Billings and others (1973), Forney and others (1975), Kaakinen and others (1975), Klein and others (1975), Fox and others (1977) and Fruchter and others (1977). This emphasis has been placed on mercury primarily due to its volatility. Studies of coal combustion by Billings and others (1973) and Klein and others (1975) indicate that more than 90% of the mercury present in coal is emitted to the atmosphere in the flue gas. Similar studies are in progress for most synfuel processes.

Preliminary investigations of simulated in-situ oil shale retorts indicate that mercury will be present in the process streams and control measures should take this into account. Fox and others (1977) estimated gaseous mercury emissions from mass balance data for two simulated in-situ retorts -- Laramie Energy Research Center's (LERC) controlled-state retort and Lawrence Livermore Laboratory's 125-kg retort. Fruchter and others (1977) made a single measurement of mercury in the gas stream from LERC's 9.1-tonne (10-ton) retort. No long-term direct gas measurements were available to corroborate these results.

The purpose of the present study was to measure gaseous mercury emissions as a function of time during simulated in-situ oil shale retorting by making direct measurements of mercury in the gas stream over an extended period, and to measure the distribution of mercury to the spent oil shale, shale oil, and

retort water. These measurements were made at LERC on the controlled-state retort (Duvall and Jensen, 1975) with a Zeeman atomic absorption spectrometer (Hadeishi and others, 1975). Retort inputs and outputs were collected and mercury mass balances completed to substantiate the gas measurement results.

It is important to realize that the measurements reported in this paper were made on process streams from a small-scale simulated retort in the absence of any environmental control technology. This is a necessary first step to determining control technology requirements. In practice, the output streams would not be directly released to the environment; they would be treated to remove any objectionable substances before disposal.

EXPERIMENTAL PROCEDURES

The distribution of mercury to spent shale, shale oil, retort water and offgas during simulated in-situ oil shale retorting was studied in 16 runs of LERC's controlled-state retort. Samples of raw shale, spent shale, shale oil, retort water, and offgas were collected and analyzed for total mercury. Offgases were continuously monitored during one run using instrumental methods and intermittently monitored during two runs with impingers.

RETORT FACILITY DESCRIPTION

The controlled-state retort and its operation have been described by Duvall and Jensen (1975) and Bartke and Duvall (1977). A schematic of this retort is shown in the insert on Figure 1. It is a bench-scale simulated in-situ retorting facility with a capacity of approximately 20 kg. It consists of a 3.96 m (13 ft) long, 7.62 cm (3 in) ID vertical stainless steel tube. Thermocouples are placed in a 2.54 cm (1 in) OD tube axially centered through the outer 7.62-cm (3-in) tube. This tube is surrounded by a contiguous series of 24 pairs of 15.2 cm (6 in) long electric heaters which are controlled by 24

The controlled-state retort is different from a field-scale retort in several ways. The maximum temperature reached in this retort, 760°C, is low compared to those reached in field retorts where temperatures may reach 1200°C. Isothermal advance rates and oil residence time in the reaction zone are low. Significant differences exist between the product collection system used in the controlled-state retort and field retorts. For these reasons, the results of this study must be verified by repeating similar measurements in the field setting.

SOLID, LIQUID AND OIL SAMPLES

Samples of raw oil shale, spent oil shale, retort water, and shale oil were collected from the 16 runs. Spent shale was collected from the top and bottom 15.2 cm (6 in) of the retort and from the middle section for most runs. For the interrupted run, 60, samples from each of 24 segments of the retort were collected. The raw and spent shales were ground to less than 3 mm (1/8 in) in an alumina-face shatter box and then to less than 0.15 mm (100 mesh) with a majority passing 0.074 mm (200 mesh) in an alumina-jaw pulverizer. Oil and water were collected from the receiver and trap at the end of each run. The nonemulsified water in the receiver was removed with a syringe (retort water). A 5- to 25-ml aliquot was vacuum filtered through a Millipore 0.45- μ m filter to collect particulates from the aqueous phase (particulate fraction). The receiver contents less the amount of water removed by syringe were combined with condensates from the two knock-out traps and a sample collected (wet oil). The oil/water emulsion on leaving the retort and before combining with the receiver contents was sampled approximately every four hours during runs 69, 70, and 71. The oil and water were separated by centrifugation and each fraction separately analyzed. Retort water samples were not acidified (Fox and others, 1978) and were stored in air-tight, acid-washed, polyethylene

bottles. All samples were refrigerated at 4°C. Samples were analyzed at 6-month intervals, and no loss in mercury was noted.

GAS MEASUREMENTS

The product gases were analyzed for total mercury (gaseous plus particulate) in runs 69 and 70. An on-line monitor and impingers were used during run 69. Impingers only were used during run 70 as the on-line monitor's furnace cracked during run 70. This may have been due to H₂S corrosion of the stainless steel tube.

The experimental setup for gas measurements is shown in Figure 1. Direct measurements of mercury in the offgas were continuously made during run 69 with a Zeeman atomic absorption spectrometer (ZAA) (Hadeishi, 1972; Hadeishi and McLaughlin, 1975). The technique uses the Zeeman effect to correct for background interferences and was previously demonstrated as a continuous monitor for ambient air (Hadeishi and others, 1974). Organics in the gas stream do not interfere with mercury measurements.

The exit gas flow rates and gas temperatures ranged from 0.1 to 2.0 l/min and 12 to 27°C. The total gas flow from the receiver, which was under a slight positive pressure, was passed through a 0.91 m (36 in) long, 0.95 cm (3/8 in) ID teflon line directly into the furnace of the ZAA detector where it was combusted and measured. There were no components between the receiver and the detector and all lines in contact with the gas were teflon except the furnace inlet tube which was a 10.2 cm (4 in) long, 1.37 cm (1/2 in) ID stainless steel tube. The mercury signal was recorded by a strip chart recorder. A typical recorder output is shown in Figure 2. The baseline represents the recorder output when there is no gas flow into the detector. When gas is allowed to flow into the detector, the recorder pen moves some distance from

the baseline. The distance moved is proportional to the concentration of mercury atoms in the gas stream.

Gas flow rates, ambient and gas temperatures, and atmospheric pressure were recorded during the run. The gas flow rate was measured with a wet test meter and stop watch in an equivalent line parallel to the sampling line to avoid contamination and adsorption. During temperature and pressure measurements, the gas flow to the detector was diverted to the parallel line by setting appropriate valves. Gas temperatures were measured with a K-type thermocouple in the receiver and with a calibrated thermometer in the parallel line at a distance equal to the receiver-to-detector distance.

The system was calibrated during the run by injecting known quantities of mercury into the gas line with a syringe pump. Approximately 5 ml of mercury were placed in a 125-ml septum-covered flask maintained at ambient temperature. A 30-cc sample of the vapor was withdrawn with a 50-cc syringe and uniformly injected over 1 min into the sampling line at a glass T while the product gas flowed in the line. An upstream injection point was used to correct for effects that might result if mercury were adsorbed on the walls. Since the calibration vapor and product gas passed through equivalent tube surface areas, adsorption would be identical. Calibration was repeated every 30 min during most of the period when mercury was detected. A typical calibration is shown in Figure 2.

The procedure used during the run was subsequently checked using a more elaborate technique. The initial calibration assumed that the mercury in the septum-covered flask was at equilibrium and uniformly distributed within the flask. This was checked by generating a well-mixed equilibrium mercury vapor using a procedure similar to Nelson's (1970). No difference between the two procedures was found. In future work, permeation tubes will be investigated for use in calibration.

Iodine monochloride (ICl) impinger trains were used to collect mercury from the gas stream during runs 69 and 70. Several different impinger train configurations which included ICl (Linch and others, 1968), concentrated acid, H_2O_2 , and NaOH were used to trap the mercury and/or remove H_2S and particulates. Analytical-grade reagents were used for the impinger solutions, and reagent blanks determined. The connecting lines in the impinger system were teflon except between the individual impingers during run 70 when Pyrex glass was used. A teflon pump and wet test meter were downstream of the impingers. The impingers were maintained at $0^{\circ}C$ with an ice bath. Sampling times ranged from 1 to 5 hrs. During sampling, dark brown, gummy deposits formed on the walls of the impingers. The empty impingers and the connecting lines were washed with methyl iso-butyl ketone (MIBK) which effectively removed the deposits, and the wash separately collected in air-tight, acid-washed, polyethylene bottles. On disassembly, each impinger solution was also separately collected for analysis. Samples were analyzed at 6-mo intervals and no loss in mercury was noted.

Laboratory air was monitored for the presence of mercury before initiation of retorting and throughout the experimental work during run 69. A syringe was used to collect 20 to 100 cc samples of air which were injected directly into the mercury monitor for analysis. After mercury was first detected, 20 to 100 cc samples of air and offgas were alternatively collected and analyzed for comparative purposes. No mercury was detected in the laboratory air at any point during the experiment. This corresponds to a background level of mercury in the air of less than 10 ppb. Likewise, no mercury was detected in the offgas from the retort during the first hours of retorting. This indicates that the mercury content of the input gases was also less than 10 ppb.

ANALYSES

The collected samples were analyzed for mercury, inorganic and organic carbon, and total sulfur, nitrogen, and hydrogen. Mercury measurements were made on all samples using Zeeman atomic absorption spectroscopy (Hadeishi and McLaughlin, 1975) except some retort water particulates. Those particulate samples with mercury concentrations greater than 20 ppb were analyzed by x-ray fluorescence spectroscopy (Giauque and others, 1977).

For the ZAA analyses, three to 10 replicates of each sample were analyzed. The reported errors are one sample standard deviation for N replicates ($\frac{\sigma}{\sqrt{N-1}}$). The samples were analyzed by inserting a measured quantity of sample into a 750°C furnace in a Pt boat mounted on a Pt-tipped probe. No sample pretreatment was used. Initial experiments indicated that poor recoveries were obtained on spiked samples of retort waters and impinger solutions; spiked samples of oils and solids gave good (greater than 95%) recoveries. Therefore, all water samples were analyzed by standard additions using mercury standards in a 0.1N HNO₃ matrix. Oil samples were analyzed using organic mercury standards prepared from commercially available 100-ppm synthetic organic mercury diluted with Singer sewing machine oil. Considerable difficulty was encountered analyzing some of the oils directly due to total light blockage by smoke. This problem resulted in a detection limit of 60-80 ppb for some of the oils. Digestion or ashing to decompose the organics is required to eliminate the smoke and is under investigation.

NBS reference standards were analyzed with the samples and an inter-laboratory calibration using samples of raw and spent shale, shale oil, and retort water was used to verify data accuracy. Select samples of all materials were analyzed at 6-mo intervals by three analysts and good agreement obtained. No evidence of mercury loss on storage was noted.

Total carbon, total hydrogen, and total nitrogen were determined on a Carlo Erba Model 1104 elemental analyzer gas chromatograph. A sample of about 2 mg was combusted in 10 ml of pure oxygen and swept through a Pora-Pak Q column. Elemental nitrogen, carbon dioxide, and water were detected and the peaks integrated. Calculations were made with factors determined from NBS standards.

Inorganic carbon was determined by reacting a sample of about 100 mg with 20 percent perchloric acid and evolving CO₂. The CO₂ was swept into a coulometric titrator. Organic carbon was calculated by subtracting inorganic carbon from total carbon.

Total sulfur was determined by burning a sample of about 100 to 200 mg in an oxygen atmosphere. The SO₂ formed was titrated automatically with KIO₃. Factors used in this determination were calculated using standards.

RESULTS AND DISCUSSION

GAS MEASUREMENTS

The results of the gas measurements made during runs 69 and 70 are summarized in Figure 3 and Table 2. These data, combined with the mercury distribution in spent shale from the interrupted run shown in Figure 4 indicate that mercury release from a batch-type oil shale retort is controlled by the successive volatilization and removal of mercury from the gas phase as the reaction front progresses down the shale bed. Mercury volatilized from shale at temperatures in excess of around 340°C is removed in the cooler regions of the shale bed that are wet with oil. Additional experimental work is required to clarify this mechanism.

Continuous Zeeman Atomic Absorption Measurements

The results of the continuous ZAA gas measurements are presented in Figure 3. This figure shows the variation in mercury emission rates ($\mu\text{g}/\text{min}$) in the gas stream as a function of time. The plotted points correspond to times when calibrations were performed. The monitor was run continuously during the run except for brief periods when other experiments were on-line. The times when impinger trains were run are indicated by the four shaded areas at the bottom of the graph. The numerals 1 through 4 correspond to four separate impinger experiments. These experiments are summarized in Table 2.

This time distribution of mercury in the offgas shows that no mercury was detected in the gas stream during the first 66% of the run by either the ZAA detector or the impingers. The lower limit of detection for these two methods are, respectively, $0.2 \mu\text{g}/\text{m}^3$ and $10 \mu\text{g}/\text{m}^3$. Mercury was detected 51 hours after the run started. At this time, the temperature in the bottom 15.2 cm (6 in) of the retort was 300°C and 0.61 m (2 ft) above the bottom of the retort, the temperature was 470°C . A sharp peak, followed by a rapid decline and four smaller peaks at 59.0, 63.2, 65.5, and 68.5 hrs were noted. The mass of mercury in each of these five peaks, based on the area under the curve in Figure 3 is, respectively, 857, 73.8, 19.8, 23.1 and 78.1 μg . The mass of mercury in the second and fifth peaks is approximately equal to the mass of mercury in one of the 15.2 cm (6-in) zones (61 μg) while the mass of mercury in the third and fourth peaks is about 35% of that present in a 15.2 cm (6-in) zone.

This type of distribution may be explained by considering the operation of the retort. Recall that the retort consists of a series of 24 15.2-cm (6-in) heaters. These are successively turned on and off to simulate the movement of a flame front down a packed shale bed. Combustion and pyrolysis

products in the controlled-state retort rapidly move out of the heated zone and travel ahead of the reaction front. Mercury present in the raw oil shale in the top of the retort is initially released when the appropriate temperature is reached. This mercury travels some distance down the retort and either condenses when it encounters a sufficiently cool region or is selectively removed from the gas stream by chemical reactions. This process continues until the reaction front is close to the bottom of the shale bed. At this point, most of the mercury released from sections above the reaction front is revolatilized when the temperature reaches about 310°C and is swept out of the retort. This corresponds to the first peak on Figure 3. Subsequently, the mercury present in the unretorted shale in the bottom two sections plus any remaining mercury from sections above the reaction front is released. This corresponds to the second through fifth peaks on Figure 3. The mass of mercury associated with the second and fifth peaks suggests that these correspond to the release of mercury present in the oil shale in the bottom two 15.2 cm (6-in) zones of the retort. The origin of the third and fourth peaks is not clear. It is hypothesized that they are due to the release of mercury from sections above the reaction front which was subsequently removed from the gas phase, similar to the first, larger peak. The different release times suggest that three different forms of mercury may be present in the bottom zones of the retort and that each is released at a different temperature due to differences in volatility. The resultant mercury level trace is reminiscent of a chromatogram suggesting the possibility of partitioning of the mercury between mobile and stationary phases.

This type of mechanism is supported by the data for the interrupted run shown in Figure 4. Retorting was stopped 2.13 m (7 ft) from the top of the retort by rapidly cooling the retort with water. Shale in the first 2.13 m

(7 ft) was completely retorted, in the next 0.61 m (2 ft) partially retorted and wet with oil, and in the bottom 0.91 m (3 ft) unheated and wet with oil. Samples from 15.2-cm (6-in) sections, corresponding to the 24 heating elements, were collected and analyzed. The concentration of mercury, organic and inorganic carbon, total nitrogen, hydrogen, and sulfur in each of these 24 sections is plotted in Figure 4. The major element analyses are included to clarify the condition of the shale at the termination of retorting.

This figure shows that the mercury is concentrated in the 0.61-m (2-ft) segment of partially retorted shale wet with oil and 2.13 m (7 ft) from the top of the retort. The temperature at the top of this zone was 540°C and at the bottom, 75°, when retorting was stopped. The maximum mercury concentration in the partially-heated zone occurred in the section that had a final temperature of 90°C. Approximately 40% of the mercury originally present in the oil shale is located in this 0.61-m (2-ft) zone.

In contrast, less than 5% of the organic carbon and total hydrogen, sulfur, and nitrogen is concentrated in this same 0.61-m (2-ft) zone. However, the fact that this zone coincides with the section where the organic carbon and total hydrogen and nitrogen reach maxima may be significant. These three parameters peak at a final shale-bed temperature of 255°C. Duvall and Jensen (1975) showed that the amount of bitumen, heavy gas oil, and residue per gram of shale reach maxima in zones with temperatures that range from 200 to 500°C. The enrichment of bitumen and these distillate fractions in this zone may influence the passage of mercury through the zone. Substances present in the heavy ends may catalyze the formation of less volatile mercury species or may form organometallic compounds with gaseous mercury. Any mercury accumulated in the 75° to 540°C zone through these types of mechanisms may be subsequently volatilized since the mercury content of the product oil is low (<52 ppb) and

since the peak mercury concentration in the water associated with the oil-water emulsion (Figure 5) and offgas (Figure 3) do not coincide.

The sulfur distribution along the shale bed in run 60, shown at the top of Figure 4, indicates that there is no relationship between sulfur and mercury. This is unexpected since mercuric sulfide could form under the conditions within the retort. This suggests that the removal of mercury from the gas phase may be related to the formation of organometallic mercury compounds.

Impinger Measurements

The results of the impinger measurements are shown in Table 2. This table presents the mass of mercury collected in each impinger, or wash, for four separate experiments during run 69 and for one experiment during run 70. Mercury was found in experiment 4 of run 69 and during run 70.

The impinger sequence used in experiment 4 of run 69 was: (1) empty gas washing bottle to collect particulates; (2) 10 ml ICl; (3) 10 ml ICl; and (4) 10 ml 1:1:1 $\text{HNO}_3:\text{H}_2\text{SO}_4:\text{H}_2\text{O}$. The connecting lines, from the receiver to the last impinger, and each impinger, were rinsed with MIBK and the wash collected for analysis. The MIBK wash was used to remove a brown, gummy deposit that adhered to the ICl impinger walls. Concentrated HNO_3 , 6N NaOH and distilled water were evaluated for deposit removal and were found to be ineffective. This deposit was present in all impinger experiments irrespective of whether mercury was found. Its composition is unknown. It apparently acted as a scavenger for mercury.

The impinger data collected during run 69 agree with the ZAA results. No mercury was detected in the impingers prior to experiment 4. The mercury levels during experiment 4 in the 2.7-hour period when both the impingers and the ZAA detector were on line are 0.74 $\mu\text{g}/\text{min}$ (impingers) and 0.71 $\mu\text{g}/\text{min}$ (ZAA). The percent difference between these values, 4%, is considered to be excellent.

In this experiment, the ICl impingers and their washes collected 88% of the mercury and 15% of this was in solution; the balance was found in the MIBK wash. The acid impinger collected 9% of the total mercury and the remaining 3% was found in the connecting lines.

No continuous ZAA data were obtained for run 70 due to the operational problem mentioned previously. However, a single impinger measurement near the end of the run was made. The impinger sequence consisted of two ICl impingers (10 ml each) followed by two 1:1:1 $\text{HNO}_3:\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ impingers (10 ml each). This yielded a mercury emission rate of 0.14 $\mu\text{g}/\text{min}$ which is equivalent to the rates obtained at the end of run 69. The ICl impingers and their washes collected 94% of the total mercury and 100% of this was found in the MIBK wash. The balance of the mercury (6%) was found in the acid impingers and of this, 28% was found in the MIBK wash.

MERCURY DISTRIBUTION

The concentration of mercury in raw oil shale, spent shale, shale oil and retort water is summarized in Table 3 and Figure 5. These data and those presented by Fox and others (1977) indicate that there is no clear relationship between mercury levels in in-situ oil shale products and retort operating conditions with the exception of the oils (Fox and others, 1977). Some trends, however, seem to be related to the composition of the raw oil shale.

Raw Oil Shales

The mercury concentration in the raw oil shale in the 16 samples analyzed ranged from 63 to 308 ppb and averaged 115 ppb. This is on the low side of ranges reported by most other investigators. Donnell and Shaw (1977) reported that the concentration of mercury in the Mahogany zone averages 370 ppb and ranges from less than 100 to 970 ppb, while Poulson and others (1977) found that mercury from the Mahogany zone ranges from 310 to 1400 ppb and from the

saline zone, from 190 to 1400 ppb. Desborough, Pitman and Huffman (1976) determined mercury concentrations in samples from cores in the Piceance Creek Basin, Colorado, and the Uinta Basin, Utah, to range from 70 to 2900 ppb. The Colorado samples analyzed in this study were from the Anvil Points mine and the Parachute Creek area, and the Utah samples were from the vicinity of the Utah lease tracts.

Spent Oil Shales

Larger variability was found in mercury concentrations in the spent oil shales than in the raw oil shales. The levels ranged from less than 2 ppb to 6935 ppb. This large variation is related to the condensation of mercury on the shale and not the concentration of mercury originally present in the oil shale. Table 3 includes analyses for top, middle and bottom spent shales for runs 63 through 71. The top and bottom spent shales were taken from the top and bottom 15.2 cm (6 in) of the shale bed; the remainder is the middle spent shale. In all of these runs except 69, the mercury concentration in the bottom spent shale is considerably higher than in the top and middle spent shales. Retorting is typically not 100% complete in the bottom 15.2 cm (6 in) due to end effects. Therefore, some of the condensed mercury from above may remain on the spent shale.

High concentrations of mercury were found in the middle sections of runs 61, 62, and 64. It is believed that this is also related to the condensation phenomenon. Condensed mercury that is not revolatilized could result in nonuniform mercury levels in the spent shales. This might occur if the heater elements were not functioning properly or if flow channeling or blockage were to occur. In the latter case, gases produced could move backwards in the retort. Mercury would then condense behind the reaction front in a cool zone that had subsequently been heated. Thus, there would be no subsequent

opportunity for volatilization. This would cause a nonuniform distribution of mercury in the spent shale and result in sampling difficulties.

Shale Oils

Concentrations of mercury in the shale oil range from 29 to 132 ppb and average 62 ppb for the nine samples analyzed. Only upper limits were obtained for the other seven samples due to light blockage by smoke during ZAA analysis. These levels are low compared to mercury values in shale oils from other simulated in-situ retorts. Poulson and others (1977) report a range of 110 to 720 ppb for eight oils produced in LERC's 9.1-tonne (10-ton) and 136-tonne (150-ton) simulated in-situ oil shale retorts. Fox and others (1977) and Fruchter and others (1977) report a range of 100 to 350 ppb for three oils from LLL's 125-kg (276-lb) simulated in-situ retort. The likely explanation for the low mercury levels in the controlled-state retort is the lower maximum temperature reached in this facility. The LERC 9.1-tonne (10-ton) and 136-tonne (150-ton) retorts often experience maximum temperatures in excess of 1000°C. In contrast, all of the runs studied here employed a maximum retorting temperature of 540°C except 69 (760°C).

There is no obvious relationship between the mercury levels in oils from the various runs and the shale composition or retort operating conditions, except temperature. The trend noted previously by Fox and others (1977), i.e., that the weight of mercury per unit weight of oil increases as a function of maximum retort temperatures, is supported by the data presented here.

Retort Water

The mercury concentration in the unfiltered retort waters ranges from 4 to 320 ppb. These levels are comparable to those reported by Poulson and others (1977), Fox and others (1977), and Fruchter and others (1977) for mercury levels in waters from retorts operated at higher temperatures. These other works report mercury ranges of from less than 10 to 100 ppb.

The retort water data presented in Table 3 and elsewhere indicate that there is no discernible relationship between the mercury level in the waters and retort operating conditions or shale type.

During runs 69, 70, and 71, 5-ml samples of the oil-water emulsion were taken every four hours starting with the first appearance of the emulsion and terminating with its last appearance. The water was removed by centrifugation and analyzed for mercury. The oils were not analyzed due to smoke interference. The result of these analyses for runs 69 and 70 is shown in Figure 5. The data for run 71 are not presented as the mercury in all but two samples was below the detection limit. These data indicate that the mercury levels in the retort water vary as a function of time from the start of the experiment and reach a maximum about 40 hours into the run. The data for both runs 69 and 70 display this trend. The concentration of mercury in the final retort water for run 70 (98 ppb) is higher than the peak (73 ppb). This suggests that samples were not withdrawn during the time that the peak occurred. These experiments are presently being repeated using a higher sampling frequency to better define the peak. In both of these runs, the mercury levels were less than 20 ppb in samples of water collected during the first 8 to 12 hours after the first appearance of the oil-water emulsion and during the final 4 to 8 hours.

The exact mechanisms responsible for this type of distribution are unknown. By comparing Figure 3 with Figure 5, it is seen that the peak mercury concentration in run 69 occurs about 11 hrs before mercury is observed in the offgas. This implies that two different mechanisms control the distribution of mercury to the oil-water emulsion and offgas. The type of distribution obtained for the retort water could be explained if two phases were moving down the bed at different rates. One might be condensed or organically bound mercury and the

second, pyrolysis products (bitumen and oil). Interactions between the two, such as leaching, may control the concentration of mercury in the retort waters. Additional experimental work is required to better define this mechanism.

The retort water samples for runs 60 through 71 except 61 were filtered through 0.45 μm pore size Millipore Type HA filter paper and the particulates collected and analyzed. The filtered samples for runs 66, 68, 69, and 71 were maintained at room temperature for two weeks and refiltered. The resulting data, which are summarized in the last two columns of Table 3, indicate that up to 100% of the mercury in retort waters may be associated with particulates.

Many investigators have noted that considerable turbidity develops in samples stored at temperatures greater than 4°C after several days. Farrier and others (1977) found that this turbidity is composed primarily of stressed rod-shaped bacterial cells. These bacteria may act as adsorption sites or assimilate elements such as mercury which are dissolved in the retort waters.

The data in Table 3 indicate that most of the mercury (> 60% - 100%) in the unfiltered waters from runs 60, 62, 63, 69, and 70 is associated with the particulates. In the remaining runs, 5% to 20% of the total mercury content of the water is associated with the particulates. The spread in particulate data could be due to differences in treatment of the samples. It is possible that some samples with high mercury particulate concentrations were not refrigerated immediately on collection. Alternatively, some of the waters may contain constituents that would inhibit bacterial growth while others may contain constituents that would promote it.

Turbidity appeared in the filtered samples after two weeks and was removed by refiltering. Mercury was found in the resulting particulates. This amounted to all of the available mercury in run 66 and 4% - 16% in the other

three runs. The turbid water at the bottom of the container was examined with an optical microscope and rod-shaped bacteria were identified. This suggests that dissolved mercury is either adsorbed on the bacteria or biologically removed by the bacteria.

The particulates from runs 60-71 were examined using a scanning electron microscope equipped with an x-ray fluorescence system (EDAX). These investigations indicated that the mercury is not localized in specific particles and is uniformly distributed in a common matrix which could be a layer of bacteria.

The bacteria phenomenon is significant for two reasons. First, if samples are not stored immediately upon collection at 4°C, bacterial growth will alter the amount of mercury in solution. Alternatively, if the samples are not carefully agitated on analysis, an erroneously low result may be obtained. This is indicated by the data in Table 4. The filtered water from run 67 was left at ambient conditions for four months and analyzed by withdrawing a sample 2 cm from the liquid surface, 2 mm from the container bottom, and 2 cm from the surface immediately after shaking. These data indicate that a large discrepancy in mercury levels in the water can be obtained. There is a factor of 12 difference between the mercury concentration, depending on where and how the sample is taken. It is recommended that agitation be achieved continuously during sample withdrawal rather than shaking and withdrawing. This may be done with a vortex mixer, magnetic stirrer or equivalent.

Mass Balances

Mercury mass balances were used to estimate the amount of mercury released from the shale bed during retorting and to corroborate the continuous gas monitoring measurements for run 69. Table 5 presents product balances for each run, and the last column shows the percent product recovery which averaged $103 \pm 3\%$ for the 16 runs. Table 6 summarizes the mercury mass balances which

were computed from the concentration data in Table 3 and the product mass balances in Table 5. In these computations, 4% of the total spent shale is associated with the top spent shale and 4% with the bottom spent shale.

The mercury mass balances in Table 6 summarize the mass of mercury in each input and output stream except the offgas. The relative imbalance ratio in the last column is used as a measure of the amount of mercury lost in the offgas (Fox and others, 1977). Relative imbalance ratios are not presented for runs 61, 62, and 64 as the mass of mercury in the spent shale exceeded that in the raw shale. The precise cause for this imbalance is unknown. It is hypothesized that it is due to sampling problems resulting from the condensation of mercury behind the reaction front. If flow blockage occurs, volatilized mercury could be swept behind the reaction front where it could condense in cool regions that would not subsequently be heated. The imbalance was not due to analytical problems, as some of these samples were also analyzed by x-ray fluorescence as a cross check and good agreement obtained.

The data in Table 6 indicate that most of the mercury originally present in the raw shale is lost in the offgas. This was confirmed by the continuous gas measurements for run 69. The balance of the mercury is distributed among the spent shale, oil, and water, in that order.

A complete mass balance for mercury for run 69 is summarized in Table 7. This table presents the mass of mercury in each input and output stream including the offgas. The mass of mercury in the offgas was determined from the area under the curve in Figure 3. The distribution of mercury to spent shale, shale oil, retort water, and offgases is shown in the second column. The relative imbalance ratio for this run was 3%. The good closure of this mass balance corroborates the observation made for other runs, to be subsequently discussed, that up to 88% of the mercury originally present in the raw oil shale is removed from the retort with the offgases.

The data in Table 6 indicate that for the Colorado shales, 19% of the mercury originally present in the raw oil shale remains in the spent shale, 7% is distributed to the oil, 1% to the water, and the balance is lost. There are not sufficient data for the other three types of shale studied - Utah, Antrim and Moroccan - to make similar generalizations. However, it is clear that for the four samples analyzed, the distribution of mercury differs from that in the Colorado shales. For the Antrim shale, run 63, 50% of the mercury remained with the spent shale, 2% was distributed to the retort water, less than 1% to the oil, and about 47% was lost. For the Moroccan shale, run 65, 29% of the mercury remained with the spent shale, 19% was distributed to the retort water, 4% to the oil, and 48% was lost.

Only 20% of the mercury originally present in the raw shale was volatilized during run 71. This is very low compared with results presented here and elsewhere (Fox and others, 1977; Fruchter and others, 1977; Donnell and Shaw, 1977). It is likely that this is due to heterogeneity of the spent shale.

No mercury was lost from the interrupted run, 60, within the limits of experimental error. The relative imbalance of 14% is probably largely due to sampling problems and is similar to the imbalance computed for run 69. The fact that no mercury was lost during the run strengthens the volatilization and condensation mechanism proposed previously.

The mass balance data agree well with similar balances presented elsewhere. Fruchter and others (1977) found that 86% of the mercury present in the raw oil shale is distributed to the offgas, 6% to the oil, 7% to the spent shale and 0.9% to the retort water in a run of LLL's 125-kg retort. Donnell and Shaw (1977) showed that during the standard Fischer Assay, 57.7% of the mercury was distributed to the offgas, 24.9% was distributed to the oil, 5.5% to the water and 1.9% to the spent shale.

ENVIRONMENTAL IMPLICATIONS

The measurements made in this study were performed on a single simulated retort with no environmental controls to provide preliminary data for evaluating environmental impacts and for assessing control technology requirements. This work has not been confirmed in the field.

A comparison of emissions determined in this study with emission standards for other industries, indicates that control technology may be required to reduce mercury in the gas and water effluents from a commercial oil shale plant. However, additional work is required to determine the fate of mercury after release from the shale bed in a large-scale field retort. The form of the mercury and its fate in the stack plume remain to be investigated. Condensation in gas lines or the stack would reduce emissions to the atmosphere.

Mercury emissions from a 50,000 barrel per day (bpd) in-situ oil shale plant processing 100 l/tonne (24 gal/ton) shale with an average mercury content of 380 ppm (Donnell and Shaw, 1977) would release about 20,000 gm of mercury per day if the plant is located in the Piceance Creek Basin and 70% of the mercury in the raw shale is volatilized.

These emissions are compared with those from other industries in Table 8. This table indicates that mercury emissions from the hypothetical in-situ oil shale facility are greater than those from coal-fired power plants and chlor-alkali plants and within the range of emissions reported for primary mercury production plants. The reason that the mercury emissions from the in-situ oil shale plant are comparatively higher than the other industries is because a relatively large mass of oil shale must be processed to produce the end product, or the mercury concentration of the starting material is high.

In another comparison, the EPA (EPA, 1975) has reported that a total of 7.2×10^8 grams of mercury are released in the United States from all mercury

emitting industries. About 27%, 17% and 19% of this is from, respectively, paint consumption, incinerators, and pulverized coal-fired power plant boilers. In contrast, a one-million bpd oil shale industry would produce about 1.46×10^8 grams of mercury per year. This is approximately equivalent to the annual emission of mercury from one of the above three existing sources of mercury, namely, paint consumption, incineration or pulverized coal-fired power plant boilers.

Table 9 compares standards and guidelines for gaseous and aqueous mercury emissions with mercury emissions measured or estimated in this study. This comparison serves to indicate which streams from an in-situ oil shale plant must be controlled and to what extent. Generally, the concentration of mercury in offgases exceeds work-room air threshold limit values (TLV) (Threshold Limit Values for Chemical Substances in Work-Room Air, 1976) and emission standards for other industries (CFR 40, 1977). Although there are no existing regulations for mercury emissions from oil shale facilities, standards set for other industries serve as a guide to assess the significance of measured mercury levels in shale gases and waters.

The TLV's for mercury in work-room air adopted by the American Conference of Governmental Industrial Hygienists (1976) are 6 and 153 ppb total mercury including alkyl mercury for long- and short-term exposure, respectively. In contrast, the concentration of mercury found in the offgas in this study ranged from 30 to 1000 ppb. These concentrations correspond to levels measured in the total gas exiting from the retort. The magnitude of these values depends on the volume of sweep gas used, the volume of pyrolysis and combustion gases produced and the emission rate of mercury. Mercury concentrations could be higher or lower than the values reported in this table, depending on the volume of input gas used. The range reported in Table 9 suggests that a

health hazard could exist for underground workers at an in-situ plant or for workers in the vicinity of a simulated in-situ retort if gas leakage occurred. Mercury monitors should be maintained in work areas.

There are no mercury emission standards for facilities burning fossil fuels. The only existing standards are for mercury ore processing and chlor-alkali plants and facilities that dry and incinerate sludges from waste treatment plants. The emission standards for these plants are 2300 and 3200 gm/day, respectively. The 20,000 gm/day from the hypothetical oil shale plant is over four times the allowable mercury emission for mercury ore processing plants and sludge disposal facilities and suggests that mercury may have to be removed from the offgas before release. The fact that uncontrolled mercury emission levels from primary production plants and from the hypothetical in-situ oil shale plant are of the same order of magnitude suggests that about 90% of the mercury may have to be removed from the offgases of such a plant.

The effect of these emissions on ambient air quality can be estimated using a simple box model. Air quality modeling that includes air-borne transport mechanisms and which uses field mercury emission rates and local meteorological conditions is required to better define these estimates. If the 20,000 gm/day of mercury were to be released from a 150-m stack and is uniformly distributed in a 1 sq km area, the resulting ambient concentration, assuming a background ambient level of 1 ppb, would be about 20 ppb. This exceeds the lower-limit total mercury TLV for work-room air by about a factor of 3. This supports the above conclusion that mercury may have to be removed from the offgas streams.

Existing control technology for gaseous and particulate mercury emissions used in other industries may be used to reduce mercury emissions from oil shale plants. Techniques conventionally used to remove mercury from related

gas streams include cooling, mist elimination, scrubbing with hypochlorite, depleted brine or hot concentrated sulfuric acid, and the use of activated carbon (EPA, 1973; Sittig, 1976). These existing control technologies need to be evaluated for application to oil shale offgases.

The nonuniform distribution of mercury in the gas stream reported in Figure 3 will affect control technology alternatives and compliance activities. If mercury release is concentrated over a short time period as suggested by this work, it will be easier to remove, and control devices can be operated intermittently instead of continuously. Compliance monitoring will be complicated by the nonuniform emission of mercury. Extensive monitoring will be required to identify when mercury release starts and when it terminates. Although it may ultimately be possible to predict when this will occur from retort operating conditions, it is not presently possible.

The concentration of mercury in the retort water would exceed recommended water quality criteria for receiving waters if the waters were discharged locally. Mercury, as well as many other constituents, would have to be removed. Treatment and discharge, however, may not be necessary if these waters are reused on site. If treatment is required, the particulate removal phenomenon noted previously would enhance mercury removal, especially if biological treatment is used.

The volatilization and condensation mechanism that apparently controls mercury release would result in mercury condensation on large areas of the shale bed if gas channeling and nonuniform heating occur. Much of this mercury would not be revolatilized and may be readily leached by groundwaters invading the retort; this needs to be studied.

SUMMARY

This work is in agreement with the findings of others that a large fraction of the mercury present in raw oil shale is released from the retort during oil shale retorting. In simulated in-situ retorting, lesser amounts of mercury are distributed to the spent shale, shale oil, and water than to the offgas.

Mercury release is controlled by the successive volatilization and removal of mercury as the reaction front progresses down the shale bed. Oil-wet shale, enriched in heavy ends, may selectively remove the mercury from the gaseous phase.

If nonuniform gas flow occurs in commercial retorts, mercury may be condensed in cool regions of the shale bed behind the reaction front where it may be subsequently leached by groundwaters. In a 50,000 bpd or larger commercial operation, it is likely that mercury will have to be removed from the gas stream to meet air quality standards or emission standards. Existing control technologies under consideration for oil shale plants need to be evaluated to determine their mercury removal efficiency. Mercury levels in retort waters would exceed water quality standards and criteria for discharge to local streams and mercury would have to be removed from these waters before discharge.

Additional work is required to determine the fate and form of the mercury in a stack plume and the effect of the oil-wet zone on the removal of mercury from the gas phase. Mercury may condense on aerosol particles during cooling which will affect downwind deposition and inhalation patterns. Oil at the bottom of a field retort may reduce or eliminate mercury emissions to the atmosphere.

Spent shales may be heterogeneous due to mercury condensation behind the reaction front. Care must be taken in sampling them. Retort waters should be

treated to arrest bacterial growth and attendant reduction in the dissolved mercury concentration.

The method used to continuously measure mercury in the gas stream needs to be refined and transferred to those charged with monitoring. Required improvements include better calibration procedures, design of a heated probe, material selection to minimize corrosion, and redesign to facilitate parts replacement in the field for long-term use.

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Table 1. Retort operating conditions for LERC's controlled-state retort.

Run	Shale type	Run type	Shale grade liters/tonnes	Run duration, hr	Shale size range, mm	Oil yield, % Fischer assay (volume basis)	Heating rate °C/min	Isothermal advance rate, m/day	Maximum temperature, °C	Sweep gas	Gas flow rate, Std liters/sec·m ²
CS-35	Colorado	C	140	62	3-13	101	1.11	1.83	540	N ₂	2.04
CS-56	Colorado	C	123	112.9 (days)	3-13	71	0.02	0.04	540	N ₂	0.04
CS-57	Colorado	C	123	62	3-13	98	1.11	1.83	540	N ₂	2.04
CS-59	Colorado	C	88	20.5	3-13	111	11.11	7.32	565	N ₂	20.4
CS-60	Colorado	I	123	34	3-13	46	1.11	1.83	540	N ₂	2.04
CS-61	Colorado	C	88	62	3-13	92	1.11	1.83	540	N ₂	2.04
CS-62	Utah	C	126	62	3-13	95	1.11	1.83	540	N ₂	2.04
CS-63	Antrim	C	40	62	3-13	77	1.11	1.83	540	N ₂	2.04
CS-64	Colorado	C	248	62	3-13	94	1.11	1.83	540	N ₂	2.04
CS-65	Moroccan	C	79	62	3-13	88	1.11	1.83	540	N ₂	2.04
CS-66	Colorado	C	128	62	3-13	91	1.11	1.83	540	75% N ₂ +25% steam	2.45
CS-67	Colorado	C	231	62	3-13	100	1.11	1.83	540	75% N ₂ +25% steam	2.45
CS-68	Colorado	C	119	62	3-13	97	1.11	1.83	540	N ₂	2.04
CS-69	Colorado	C	118	78	3-13	98	1.11	1.83	760	56%N ₂ + 30% steam,+14%O ₂	2.45
CS-70	Colorado	C	134	62	3-13	96	1.11	1.83	540	75% N ₂ +25% steam	2.45
CS-71	Utah	C	137	62	3-13	91	1.11	1.83	540	75% N ₂ +25% steam	2.45

^a
C = completed run; I= interrupted run.

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Table 2. Summary of impinger data for controlled-state retort runs 69 and 70.

Run	Mass of mercury recovered, μg
<u>CS - 69</u>	
Experiment 1	
IC1 (1)	< 2
IC1 (2)	< 2
Experiment 2	
6.3 N NaOH (1)	< 9
IC1 (2)	< 2
IC1 (3)	< 2
Washes	< 8
Experiment 3	
10% H ₂ O ₂ (1)	< 7
IC1 (2)	< 2
IC1 (3)	< 2
1:1:1 HNO ₃ :H ₂ SO ₄ :H ₂ O (4)	< 2
6.3 N NaOH (5)	< 7
Washes	< 8
Experiment 4 ^a	
MIBK wash of empty impinger (1)	< 2
IC1 (2)	11.8
IC1 (3)	4.8
1:1:1 HNO ₃ :H ₂ SO ₄ :H ₂ O (4)	9.5
MIBK wash of connecting lines	4.1
MIBK wash of (2) and (3)	88.8
MIBK wash of (4)	0.7
<u>CS - 70^b</u>	
Experiment 1	
IC1 (1)	< 2
IC1 (2)	< 2
1:1:1 HNO ₃ :H ₂ SO ₄ :H ₂ O (3)	2.2
1:1:1 HNO ₃ :H ₂ SO ₄ :H ₂ O (4)	2.2
MIBK wash of (1) and (2)	24.6
MIBK wash of (3) and (4)	1.7

^a Total volume of gas passed through impingers was 233 liters in 2.7 hr. Impingers started 55.8 hrs after start of run.

^b Total volume of gas passed through impingers was 127 liters in 3.75 hr. Impingers started 53 hr after start of run.

Note: Numbers in parenthesis identify the order of the impingers. For example, IC1 (1) was the first impinger, and IC1 (2) the second impinger in a two impinger train.

Table 3. Concentration of mercury in raw oil shale, spent oil shale, shale oil and retort water from runs 35, 56, 57, and 59-71.

Run	Raw oil shale, ppb	Spent oil shale, ppb			Shale oil, ppb	Retort water, $\mu\text{g/liter}$		Refiltered particulates $\mu\text{g/liter}$
		Top	Middle	Bottom		Total	Particulate	
CS-35	78 \pm 6	N.S. ^a	29 \pm 2	N.S. ^a	<60	4 \pm 1	N.S. ^a	N.S. ^a
CS-56	78 \pm 6	N.S. ^a	42 \pm 3	N.S. ^a	<60	12 \pm 1	N.S. ^a	N.S. ^a
CS-57	78 \pm 6	N.S. ^a	8 \pm 2	N.S. ^a	70 \pm 5	11 \pm 1	N.S. ^a	N.S. ^a
CS-59	63 \pm 6	N.S. ^a	<20	N.S. ^a	<80	34 \pm 4	N.S. ^a	N.S. ^a
CS-60	163 \pm 13	205 \pm 16 ^b	205 \pm 16 ^b	205 \pm 16 ^b	<52	29 \pm 3	29 \pm 4 ^c	N.S. ^a
CS-61	81 \pm 4	N.S. ^a	1811 \pm 79	N.S. ^a	56 \pm 3 ^d	N.S. ^a	49 \pm 4 ^c	N.S. ^a
CS-62	73 \pm 5	N.S. ^a	121 \pm 15	N.S. ^a	<79	49 \pm 5	52 \pm 4 ^c	N.S. ^a
CS-63	138 \pm 7	63 \pm 7	69 \pm 37	261 \pm 55	<61	80 \pm 5	55 \pm 2 ^c	N.S. ^a
CS-64	215 \pm 13	37 \pm 6	6935 \pm 920	207 \pm 9	48 \pm 2	196 \pm 3	15 \pm 1 ^c	N.S. ^a
CS-65	101 \pm 11	11 \pm 1	25 \pm 3	288 \pm 59	59 \pm 1	320 \pm 25	67 \pm 2 ^c	N.S. ^a
CS-66	93 \pm 6	14 \pm 1	15 \pm 1	28 \pm 4	<82	152 \pm 13	33 \pm 2 ^c	136 \pm 3
CS-67	308 \pm 33	43 \pm 2	13 \pm 2	385 \pm 21	59 \pm 4	95 \pm 9	5.1 \pm 0.2	N.S. ^a
CS-68	80 \pm 6	24 \pm 2	11 \pm 1	238 \pm 10	46 \pm 2	150 \pm 14	16 \pm 1	6.2 \pm 1.5
CS-69	86 \pm 7	<2	15 \pm 2	3.0 \pm 0.9	54 \pm 11	103 \pm 9	79 \pm 2 ^c	14 \pm 3
CS-70	62 \pm 2	1.5 \pm 0.2	9.5 \pm 1.5	34 \pm 2	29 \pm 10	98 \pm 5	73 \pm 2 ^c	N.S. ^a
CS-71	70 \pm 1	47 \pm 3	44 \pm 3	58 \pm 2	135 \pm 20	50 \pm 2	1.9 \pm 0.3	7.9 \pm 1.2

^aN.S.: no sample.

^bInterrupted run, 23 samples analyzed; average of the 23 is 205 \pm 16 ppb.

^cMeasured by X-ray fluorescence.

^dOil dewatered with pentane.

Table 4. - The effect of bacterial growth on the homogeneity of retort water for run 67

Sample	Mercury Concentration ppb
Sample taken 2 cm from liquid surface (no shaking)	34 ± 6
Sample taken 2 mm from container bottom (no shaking)	416 ± 15
Sample taken 2 cm from liquid surface after shaking	121 ± 15

Table 5. - Mass balance data for LERC controlled-state retort runs (mg of material)

Run	Raw oil shale	Input gas (O ₂ +H ₂ O)	Spent shale	Product gas	Oil (wet)	Retort water	Percent recovery
CS-35	17,748	-	14,376	996	2142	244.0	101
CS-56	17,369	-	13,841	804	1540	241.3	95
CS-57	17,259	-	13,903	823	2294	67.9	99
CS-59	18,603	-	15,670	1542	1595	52.9	101
CS-60	17,140	-	15,306	310	907	37.1	97
CS-61	18,624	-	16,161	418	1587	99.7	98
CS-62	16,865	-	13,989	766	2163	74.1	101
CS-63	16,511	-	14,918	1306	535	495.1	105
CS-64	14,009	-	10,074	1206	3377	92.9	105
CS-65	15,820	-	13,109	633	1125	927.3	100
CS-66	16,395	618	13,114	1530	2151	338.2	101
CS-67	13,948	580	9,400	1794	3413	393.3	103
CS-68	16,252	-	13,376	656	1959	158.5	99
CS-69	16,954	976	11,380	4942	2233	351.5	105
CS-70	17,377	600	13,654	1513	2358	401.6	100
CS-71	16,927	651	13,513	1313	2384	334.5	100

Table 6. Mercury mass balances for LERC controlled-state retort

Run	Raw oil shale, µg	Spent oil shale, µg	Oil (wet), µg	Retort water, µg	Relative imbalance, ^a %
CS-35	1380	420	40	< 1	≥+67
CS-56	1350	580	< 90	3	≥+50
CS-57	1350	< 110	160	< 1	≥+80
CS-59	1170	< 320	< 130	2	≥+61
CS-60	2790	3140	< 50	1	≈-14
CS-61	1510	(b)	90	-	-
CS-62	1230	(b)	< 170	4	-
CS-63	2280	1140	< 30	40	≥+47
CS-64	3010	(b)	160	18	-
CS-65	1600	460	66	300	+48
CS-66	1520	200	< 180	50	≥+72
CS-67	4300	270	200	37	+88
CS-68	1300	280	90	24	+70
CS-69 ^c	1460	210	120	35	+75
CS-70 ^c	1080	140	69	38	+77
CS-71	1180	610	320	16	+20

Note: The symbol \gtrsim means that the actual value is slightly larger than the absolute magnitude of the recorded value, and the symbol \lesssim means that the actual value is slightly smaller than the absolute magnitude of the recorded value.

$$^a \text{Relative imbalance} = \left[\frac{\text{mass of Hg in inputs} - \text{mass of Hg in products}}{\text{mass of Hg in inputs}} \right] \times 100$$

^bNo value reported due to suspected spent shale heterogeneity.

^cExcludes the mass of Hg measured in the offgas.

Table 7. Mass balance and mercury distribution during run 69 of the controlled-state retort.

	Mass of mercury (μg)	Percent distribution (%)
<u>INPUTS</u>		
Raw oil shale	1460	-
<u>OUTPUTS</u>		
Spent oil shale	210	15
Wet shale oil	120	8
Retort water	35	2
Offgases	1050	75
Total outputs	1415	100
<u>RELATIVE IMBALANCE</u>	3%	-

Table 8. - Comparison of uncontrolled mercury emissions from various industries with a hypothetical in-situ oil shale plant.

	Uncontrolled mercury emissions gm/day	Reference
<u>COAL-FIRED POWER PLANTS</u>		
750-MW electric generating station	2,500	Billings and others, 1973
290-MW electric generating station (3.2×10^9 gm/day)	140	Klein and others, 1975
<u>PRIMARY MERCURY PRODUCTION</u>		
Rotary furnace (9.1×10^7 gm/day)	8,200-26,800	EPA, 1973
<u>CHLOR-ALKALI PRODUCTION</u>		
End-box ventilation system (9.1×10^7 gm/day)	900-6,800	EPA, 1973
Cell-room ventilation system (9.1×10^7 gm/day)	230-2,300	EPA, 1973
<u>IN-SITU OIL SHALE PLANT</u>		
50,000 bpd plant (7.9×10^{10} gm shale/day)	20,000	This paper

Table 9. Comparison of mercury standards and regulations to corresponding values for simulated in-situ oil shale offgas

		STANDARD OR RECOMMENDED VALUE	ESTIMATED VALUE FOR AN UNCONTROLLED 50,000 BPD OIL SHALE PLANT
GASEOUS AND AMBIENT	<u>TLV for Work-room Air</u> ^a	Lower Limit Short-term Exposure	
	Alkyl Hg	1 ppb 3 ppb	
	Total Hg except alkyl Hg	5 ppb 150 ppb	
	<u>Oil Shale Offgas</u>		
	Total Hg		<1 ^(b) - 1000 ^(c) ppb
	Methyl Hg		0.1 ppb ^(b)
WATER	<u>Ambient Air</u>		
	Total Hg		20 ppb ^(d)
	<u>Emission Standards</u> ^e		
	Ore processing & chlor-alkali plants	2300 gm/day	
	Sludge drying & incineration plants	3200 gm/day	
<u>In-Situ Oil Shale Plant Emissions</u>			
Uncontrolled			20,000 gm/day
WATER	<u>Water Quality Criteria and Standards</u>	<u>Concentration in Main Water Mass</u>	
	Domestic water supplies ^f	2 ppb	
	Freshwater aquatic life ^h	0.2 ppb	
	Livestock watering ^h	10 ppb	
	<u>In-Situ Oil Shale Plant</u>		
	Untreated retort water		4 - 320 ppb
Main water mass		1 - 140 ppb ^(g)	

^aThreshold Limit Values for Chemical Substances in Work-Room Air, 1976.

^bBased on a single measurement at LERC's 10-ton retort (Fruchter and others, 1977).

^cThis is the maximum concentration measured in the gas exiting from the bottom of the retort in run 69. The magnitude of this value depends on the amount of sweep gas that dilutes the gases produced from pyrolysis and combustion of the oil shale.

^dComputed for a 1 sq. km area and a 150-m stack height. Assumes complete mixing within this volume and that 70% of the Hg in 24 gpt shale with an average Hg content of 0.38 ppm is volatilized.

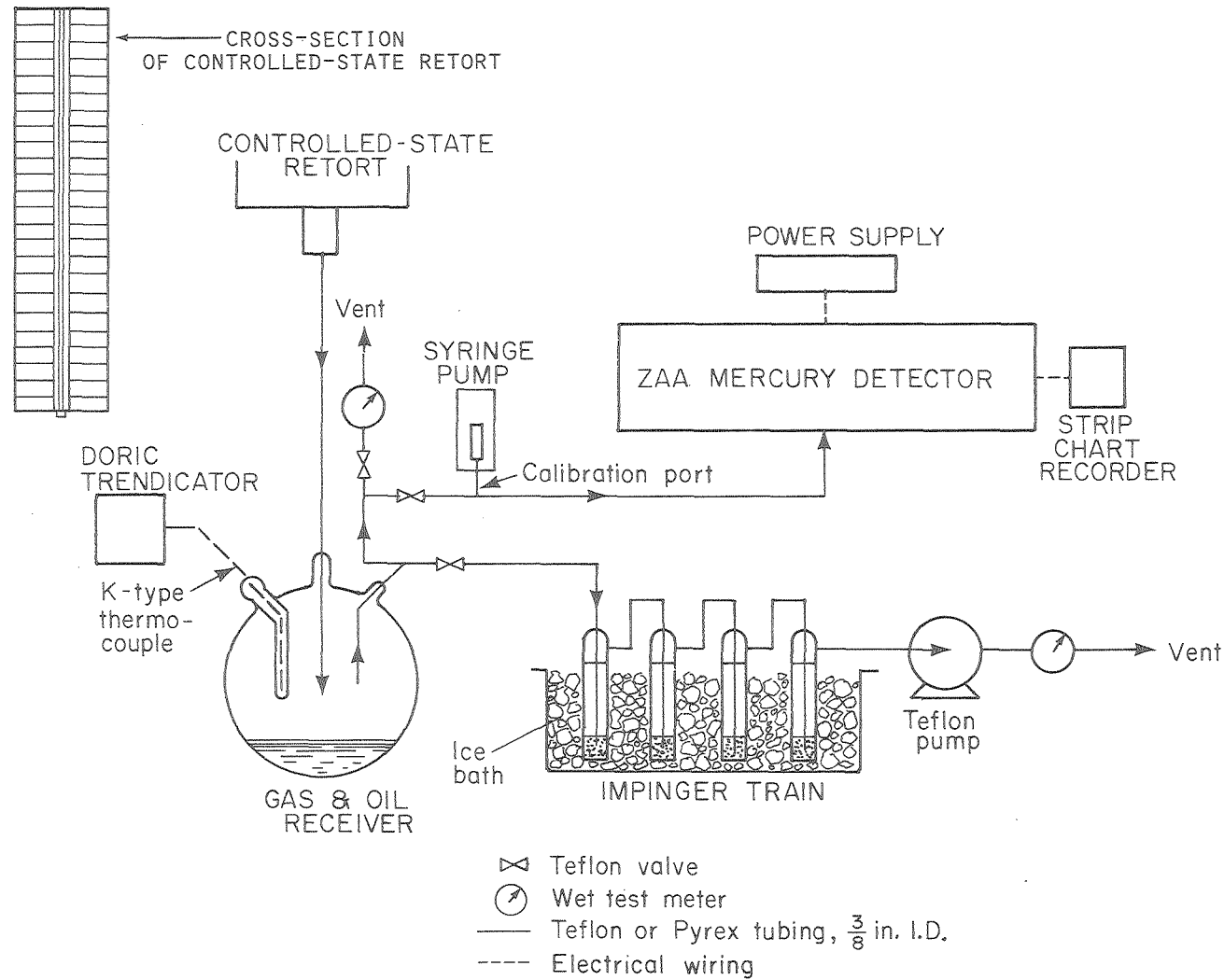
^eCFR 40, 1977

^fFederal Register, December 24, 1975

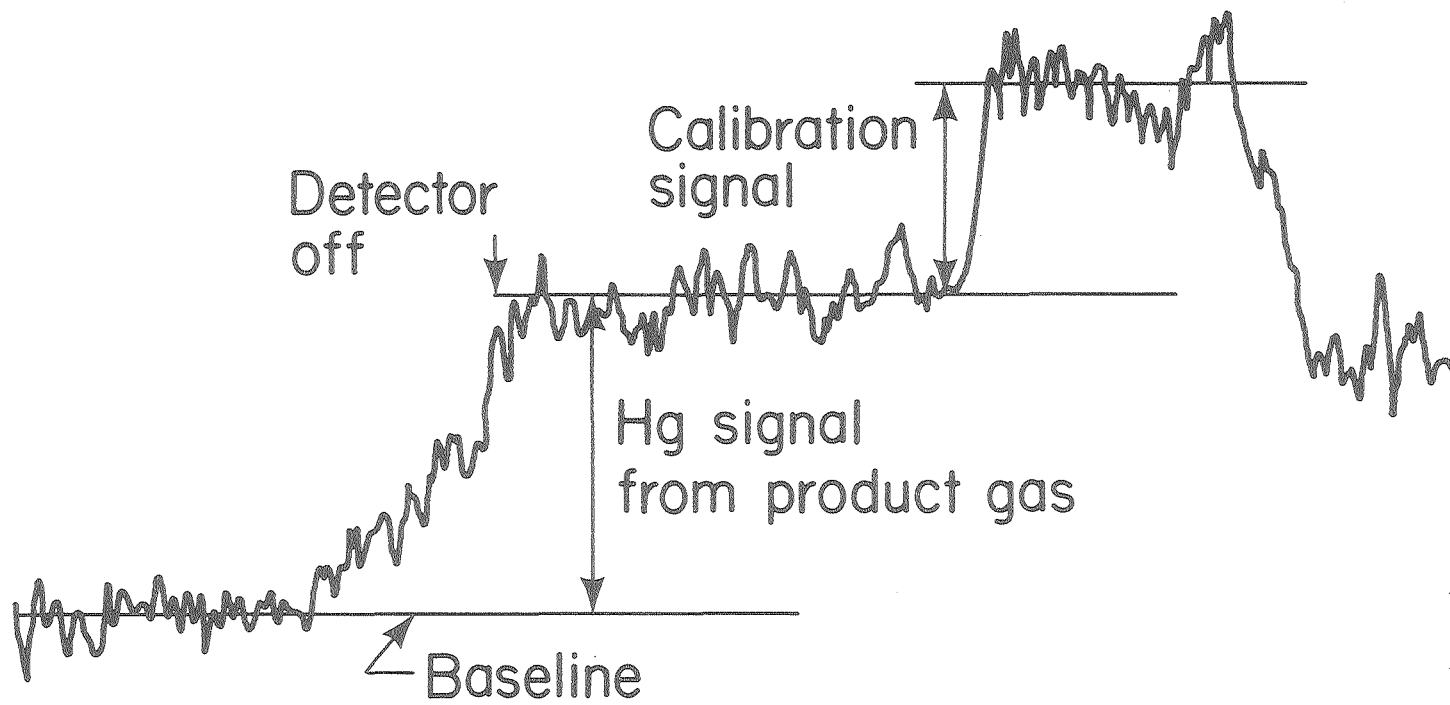
^gCalculated assuming 1 liter of water per liter of oil is produced and this is discharged directly into a local stream with a flow of 4.2 cfs.

^hWater Quality Criteria, 1973

FIGURE 1. Experimental setup for gas measurements during runs 69 and 70.

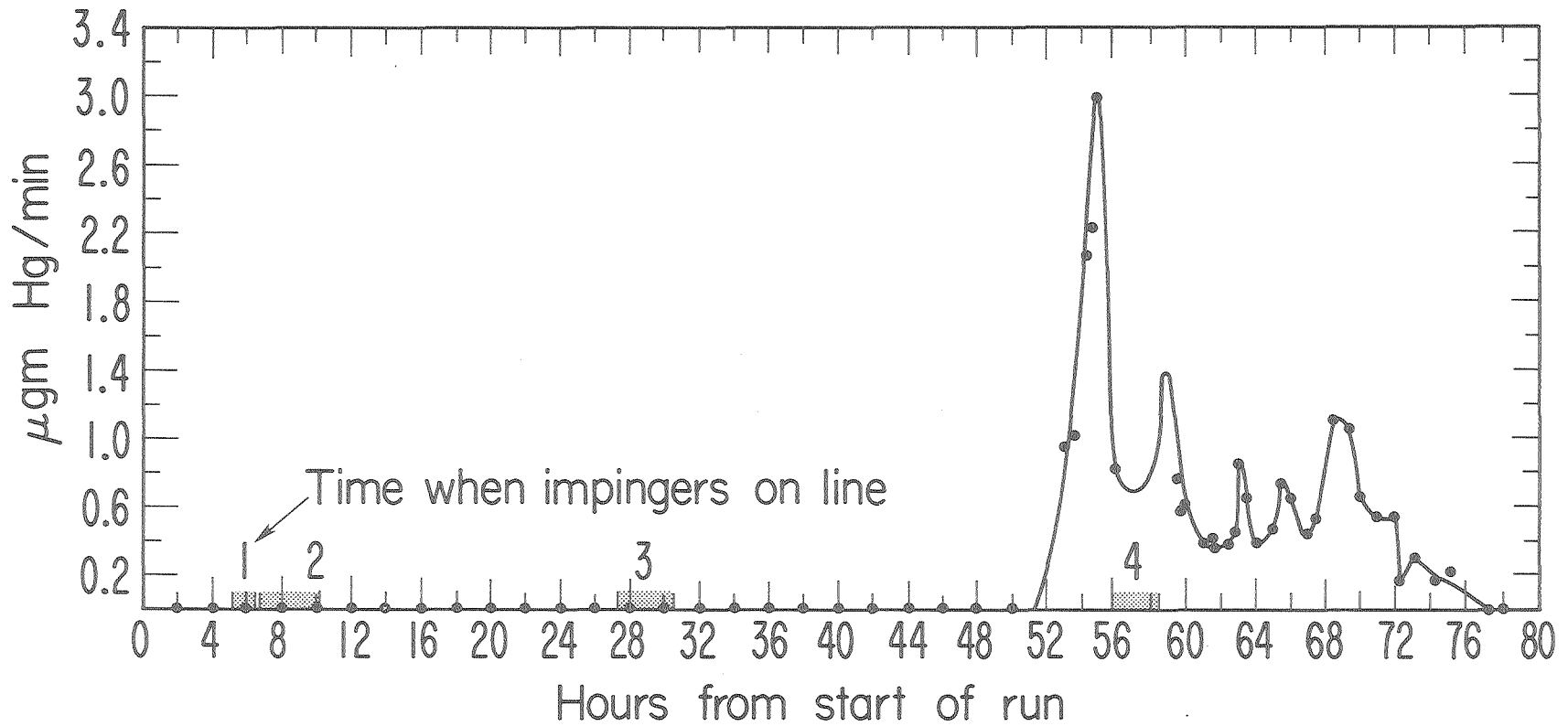


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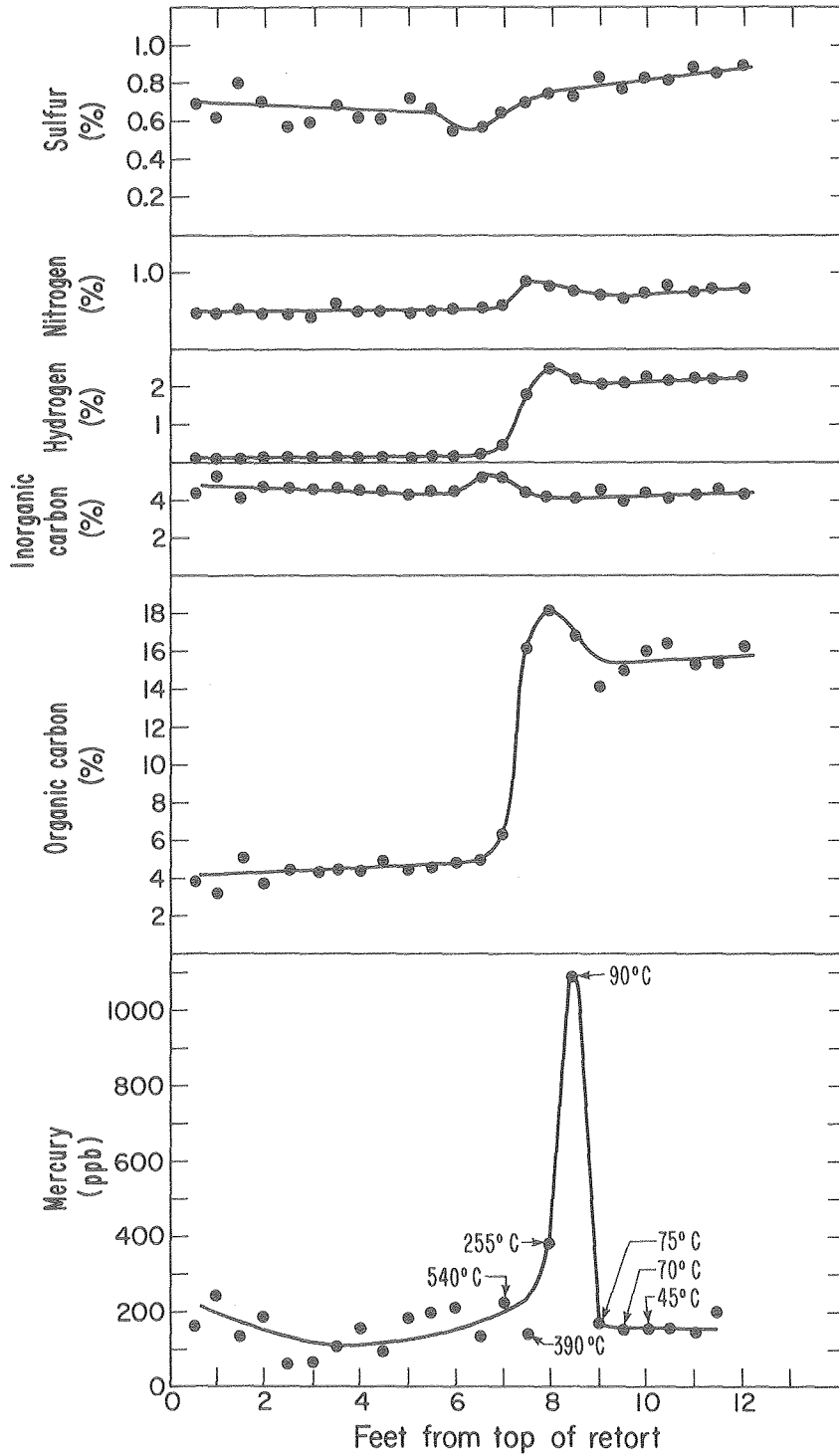
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FIGURE 2. Typical strip chart recording from continuous gas monitoring with a Zeeman atomic absorption spectrometer.



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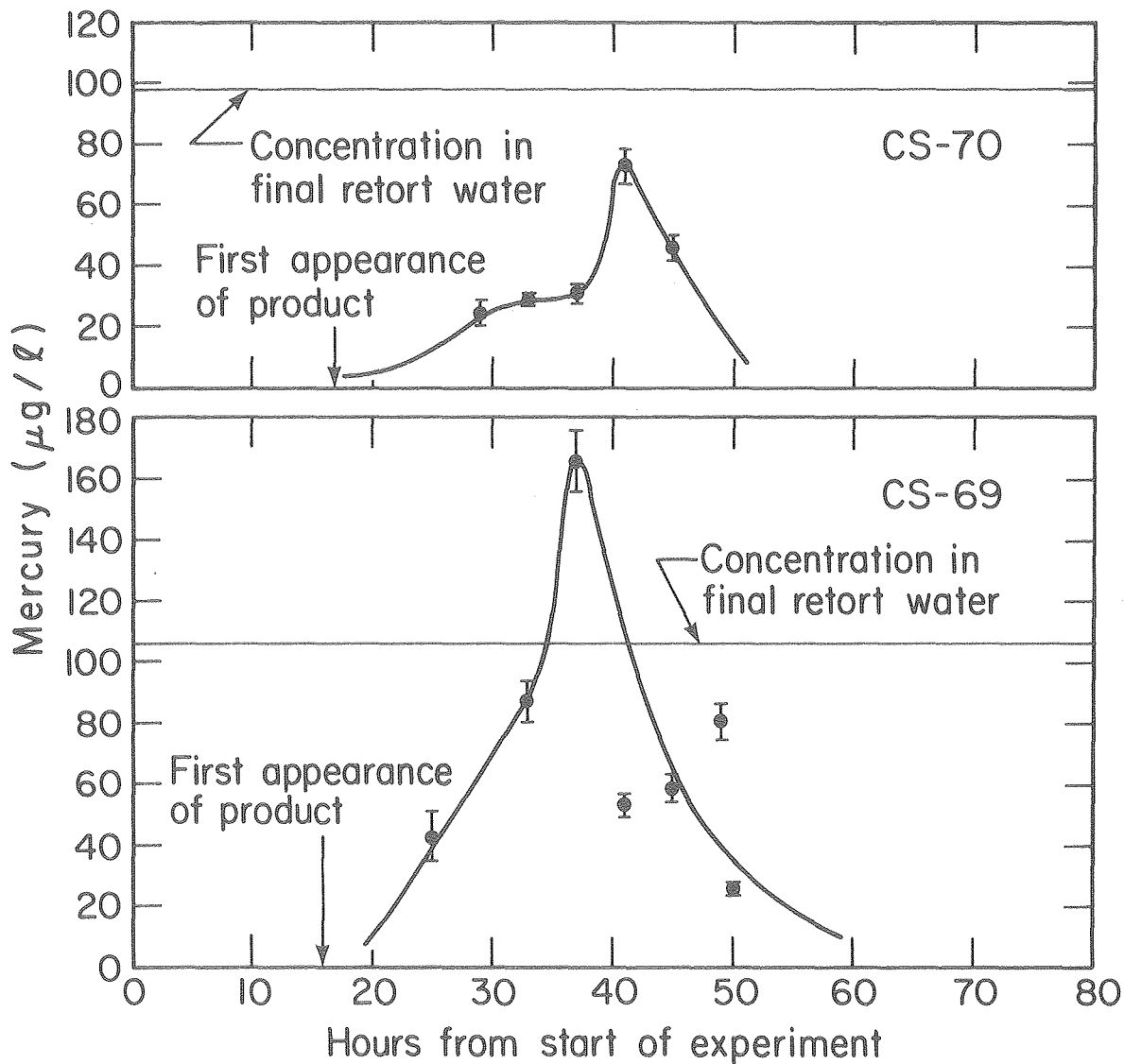
Figure 3. Time distribution of total mercury in the offgas from run 69 of the controlled-state retort



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Figure 4. Distribution of mercury, organic carbon, inorganic carbon, total hydrogen, nitrogen, and sulfur throughout the shale bed of an interrupted run of the controlled-state retort, run 60.

FIGURE 5. Time variation in mercury concentration in retort water from runs 69 and 70.



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