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Project Summary

Mercury Mass Distribution During Laboratory and Simulated *In-Situ* Oil Shale Retorting

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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 using a continuous on-line Hg monitor. For all experiments total Hg mass in the raw shale feedstock and in the processed shale was quantified. For the laboratory experiments, total Hg mass in the product oil and water was quantified.

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_2. 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 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 certain assumptions made possible estimation of atmospheric Hg emissions for underground retorting at a MIS oil shale facility producing 8×10^6 liters (50,000 barrels) of oil per day. Within the bounds imposed by the assumptions invoked, uncontrolled Hg emissions from a MIS facility could exceed emissions limitations established for other industries. Possibly, retort design parameters and retort operating procedures can be used to control Hg emissions from MIS retorting.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Shale oil derived from Green River Formation oil shale in Colorado, Utah, and Wyoming is a relatively dilute hydrocarbon resource requiring processing of approximately 8-16 kg of shale for each liter of product oil. The potential public health and environmental impacts directly associated with extensive oil shale development result largely from the vast quantity of rock heated to a minimum temperature of 500°C needed to produce a significant quantity of oil. A primary concern about oil shale development is the emission of potential atmospheric

pollutants such as sulfur dioxide, hydrogen sulfide, oxides of nitrogen, hydrocarbons, carbon monoxide, carbon dioxide, particulates, and trace elements.

Of the toxic trace elements contained in oil shale, Hg is the most likely to become an atmospheric contaminant from a large-scale oil shale development. Mercury occurs in Green River Formation oil shale in typical concentrations for sedimentary materials; on the order of one hundred to several hundred parts per billion. Although these concentrations are low, the potential exists for evolution of almost all of this Hg concentration into offgas during retorting due to the volatility of Hg and its compounds. Should this occur in the absence of control mechanisms, atmospheric emissions of Hg would significantly exceed air pollution standards established for other industries.

Existing data on the release of Hg from oil shale during retorting are rudimentary. This investigation used an experimental mass balance approach, in which offgas Hg is directly quantified, to provide additional requisite data about the mass distribution of Hg from shale to offgas and other products of retorting. Major emphasis was placed on implications of the experimental results for MIS retorting, since this extraction process appeared to be the most feasible at the inception of the investigation.

Offgas composition was determined by gas chromatography.

The laboratory experiments were augmented by a single experiment conducted during burn L-3 of Lawrence Livermore National Laboratory's 6000-kg capacity, simulated in-situ retort. In this retort, the shale is ignited at the top of the 6-m-high packed bed and the reaction front is driven downward by injecting a gas from the top. Shale originating from Federal Lease Tract C-a, Colorado was used for the L-3 burn. Input gas was an equimolar mixture of air and steam. The isothermal advance rate was 1.8 m/day, and the average maximum center-line temperature was 850°C. The experiment was terminated 100 hours after ignition with approximately the lower 0.5 m of the shale column incompletely retorted.

On-Line Hg Gas Monitor

An on-line Hg gas monitor was used to quantify total Hg in the offgas produced by the experimental retorts. This instrument is based upon a source-shifted Zeeman atomic absorption (ZAA) spectrometer. The unique background correction capability of ZAA spectrometry allows the instrument to measure Hg in retort offgas with up to 90% extinction of the analytical and reference beams due to broadband absorption phenomena. Determinations of the temporal variability of Hg

emissions and the total mass of offgas Hg emitted during an experiment were made possible by the continuous on-line feature of the instrument. Calibration gas with Hg concentrations ranging from 0-20 mg/m³ was produced by a dynamic Hg vapor generator. Additions of known concentrations of Hg were made to the offgas throughout an experiment, and calibration curves were constructed from the peak height responses to these additions.

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 gas monitor. The U.S. Environmental Protection Agency reference method 101 for the determination of gaseous Hg emissions was tested during the LLNL 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. Further, the method is too laborious for the rapid analysis of samples. Following the LLNL experiment, other techniques for the collection and analysis of inorganic, organic, and total Hg in ambient air were tested. Methods based upon gold (Au) amalgamation and/or activated carbon adsorption in packed columns proved to be superior to the reference method. These were adap-

Experimental Retorts

A laboratory retort was constructed of noncontaminating materials specifically for this investigation. The batch process retort has a 4.0 to 5.5-kg capacity; heat is supplied to the shale through the walls of the containing vessel by a tube furnace. Although larger in size, the retort is similar to the Fischer assay retort. The laboratory retort is shown schematically in Figure 1.

Replicate batches of raw shale for the laboratory experiments were prepared using Mahogany Zone shale from the Anvil Points mine in Colorado. Particle sizes retained for use after crushing ranged between 0.6 and 6.4 mm. The shale grade was 145 L/metric ton (34.8 gallons per ton) by Fischer assay. Shale grade, shale particle size distribution, and heating rate were identical for all experiments. With the furnace in full power mode, the vertical shale column was heated to a center-line temperature of 150°C and then ramped at 1°C/min to a maximum temperature of 500°C. The retort was swept from top to bottom with N₂ at a flow rate of 2 standard L/min.
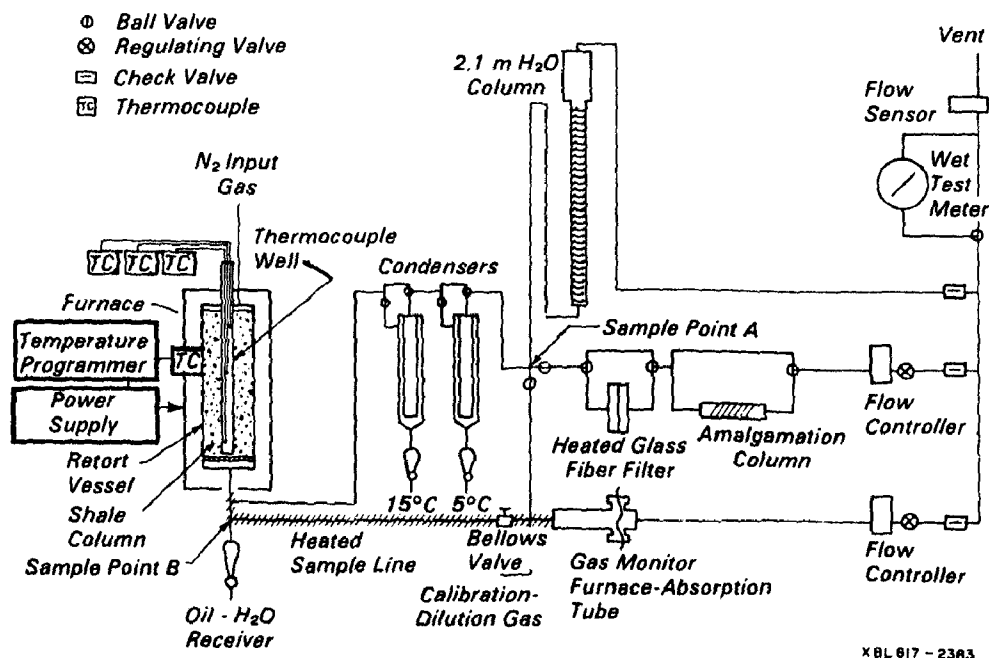

Figure 1. Schematic of laboratory retort showing installations of on-line Hg monitor and discrete gas sample apparatus.

ted and used as the alternate method for the collection and analysis of total Hg in retort offgas, as well as for the analysis of Hg in oil, water, shale, and offgas particulate samples. The separation of inorganic and organic forms of gaseous Hg was accomplished by a close adaptation of a method which combines Au-amalgamation and activated carbon adsorption.

A multi-step method was used for analysis of Hg in discrete gas samples. The first step, oxidation of the sample, is accomplished with a 1000°C quartz combustion tube packed with tungsten trioxide. Mercury evolved during oxidation is trapped in dilute hydrochloric acid and then reduced to the metallic state by the addition of a basic sodium borohydride solution. A two-stage Au-amalgamation step, which further separates interfering substances from Hg vapor and enhances analytical precision, is followed by cold vapor atomic absorption detection.

Results

Seven retorting experiments were conducted with the laboratory retort. The three initial experiments primarily were used to gain familiarity with the operation of the retort, and to develop analytical techniques. In the four subsequent experiments, accurate determinations of the distribution of Hg among the products of retorting were made.

Temperatures along the vertical axis of the shale column were monitored throughout each experiment. Vertical temperature variations were maintained within 20°C for all but one experiment. Offgas volume was continuously monitored with an electronic flow sensor which was calibrated periodically with a wet test meter. The offgas was sampled every 30 min and analyzed by gas chromatography. The major components of the offgas, excluding N_2 input gas, were H_2, CO, CO_2, and C_1-C_6 hydrocarbons. The mass of product gas was calculated by integrating product gas volume at standard temperature and pressure with gas density as determined from gas composition. Oil, water, and processed shale were collected and weighed. Material distribution for the laboratory experiments was similar to the distribution for a Fischer assay of the raw shale. The distribution for the final two experiments is shown in Table 1. For all experiments, spent shale accounted for 81% of the raw shale mass. About 12% of the initial mass distributed to oil. Mass distribution to water and gas was 1% and 2.5%, respectively. The average weight of unaccounted for material per experiment

was 3.8% of the raw shale mass.

The laboratory retort was modified throughout the course of the investigation in an attempt to obtain closure of an elemental balance equation for Hg. Substitution of a stainless steel retort vessel for the original ceramic vessel, and the use of a stainless steel heated sample line in place of an unheated line, substantially decreased the observed imbalance in the equation. Ancillary experiments demonstrated that Hg was condensing and adsorbing on the ceramic and unheated stainless steel components of the retort. Mercury mass distributions for the final two experiments, after the modifications to the retort were made, are shown in Table 1. Eighty percent to almost 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 product oil. Approximately 2% of the Hg remained in the processed shale. The small quantities of product water combined with relatively low Hg concentrations in water resulted in negligible mass distribution of Hg to water.

Mercury evolved from shale over a shale temperature range of 160°-320°C at the 1°C/min heating rate used in the laboratory experiments. The peak in Hg evolution occurred at approximately 240°C. The evolution of low molecular weight hydrocarbon gases corresponds closely (±25°C) to the production of oil at

the 1°C/min heating rate. From this relationship and the temperature profile for the evolution of C_1-C_5 hydrocarbons, oil production was estimated to begin at 275°C and to achieve a maximum value at 400 °C. Thus, Hg in raw shale volatilized almost entirely in advance of oil formation.

During one laboratory experiment, the temperature at the bottom of the shale column lagged substantially behind the temperatures at the center and top of the column. Mercury was not detected in the offgas until the bottom shale column temperature reached 160°C, even though the center of the column was at the temperature of maximum Hg volatilization.

A gaseous Hg speciation sample was collected during the Hg evolution peak of the final laboratory experiment. Results of the analysis of this sample indicated that organomercurials were the dominant chemical species of Hg as the offgas left the retort. Additional work is required to substantiate this observation. Several particulate samples were obtained from the offgas of the laboratory retort. Concentrations of particulate phase Hg were less than 2% of total offgas Hg concentrations.

Intercomparisons of the on-line gas monitor method and the discrete gas sample method for the determination of offgas Hg concentrations were made during two laboratory experiments. No

Table 1. Material Distribution and Mercury Mass Distribution Patterns for Final Two Laboratory Experiments in Which Losses of Gaseous Mercury to Components of Retort Wire were Minimized

	Material Distribution		Mercury Mass Distribution		
	Mass (g)	Distribution (%)	Hg Conc. (µg/g)	Hg Mass (µg)	Distribution (%)
Experiment E6					
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	79.7±2.9
Total		96.0			88.4±4.7
Imbalance		-4.0			-11.6
Experiment E7					
Raw Shale	4081		0.155±0.007	632.6±28.6	
Spent Shale	3297	80.8	0.004±0.002	13.2±0.7	
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	104.5±6.3
Total		96.3			111.3±8.2
Imbalance		-3.7			+11.3

statistically significant difference was found between Hg concentrations determined by the two methods when samples were obtained from the same location.

Partitioning of Hg from shale to offgas was determined for the LLNL simulated *in-situ* retort experiment. The pre- and post-retorting contents of the shale column were estimated from analyses of representative shale samples. After retorting, 15% of the initial Hg remained in the column. The majority of the remaining Hg was present in the bottom 0.5 m of the column which mostly was unretorted due to early termination of the burn. Offgas Hg concentrations at a point downstream from the retort were determined periodically with the on-line gas monitor. An estimated 11% of the initial Hg content of the shale partitioned to the offgas during the first 96 hours of the burn. A large portion of the 74% Hg unaccounted for may have evolved during the final four hours when the bottom of the shale column reached the temperature of Hg volatilization. However, because of electronic problems associated with the abnormally high ambient temperature no offgas Hg measurements were obtained during this period.

Discussion and Conclusions

The Hg mass distribution results obtained during this investigation were compared to previously observed Hg mass distributions for LLNL's simulated *in-situ* retorts; Laramie Energy Technology Center's controlled-state retort; the Paraho semi-works; combustion surface retort; and a Fischer assay. The comparison emphasized the fact that the majority of Hg in raw shale will be emitted to the offgas during retorting. Gaseous Hg emissions are not, however, expected to be uniform throughout an MIS retort burn.

In an 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. One of the authors (Fox) previously presented evidence which indicated that the timing of the appearance of Hg in the offgas from an MIS retort would be controlled by the adsorption of Hg on unretorted or partially retorted shale.

The laboratory experiment in which the bottom shale column temperature lagged behind the center temperature provided additional evidence that adsorption of Hg on unretorted or partially retorted shale would control the timing of the release of offgas Hg from an MIS retort. The ob-

served Hg emissions behavior for that experiment can be explained by the adsorption of Hg volatilized from the center of the shale column on cooler shale at the bottom of the column and subsequent revolatilization when the bottom of the column reached 160°C.

The difficulties encountered in obtaining closure of the Hg mass distribution equation for the laboratory retorting experiments were attributed to adsorption and condensation losses of gaseous Hg to components of the retort. These losses were substantial, amounting to 50% or more of the Hg content of the raw shale. Losses of gaseous Hg to retort materials also are expected to limit extensively the quantity of Hg reaching the atmosphere during MIS retorting.

Atmospheric Hg emissions were estimated for underground retorting at an MIS oil shale facility. Production of 8×10^6 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 ppb; (2) processing of 2000 kg of shale per barrel of oil produced, (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 from Hg ore processing facilities and Hg cell chlor-alkali plants to 2300 grams of Hg per 24-hour period. Emissions from wastewater sludge drying and incineration plants are not to exceed 3200 grams per 24-hour period.

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 an 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 an 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 developed concerning the future necessity for offgas Hg emissions monitoring or controls at MIS oil shale facilities.