**Title**

OCTOBER MONTHLY PROGRESS REPORT - DISTRIBUTION OF As, Cd, Hg, Pb, Sb AND Se DURING SIMULATED IN-SITU OIL SHALE RETORTING



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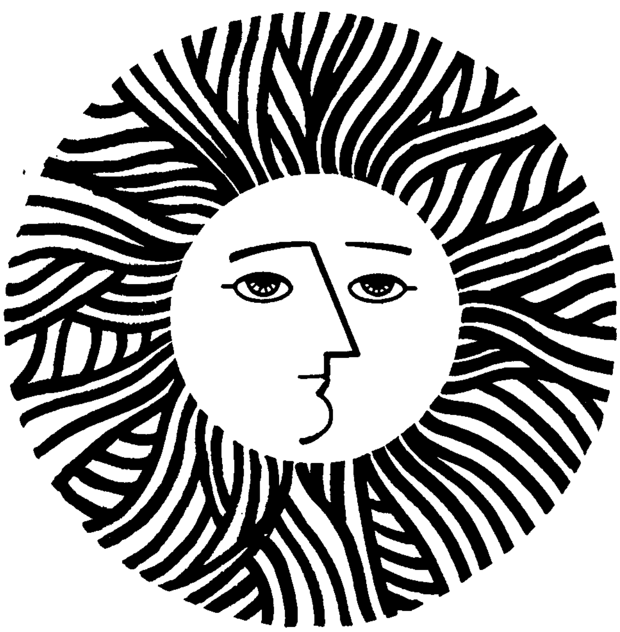
## ENERGY & ENVIRONMENT DIVISION





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November 8, 1979

TO: Bob Thurnau

FROM: D. C. Girvin, A. T. Hodgson and P. Fox

RE: October Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb and Se during
Simulated In-Situ Oil Shale Retorting
LBID-136

The progress reports to be submitted this year will maintain the same format used in previous reports. Before describing the progress for October 1979, I would like to briefly summarize the current status of each task and describe what is to be included under each of these task headings in this and future reports.

Work on Task 1, Analytical Methods for Oil and Water Samples, is nearing completion. Additions, modifications and improvements to these methods will be reported as part of Task 1. The level of effort devoted to this task will be significantly reduced in the following months.

Work on Task 2, Analytical Methods for Gas Samples, is not complete. Considerable testing and modification of the ZAA spectrometer for analysis of arsenic, cadmium and selenium in the offgas stream will continue during the laboratory retort experiments. This will include testing and modification of the ZAA furnace and development of calibration techniques for these elements. Work on the mercury gas monitor and dynamic calibration system is complete. However, improvements will be incorporated into the mercury instrument, and experiments will be conducted to help elucidate the matrix effects encountered during offgas sampling. This work will be described under Task 2.

Task 3, Design and Construction of Experimental Apparatus, has been completed. If significant modifications to the retort are made they will be described under this heading.

Task 4, Laboratory Partitioning Studies, is just getting started and will be the major focus of activity during this second year of the project.

Task 5, Pilot-Scale Partitioning Studies, was originally intended to begin during the third year. However, due to the margins of this project and the mercury field studies project, Task 5 will be retitled Field Studies. Progress toward the proposed field measurements of mercury at Lawrence Livermore Laboratory, Laramie Energy Technology Center and Tract C-a will be presented as part of Task 5.

## WORK PROGRESS

### Task 1. Analytical Methods for Oil and Water Samples

In October, development of analytical methods for oil and water samples was confined to the analysis of oil for arsenic using graphite furnace atomic absorption spectroscopy. Two different techniques were investigated.

The first technique employs a nitric acid digestion followed by direct injection into the graphite furnace. Initial attempts in which oil was digested in a beaker resulted in a large loss of arsenic. As a result, the digestion is now carried out in a boiling flask fitted with a condenser. Even with this apparatus, the digestion must proceed slowly under carefully controlled temperature conditions. In addition, a nickel nitrate solution must be added to the flask to help reduce the volatilization of the analyte. Quantitative recovery of arsenic from oil which has been spiked with an organic arsenic compound has been obtained using this technique. Since approximately 50 ml of acid is required to digest one gram of oil and concentration of the acid by evaporation is prevented by the volatility of arsenic, the overall sensitivity of the method is 1.0 mg/L.

The second technique for the analysis of arsenic in oil employs a simple dilution of the oil with xylene and direct injection of the diluted sample into the graphite furnace. Nickel is added to the furnace in a separate injection and dried prior to the introduction of the diluted oil. This is done to prevent loss of analyte during drying and charing. Several difficulties have been encountered with this technique. The observed concentrations are dependent upon the dilution factor up to dilutions of 1:200. In addition, analyses must be performed by the method of standard additions and, even then, the imprecision in the results is approximately 10-15%. Although the relative ease of this technique makes it attractive for routine analyses, it may have to be dropped in favor of the digestion technique due to the lack of precision.

Task 2. Analytical Methods for Gas Samples

Matrix effects necessitated the use of the method of standard additions to quantify mercury levels during the field test of the Zeeman mercury monitor at Lawrence Livermore Laboratory in May 1979. These matrix effects were not directly related to the broadband UV extinction of the analytical line. With the furnace operating at 900$^{o}$C, the matrix effect manifested itself as a factor of two reduction in the slope of calibration curves obtained by introducing mercury vapor into the offgas stream relative to the slope obtained by introducing mercury vapor into air.

A series of experiments are being conducted to elucidate this effect and possibly minimize it during future retort experiments. The objectives of these experiments are: 1) to examine the effect of hydrogen sulfide gas and thiophene and pyridine vapors on the response of the ZAA to a constant concentration of mercury and 2) to examine the resistance of the organic vapors to thermal decomposition in the furnace. Hydrogen sulfide was chosen because it was present in large concentrations in the Livermore L-3 offgas and because it reacts readily with mercury to form highly stable sulfides which possibly may not be detected by the ZAA. Pyridine and thiophene were chosen since they may be representative of nitrogen and sulfur-containing cyclic organic compounds in the offgas. In addition, the sulfur in thiophene may react with mercury. These experiments will continue into November, and the results will be reported next month.

Two changes in the design of the mercury monitor system were made this month. First, the seals on the heated sample probe were improved to eliminate possible leaks of offgas to the atmosphere. This redesign included modification of the nose piece of the probe and the bushings in the gate valve (See 2nd quarterly report). These components are being built and will be tested next month. Second, the ZAA furnace has been redesigned to minimize broadband UV absorption of the analytical line due to condensation of UV absorbing organic vapors on the quartz windows. This modification will increase the temperature of the windows by decreasing the distance between the windows and the supports used to supply current to the furnace. In addition, the dead volume and the residence time of gas trapped between the window and the gas exit tube has been reduced by a factor of five. Gold O-rings will be used to seal the quartz windows to the furnace. The new furnace will be built and tested next month. Since thiophene vapor strongly absorbs in the region of 253.7 nm and readily condenses on the quartz windows of the old style furnace, thiophene can be used to test the effectiveness of the furnace modifications.

Task 3. Design and Construction of Experimental Apparatus

During October, construction of the laboratory-scale oil shale retort was completed, preliminary tests were conducted, and preparations were made for the first retort run.

The gas handling system for the retort has been modified by the installation of a bypass line for offgas flow which is in excess of the regulated flow through the furnace of the spectrometer. Pressure drop to the atmosphere across the flow controller is slightly less than 3 psi. As gas is evolved from the shale during retorting, pressure upstream of the flow controller will begin to increase. When the pressure exceeds 3 psi, the excess gas will bubble through a 2.1 meter high water column, and the amount in excess of the regulated flow will bypass the controller. A flow sensor has been ordered and will be placed in the bypass line or in the recombined offgas stream immediately upstream of the wet test meter (WTM). Total gas flow is currently being determined with the WTM.

Task 4. Laboratory Partitioning Studies

Three barrels of shale from the Anvil Points Mine have been obtained. A small quantity of this shale has been crushed, ground and sieved with 85% of the total weight of the particles falling between 1/4 inch and 30 mesh. Particles smaller than 30 mesh will not be retorted.

The first batch of shale will be retorted early in November. Since the purpose of this run will be to evaluate the performance of the retort, no attempt will be made to analyze the offgas with the ZAA mercury monitor. Temperatures will be measured throughout the system, gas flows will be determined with the flow controller and the WTM, and liquid products will be collected and weighed. Any significant problems which are encountered will be corrected before additional retort runs and offgas monitoring are initiated.

Task 5. Field Studies

Plans to measure mercury at the Laramie 150-ton retort in November 1979 have been abandoned since the primary objective of the November run is to cure the new refractory lining which was installed this summer. Instead, we are planning to participate in the subsequent air-steam run at the 150-ton retort as part of our currently funded field program. This next run is scheduled for May 1980.

Arrangements have been made to use the Zeeman mercury field monitor to measure mercury during Lawrence Livermore Laboratory's one day run of their small retort in January 1980. This will be run S-19.

Plans are also being made to measure mercury with the Zeeman mercury monitor during Rio Blanco's in-situ field experiment at tract C-a in the summer of 1980. The scope of work for this experiment and the proposed budget are being drafted and will be submitted for your consideration and comment in the near future.

## PROJECTED WORK

The projected work for November 1979 is as follows:

Task 1. Set up instrumentation to examine AAS cold vapor and ZAA techniques for the analysis of mercury in retort water and oil.

Task 2. Test modified heated sample probe and furnace. Design a furnace for arsenic, cadmium and selenium gas analyses and initiate fabrication. Fabricate a light source temperature control unit for the ZAA. Complete mercury matrix interference tests.

Task 4. Retort the first batch of oil shale and make modifications to the system as required.

Task 5. Make initial preparations for the January 1980 Lawrence Livermore Laboratory retort run.

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