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

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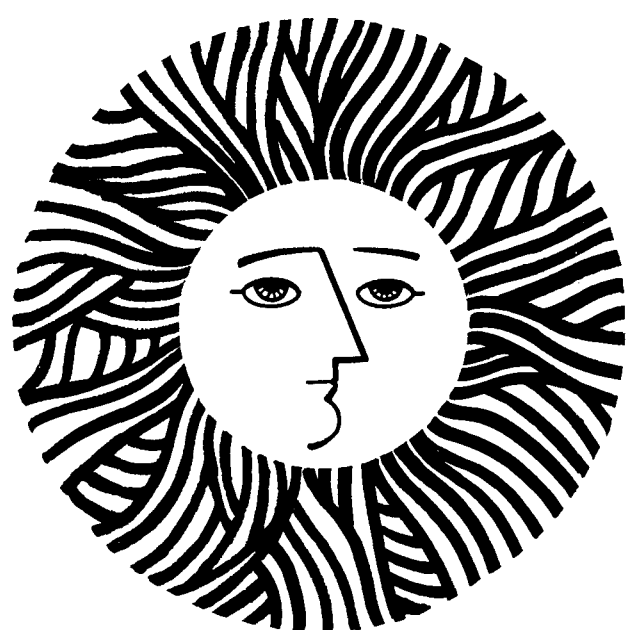
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February 8, 1980

TO: Bob Thurnau

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

RE: January Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb and Se During
Simulated In-Situ Oil Shale Retorting
LBID-174

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

The batch sample mercury ZAA is not operational yet due to delays in the fabrication of the dual chamber nickel furnace. However, a batch sample cadmium ZAA, equipped with the newly developed cadmium gas monitor light source, was set up and used to determine cadmium concentrations in raw and spent shale from our retort run LBL-1 and from Lawrence Livermore Laboratory's (LLL) retort run L-3 (see Task 5).

Water produced during retort run LBL-1 was reanalyzed for mercury by cold vapor AAS. No mercury was detectable after a month of storage. Consequently, we will continue to immediately analyze water samples for mercury and will reevaluate sample storage procedures.

Waters produced during retort run LBL-2 were oxidized on the day of collection with potassium permanganate/persulfate prior to mercury analysis by cold vapor AAS. The oxidation step introduced a variable mercury blank which obscures the comparison of results of oxidized and unoxidized samples. Additional work is required to eliminate the blank or to develop an alternate oxidation procedure.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

The ZAA mercury light source temperature stability tests were conducted for fixed ambient temperatures of 14°C and 34°C. The objective of these tests was to establish whether the Borg-Warner thermoelectric heat pump (bi-directional P-N junction) has the heating and cooling capacity and the control sensitivity necessary to maintain the light source at 25°C under static thermal loads which may be encountered during field use of the ZAA mercury monitor. The tests

showed that with constant ambient temperatures of 14°C and 34°C, the thermoelectric device can maintain the light source assembly at 25±0.2°C. An identical result was obtained in November for an ambient temperature of 20°C. These results demonstrate that the heat pump has the necessary heating and cooling capacity and temperature stability to maintain a lock-in amplifier baseline drift of less than ±0.02 mg Hg/m³, with a light source operating temperature of 25°C. Completion of the mercury light source temperature controller will require modification of the control circuit, which drives the thermoelectric device, so that the desired temperature of 25±0.2°C is maintained during major changes (5°C/hr) in ambient temperature. This will be done during February, March, and April.

TASK 4. LABORATORY PARTITIONING STUDIES

A laboratory retort experiment LBL-2 was conducted in late January with ZAA instrumentation used to make on-line mercury measurements in the offgas. The objectives of the experiment were (1) to determine the mercury volatilization rate and the offgas mercury concentration as a function of retort temperature for retorting conditions which will be used in subsequent mercury partitioning experiments and (2) to evaluate retorting procedures and analytical strategies for mercury measurements in offgas, oil, and retort water. The experiment was highly successful, and both objectives were achieved.

The shale grade, size distribution, nitrogen input-gas flow rate (2 L/min) and other retorting parameters used for LBL-2 were the same as those used for LBL-1. The shale column was heated to 150°C then the furnace was programmed for a 1.0°C/min temperature increase to 550°C. The observed temperatures along the center line of the shale column increased at a rate which was virtually identical to the furnace's programmed rate of increase. The total volume and flow rate of the offgas were measured, and oil, water, and spent shale were collected in order to obtain a material balance. Oil and water were retained for mercury analysis. Untreated and potassium permanganate/persulfate oxidized water samples were immediately analyzed by cold vapor AAS.

Offgas sampling and ZAA operating conditions were identical to those used for LBL-1 except that a "short" ZAA furnace with a 5-cm, rather than an 18-cm, absorption tube was used in order to extend the concentration range over which ZAA response is linear. The concentration of mercury in the offgas as a function of the temperature at the center of the shale column is shown in Figure 1. Below 177°C and above 350°C mercury concentrations were less than or equal to 0.01 mg/m³. A single broad mercury peak was observed between 180°C and 340°C with a maximum concentration of 2.14 mg/m³ occurring at 243°C. The slopes of ZAA calibration curves in offgas were equal, within experimental errors, to the slopes obtained in nitrogen, indicating an absence of matrix effects throughout the experiment. Mercury was volatilized before oil production began. At 350°C, oil started to collect in the oil/water receiver below the retort, and broadband UV absorption of the ZAA photomultiplier tube signal increased dramatically. Dilution of the sample gas with nitrogen was necessary in order to continue ZAA mercury measurements above 350°C.

TASK 5. FIELD STUDIES

Cadmium concentrations were determined in raw and spent shale samples from the interrupted LLL retort run L-3. Cadmium measurements were made on composite samples taken at 0.3 m intervals from the retorted shale column. Mercury measurements will also be made on these samples. Before these results can be reported they must be normalized to a consistent weight basis to account for the change in density of the shale which occurs during retorting.

PROJECTED WORK

The projected work for February is as follows:

Task 1. Analytical Methods for Oil and Water Samples.

- The assembly of the batch ZAA spectrometer for Hg analysis in oil and raw and spent shale will be completed.
- An attempt will be made to use ozone/UV oxidation for treatment of retort water prior to mercury analysis by cold vapor AAS.

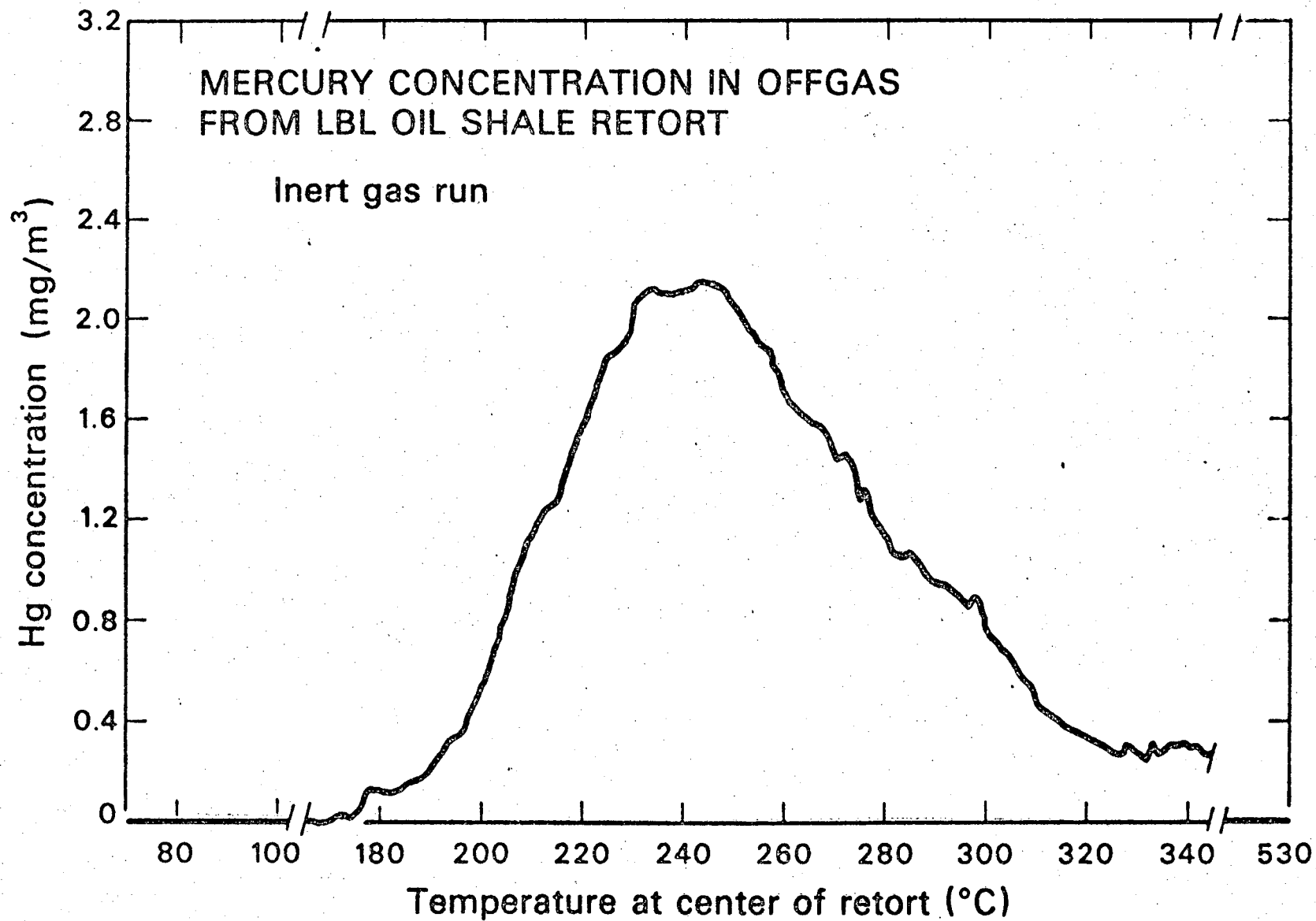
Task 2. Analytical Methods for Gas Samples.

- The circuitry for the Hg light source temperature controller will be designed.

Task 4. Laboratory Partitioning Studies

- Analysis of data from LBL-2 will be completed. Preparations for the third retort experiment, LBL-3, will be made. LBL-3 will be conducted in late February or early March. The objective of LBL-3 will be to conduct the first complete mercury partitioning experiment and to obtain preliminary partitioning data for As, Cd, and Se.

Figure 1. Mercury concentration in offgas from oil shale retort.
Inert gas run LBL-2



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