Title

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

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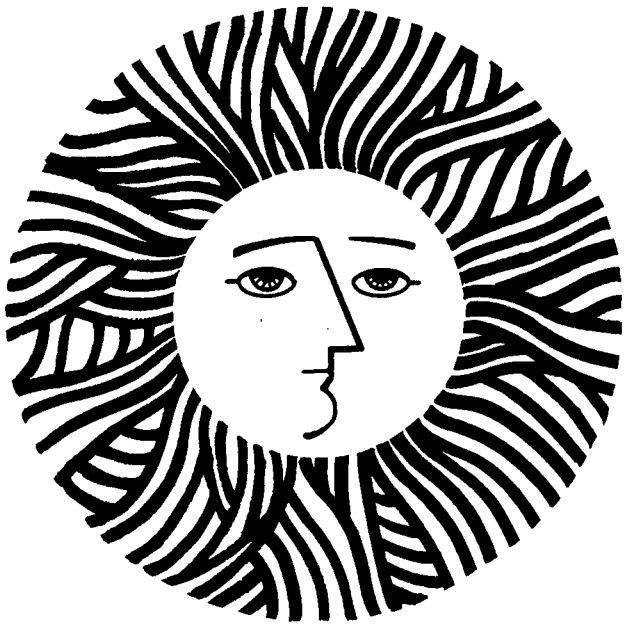

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September 11, 1980

TO: Bob Thurnau and Pat Fair

FROM: D. C. Girvin and A. T. Hodgson

RE: August Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb, and Se
During Simulated In-Situ Oil Shale Retorting
LBID- 291

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

In July, five samples of shale oil, produced during retort runs LBL-02 and LBL-03, were submitted for neutron activation analysis. The results of this analysis have not been received. Consequently, we have not been able to evaluate the accuracy of the WO_3 combustion-amalgamation-ZAA method for Hg in shale oil, nor have we done any additional developmental work on the method.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

Gold-plated glass-bead amalgamation tubes were placed in the auxillary sampling line of the retort during run LBL-04 (see Task 4, Laboratory Partitioning Studies). Offgas Hg samples were collected on Au amalgamation tubes placed in two positions. In the first position, offgas passed directly through the amalgamation tube without any prior heating or oxidation. In the second position, offgas first passed through a WO_3 packed quartz combustion tube heated to 1000°C then through the amalgamation tube. Samples collected in the first position were analyzed by thermally desorbing the Hg into nitrogen carrier gas which passed through a WO_3 combustion tube at 1000°C. Subsequent analytical steps were identical to those described in the July monthly progress report for the analysis of oil samples. The samples collected in the second position were analyzed by thermally desorbing the Hg into helium and recollecting it on another amalgamation tube. The Hg was then thermally desorbed from the second tube and swept directly into a ZAA spectrophotometer. The results of these analyses are summarized in Task 4.

As described in the July monthly progress report, a Perkin Elmer HGA 2000 graphite furnace was modified to heat a continuous stream of offgas.

Tests prior to retort run LBL-04 showed that the device could heat the offgas stream to approximately 2000°C for 7 to 10 minute intervals before overheating. In addition, repeated use of the baffled graphite tube with nitrogen for a total of 40 minutes did not significantly deteriorate the tube.

For retort run LBL-04, the HGA-2000 was installed immediately upstream of the stainless steel ZAA furnace so that offgas could be periodically routed through the HGA-2000 before it entered the ZAA furnace. Only limited use of the HGA-2000 was made during run LBL-04 (see Task 4). Therefore, additional testing and use of the device during the next retort run are warranted.

During September, the ability of the HGA-2000 to reduce or eliminate matrix suppression due to the presence of hydrogen sulfide will be examined. The effect of H_2S on the ZAA absorbance was previously examined and reported in the December 1979 monthly progress report. The H_2S test will also provide an opportunity to optimize the HGA prior to its use during LBL-5.

TASK 4. LABORATORY PARTITIONING STUDIES

An inert gas, laboratory retort run, LBL-04, was conducted on August 14. The shale grade, particle size distribution (-¼ inch to +30 mesh), nitrogen input-gas flow rate (2 l/min), heating rate (1.0°C/min), and maximum temperature (500°C) were the same as those used for runs LBL-2 and LBL-3.

Reduction of the offgas Hg data for run LBL-04 is complete. The profile of offgas Hg concentration versus retort temperature is nearly identical to that reported for run LBL-02 in the February monthly progress report. A total of 295 µg of Hg, or 38% of the total Hg initially present in the raw shale, was observed in the offgas. This is in good agreement with results from runs LBL-02 and LBL-03.

Offgas Hg concentrations were also determined by the Au amalgamation technique and compared with Hg concentrations determined by the ZAA monitor. Three of the four amalgamation samples that were collected in position one without prior WO_3 oxidation, produced concentrations which agreed with the corresponding ZAA monitor concentrations (±2%). The remaining sample from position one and all of the samples from position two yielded concentrations which were significantly less than ZAA monitor concentrations. Consequently, collection of amalgamation samples without prior WO_3 oxidation appears to be the preferred technique. More amalgamation samples will be collected using this technique during the next retort run.

The HGA-2000 was used twice during run LBL-04, once near the peak in the Hg profile and once on the tailing edge of the profile. No significant increases in the ZAA Hg signal were observed. Although each test was of short duration, this result indicates that Hg present in the offgas is entirely reduced to elemental Hg^{o} by thermal decomposition in the 900°C ZAA furnace. Use of the HGA-2000 during the next retort run is planned in order to substantiate the LBL-04 observations.

Since the ZAA monitor and the Au-amalgamation sample results agree, and the HGA-2000 does not reveal the presence of Hg which is not detected by the ZAA monitor, the low fraction of the total Hg observed in the offgas of runs LBL-02 through LBL-04 may be due to adsorption of Hg on the cool portions of the retort walls. Two experiments were conducted in order to examine this possibility.

The shale bed is supported inside the retort on a removable pedestal. This pedestal and the retort vessel are mullite ceramic (75% Al_2O_3, 25% SiO_2). Offgases exiting the retort contact the pedestal. Since the bottom portion of this pedestal is near room temperature, some Hg may condense on it. The day after run LBL-04, the pedestal was heated to 400°C in a stream of nitrogen which was then passed through the ZAA monitor. Approximately 5% of the total Hg in the raw shale for run LBL-04 was detected. Since the pedestal accounts for about one half of the total, cool, mullite surface area inside the retort, the experiment suggests that as much as 10% to 15% of the total Hg could be lost to this sink.

In the second experiment, Hg calibration gas was passed through a container of mullite chips. The total surface area of the chips was estimated to be approximately one half of the cool mullite surface area inside the retort. Of the 414 µg of Hg passed through the chips, 57 µg were lost. Thirty-four µg of Hg were recovered by heating the chips to 455°C.

These crude experiments demonstrate that cool mullite surfaces act as a sink for Hg. Consequently, we are going to fabricate a stainless steel (SS) retort vessel which will be held entirely within the heated zone of the Lindberg furnace. In this way, all retort surfaces will be heated in order to prevent the loss of Hg from the vapor phase. Heating of all retort surfaces cannot be accomplished with the present mullite retort vessel because

the seals between the mullite tube and the SS end caps must be kept cool. The new SS retort vessel will be built during September, and a retort run will be conducted in early October.

MISCELLANEOUS

Project staff made a site visit to Logan Wash, tracts C-a and C-b, Anvil Points, and the Colony mine to inspect facilities in anticipation of future field sampling.

PROJECTED WORK

The projected work for September is as follows:

Task 1. Analytical Results for Oil and Water

o Neutron activation analysis for Hg in five shale oil samples should be completed in September. A comparison of these results with those obtained with the WO_3-combustion-amalgamation ZAA method will be made to evaluate the accuracy of this method.

Task 2. Analytical Methods for Gas Samples

o Improvements in the HGA-2000 hook-up to the ZAA mercury monitor will be made for use during LBL-5. A test of the effectiveness of the HGA-2000 in reducing H_2S matrix supression on the Hg ZAA will be conducted. The ZAA light source, light source high voltage driver, and monochromator to be used to measure Cd in offgas streams will be tested.

Task 3. Design and Construction of Experimental Apparatus

o A new Stainless Steel (SS) retort vessel will be fabricated to eliminate the cold surface within the retort.

Task 4. Laboratory Portitioning Studies

o Preparation will be made for LBL-5 using the new SS retort vessel. The major objectives for LBL-5 are: (1) to determine if losses of Hg from the vapor phase are reduced using the new SS retort vessel; (2) to obtain additional data for the Au-amalgam and ZAA method comparison; and (3) further examine the effect of the high temperature combustion tube (HGA-2000) on the ZAA mercury response.

Task 5. Field Studies

The ZAA, for batch analysis of liquid and solid samples, will be used to analyze the spent shale samples from Lawrence Livermore Laboratories interupted

steam-air retort run L-3 to determine if Hg has been concentrated in the unretorted bottom layers of shale.

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