Title

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

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For Reference

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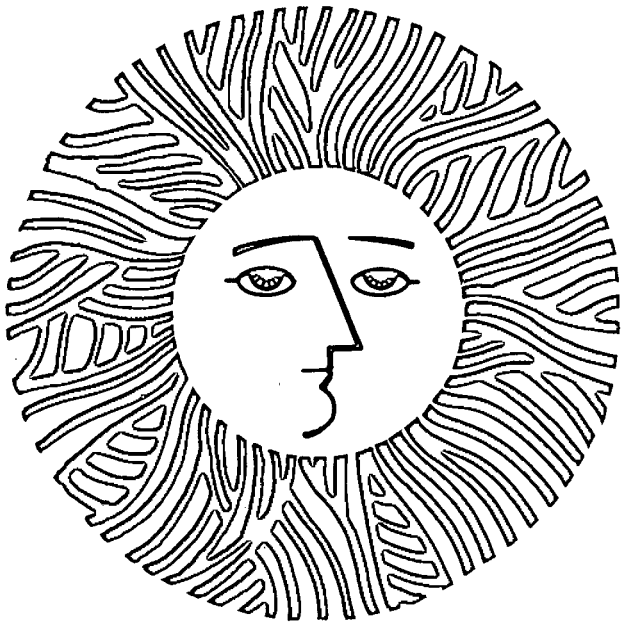

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July 9, 1980

TO: Bob Thurnau

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

RE: June Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb and Se
During Simulated In-Situ Oil Shale Retorting
LBID-251

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

The CuO furnace-combustion technique previously described for decomposition of oil samples prior to Hg analysis was applied to the fresh shale oil obtained from retort run LBL-03. Although we had obtained acceptable results for the analysis of shale oils from other retorts using this technique, inconsistent results were obtained with the LBL-03 oil due to incomplete combustion and/or inorganic interferences not previously encountered. As a result, the combustion technique has been extensively modified. A quartz combustion tube was fabricated, and the cupric oxide was replaced with tungsten trioxide (WO_3) mixed with ceramic beads to maintain permeability. Oil samples (10-50 mg) are now heated in a stream of nitrogen saturated with water vapor which then flows through the WO_3 zone of the combustion tube maintained at 1000°C. A bubble trap containing a solution of lead acetate is placed downstream of the combustion tube to remove sulfur compounds. The gas then passes through a ascarite column which removes acetic and other acids. Mercury is trapped on a silver-plated quartz wool or gold-plated glass bead amalgamation tube immediately following the ascarite column.

A number of Hg analyses of oil from LBL-03 have been attempted with various configurations of the WO_3 combustion technique. However, when the analysis was performed using standard additions, the Hg signals were suppressed relative to the calibration curve. Consequently, standard addition

analyses are required. In addition, the accuracy of the combustion technique will be checked against neutron activation analysis.

Retort water produced during retort run LBL-03 was preserved upon collection and analyzed the following day using the Perkin Elmer Model MHS-10 Hg/hydride system. In addition, a subsample was oxidized with ozone and analyzed using the same instrumentation. Although matrix suppression was present with both unoxidized and oxidized samples, linear standard addition plots were obtained.

In April, we reported on the use of a stannous chloride bubble system to evolve Hg from water samples. The Hg was collected on amalgamation tubes and analyzed by thermal desorption, ZAA cold-vapor detection. Our attempts to analyze preserved LBL-03 retort water by this method were unsuccessful; standard addition plots were often non-linear, and the results which were obtained were inconsistent.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

When the condensers were switched into the offgas stream during the past two retort runs, the ZAA Hg signal was depressed for approximately one minute before returning to its original level. This effect was confirmed by a simple test conducted in June following the cleanup for run LBL-03. Nitrogen calibration gas containing 2 mg Hg/m^3 was passed through two condensers in series before entering the ZAA. The condensers had been equilibrated at 4°C. When the condensers were first switched into the line, Hg concentration dropped to less than 0.5 mg/m^3. After one to two minutes, the concentration returned to its original value. Dilution of the calibration gas by the gas originally in the condensers could account for this decrease. When the condensers were switched in a second time, the drop in Hg concentration was considerably less.

Nitrogen calibration gas containing 2 mg Hg/m^3 was also passed through a glass fiber filter and stainless steel holder maintained at 128°C to determine if these components have an effect on gaseous Hg concentrations. Only a small transient fluctuation in Hg concentration was observed. This fluctuation is probably attributable to a pressure wave travelling through the plumbing system.

TASK 4. LABORATORY PARTITITIONING STUDIES

Reduction and analysis of the online data produced during retort run LBL-03 is nearly complete. Shale bed heating profiles and offgas flow rates have been plotted versus time, Hg calibration curves have been constructed, and offgas Hg concentrations and the total quantity of Hg in the offgas have been calculated.

A material balance was determined for LBL-03 using the calculated volume of offgas produced and the measured weights of the starting material and the other products. The combined weight of the products was 103% of the raw shale. Recovery in excess of 100% is probably due to errors in the measurement of offgas flow rates. During subsequent retort runs, the total offgas flow rate sensor will have to be calibrated more frequently since changing offgas composition seemed to have a relatively large effect on the sensor's calibration.

Elemental balances for Hg in retort runs LBL-02 and LBL-03 are incomplete pending the resulution of the analytical difficulties encountered with Hg in the product oil. However, the total weights of Hg in the offgas have been calculated. Total offgas Hg during run LBL-02 was 314 ug or 39% of the Hg initially present in the raw shale. For run LBL-03, total offgas Hg was 352 ug or 43% of the Hg in the raw shale.

PROJECT WORK

The projected work for July is as follows:

Task 1. Analytical Methods for Oil and Water

- We are continuing our efforts to resolve the analytical difficulties encountered for Hg in the fresh oil sample from run LBL-03. Samples of this and other oils will be submitted for neutron activation analyses.

Task 2. Analytical Methods for Gas Samples

- We are modifying the alternate sampling procedure for Hg in offgas streams. The procedure will utilize a high temperature combustion tube and gas scrubbers to remove interferences. It will be tested during the next retort run.

Task 4. Laboratory Partitioning Studies

- An inert gas retort run with continuous on-line Hg monitoring is scheduled for August.

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