Title

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

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June 12, 1980

TO: Bob Thurnau

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

RE: May Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb, and Se
During Simulated In-Situ Oil Shale Retorting
LBID-236

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

In April, we initiated an evaluation of Parr acid digestion bombs for the decomposition of oil samples prior to Hg analysis. Shale oil samples and Hg in oil standards were digested in these bombs with nitric acid and were analyzed for Hg by the previously described stannous chloride bubbler, amalgamation, thermal desorption, cold-vapor ZAA detection method. Precision of the analysis was poor and recovery of inorganic Hg added to shale oil samples prior to digestion was low, on the order of 75%. For these reasons, we tested a combustion technique for the decomposition of oil samples. With this technique, oil samples are heated to 500°C in a stream of N_2 which passes through a cupric oxide (CuO) combustion tube maintained at 500°C. The Hg is collected at room temperature downstream of the combustion tube by amalgamation on silver-plated quartz wool or gold-plated glass beads. Precision of analysis for shale oil samples was considerably better than with the acid digestion method and quantitative recovery was obtained for inorganic Hg added to shale and mineral oil samples prior to decomposition. Since the CuO oxidation method appears to be the superior technique, it will be employed for the analysis of Hg in the fresh oil samples produced during the latest retort run, LBL-03.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

Modifications were made to the laboratory retort to accommodate in-line filters for sampling of particulates in the offgas stream and amalgamation tubes for sampling of total or gaseous Hg in the offgas stream.

Two stainless steel, 47 mm, in-line filter holders were installed in parallel in an auxillary leg of the offgas stream plumbing (Figure 1). Flow is switched through either one or the other filter holder or around both filter holders by three-way stainless steel ball valves. Both filter holders are mounted inside a small laboratory oven which can be maintained at 120±5°C. Particulates are collected on 47 mm, Gelman, spectro grade, glass fiber filters. Prior to use, these filters are blanked for Hg by heating them at 400°C for one hour in a muffle furnace. Analysis of the filters for Hg is accomplished using the CuO combustion apparatus described for oil samples. Whole filters are inserted into the prechamber of the combustion tube and heated to 500°C in a stream of N_2; Hg is collected downstream of the combustion tube by amalgamation.

Amalgamation tubes for sample collection are placed downstream of the filter holders (Figure 1). Offgas can be routed directly through an amalgamation tube for total Hg in offgas measurements or first through a filter for gaseous phase only measurements. The amalgamation tubes, themselves, can be placed either before or after a CuO combustion tube maintained at 500°C. The purpose of this CuO combustion tube is to determine if oxidation of the offgas has an effect on the quantity of Hg collected by amalgamation.

An attempt was made to sample Hg in the offgas stream with both the filters and the amalgamation tubes during retort run LBL-03. The preliminary data obtained with these devices were insufficient for comparison with the data obtained with the on-line ZAA Hg monitor. We did, however, gain valuable experience which will allow us to design a more adequate alternate sampling procedure for Hg in offgas streams to be tested during subsequent retort runs.

TASK 3. DESIGN AND CONSTRUCTION OF EXPERIMENTAL APPARATUS

As noted in Task 2, modifications were made to the laboratory retort to accommodate discrete sampling of the offgas stream during retort run LBL-03. An auxillary sampling line was installed which originates at the same location as the ZAA monitor sample line and runs parallel to the ZAA line. Flow through the auxillary line is controlled by a Brooks electronic flow controller. During LBL-03, the auxillary line was used for sampling of particulates on heated glass fiber filters and for collection of Hg on amalgamation tubes. Other offgas sampling experiments can also be incorporated into this line.

Another retort modification for run LBL-03, was the addition of a Brooks electronic flow sensor to continuously monitor total offgas flow rates. The sensor is periodically calibrated during the run with a wet test meter. The output signal from the sensor is recorded by the Doric 203A data logger.

TASK 4. LABORATORY PARTITIONING STUDIES

An inert gas, laboratory retort run, LBL-03, was conducted on May 30. Continuous measurements of Hg in the offgas were made with the ZAA monitor. In addition, heated glass fiber filters were used for the collection of particulate samples from the offgas, and amalgamation tubes were used as an alternate sampling procedure for the determination of Hg in the offgas.

The objectives of retort experiment LBL-03 were: (1) to determine Hg volatilization rates and Hg concentrations in the offgas as functions of retort temperature, (2) to determine Hg concentrations in product oil and retort water, (3) to determine Hg concentrations in the particulate phase of the offgas, (4) to determine an elemental balance for Hg, and (5) to further evaluate analytical methods.

The shale grade, particle size distribution (-1/4 inch to +30 mesh), nitrogen input-gas flow rate (2 l/min), and heating rate for retort run LBL-03 were the same as those used for run LBL-02. The shale column was heated to 180°C and then ramped at 1.0°C/min to a maximum temperature of 535°C. LBL-03 differed

from LBL-02 in that the shale column was heated to a temperature of 180°C on the day previous to the retort run and was then allowed to cool to room temperature before the run was initiated. Offgas flow rates were measured during the run; product oil, retort water, and spent shale were collected, weighed, and retained for elemental analyses. Preliminary analysis of the ZAA monitor data for Hg in the offgas of LBL-03 indicates that the Hg concentration profile as a function of retort temperature is similar to the profile produced during LBL-02.

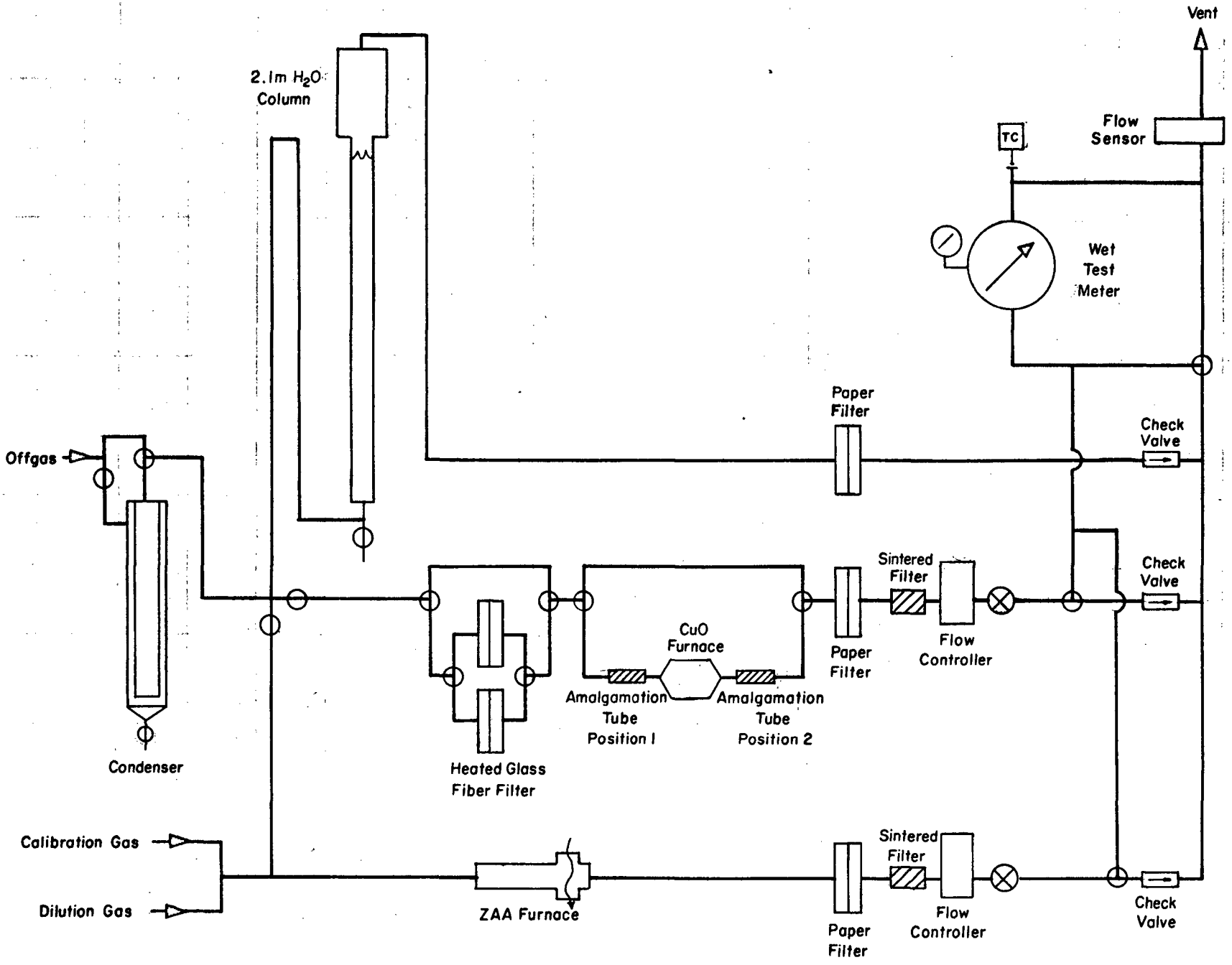
PROJECTED WORK

The projected work for June is as follows:

Task 4. Laboratory Partitioning Studies

Shale oil and retort water produced during LBL-03 will be analyzed for Hg, and the ZAA monitor data will be evaluated. Any necessary modifications to sampling or analytical procedures will be made in preparation for the next retort run. This run is currently scheduled for mid-July to allow for adequate evaluation of LBL-03 and for annual vacation leaves which will reduce our staff by 50% during June.

Figure 1. Schematic of modified gas handling system for laboratory retort.



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