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

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April 7, 1980

TO: Bob Thurnau

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

RE: March Monthly Progress Report
Distribuition of As, Cd, Hg, Pb, Sb, and Se
During Simulated In-Situ Oil Shale Retorting
LBID-194

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

The batch ZAA spectrometer for Hg analysis was tested and used to analyze a number of solid and liquid samples. The literature review of preservation and storage procedures for water samples intended for subsequent Hg analysis was completed. From this literature, we selected a procedure for use with our retort water samples (Feldman 1974, Lo and Wai 1975). The procedure employs 5% (v/v) HNO₃ plus 0.05% K₂Cr₂O₇ as preservatives and storage in glass containers. We are currently testing the efficacy of the method by periodically analyzing a preserved spiked sample.

In February, we began evaluating the use of ozone as an oxidant for retort water prior to Hg analysis by cold vapor atomic absorption spectroscopy (AAS). At that time we were losing up to 25% of Hg spikes added to retort water during the oxidation process with 5% (v/v) HNO₃ as a preservative. Addition of 0.05% K₂Cr₂O₇ plus 5% (v/v) HNO₃ resulted in quantitative recovery of Hg spikes after ozonolysis. Consequently, ozone oxidation in conjunction with cold vapor AAS appears to be a viable method for Hg analysis of retort water.

We have made initial attempts to analyze oil samples for Hg using the new batch-sample ZAA spectrometer. We began by comparing a commercially available oil standard diluted in xylene with aqueous standards and obtained good
results. However, direct analysis of undiluted oil samples resulted in severe matrix suppression. As a consequence, oil samples may have to be diluted and analyzed by the method of additions.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

We have assembled an apparatus for the collection and analysis of gaseous Hg. Collection is accomplished by amalgamating the Hg on silver-plated quartz wool. The Hg is then thermally desorbed in an inert gas stream and detected by cold vapor AAS. If the apparatus performs well, it will be used to check the dynamic Hg calibration device and to collect gaseous Hg in the offgas steam of the laboratory retort.

The Hg ZAA monitor, equipped with the short 5-cm furnace, was tested and found to be linear up to a concentration of 1500 ppb Hg. Several electronic repairs and modifications to the monitor have eliminated a major baseline drift problem. The light source temperature controller was not constructed this month due to a delay in the delivery of an appropriate sized immersion heater.

TASK 4. LABORATORY PARTITIONING STUDIES

Raw shale was prepared for the next 15 retort runs. Chunks of shale were crushed, ground, and sieved. Four size classes ranging between -1/4 and +30 mesh were selected for use. Each of the four size classes was split into 16 equal fractions using riffle splitters. One fraction from each size class was retained for analytical purposes. Fifteen equivalent batches of shale, weighing 5500 g each, were prepared by randomly recombining the four size classes. A 100-g reference sample was obtained from each batch during the recombination step.

The four size fractions that were set aside for analyses were split two additional times, and, randomly selected 1/4 fractions were combined to produce a sample representative of the entire batch. This sample was ground to -50 mesh in a
planetary-type ball mill. Analytical work has been initiated on small subsamples of this material. Cadmium and Hg analyses are being performed by ZAA using direct injection, and As and Se analyses are being performed by X-ray fluorescence spectroscopy. Neutron activation analysis may also be used to determine As and Se, as well as Sb. In addition, we are planning to decompose the shale in an acid digestion bomb and analyze the sample for As, Pb, Sb, and Se by graphite furnace AAS.

Two additional Brooks flow sensor/controllers have been acquired for use with the laboratory retort. The requisite electronic power supplies for these devices have been constructed. The devices are currently being tested and calibrated. One new flow controller will be used to regulate flow through a bubbler train or amalgamation device for collection and subsequent determination of Hg as a check on the ZAA monitor. The other device will be used in the sensor mode to measure either total or bypass offgas flow rates.

The complete results and data interpretation of retort run LBL-2 will be reported along with the results and interpretation of the following three retort runs during which Hg in the gas phase will be monitored.

PROJECTED WORK

The projected work for April is as follows:

Task 1. Analytical Methods for Oil and Water Samples
- We will continue working on the development of a method for the determination of Hg in shale oil.
- We will begin to develop methods for the determination of Cd and Pb in shale oil.

Task 2. Analytical Methods for Gas Samples
- The amalgamation device for collection and analysis of gaseous Hg will be tested.

Task 4. Laboratory Partitioning Studies
- A series of three inert gas retort runs will be initiated
in April. Maximum temperatures of these runs are projected to be 500°C, 750°C, and 1000°C. The Hg ZAA monitor will be in operation during all three runs which should complete the majority of the laboratory studies involving this element. During the three runs, as much information as possible will be obtained about the partitioning of the other elements of interest through careful analyses of all products except the gas phase. This information will be used to design subsequent retorting experiments.

REFERENCES


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