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

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April 13, 1981

TO: Pat Fair
FROM: Al Hodgson and Phyllis Fox
RE: Monthly Progress Report for March Distribution of As, Cd, Hg, Pb, Sb, and Se During Simulated In-Situ Oil Shale Retorting LBID-382

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER SAMPLES

Oil samples from retort experiments 2 through 7 were digested with nitric and perchloric acids and were analyzed for Cd by graphite furnace atomic absorption spectroscopy (AAS). Sample concentrations ranged from 0.06 to 0.11 µg Cd/g. Additional work is needed to improve analytical precision.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

Our initial approach to the on-line instrumental analysis of Cd in retort offgas was to develop a gas-tight, high temperature, graphite furnace analogous to the stainless steel furnace used for Hg analysis. This approach is hindered by the necessity for a gaseous Cd standard. In addition, our development work with the graphite furnace brought to notice the great difficulty of maintaining gas-tight seals in a high temperature furnace. These problems lead us to reevaluate our approach to the on-line analysis of Cd. Calculations based upon conservative estimates of possible Cd concentrations in offgas from the laboratory retort indicated that it might be possible to use a conventional AAS air-acetylene burner as the atomization device for the analysis. The advantage of the burner over the graphite furnace is that standards can be introduced into the burner in liquid form. The disadvantage of the burner is that gas flow rate measurement and control must be accomplished before the offgas reaches the burner. This disadvantage appeared to be outweighed by the overall simplicity of the method, and we preceded with the development of the air-acetylene burner method for on-line Cd analysis.
A Perkin-Elmer Model 306 AAS equipped with a Cd hollow-cathode lamp and deuterium arc background corrector was used as the detector for the retort experiment described in Task 4. The short sample line running from the outlet of the retort to the AAS was maintained at 300°C by joule heating. Gas flow rate measurements were made by periodically switching in a rotameter connected in parallel with the heated line. The rotameter was calibrated with a wet test meter prior to the experiment. Analytical calibration was accomplished by nebulizing aqueous Cd standards into the burner. The apparent Cd concentrations in the flame were calculated from aqueous standard concentrations, nebulization rate, nebulization efficiency, and air and fuel flow rates. Linear calibration curves were obtained with aqueous standards ranging from 0.025 to 2.0 µg Cd/ml. Offgas flow rates were varied from 300 scc/min to 1500 scc/min. With these flows, the range of measurable offgas Cd concentrations is approximately 0.01 to 5.0 mg Cd/m³.

As expected, we experienced difficulty with offgas flow rate measurement and control. Accurate flow rate measurements were not achieved during the retort experiment. In addition, offgas Cd concentration required 5-10 min to recover to its prior level after reestablishment of direct gas flow to the burner following a flow rate measurement. We are currently investigating several alternate methods of flow rate measurement which would eliminate the necessity to interrupt offgas flow to the burner.

TASK 4. LABORATORY PARTITIONING STUDIES

An inert gas, laboratory retort experiment, LBL-08, was conducted on March 27. The stainless steel retort vessel and a heated offgas sample line were used. The shale grade, particle size distribution, and nitrogen input-gas flow rate were the same as for previous experiments. The shale column heating rate was 1.5°C/min, and the final shale column temperature was 890°C at the bottom. The objective of the experiment was to attempt an analysis of Cd in the offgas using the air-acetylene burner for atomization.

Experiment LBL-08 produced the first measurements of Cd in retort offgas. Cadmium was initially detected in the offgas at a bottom shale
column temperature of \(760^\circ C\). Evolution of offgas Cd continued until termination of the experiment at \(890^\circ C\). Due to the flow rate measurement problems discussed above, the results are semi-quantitative. Calculated offgas Cd concentrations ranged up to approximately \(1 \text{ mg/m}^3\). The data are preliminary, and the experimental results may change significantly as the analytical technique is refined.

PROJECTED WORK

Three areas of effort are planned for April. We will attempt to design and assemble a relatively simple apparatus for flow rate measurement in the heated, offgas sample line. We will attempt to improve the precision of the analytical technique for Cd in raw and spent shales. Preparation of the report on the results of the Hg partitioning studies is to continue.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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