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LAWRENCE BERKELEY LABORATORY
Room: 288 Bldg.: 70 Ext.: 4140

December 6, 1979

TO: Bob Thurnau

FROM: D. C. Girvin, A. T. Hodgson and P. Fox

RE: November Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb and Se during
Simulated In-Situ Oil Shale Retorting
LBID-147

WORK PROGRESS FOR NOVEMBER 1979

Task 1. Analytical Methods for Oil and Water Samples

In the quarterly progress report for April 1-June 30, 1979, we presented results of elemental analyses of two subsamples (Omega-9-1 and Omega-9-2) of Omega-9 retort water. Large discrepancies in elemental abundances were apparent when our results for subsample Omega-9-2 were compared to the results of the interlaboratory, multimethod study for this water (1). Contamination and filtration were cited as possible sources of these errors.

In November we collected and analyzed a third subsample of Omega-9 water and were able to resolve the discrepancies. The second subsample, which we reported as Omega-9-2, was not Omega-9 water; it was apparently mistakenly collected in March 1979 from a 30-gallon drum containing Geokinetics-Site 9 water. The November subsample, on the other hand, was taken from a positively identified drum of Omega-9 water. Analyses of this subsample by our previously reported direct AAS techniques produced results for As, Sb and Se which fall within the ranges established for these elements by the multimethod study (Table 1). Our Cd concentration is higher than the established value, and no comparison can be made for Pb due to the insufficiency of the multimethod data. Table 1 also shows that there were only minor and probably

Table 1. Comparison of As, Cd, Pb, Sb and Se concentrations in Omega-9 retort water as determined by an interlaboratory, multimethod study and by flameless atomic absorption spectroscopy analyses of untreated and refiltered (0.4 μm) samples

Element	Concentration (mg/L)		
	Interlaboratory Multimethod Study Best Value (1)	Atomic Absorption Spectroscopy - LBL	
		Untreated	Refiltered
As	1.0 ± 0.2	0.90	0.85
Cd	0.0016 ± 0.0008	0.0010	0.0009
Pb	0.02 - 0.0045	0.02	0.03
Sb	1.9 ± 0.5	2.15	1.90
Se	0.21 ± 0.11	0.13	0.15

insignificant differences between elemental concentrations in untreated and refiltered (0.4 μm Nuclepore) aliquots. Filtration, however, could result in lower concentrations for retort water samples in which bacterial growth has occurred, such as our first Omega-9 subsample (Omega-9-1).

The ZAA spectrometer for batch analysis of mercury in retort water and oil is not yet operational. It was necessary to move this instrument to a different laboratory, and a new exhaust hood and 220 volt power must be installed prior to its use. We have also taken this opportunity to install a new dual chamber nickel furnace and new light source electronics. The relocated instrument should be in operation in January.

Task 2. Analytical Methods for Gas Samples

The redesigned heated sample probe and stainless steel ZAA furnace for the mercury field monitor have been tested. The probe was maintained at 350°C for 24 hours without evidence of gas leakage around the seals. The new quartz window mounts on the ZAA furnace have successfully reduced UV absorption due to condensation of organic residues on the windows.

A compact light source temperature controller has been fabricated. This unit consists of a Borg Warner thermoelectric heat pump (bi-directional P-N junction) and a small centrifugal pump which circulates 500 mL of cooling water between the light source water jacket and the heat pump. Preliminary tests have demonstrated that the device can maintain the light source at 25° ± 0.2°C when the ambient temperature is 20°C. This degree of stability will maintain the LIA baseline drift at less than ±0.02 mg Hg/m^3 (2). In December, tests will be run to determine light source temperature stability about a set temperature of 25°C for ambient temperatures of 15°C and 35°C.

A series of matrix interference tests were conducted to examine the effects of hydrogen sulfide gas and thiophene and pyridine vapors on ZAA response to a fixed concentration of mercury. These tests were conducted using both air (oxidizing atmosphere) and nitrogen (inert atmosphere) as the carrier gas. A constant concentration of mercury (0.52 mg Hg/m^3) was metered into the carrier gas stream. Pure H_2S gas, or streams of nitrogen or air containing thiophene or pyridine vapor were also metered into the carrier gas stream.

Preliminary results are qualitatively summarized in Table 2 for a furnace temperature of 750°C. Broadband UV absorption is indicated by a decrease in the photomultiplier tube (PMT) signal. A decrease in the lock-in amplifier (LIA) signal indicates matrix suppression. At 25°C, pyridine in air totally extinguished the PMT signal. However, thermal decomposition of pyridine in the furnace at 750°C eliminated UV absorption and no effects on either the PMT or LIA signals were observed. Tests with pyridine in nitrogen were not conducted.

In air, H_2S (2% by volume) suppressed the LIA signal by approximately 27%. Thiophene in air also suppressed the LIA signal. In nitrogen, the effects of H_2S and thiophene on the LIA signal were less than or equal to the measurement error of $\pm$7%.

These results indicate that, under certain circumstances, the presence of sulfur-containing compounds result in a matrix suppression of the mercury signal similar to that observed during the May 1979 test of the ZAA monitor at Lawrence Livermore Laboratory. The use of standard addition techniques to quantify mercury in offgas streams are therefore mandatory. Several additional experiments will be conducted in the next few months to verify and further elucidate these results.

Task 3. Design and Construction of Experimental Apparatus

In general, the laboratory-scale retort functioned properly during the first trial run (see Task 4); however, several problems were encountered which are now being corrected. The most serious problem was the development of an offgas leak at the O-ring seal between the ceramic retort vessel and the stainless steel flange on the bottom of the vessel. The mounting bracket for the flange is being strengthened to allow for more compression of the O-ring which should eliminate the leak. Another problem was uneven heating of the shale column. Temperatures 10 cm from the bottom of the column were typically 75°C lower than respective temperatures at the center of the column, while temperatures 10 cm from the top were only about 20°C lower than center temperatures. The furnace was tested and found to be functioning properly; therefore, low temperatures at the bottom probably resulted from the vertical operation of the furnace. A Variac is being installed to reduce the wattage of the upper elements

Table 2. Summary of matrix suppression tests for a ZAA furnace temperature of 750°C.

Test Constituent	Signal	Carrier Gas: Air, Without Hg	Air, With Hg	N_2, Without Hg	N_2, With Hg
Pyridine	PMT[1]	NE[2]	NE	-	-
	LIA[3]	NE	NE	-	-
Thiophene	PMT	DEC[4]	DEC	-	DEC
	LIA	NE	DEC	-	NE
H_2S	PMT	NE	DEC	-	DEC
	LIA	NE	DEC	-	NE

1 PMT = photomultiplier tube signal

2 NE = no effect

3 LIA = lock-in amplifier signal

4 DEC = signal decreases in magnitude

relative to the bottom elements. By adjusting the Variac, we should be able to obtain a smaller temperature differential throughout the shale column.

Task 4. Laboratory Partitioning Studies

We successfully retorted the first batch of oil shale in the laboratory apparatus early in November. A charge of raw shale weighing 5.5 kg was heated in a nitrogen atmosphere at a rate of 1.0 - 1.5^{o}C/min to a maximum temperature of 700°C. Temperatures in the shale column and throughout the system were monitored, oil and water were collected, and offgas flow rates were determined with a wet test meter. After the run, the spent shale, oil and water were weighed, and a material balance was attempted using estimates for the quantity and density of gas produced. No attempt was made to measure Hg in the offgas with the ZAA Hg monitor since the sole purpose of the run was to evaluate the performance of the retort.

The second retort run is scheduled for mid-December. During that run we plan to continuously measure Hg in the offgas with the ZAA monitor. The primary objective will be to further evaluate the performance of the instrumentation. Secondarily, we should obtain some preliminary data about the timing and rate of Hg vaporization during retorting.

Task 5. Field Studies

In the October progress report we stated that the ZAA field monitor would be tested during Lawrence Livermore Laboratory's one-day run of their 125 kg retort in January. This run has been postponed by LLL until March due to relocation of the retort in another building. Those tests of the mercury monitor which were to have been made at LLL in January will be made using the new LBL retort.

PROJECTED WORK FOR DECEMBER 1979

The work schedule for December is limited due to LBL's holiday season shutdown from December 22 to January 2. The projected work for December is as follows:

Task 2. Continue the light source temperature control tests and the matrix interference tests.

Task 4. Conduct the second LBL oil shale retort run. The offgas from this run will be used to test the ZAA mercury monitor. Preliminary mercury offgas data will also be obtained; however, data collection will be a secondary objective.

REFERENCES

1. D. S. Farrier, J. P. Fox and R. E. Poulson, "Interlaboratory, multimethod study of an in-situ produced oil shale process water", Lawrence Berkeley Laboratory Report LBL-9002, March 1979.

2. D. C. Girvin and J. P. Fox, "On-Line Zeeman Atomic Absorption Spectroscopy for Mercury Analyses in Oil Shale Gases", Lawrence Berkeley Laboratory Report LBL-9702, August 1979.

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