Title

AUGUST MONTHLY PROGRESS REPORT - THE PARTITIONING OF MAJOR, MINOR AND TRACE ELEMENTS DURING SIMULATED IN-SITU OIL SHALE RETORTING

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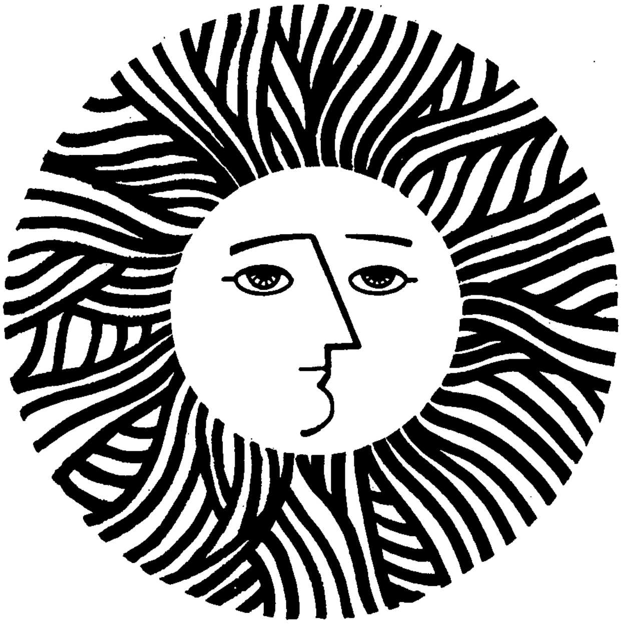

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LAWRENCE BERKELEY LABORATORY
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September 15, 1980

TO: Brian Harney and Art Hartstein

FROM: Phyllis Fox and Richard Fish

RE: August Monthly Progress Report
The Partitioning of Major, Minor, and Trace Elements during Simulated
In-Situ Oil Shale Retorting
LBID-290

SPECIATION OF INORGANIC AND ORGANOMETALLIC COMPOUNDS IN OIL SHALE PROCESS WATERS

We previously identified arsenate and methyl- and phenylarsonic acids in seven in-situ oil shale process waters. This month we continued our studies on the origin of these species. We are investigating the hypothesis that contact between the produced water and the oil and raw or partially retorted shale ahead of the reaction zone of a MIS retort results in the partitioning of As compounds from the raw shale and oil to the water. This is being investigated by extracting raw shales and shale oils with ammonium bicarbonate (major constituents in the aqueous phase) at temperatures expected in the condensation zone of a MIS retort and analyzing the extracts by HPLC-GFAA.

Anvil Points oil shale and shale oils from LLL small retort runs S-12 (air/N_2) and S-13 (air/steam) were extracted with 0.16 M ammonium bicarbonate at 21°C and 53°C. HPLC-GFAA analyses indicate that the oil shale extracts contain arsenate and methyl- and phenylarsonic acids, two unidentified arsenic compounds, and the unknown neutral compound that elutes with the solvent front. A control experiment with the 0.16 M ammonium bicarbonate solution indicated the presence of trace amounts of phenylarsonic acid. The concentration of arsenate and phenylarsonic acid in raw shale extracts was higher than the concentration of methylarsonic acid and the unknown compounds. The presence of large concentrations of arsenate and methyl- and phenylarsonic acids in the raw shale extract suggests a biogeochemical origin for these compounds in oil shale systems. This is the first instance, known to the authors, in which evidence for the biogeochemical origin of phenylarsonic acid has been advanced. Because of the potential scientific significance of this finding, we are carefully repeating these experiments with appropriate controls.

The extracts of oil S-12 contained significant concentrations of arsenate and methylarsonic acid and smaller concentrations of phenylarsonic acid, a new unidentified compound, and the neutral species at the solvent front. Spiking the sample with authentic arsenicals (10, 20, and 40 ng/peak) increased the histogramic peak heights of arsenite and methyl- and phenylarsonic acids, providing further evidence for their identification. The S-13 oil also contained arsenate and methyl- and phenylarsonic acids as well as three unknown compounds.

IDENTIFICATION OF POTENTIAL ORGANIC COMPOUNDS AS LIGANDS OF METALS IN OIL SHALE PROCESS WATERS

We previously identified C_2 through C_4 monocarboxylic acids in Occidental's Heater-Treater water. This month, we modified the butylation procedure to improve ester yields. We previously lyophilized the sample and dissolved the residue in H_2SO_4 in butanol. After the usual workup, benzene extracts were concentrated by fractional distillation and analyzed by capillary column gas chromatography. This month, we investigated the use of boron trifluoride in butanol and HCl in butanol to improve yields and to eliminate the formation of ethers. Preliminary work suggests that HCl in butanol is the preferable method.

GEOKINETICS CORE STUDY

A WPAS was submitted to LETC for the new program, and work was initiated to select cores and compositing techniques that will be used to prepare samples for analysis.

PROCESS WATER INTERCOMPARISON STUDY

LBL is collaborating with LETC and the University of Wyoming in an intercomparison study on oil shale process waters. The purpose of the program is to fully characterize six oil shale process waters (2 samples of Paraho retort water, Occidental retort water and gas condensate, and retort water from a Geokinetics experiment and a recent run of the 150-ton retort) and to investigate analytical problems. LBL will coordinate the national laboratory participation in the program and will perform detailed analyses of the six samples.

This month, we received three sets of the six samples and initiated analytical work on them. They are being analyzed by neutron activation analysis, x-ray fluorescence spectrometry, atomic absorption spectroscopy, Zeeman atomic absorption spectroscopy, and HPLC-GFAA as well as for water quality parameters.

MISCELLANEOUS

Phyllis Fox presented the paper, "Trace Elements in Oil Shale Materials" at the ACS Las Vegas meeting on August 25. Dr. R. H. Fish attended two Gordon Research Conferences: Organometallic Chemistry in Energy-Related Areas at the Proctor Academy, Andover, N. H., from August 11-15 and Organic Geochemistry at Holderness School, Plymouth, N. H., from August 17-22. A poster session was presented at the Organometallic Gordon Conference entitled "Speciation of Inorganic and Organoarsenic Compounds by HPLC-GFAA Analysis." Laura Joseph visited oil shale field sites August 18-22 at Logan Wash, tracts C-a and C-b, the Colony Mine, Paraho, and Geokinetics.

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