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LAWRENCE BERKELEY LABORATORY
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October 8, 1980

TO: Brian Harney and Art Hartstein

FROM: Phyllis Fox, Jeremy Cantor, and Laura Joseph

RE: September Monthly Progress Report
The Partitioning of Major, Minor, and Trace Elements during Simulated In-Situ Oil Shale Retorting
LBID-302

SPECIATION OF INORGANIC AND ORGANOMETALLIC COMPOUNDS IN OIL SHALE PROCESS WATERS

This month we continued our studies on the origin of arsenicals in oil shale process waters and initiated studies to identify arsenicals in leachates from in-situ spent shales. Samples of raw and spent shale are being extracted with 0.16 ammonium bicarbonate at ambient and elevated temperatures to simulate conditions ahead of the reaction zone in a MIS retort and leaching of in-situ spent shale by local groundwaters. These experiments are using pulverized Anvil Points raw shale and spent shale from runs S-9 (inert gas), S-10 (air/recycle), S-12 (air), and L-1 (air) of LLL's simulated in-situ retorts.

Ground shale samples and a 0.16 M solution of ammonium bicarbonate (prepared from distilled water and reagent grade ammonium chloride and ammonium carbonate) in a ratio of 1 gm shale/1 ml buffer were agitated together for 48 hours at 60°C and at room temperature. All samples were agitated with a "wrist-action" shaker, and half were immersed in a constant temperature water bath for the duration of the experiment. The samples were centrifuged where necessary, vacuum filtered through a 0.45 micron Millipore type HA filter, stored under refrigeration, and analyzed by HPLC-GFAA. A control sample containing only the buffer solution and a distilled water blank were also analyzed. Arsenic species were identified by retention times without spiking and are thus tentative.

HPLC-GFAA analyses of the raw shale extracts differed from those of earlier experiments. We previously reported the presence of arsenate and methyl- and phenylarsonic acids, two unidentified arsenic compounds, and the unknown neutral compound that elutes with the solvent front. The present experiments indicate the absence of methylarsonic acid and arsenate and the presence of phenylarsonic acid. This confirmation of the presence of phenylarsonic acid suggests a biogeochemical origin for this specie.

Because of the potential scientific significance of this finding, additional control experiments are being conducted and work is in progress to resolve the discrepancy between these experiments and those reported in August.

HPLC-GFAA analysis with known retention times was also used to tentatively identify arsenicals in spent shale extracts. This work indicates that arsenate is the predominate specie in all four samples. Phenylarsonic acid was also identified at lower concentrations in samples S-10, S-12, and L-1. Next month, these samples will be spiked with authentic arsenicals to confirm these identifications.

We also investigated potential interferences in the speciation studies, contamination problems, and sample preservation methods. Several analyses were performed at the 197.2 nm arsenic line instead of at 193.7 nm since it had been reported that the strong carbon line at 193.09 nm can interfere with background-corrected arsenic determinations. This wavelength showed the expected decrease in sensitivity, but no other changes were noted. Presumably, by the time the eluate reaches the graphite furnace, the matrix is no longer concentrated enough to cause interference.

The control sample showed considerable contamination by at least two species (or groups of species). Further tests identified the chemicals used to make the buffer as the source of contamination. This contamination includes neutral compounds which elute with the solvent front and are visible in the undiluted buffer but not at the 1:10 dilution used for most of the analyses. A set of standards made up in the diluted buffer showed this neutral peak, which was not observed in either the standards or the diluted buffer alone; the cacodylic acid peak disappeared almost entirely in this run, Retention times, however, were unaffected by the buffer matrix. Further investigation of this effect will be necessary to determine its impact on analyses.

It had been previously suggested that speciation studies should be conducted on fresh or freshly frozen samples. This month we studied the effect on sample integrity of freezing and refrigeration at $4^{o}C$. Freezing produced a precipitate which would not dissolve at room temperature. This work is still in progress and results will be reported at a later time.

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

Five process waters (Occidental's boiler blowdown and retort water, Geokinetics' retort water, LETC's 150-ton retort water, and Omega-9 retort water) were reacted with HCl in butanol to form the butyl ester derivitives of those mono- and di-carboxylic acids present in each lyophilized sample. The procedure followed to prepare the product mixtures for capillary GC analysis was identical to that which was previously used in the butylation of Occidental's heater-treater Water.

Two gas chromatograms were obtained for each product sample: one containing only the sample and one containing the sample spiked with a standard mixture of the butyl esters of acetic, propionic, and butyric acids (C_2-C_4). Correlation between each set of chromatograms indicates that the C_2-C_4 mono-carboxylic acids are present in all process waters studied. The samples will soon be analyzed by GC-MS to confirm these tentative identifications.

Quantitation was not attempted due to the unavoidable loss of low molecular weight esters (particularly butyl acetate) during the preparation of the product mixtures for GC analysis.

Preparation of Standards

The butyl propionate used in the standard mixture was synthesized by reacting propionic acid with HCl in butanol and purified by fractional distillation. Our new Perkin-Elmer model 598 Infrared Spectrophotometer was used to obtain its IR spectrum. Needed confirmation of its synthesis was quickly obtained by comparing this spectrum to a published spectrum of butyl propionate. Butyl acetate was synthesized previously. Its structure was confirmed by NMR. Butyl butyrate was purchased commercially.

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