Title

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

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LAWRENCE BERKELEY LABORATORY
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June 13, 1980

TO: Brian Harney and Art Hartstein

FROM: Richard Fish and Phyllis Fox

RE: May Monthly Progress Report
The Partitioning of Major, Minor, and Trace Elements During Simulated In-Situ Oil Shale Retorting,
LBID-239

SPECIATION OF INORGANIC AND ORGANOMETALLIC COMPOUNDS IN OIL SHALE PROCESS WATERS

Dr. Ken Jewett, a visiting scientist from the National Bureau of Standards, assisted in setting up the high performance liquid chromatograph-graphite furnace atomic absorption detector (HPLC-GFAA) combination.

We reanalyzed the seven process waters previously studied at NBS for inorganic and organoarsenic compounds. This allowed us to ascertain that several of our previous tentative identifications were misleading. By diluting the process water samples, we were able to eliminate the organic matrix problem and dramatically improve our separations. This work indicates that arsenate (AsO_4^{3-}) was the predominant compound in all of the process waters studied. Smaller but significant amounts of phenyl- and methylarsonic acid were also present in most of the process waters studied.

The samples were spiked with known arsenic standards to enable us to more clearly define our identifications. We are presently attempting to define the detection limits for arsenite, a known carcinogen, that we have not been able to detect in any of the process waters to date.

We have also made a simple collection device for preping unknown inorganic or organometallic compounds by placing a peristaltic pump in line with the effluent being removed from the laminar flow cell. The effluent from the outlet of the

pump is collected by an automatic fraction collector. As far as we know, there have been no attempts by people using HPLC-GFAA to preparatively isolate unknown compounds emerging from the HPLC column during GFAA detection.

We are presently investigating the possible origin of the inorganic and organoarsenic compounds identified in process waters by repeating our speciation studies on artificial retort water samples. These samples were produced by contacting samples of oil shale and shale oil with an ammonium bicarbonate solution to simulate the contact between water, dissolved gases, and raw shale within an in-situ retort.

ARSENIC COORDINATION CHEMISTRY

Arsenic occurs at high concentrations, 5 to 50 ppm, in shale oils and is considerably enriched compared to conventional crudes which typically have As concentrations of about 0.01 ppm. These elevated levels are significant from both an environmental and processing standpoint. If shale oils are combusted directly, as in an oil-fired boiler, As emissions may be a factor of 1000 or more higher than from boilers fired with conventional crude. Additionally, As is a known cracking catalyst poison and must be removed before shale oil can be refined. Previous attempts to remove As on an adsorption bed have limited commercial application due to the high costs associated with bed replacement or regeneration. Therefore, we have initiated work to develop an alternate method to remove As from shale oils using the techniques and knowledge we have developed in oil shale speciation work.

Our approach is to coordinate various arsenic species with ligands that can be readily placed in a polymeric backbone. We have begun a study to ascertain how these species, e.g., arsenate, methyl- and phenylarsonic acids, and trialkylarsine oxides, coordinate with a variety of new organic ligands being synthesized by colleagues in LBL's Materials and Molecular Research Division (MMRD). Several new arsenic coordination complexes were synthesized and their structures elucidated by 90 and 250 mHz

nuclear magnetic resonance spectroscopy. We hope to be able to define their rates of formation and continue to evaluate more functionally substituted ligands capable of coordinating any arsenic compound.

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