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

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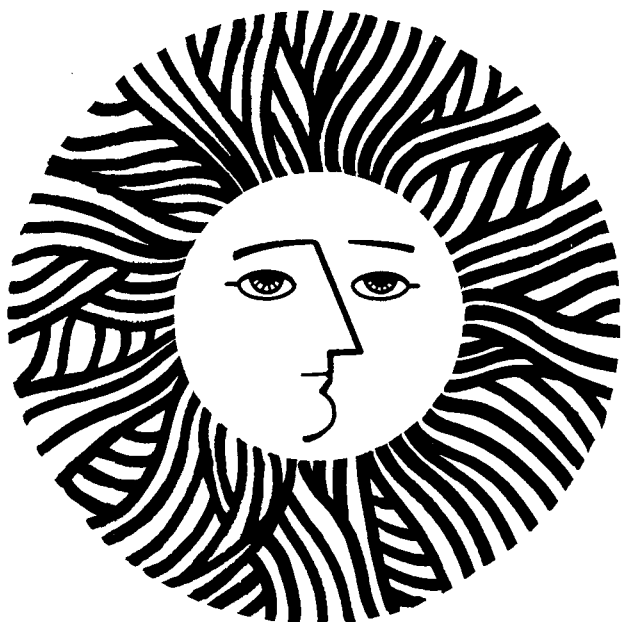
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February 19, 1980

TO: Art Hartstein

FROM: Richard Fish, Bob Giaouque, Barbara Branstetter, and Phyllis Fox

RE: January Monthly Progress Report
The Partitioning of Major, Minor, and Trace Elements during
Simulated In-Situ Oil Shale Retorting
LBID-173

NAVY CORE PROJECT

Data Analysis

John Ward Smith visited the Laboratory on January 10 and 11 to collaborate with Phyllis Fox and Bob Giaouque on the interpretation of the results of the elemental and mineral analyses of two cores from the Naval Oil Shale Reserve. The resulting discussions led to a number of modifications and additions to the data analysis procedures previously employed. Work completed as a result of these discussions is summarized here.

Pearson correlation coefficients and statistical significance values were recalculated for Core Hole 25 minerals, elements, and Fischer Assay data incorporating the following changes:

- Mineral x-ray diffraction peak height data were used for all minerals. (Previously, estimated weight percent values were used for some of the nine minerals -- analcime, quartz, calcite, and dolomite.) This permits slightly improved sensitivities to be realized.

- All x-ray diffraction peak heights were adjusted to compensate for organic volume content using the Fischer Assay gallons of oil/ton data. The organic volume was estimated using procedures developed by Robb, Smith, and Trudell (1978). This was done since the organic matter in an individual sample controls how much mineral fraction is available for x-ray diffraction. If the effect were not compensated, many minerals would show an inverse correlation with organic matter due to dilution by organic matter.

• A similar procedure was used to attempt to correct for the dilution by carbonate minerals. These minerals are a major component of the samples (20 to 60 weight percent). Using the Ca and Mg results determined for each sample, total carbonate minerals were calculated. All values except Mg, Ca, Sr, Ba, inorganic carbon, calcite, and dolomite were corrected for dilution by the carbonate minerals.

Using the above adjusted results, Pearson correlation coefficients and statistical significance values were determined. The results obtained appeared to be very questionable, e.g., many previous positive correlations obtained between elements and minerals using the initial uncorrected results were severely reduced or not correlated at all. Subsequently, we eliminated the corrections made for the dilution by the carbonate minerals, and more reasonable correlations were obtained, including positive correlations between minerals and organics which were not apparent using the uncorrected results.

The failure of the correction for dilution by carbonate minerals to yield meaningful correlation results can possibly be attributed to the fairly sizeable analytical uncertainties in the Mg results. Furthermore, other elements, e.g., Fe or Sr, can substitute for Mg or Ca in some of the carbonate minerals. Consequently, x-ray diffraction peak heights, corrected for the dilution by the organic volume content, are the only corrections being made to the analytical data before the determination of correlation coefficients and statistical significance values.

Cadmium Measurements

During January, Cd analyses on Core 25 were initiated. Forty samples were run in triplicate. A new furnace, the Extended Range High Gas Temperature Furnace, was developed to facilitate sample analysis without dilution. The development was based on the solution of equation:

$$\frac{dN}{dt} = R_1(i)N_0 - R_2(i)N$$

where $R_1(i)$ is the atomization rate of trace element and $R_2(i)$ is the rate of escape of trace element in the sample. The general solution of the above rate equation shows that

$$N = \int_0^{\infty} N dt$$

is independent of vaporization rate of cadmium and is dependent only on the escape rate. This matrix independence was tested on several NBS Standard Reference Materials -- Coal, Coal Fly Ash, Bovine Liver, Wheat -- and was found to be in good agreement.

IDENTIFICATION AND QUANTIFICATION OF FATTY ACIDS AS LIGANDS OF METALS IN OIL SHALE WATERS

The fatty acid profiles of various oil shale process waters were extended to include Livermore's L-2 retort water and LETC's Omega-9 retort water. The previous retort or process waters examined were Occidental's heater-treater, product, and boiler blowdown waters; LETC's 150-ton retort water, and Geokinetic's retort water.

We found a characteristic profile of fatty acid methyl esters for each process water. Thus, fingerprinting of organic ligands of metals found in retorting process products will be useful in being able to environmentally differentiate one process from another. These studies were thus expanded to include nitrogen aromatic heterocyclic compounds.

SPECIATION OF ORGANOARSENIC COMPOUNDS IN SHALE OILS

The speciation of organo- and inorganic arsenic compounds in retort process waters has been extended to shale oils. We are now in the process, through our collaborative research effort with colleagues at the National Bureau of Standards, of examining several normal and reverse phase columns for the separation of the organoarsenic compounds that we suspect are present in the shale oils.

Additionally, we are hoping to extend our studies to other metals such as selenium, cadmium, mercury, and zinc with our high performance liquid chromatograph-graphite furnace atomic absorption detector combination.

The paper, "Environmental Organometallic Chemistry: The Use of a High Performance Liquid Chromatograph in Combination with a Graphite Furnace Atomic Absorption Detector in the Speciation of Environmentally Toxic Organometallic and Inorganic Compounds", was presented by Dick Fish at the Third Annual Oil Shale Conversion Symposium in Denver on January 15.

REFERENCES

W. A. Robb, J. W. Smith, and L. G. Trudell, "Mineral and Organic Distributions and Relationships Across the Green River Formation's Saline Depositional Center, Piceance Creek Basin, Colorado", Laramie Energy Technology Center Report LETC/RI-78/6, 1978.

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