Title

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

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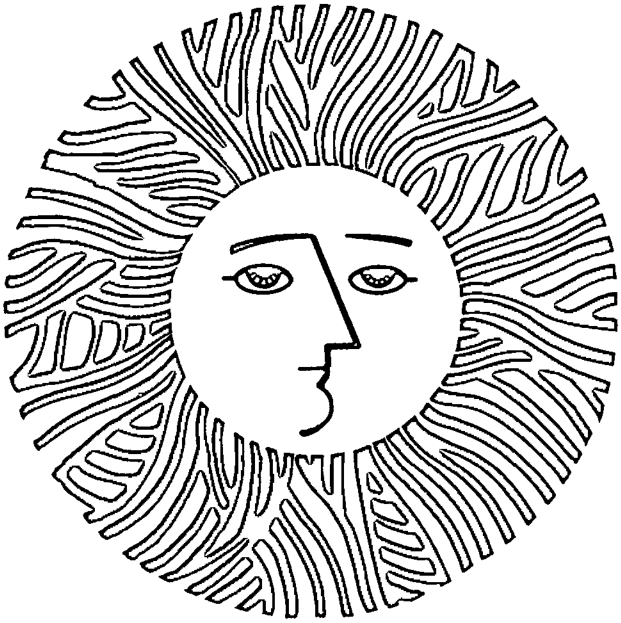

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July 21, 1980

TO: Brian Harney and Art Hartstein

FROM: Phyllis Fox and Richard Fish

RE: June Monthly Progress Report
The Partitioning of Major, Minor, and Trace Elements
during Simulated In-Situ Oil Shale Retorting
LBID- 247

SPECIATION OF INORGANIC AND ORGANOMETALLIC COMPOUNDS IN OIL SHALE PROCESS WATERS

Progress was slow this month due to several electronic problems with the new atomic absorption spectrometer. These have now been resolved. However, we did investigate the detection limit of arsenite (AsO_2^{1-}) by high performance liquid chromatography-graphite furnace atomic absorption analysis. The detection limit for arsenite was determined to be 0.01 ppm by adding known amounts of the compound to Geokinetics and Occidental retort water. This value is now being used to screen previous data to determine whether any arsenite was present. The column and solvent conditions we previously used to separate arsenic species were not adequate to completely separate arsenite from a neutral organoarsine oxide that eluated with the solvent front. Thus, we are presently using this new detection limit to verify the absence of arsenite in previous data.

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

We have been investigating organic ligands that have the potential to coordinate with trace metals in oil shale process waters. We previously identified 42 mono- and dicarboxylic acids in seven process waters. The smallest identified compound was a C_4 monocarboxylic acid, butanoic acid. This month we investigated the presence of lower melecular weight carboxylic acids that may not have been detected in the original analyses for volatility reasons. Occidental heater-treater water was reacted with butanol to form butyl esters of any mono- and dicarboxylic acids present. A preliminary capillary gas chromatography-mass spectrometry analysis (GC-MS) positively identified butyl acetate. Thus, the presence of acetic acid has been established in this water. This suggests that it may be present in other waters. We are presently evaluating the GC-MS data to determine if the C_3 ester, butyl propionate, is also present in the heater-treater water.

ARSENIC COORDINATION CHEMISTRY

We are continuing our experiments on the coordination of arsenic species with ligands that can be readily placed in a polymeric backbone as a means to remove arsenic from shale oils. Several new ligands have been used and reactions with methyl and phenylarsonic acid and arsenate have provided insights into the conditions necessary for coordination. The resulting new coordination compounds are presently being characterized by nuclear magnetic resonance spectroscopy and mass spectrometry.

MASS BALANCE STUDIES

The mass balance studies of simulated in-situ retorts have been completed and a final report prepared. This report will be distributed next month. The following summarizes pertinent conclusions from this work. The purpose of this work was to determine the fate of inorganic constituents in Green River, Antrim, and Moroccan oil shales during in-situ oil shale retorting. The partitioning, or distribution, of 50 elements to the spent shale, shale oil, retort water, and offgas was studied by completing mass balances for several runs of three simulated in-situ retorts. Analytical methods were developed or adapted to make accurate and precise measurements and used to characterize the products and by-roducts from 24 simulated in-situ retort runs. The effect of shale origin and retort operating conditions, including temperature, particle size, atmosphere, and gas flow rate, on partitioning patterns was investigated; and the resulting data were used to develop a conceptual model of elemental partitioning during simulated in-situ retorting.

The major conclusions from this work are summarized and recommendations for additional work are presented.

Elemental Abundances

The elemental composition of raw and spent oil shales, shale oils, and retort waters was determined using neutron activation analysis, x-ray fluorescence spectrometry, Zeeman atomic absorption spectroscopy, and other techniques. Fifty elements were measured in each of these phases from 15 runs of LETC's controlled-state retort and in nine runs of LLL's two simulated in-situ retorts. Major elements (C, H, N, and S) and Hg were also measured in the offgas of the same runs.

The relative elemental abundances in Green River oil shales and their by-products are summarized in Table 1. This table indicates that C, H, N, and S are the major components of raw shales and their byproducts while most other constituents occur at concentrations of less than 0.1%. The predominately organic constituents C, H, and N and the conventionally chalcophile elements As, Se, Mo, S, and Sb are significantly enriched in Green River oil shales while most other elements are very similar to average crustal abundances. The elemental composition of raw and spent shales is similar for most elements while the mineral compositions may vary widely. Differences in the elemental and mineral composition of raw and spent shales are due primarily to high temperature mineral and gaseous reactions during oil shale retorting and to the loss of organics. The abundance of nonvolatile elements in spent shale is about 20% higher than in raw shale because about 20% of the matrix is volatilized.

The elemental composition of shale oils is quite different from conventional crudes. The elements Al, As, Ba, Cu, Fe, Ga, La, Mg, N, Na, Se, U, and Zn are enriched in Green River shale oils while Mo, V, and H are deficient compared to conventional crudes. The retort operating conditions studied here--temperature, atmosphere, particle size, and gas flow rate--did not significantly affect the elemental composition of shale oils; shale source and retort design and operation exerted the greatest influence on oil composition.

Table 1. Summary of elemental abundances in raw and spent oil shale, shale oil, retort water, and gases[a].

Product	Major Elements[b]	Minor Elements[c]	Trace Elements[d]
Raw and Spent Oil Shale	Si, C, Ca, Mg, Na, Al Fe, K, S, N, H, Ti	Mn, V, Zn, Cr, As, Cu, Mo, Ni, Pb, Co, Th, U, Sb, Se, W, Ba, Sr, Rb, Ce, La, Nd, Ga, Y, Sc, Cs, Dy, Sm, Hf, Yb	Cd, Hs, Eu, Lu, Ta, Tb
Shale Oil	C, H, N, S	Al, As, Ba, Co, Cu, Fe, K, Mg, Na, Ni, Se, Zn, Cl	Cd, Ce, Cr, I, Dy, Eu, Ga, Br, Ge, Hf, Hg, La, Mn, Mo, Sb, Sc, Sm, Th, U, V, Y
Retort Water	C, H, N, S	Al, As, Ca, Cl, Fe, K, Na, Ni, Zn, Mg	Ba, Br, Cd, Ce, Co, Cr, Cs, Cu, Eu, Ga, Ge, Hf, Hg, I, La, Mg, Mn, Mo, Pb, Rb, Sb, Se, Sm, Sr, Ta, Th, Ti, U, V, W, Y, Yb,
Gases	C, H, N, S	Hg	No data

[a] Excludes Antrim and Moroccan shale and their byproducts

[b] Concentration >0.1%

[c] Concentration $\leq$0.1% to 1 ppm

[d] Concentration <1 ppm

Retort waters are produced within the retort as a vapor that is condensed with the oil and travels over the cool shale ahead of the reaction zone. The composition of these waters depends on retort operating conditions and product collection system design and operation. In this work, there was a large range in the Green River retort water elemental abudances, and the ratio of the maximum to the minimum concentration ranged from 1.3 to 582 and averaged 75. This variability is consistent with that reported by others and is hypothesized to be due to differences in the product collection systems. The elemental composition of raw and spent oil shale did not significantly effect the composition of retort waters and there was no statistically significant difference in the composition of Green River, Antrim, and Moroccan retort waters. There were, however, statistically significant differences between waters produced by the two retort systems which is likely related to differences in the product collection system. The only retort operating conditions that had a significant effect on elemental compositions of retort waters were temperature and input gas (especially steam).

The particulate fraction (collected by vacuum filtration on a 0.45 μm filter paper) of retort water ranged from 203 to 2984 mg/l and consists of oils and tars, raw and spent shale fines, bacterial residue, and crystals that precipitate during filtration. The major elements (concentration >0.1 mg/l) in the particulate phase are Fe, Ni, K, and Ca (C, H, N, and S were not measured here). Scanning electron microscopy analysis indicated that the particulate fraction of retort waters consists of crystals and amorphous solids embedded in a uniform background of spong material. The amorphous particles (raw and spent shale fines) were rounded and their chemical composition was Si-Al-(Ca, K, Fe, Na). The crystalline particles ranged in size from a micron or less to about 100 μm on a side, were of varied shape, and composed principally of Fe, Ca, Mg, or Ni. Aragonite was positively identified as one of the crystalline phases by x-ray diffraction. These crystalline phases form from the precipitation of metal carbonates when CO_2 is stripped from solution during filtration according to the reaction $MeCO_3(s) + CO_2(g) + H_2O \rightleftarrows Me^{+2} + 2HO_3^-$. The spongy background material consists of oils, tars, and bacterial cells. Bacterial growth in unrefrigerated samples may remove significant amounts of the elements Hg, Ni, As, Fe, Ge, Br, and Se from retort waters.

The pyrolysis of oil shale produces a low Btu gas that contains elevated concentrations of hydrocarbons, sulfur compounds, and oxides of carbon. The composition of these gases was determined in this study and related to retort operating conditions. The concentration of H_2, CH_4, C_2 through C_5 hydrocarbons, H_2S, CO, CO_2, COS, and NH_3 in shale gases was determined by gas chromatography and mass spectrometry. These analyses indicate the CO_2, H_2, CH_4, and CO constitute about 90 mole percent of the gas and that the C_2 through C_5 hydrocarbons, NH_3, and H_2S are minor constituents (<5 mole %). The organic and inorganic composition of these gases depended primarily on retorting temperatures and atmosphere. Elevated temperatures decomposed a larger fraction of the carbonate minerals, producing higher concentrations of CO_2 in the gas than in runs at lower temperatures. The presence of oxygen in the offgas reduced the concentration of C_1 through C_5 hydrocarbons by oxidation to CO_2 and H_2O and increased the concentration of CO_2 through the char-oxygen reaction. Steam in the input gas reacted with CO and char to increase the Btu content of the gas by enchanced H_2 production in LLL runs.

The concentration of Hg in the offgas from two runs of the LETC controlled-state retort was determined by on-line Zeeman atomic absorption spectroscopy and ICl impinger trains. These analyses indicate that mercury concentrations in the offgas of the simulated in-situ retort may vary over several orders of magnitude, from 1 to 1000 ppb. Mercury was non-uniformly emitted in a pulse about two-thirds of the way through an O_2/steam/N_2 run of the LETC retort; no Hg was detected during the first two-thirds of the experiment. This type of emission pattern is hypothesized to be due to successive volatilization and condensation of mercury along the packed bed of shale.

Partitioning Patterns

The elemental abundance data were used to determine mass balances for each element for the 24 runs. These mass balances were used to study the partitioning of each element among the products--spent shale, retort water, shale oil, and offgas. Product closures, or the ratio of mass outputs to mass inputs, were determined for each element and run and used to assess the adequacy of experimental procedures and the possible volatilization of elements. Mobility, or the fraction of the total elemental mass charged to the retort that is distributed to the oil, gas, and water phases, was computed for each element and run.

The elemental closures indicate that sampling and analysis procedures were adequate and that good mass recovery was obtained in most instances. The average closure for all elements and runs (excluding Cd and Hg) for the LETC runs was 101 ± 7% and for the LLL runs it was 101 ± 10%. Good closures were not obtained for Hg and Cd due to the volatilization of these elements. (Mercury and Cd were not measured in the offgas of most runs and, therefore, a closure of less than 100% indicates possible volatilization). About 68% of the Cd and 42% of the Hg originally present in the raw shale in LETC runs were recovered in the products while in the LLL run 88% of the Cd and 34% of the Hg were recovered.

The elements were divided into three groups based on their relative mobility. Mass distribution patterns depended on retorting temperature, atmosphere, and shale source. The most volatile elements (Group 1) were H, N, S, C, Cd, and Hg. From 10% to nearly 100% of these elements were distributed to the oil, water, and gas phases during retorting. From 1% to 4% of the elemental mass of the Group 2 elements, As, Se, Ni, and Co, were mobilized and about 95% of that was distributed to the oil. The retort operating conditions studied had no statistically significant effect on Group 2 mass distribution patterns except for Se. Selenium was apparently vaporized and removed from the retort at elevated temperatures. About 16% of the total elemental mass of Se charged to the retort was lost from the system at retorting temperatures greater than 900°C; no Se loss was noted at lower temperatures. The Group 3 elements, which include Cr, Sb, Zn, Cu, Mo, Fe, and Mn, had mobilities of less than 1% and large coefficients of variation. No significant relationships were observed between operating conditions and mobility for these elements due to the large experimental error.

Partitioning Model

A theoretical framework was developed to interpret the elemental abundance and partitioning data, and theoretical calculations and experiments were carried out to validate the model. This model assumes that an element may be partitioned from the raw oil shale to its products either because its compounds are volatile under retorting conditions or because its compounds are soluble or entrained in these products.

Elements may be volatilized from oil shale as a consequence of mineral decomposition, kerogen conversion, or reduction by C, CO, and other species. Volatile species formed from these types of reactions would be swept ahead of the reaction zone by input gas where they may be condensed on the cool shale bed, entrapped in the oil-water emulsion, or swept out of the retort as gaseous or condensed species. The water that condenses with the oil in cool regions of the retort could leach some constituents from the unreacted shale, and elemental partitioning between the oil and water phases would occur. Finally, raw and spent shale fines may be entrained in the gas stream or may be picked up by the oil-water emulsion as it passes over the cool shale.

These types of mechanisms were investigated using thermodynamic calculations and in leaching experiments. The volatilization of elements from the mineral matrix and the stable gas phase species were estimated for Hg using thermodynamic procedures. Equilibrium constants were determined for 30 possible reactions from free energies of formation and used to compute species distributions. These calculations indicate that the principal gaseous species of Hg are $Hg(g)$, $HgO(g)$, $Hg(CH_3)_2$, and $Hg_2(g)$. These calculations suggest that mercury may occur as HgS in oil shale and that it is released during retorting by decomposition of the sulfide, by reduction with H_2 and CO, and by combustion. Mercury volatilized by one of these mechanisms may then be removed from the gas stream by formation of HgO or HgS in cool regions ahead of the reaction front. These results are consistent with experimental measurements made in this study and elsewhere.

Some elements may be partitioned from the raw shale into the oils and waters by contact between shale, water, and gases and by entrainment of solids in the reaction zone. This was investigated in a series of experiments in which samples of oil shale and shale oil were leached with an NH_4HCO_3 (major minor, and trace elements. This study indicated that ppm concentrations of dissolved Al, As, B, Ca, Fe, K, Mg, P, and Si were leached from both the raw shale and shale oil by the NH_4HCO_3 solution. Parts per million concentrations of Cr, Li, Mo, Se, V, and Zr were also leached from the raw shale. Filtration of raw shale leachate significantly reduced the concentration of As, Fe, Mn, Ni, Pb, Rb, Sr, Zn, and Ti suggesting that these elements are partially associated with raw shale fines that coated the shale prior to leaching. These results substantiate the hypothesis that significant concentrations of some elements, notably As, B, Fe, P, and Si, are incorporated into retort water by virtue of its contact with raw shale and oil ahead of the reaction zone.

Recommendations

This investigation has surveyed the partitioning of 50 major, minor, and trace elements during simulated in-situ retorting. This work indicates that most of these elements are not significantly mobilized during retorting. The only elements that are distributed in large quantities to the by-products are C, H, N, S, Cd, and Hg. Lesser but significant quantities of Se, As, Ni, and Co are also distributed to the oils and water; and, at retorting temperatures in excess of about 900°C, Se is mobilized to the gas phase.

These major conclusions should serve as a starting point for further investigations of elemental partitioning during in-situ oil shale retorting. Specifically, the following are recommended:

1. Additional Detailed studies should be conducted on the partitioning of the mobile and environmentally important trace elements As, Se, Co, Ni, Cd, and Hg. These studies should be carried out in laboratory-scale retorts designed specifically for partitioning studies to facilitate close experimental control and to minimize contamination. High precision analytical methods need to be developed to decrease experimental error and, hence, mass balance closure.
2. Direct gas-phase measurements need to be made of the volatile elements As, Se, Cd, and Hg. These measurements should be made throughout the duration of retorting experiments to investigate the pulsing patterns observed here for Hg and in real time to avoid sample alteration.
3. This work should be corroborated by conducting similar partitioning studies using field in-situ retorts.
4. The inorganic and organometallic compounds and complexes present in the retort waters, shale oils, and offgases should be determined so that the environmental implications of use and disposal of these products and by-products can be assessed. The mineral residence of the volatile elements, As, Se, Co, Ni, Hg, and Cd in raw oil shale should also be determined.

PUBLICATIONS AND PRESENTATIONS

A final draft of the paper, "Fingerprinting Inorganic and Organoarsenic Compounds in Oil Shale Process Waters using a Liquid Chromatograph Coupled with an Atomic Absorption Detector" was prepared for submission to Science. Dr. Richard Fish presented a talk entitled "Speciation of Inorganic and Organoarsenic Compounds in Oil Shale Process Water" at the Second Symposium on Environmental Analytical Chemistry, June 18-20, 1980, held at the Brigham Young University, Provo, Utah. This talk was co-authored with F. E. Brinckman and K. L. Jewett of the National Bureau of Standards. Phyllis Fox prepared the final report on the mass balance studies, *Partitioning of Major, Minor, and Trace Elements during Simulated In-Situ Oil Shale Retorting*.

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