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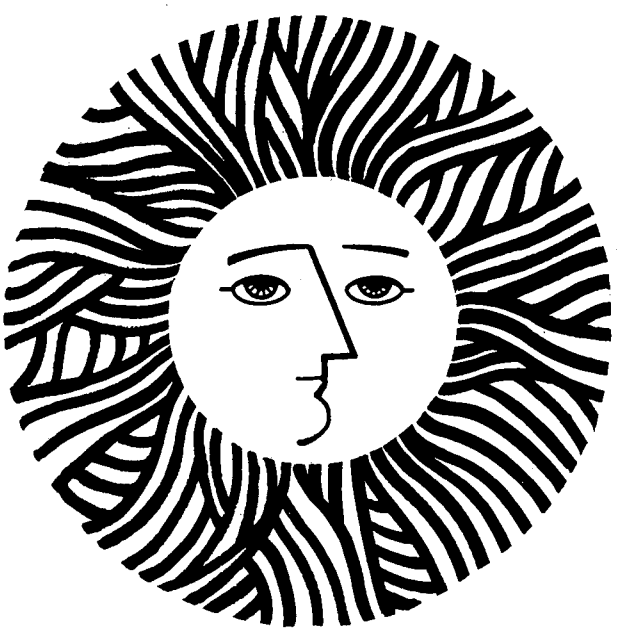

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September 2, 1981

TO: Charles Grua

FROM: Richard H. Sakaji, Bonnie M. Jones, and Jerome F. Thomas;
Christian G. Daughton (SEEHRL) Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

RE: Monthly Progress Report for August
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-440

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

The major remaining difficulty with the reverse-phase chromatographic/IR spectrophotometric determination for oil and grease has been the erratic background absorbance contributed by the C-18 Sep Paks. This background absorbance appears to be caused by compounds that are leached from the cartridges (e.g., plastisizers from the cartridge casing). A 20-mL pre-wash of Freon has not been sufficient to eliminate the significant background contribution. We have tried seven different pretreatments (no wash, 1.0 and 0.1% acetic acid, Freon, tetrahydrofuran, acetonitrile, and methylene chloride) in an attempt to attenuate the background absorbance. Among these, a pre-wash with 10 mL of HPLC grade tetrahydrofuran (THF) reduced the background absorbance (log P_o/P) to 0.011 (rsd = 39.3%, n = 8); this was 50% lower than the absorbance contribution from cartridges that were pre-washed with Freon.

We determined the reproducibility of the oil-and-grease determination for Oxy-6 retort water, incorporating the THF pre-wash and a 2-mL ASTM Type I water wash after sample application. The oil-and-grease value was 204 mg/L (rsd = 13.2%, n = 8); this was lower than previously reported values (405 to 313 mg/L) and reaffirmed our view that oil-and-grease values should be expressed as a range for any particular synfuel wastewater.

The necessity for lyophilization was demonstrated. The absorbance scans from both blank and sample cartridges that were partially dried with compressed air were unusually shaped; two auxillary peaks at 2970 and 2850 cm^{-1}, which corresponded to asymmetric methyl and symmetric methyl C-H stretches, respectively, were quite pronounced and made accurate quantitation at 2930 cm^{-1} difficult. The blanks exhibited the same spectrum. These

results indicated that the methanol that was applied to activate the chromatographic packing material was subsequently eluted with the Freon from the non-lyophilized cartridges. Lyophilization of C-18 Sep Paks apparently is essential for accurate oil-and-grease quantitation.

TASK 4. SPENT AND RAW SHALE STUDIES

Batch Isotherm Studies

We repeated our investigation of the sorptive equilibria between fractionated Oxy-6 retort water (C-18 separation) and TOSCO II spent shale. The results from batch equilibrium experiment #9 included:

1. The organic solutes from the polar fraction were not sorbed within the first 24 hours of contact with the spent shale. The DOC concentration declined between 24 and 96 hours (C_i/C_o = 0.40 at 96 hours). Biooxidation of the easily degradable compounds in the polar fraction probably accounted for this reduction.
2. A significant portion (52%) of the DOC was removed from the nonpolar fraction by sorption. The sorptive process approached equilibrium within eight hours (C_i/C_o = 0.50), but the DOC reduction continued through the entire investigation (C_i/C_o = 0.37 at 96 hours).

These data confirmed our conclusions from batch equilibrium experiment #8 (July 1981); TOSCO II spent shale preferentially sorbs the nonpolar organic constituents from Oxy-6 retort water and has a very low sorptive capacity for the easily biodegradable polar compounds.

TASK 5. SYSTEM STUDIES

Biological Oxidation Studies

The investigation of the biotreatability of the polar and nonpolar fractions of retort water (July 1981) was repeated incorporating pH control (phosphate buffer addition) and trace metal addition to the nonpolar fraction. We had postulated that the nonpolar fraction was unbuffered and trace metal deficient because of the fractionation procedure, and that these factors were limiting the biodegradation of the organic solutes. The results are summarized in Table I. The percentage of DOC removal from the nonpolar fraction was equivalent to the previously reported values. These factors, therefore, were not limiting microbial mineralization of the organic solutes; these results support our hypothesis regarding the recalcitrance of the remaining organic solutes in the nonpolar fraction.

With the use of our Oxy-6-retort-water acclimated bacteria, carbon-unsupplemented Oxy-6 gas condensate appears to be incapable of supporting microbial growth. To elucidate the factors that limit biooxidation of gas condensate, we separated the wastewater into polar and nonpolar fractions using C-18 Sep Paks. Each fraction was diluted 50%, supplemented with inorganic orthophosphate and trace metals, inoculated, and incubated at 30 C for several days. The results from this investigation included:

1. Eighteen per cent (115 mg/L) of the gas condensate DOC resides in the polar fraction.
2. Of the remaining 82 per cent, which was present in the dried residuum that was obtained by fractionation and subsequent elution, 69 per cent would not resolubilize in water.
3. Neither fraction was capable of sustaining microbial growth.

The absence of microbial activity in the polar fraction was surprising. A possible explanation may be that the individual organic solute concentrations were below the affinity constants of the requisite enzymes. We have hypothesized that the major portion of the organic material in Oxy-6 gas condensate is analogous to the biologically recalcitrant solutes in Oxy-6 retort water. We plan to include gas condensate in our investigation of the biorefractory solutes of Oxy-6 retort water.

This work was supported by the U.S. Department of Energy under Contract number W-7405-ENG-48.

Table I
Bacterial Removal of DOC from Oxy-6 Retort Water
Fractionated by Reverse-Phase Separation

Fraction[1]	Dissolved Organic Carbon Concentration (mg/L) initial	Δ[2]
control (unfractionated)	1379 1.00[3]	730 53[4]
polar	742 0.54	549 74
nonpolar[5]	586 0.43	176 30
recombined polar + nonpolar	1340 0.97	750 56

[1] each control and fraction of Oxy-6 retort water was diluted 50% prior to inoculation
[2] DOC removed by biooxidation
[3] portion of DOC in fraction compared with initial unfractionated DOC
[4] % of DOC removed by biooxidation compared with initial DOC
[5] supplemented with 2.5 mM ammonium chloride, phosphate buffer, and trace metals

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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