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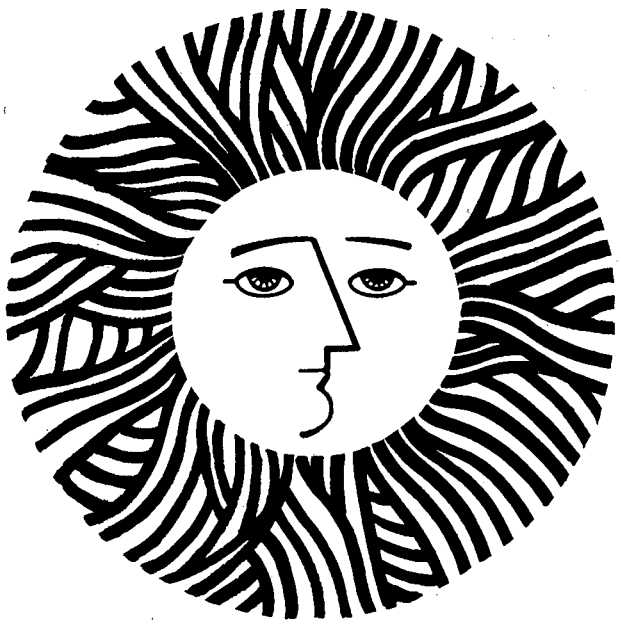

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May 1, 1981

TO: Charles Grua

FROM: Richard Sakaji and Bonnie Jones; Christian Daughton (SERL)

RE: Monthly Progress Report for April
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-399

PRESENTATION

B. Jones presented an invited paper, "Oil Shale Wastewater Treatment: Analytical Methods Development" (C.G. Daughton, B.M. Jones, and R.H. Sakaji), at the 53rd Annual California Water Pollution Control Association Conference, Long Beach, California, April 29-May 1, 1981. A copy of the abstract is enclosed.

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

We have demonstrated the retention efficiency of activated and unactivated C-18 Sep Paks. Two sets of C-18 Sep Paks were used in this experiment. One set was activated with methanol and rinsed with water; the other set was left unactivated. Both sets had a known quantity of mineral oil applied to each cartridge. A known volume of distilled-deionized water was then passed through each cartridge to simulate sample preparation. After lyophilization, the cartridges were eluted with Freon and the eluate was quantitatively analyzed by infrared spectroscopy for oil content. There was no statistical difference in the recovery of mineral oil between the activated and the unactivated C-18 Sep Paks. The oil recoveries were 86.6 and 90.7%, respectively. From this experiment, we can conclude that, for standard additions by this method, C-18 Sep Pak activation has no effect on the retention efficiency of mineral oil. We believe that the mineral oil was able to partition into the octadecylsilyl stationary phase of the unactivated cartridge because the oil was applied in "pure" form without an aqueous (polar) solvent. The presence of an aqueous solvent would necessitate

indicates that activation of the raw shale should be investigated.

To determine the effects of sequential treatment processes on organic solute removal from retort water, biologically treated or "spent" media from a microbial batch culture was used in two batch equilibrium experiments with both spent or raw shale. The batch culture media consisted of 50% Oxy-6 retort water and 50% phosphate buffer. Upon reaching stationary phase (conclusion of microbial growth), the retort water is depleted of easily degradable carbon and further growth is limited. The resultant extracellular fluid is "spent" media. Bacterial action reduces the DOC of retort water by 50%. The combination of Colony raw shale and Oxy-6 "spent" media yielded batch experiment data that were inconclusive because of data scatter. The data from the TOSCO II spent shale and Oxy-6 "spent" media combination revealed that equilibrium was reached within 24 hours ($C_i/C_o=0.565$). DOC was reduced 44% in the "spent" media. This sequential biological:physical-chemical treatment effected an overall reduction of 72% of the organic solutes present in retort water. This indicated that spent shale treatment is complementary to biological treatment; each treatment process is capable of removing different classes of organic compounds from retort water.

TASK 5. SYSTEM STUDIES

Biological Oxidation Studies

Our previous research has indicated that 50% of the organic solute carbon in Oxy-6 retort water was refractory to biological degradation. We feel that our research efforts should focus on the biological treatment of this recalcitrant fraction of organic compounds.

Repeated efforts to isolate microorganisms that are capable of metabolizing the recalcitrant solutes have been unsuccessful. We have begun to investigate the capabilities of commercially-acclimated bacteria, LLMO and Hydrobac, to degrade this portion of organic compounds present in the wastewater. The LLMO culture was unable to grow in spent retort water or in raw gas condensate water. Initial growth was observed, however, in ammonia-stripped raw retort water inoculated with the Hydrobac culture.

We suspect that many of the recalcitrant species are sulfur- and nitrogen- heterocycles. Analog enrichment for a microbial population that can ultilize a nitrogenous-heterocyclic compound as a sole nitrogen source was

successful. We have isolated a culture, in the presence of an easily degradable carbon source, that can use quinoline as a sole nitrogen source; by making nitrogen the limiting nutrient, the requisite enzymes are derepressed. This culture will be introduced and acclimated to the retort water environment. It may be necessary to prevent inhibition or repression of the enzyme complement that is synthesized for heterocycle degradation. Further experiments will be conducted to investigate the action of these organisms on other nitrogenous heterocycles.

April 30, 1981 Laboratory

Oil Shale Wastewater Treatment: Analytical Methods Development

C. G. Daughton: Sanitary Engineering Research Laboratory, University of California, Berkeley.
B. M. Jones and R. H. Sakaji: Lawrence Berkeley Laboratory.

Shale oil production generates large volumes of several types of wastewater. One waste stream, retort water, is highly contaminated from contact with hot shale, kerogen, and oil during the retorting process. The analysis of retort water involves two major problems: (i) the acquisition of representative samples and subsamples, and (ii) interferences with and inappropriateness of "standard methods." Development of waste treatment schemes for retort water requires methods for specific and sensitive detection of constituents that reflect the extent of treatment.

Characteristics of retort water (e.g., intense color, abiotic particulates, surface-active agents, propensity to foam, and large quantities of tarry materials) often interfere with commonly used analytical methods, and have necessitated development of compatible methodology. The methods required for experimental work may differ from those for process monitoring because of these characteristics and the sample size dictated by experimental design. Two measures of the extent of wastewater treatment necessary for experimental work are cellular biomass (an indirect measure of biodegradation) and oil and grease. For quantitation of biomass, we have modified a protein assay method. Microbial cells were separated from retort water and digested in alkali; the solubilized protein was quantitated colorimetrically using Folin-Ciocalteu "phenol" reagent. A new approach to dissolved oil determination involved its separation from aqueous medium by reverse-phase chromatographic partitioning, elution with an organic solvent, purification by normal-phase partitioning, and quantitation by infrared spectroscopy.

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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