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MONTHLY PROGRESS REPORT FOR JUNE. SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATERS

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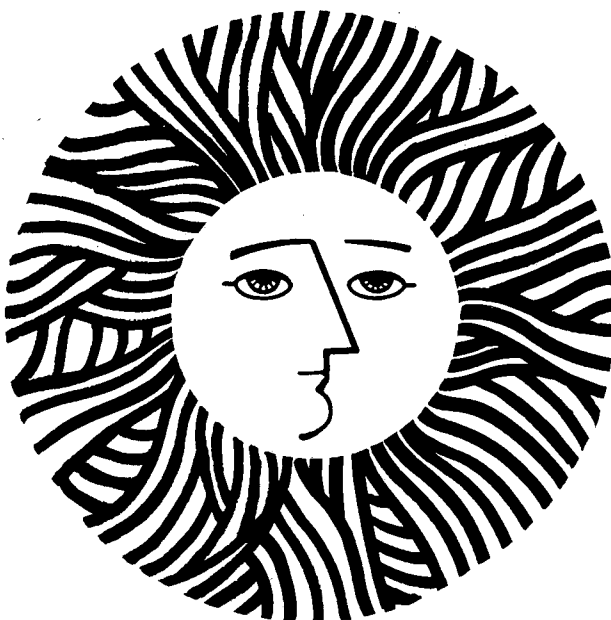
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July 1, 1981

TO: Charles Grua  
FROM: Richard Sakaji and Bonnie Jones; Christian Daughton (SERL)  
RE: Monthly Progress Report for June  
Spent Shale as a Control Technology for Oil Shale Retort Waters  
LBID- 422

#### PRESENTATION

B. Jones and R. Sakaji attended the Second Processing Needs and Methodology for Wastewaters from the Conversion of Coal, Oil Shale and Biomass to Synfuels Workshop, June 24-25, 1981, DOE Headquarters, Germantown, Maryland. R. Sakaji presented an invited review of our work, "Spent Shale as a Control Technology for Oil Shale Process Wastewaters" (J. Cantor, B. M. Jones, G. Langlois, R. H. Sakaji, K. Yu, and C. G. Daughton). A manuscript will be submitted for the workshop proceedings.

#### TASK 5. SYSTEM STUDIES

##### Biological Oxidation Studies

##### Nitrogenous Heterocycles.

We have demonstrated that approximately 50% of the organic carbon in Oxy-6 retort water is resistant to microbial mineralization. Our research has focused on the microbial alteration and degradation of the organic compounds in this recalcitrant fraction. Nitrogenous heterocyclic compounds, postulated to be major constituents of this fraction, are resistant to catabolism and represent a major problem in the treatment of oil shale wastewater. This recalcitrance is partially a result of the inability of bacteria to attack these compounds unless they are present as sole sources of nitrogen. The availability of an easily utilizable nitrogen source represses the synthesis of enzymes required for heterocyclic-nitrogen abstraction. Unfortunately, oil shale process waters contain excessive concentrations of ammonia, a preferred form of nitrogen for many bacteria.

Dr. Daughton has proposed a treatment scheme that circumvents this enzyme repression problem. Attached is a report that was submitted to document a Record of Invention (not for circulation). The documented protocol details the selective enrichment for microorganisms capable of using nitrogenous heterocycles as sole nitrogen sources, concentration of the resulting cell mass, and introduction of the induced bacterial culture into the wastewater. This procedure obviates the enzyme repression difficulty by introducing a large quantity of previously induced enzyme into the wastewater.

We have succeeded in isolating a microbial community that is capable of utilizing quinoline, a nitrogenous heterocycle, as sole nitrogen source. Carbon was supplied in the form of easily degradable carboxylic acids. We have been unable, however, to grow sufficient quantities of cells for introduction into retort water. We will continue this work using a synthetic wastewater composed of a variety of nitrogenous heterocyclic compounds to ensure the selection of competent microorganisms.

#### General Studies.

An investigation of the biotreatability of 100% Oxy-6 retort water revealed that microbial activity eliminated 55% of the dissolved organic carbon (DOC). This removal was consistent with our studies using 50% Oxy-6 retort water, however, cell yield calculations (mg protein produced/mmmole carbon consumed) revealed that retort water concentration had a moderately adverse effect on microbial efficiency. These data are consistent with our conclusions from our toxicity studies.

Initial characterization of sour water from a near-commercial surface retorting operation revealed that the DOC content of this sample is 1.6 times the DOC concentration of Oxy-6 retort water. We have begun enrichment cultures using this surface process water and plan to include it in our biotreatability investigations.

#### Combined Biological Oxidation/Spent Shale Treatment

The second batch experiment combining biological and sorbent treatments of retort water was completed this month. Either powdered activated carbon (PAC; I.C.I. 12-40 mesh) or TOSCO II retorted shale (60-80 mesh) was added to flasks containing either raw or spent Oxy-6 retort water and an acclimated inoculum. Spent retort water was the extracellular fluid that remained after exhaustive biooxidation. The results and conclusions from the inoculated raw

retort water/sorbent mixtures (Table I) include:

1. Bacterial metabolism effected a 50% DOC reduction (i.e., control without sorbent).
2. PAC and spent shale sorption removed 8 and 6%, respectively, of the DOC (i.e., as determined after one hour of incubation).
3. The total reduction of DOC in raw retort water by simultaneous biological treatment and addition of PAC or spent shale was 79 and 77%, respectively.
4. Simultaneous treatment of inoculated raw retort water with either spent shale or PAC yielded total reductions that were greater than the sums of the individual reductions effected by biooxidation and sorption. For either treatment, this unexplained portion of the total percentage removal was 21 percent. We hypothesize that removal of the unexplained portion (i.e., synergism) was by enhancement of biodegradation.

The results and conclusions from the inoculated spent retort water/sorbent mixtures (Table I) include:

1. Reinoculation of spent water effected a further DOC diminution of 4 percent (total DOC removal of 52% compared with raw retort water). This could result from (i) incomplete biological pretreatment, (ii) presence of cellular lytic products, or (iii) variations in inoculum composition.
2. PAC and spent shale sorption removed 11 and 8%, respectively, of the DOC.
3. The unexplained portions of the total percentage removal of DOC by simultaneous treatment of inoculated retort water with either PAC or spent shale were 16 and 17%, respectively.

The treatment of spent retort water by inoculation and sorbent addition represents a treatment scheme that includes: thorough biological pretreatment of raw retort water, separation of cells, and collection of spent retort water followed by sorbent treatment of reinoculated spent retort water. The total DOC reductions achieved by this process were identical to those obtained when PAC or spent shale was added directly to inoculated raw retort water. This indicated that biological pretreatment of raw retort water to produce spent water may be unnecessary for the enhancement of biooxidation by sorbent addition.

An apparent incongruity was the greater enhancement of DOC removal from raw retort water compared with spent retort water. One explanation for this observation is that sequential cometabolism occurred in the mixed acclimated culture; organic compounds altered by one population were utilized by another. This mechanism would be more likely to occur in raw retort water which, unlike spent retort water, contains easily degradable compounds that could serve as cosubstrates.

A third biological/sorbent treatment batch experiment was conducted to determine if the enhanced removals of DOC were reproducible. The total reduction of DOC observed in these experiments was equal to the additive removals of biooxidation and sorption. The nonreproducibility of enhanced DOC removal may be caused by variability in the composition of the microbial inoculum.

Table I  
 Percentage DOC Removal from 50% Oxy-6 Retort Water  
 by Combined Biological/Sorbent Treatment

<u>sorbent</u>	<u>% DOC Removal from Inoculated Medium</u>					
	<u>Raw Retort Water</u>			<u>Spent Retort Water</u>		
	<u>total</u>	<u>sorption</u>	<u>enhancement<sup>1</sup></u>	<u>total</u>	<u>sorption</u>	<u>enhancement</u>
none (control)	50 <sup>2</sup> (692) <sup>3</sup>	na <sup>4</sup>	na	52 <sup>2</sup> (731) <sup>3</sup>	na	na
PAC <sup>5</sup>	79 (1102)	8 (118)	21 (292)	79 (1108)	11 (154)	16 (223)
spent shale <sup>6</sup>	77 (1083)	6 (84)	21 (307)	77 (1073)	8 (116)	17 (226)

<sup>1</sup> total % removal minus removals from biooxidation (i.e., control) and sorption

<sup>2</sup> percent reduction from raw Oxy-6 retort water (DOC = 1396 mg/L)

<sup>3</sup> DOC (mg/L) removed, compared with raw retort water

<sup>4</sup> not applicable

<sup>5</sup> powdered activated carbon, 12-40 mesh (1.3 g/L)

<sup>6</sup> TOSCO II spent shale, 60-80 mesh (100 g/L)



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