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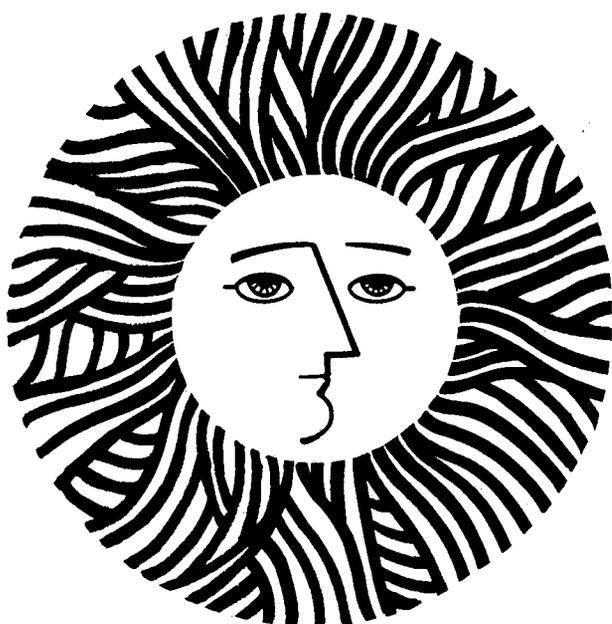
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April 2, 1981

TO: Charles Grua

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

RE: Monthly Progress Report for March
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-384

PRESENTATION

R. Sakaji and B. Jones attended the Fourth Annual DOC Oil Shale Conversion Symposium, March 24-26, 1981, Denver, Colorado. B. Jones presented an invited paper, "Factors Limiting Biodegradation of Oxy-6 Process Water Constituents" (B. M. Jones, R. H. Sakaji, J. P. Fox, and C. G. Daughton). A copy of the abstract is enclosed.

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

As mentioned last month, the protocol that we have developed for quantitating oil and grease is actually a measure of true hydrocarbon oil. This method employs a Si cartridge clean-up of the eluate from a C-18 cartridge. We discovered that eluate from the Si cartridge could contribute a significant interference to the quantitation of oil at 2920 cm^{-1} . Freon pre-wash did not alleviate the problem. The interference was found to be inherent to one particular lot of Si Sep Paks. When the established protocol was followed, the eluate of Si Sep Paks from other lots did not interfere with the analysis.

A second study of the retention capacity of C-18 cartridges was conducted. Two cartridges were connected in series, and various quantities (5-30 mL) of Oxy-6 retort water were passed through the two cartridges. Each cartridge was lyophilized and eluted separately. The eluate from each cartridge was then analyzed for oil content. If the oil (i.e., substances that absorb at 2920 cm^{-1}) in retort water either exceeded the capacity of or was not retained by the first cartridge, then oil should be detected on the second cartridge. For quantities of retort water greater than 5 mL, there was

a detectable amount of oil present on the second cartridge. The range of oil concentrations in Oxy-6 retort water from this study was 29-35 mg/L when the oil retained by the two cartridges in series was considered in the calculations. We plan to investigate this apparent breakthrough of oil by applying larger quantities of retort water to C-18 cartridges connected in series. The oil and grease method that we have developed is apparently affected by samples of high osmolality such as retort water.

TASK 4. SPENT AND RAW SHALE COLUMN STUDIES

Batch Isotherm Studies

The batch experiment to determine the time required for the sorbent-solute system to reach equilibrium was repeated early this month. The sorbents in these studies were TOSCO II spent shale and granular activated carbon (GAC) from Calgon and ICI Americas, Inc. Organic solute concentration in Oxy-6 retort water was quantitated as dissolved organic carbon (DOC).

Sample vials containing replicate mixtures of retort water and GAC were agitated on a shaker for periods up to 30 days. At selected time intervals, the sample vials were removed and the liquid and particulates were separated by filtration. The filtrate was analyzed for DOC. The fraction of DOC remaining in solution was plotted as a function of time. This procedure was repeated using TOSCO II spent shale as the sorbent.

For both GAC's, apparent equilibrium was reached within 8 hours. TOSCO II spent shale reached an apparent equilibrium in 24 hours, but exhibited further DOC removal during the following 144 hours. This additional DOC removal was attributed to biological activity; 24 hours is the typical incubation time required to achieve biological growth in our batch biological oxidation experiments. Therefore, the time required to reach equilibrium in the TOSCO II sorbent-solute system was estimated to be 24 hours.

Isotherm experiments were conducted using this 24 hour time period. Various quantities of sorbent were weighed into sample vials. An equivalent volume of retort water was then added to each sample vial. The vials were agitated on a wrist-action shaker for 24 hours. The sample vials were then removed, the liquid-solid mixture was filtered, and the filtrate was analyzed for DOC. The data from these experiments were plotted as mg of DOC removed/g of sorbent vs. the equilibrium concentration of DOC in the aqueous phase (i.e., nonsorbed DOC).

Two sorption isotherm experiments were completed using TOSCO II spent shale. The first sorption isotherm experiment used 25-120 mesh TOSCO II spent shale. The resulting scatter of data made the results impossible to interpret. The poor results in this experiment were believed to result from the broad distribution range of particle sizes and variability among spent shale samples in the vials. The second sorption isotherm experiment, which used shale of a restricted size range, was successful. The sorption isotherm from the DOC data resembled a flattened "S"-shaped curve. The linearized data fit both the Langmuir and Freundlich adsorption models ($r^2 = 0.979$ and 0.983 , respectively). This is acceptable, as these two models agree with one another over a moderate range of equilibrium values. The shape of the isotherm suggested that adsorption was not the only process by which the DOC was removed from solution. The term "sorption" is possibly more appropriate for describing the complex chemical interactions that were occurring in this system, because the removal mechanisms could be a combination of adsorption, absorption, and precipitation.

Two isotherm experiments using Calgon GAC were also conducted. The first experiment used an inadequate range of carbon dosages and resulted in an incomplete isotherm. The second experiment was more successful, and the resulting isotherm resembled a flattened "S"-shaped curve that best fit the Freundlich adsorption model. As in the spent shale studies, the isotherm suggests that a complex series of chemical and physical interactions was occurring. The data also show that GAC had a much higher sorptive capacity than the spent shale.

TASK 5. SYSTEM STUDIES

Biological Oxidation Studies

The effect of nutrient addition on bacterial growth and removal of organic solutes from 50% Oxy-6 retort water was investigated. Previous studies showed that the addition of magnesium and iron did not enhance microbial growth or the microbial degradation of organic material. An experiment was conducted to determine if other micronutrients (vitamins and other trace metals) would serve to improve the biological treatment of retort water. The results from this work are summarized in Table I.

Table I.

Effect of Nutrients on DOC Removal from Oxy-6 Retort Water

	<u>% DOC Removal</u>	
	<u>Supplemented</u>	<u>Unsupplemented</u>
Mg & Fe	45	48
trace metals & vitamins	46	50

There are two possible explanations for these results; (i) these compounds were not the factors limiting microbial growth, or (ii) the added nutrients were unavailable to the bacteria. In either case, the addition of these nutrients did not enhance the biodegradation of the organic solutes in Oxy-6 retort water.

Initial biological treatment studies have revealed that Oxy-6 gas condensate (50%) is not amenable to microbial degradation. Our initial hypothesis was that ammonia toxicity was limiting microbial growth. Further investigation revealed that ammonia-stripped gas condensate (50%) also could not support microbial growth. When easily degradable carbon was added to both stripped and unstripped gas condensate, we found that bacterial growth ensued and that it was not affected by ammonia concentration. The growth was solely at the expense of the exogenous carbon source. Microbial growth in this wastewater was therefore carbon limited; the organic solutes were recalcitrant to biological degradation. Ammonia toxicity did not appear to limit microbial growth in 50% Oxy-6 gas condensate. We intend to do parallel investigations with Oxy-6 gas condensate and Oxy-6 spent retort water on the microbial alteration of bioreactory compounds.

We observed that up to 25% of the DOC disappeared from solutions of gas condensate during incubation without concomitant microbial growth. These organic compounds were apparently volatilized. This emphasizes the importance of monitoring both microbial density by protein quantitation, as well as organic solute concentration.

FACTORS LIMITING BIODEGRADATION OF OXY-6 PROCESS WATER CONSTITUENTS

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Microbial removal of contaminative constituents from Oxy-6 retort water rarely has exceeded 50% of either dissolved organic carbon (DOC) or soluble chemical oxygen demand (SCOD). Removal of this fraction of organic solutes is easily accomplished; in contrast, the remaining fraction is extraordinarily resistant to degradation. Furthermore, the specific COD (i.e., SCOD/DOC) is generally not reduced below 3.00. These studies have involved highly acclimated aerobic seed grown in 50% Oxy-6 retort water.

Possible explanations for the incomplete removal of retort water solutes by microbial degradation include: (i) trace nutrient limitation (e.g., metals, vitamins), (ii) macro-nutrient limitation (e.g., P, S, N), (iii) substrate or metabolite toxicity (e.g., NH₃), and (iv) recalcitrant organic substrates or incompetent microbial species.

We have investigated these possibilities with the following results: (i) Addition of trace nutrients does not enhance the removal of the recalcitrant fraction. (ii) Endogenous inorganic orthophosphate (Pi) concentration in Oxy-6 retort water rapidly becomes limiting; the addition of Pi to a final concentration of about 0.1 mM is necessary for complete degradation of the usable carbon. (iii) Oxy-6 gas condensate, inoculated with our retort water acclimated seed, has not been conducive to microbial growth. This is possibly a result of ammonia toxicity. (iv) Recalcitrant organic molecules may compose the remaining undegraded fraction. Classical enrichment techniques have been surprisingly unsuccessful for obtaining microorganisms capable of growth on the "spent" retort water (extracellular fluid remaining after cessation of growth on the easily utilized fraction).

We have achieved, however, the highest reported degree of retort water solute removal for biological and non-technological approaches. By linking two retort water treatment processes, spent shale pretreatment and biological treatment, we have effected the removal of 80% of DOC in retort water. Spent shale and biodegradation appear to remove different classes of organic compounds; we feel that they are complementary processes for the treatment of retort water.

April 2, 1981

TO: Charles Grua

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

RE: Monthly Progress Report for March
Steam Stripping Project
LBID-387

ANALYTICAL METHODS DEVELOPMENT

Ammonia Determination

We have investigated M. W. Weatherburn's version of the phenate or indophenol blue method for ammonia determination (Analytical Chemistry, 1967, 39, 971-974) as a possible alternative to the distillation/acidimetric titration method. The distillation/acidimetric titration method is recommended in Standard Methods for samples that contain either high concentrations of ammonia or interferences such as color and turbidity. Weatherburn's test is quick and simple to perform and has the advantage of diluting the sample with the assay mixture by 1:500 which may eliminate any color or turbidity interference of the sample matrix. Even more significantly, the test is specific for ammonia, whereas acidimetric titration cannot distinguish between ammonia and other distillable bases. Shale oil process waters have not been sufficiently characterized to assume that such interferences would not occur.

Standard curves from the Weatherburn method are linear ($r^2 = .999$) in the range from 100 to 1000 mg/L ammonia nitrogen (using an ammonium sulfate standard), but samples of gas condensate have not yielded reproducible results. Degassing of ammonia during sampling has been hypothesized as the most likely explanation; sample reproducibility will require further study. The effect of acidification of samples on the accuracy and precision of the test must also be investigated; acidification may be required to prevent loss of ammonia during storage, and samples may be collected by sparging the gas stream through acidic medium.

Scheduling requirements of the Steam Stripper project have necessitated postponement of development and validation of the colorimetric ammonia determination until validation of the carbon analysis methods has been

completed. If time is not available for completion of the ammonia analytical method development, the distillation/acidimetric titration method will be used for steam stripper samples.

STEAM STRIPPER DESIGN

Preliminary Work

Sufficient materials have been obtained to fabricate a skeleton frame for the steam stripper. Detailed design and documentation thereof continued.

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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