Title

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

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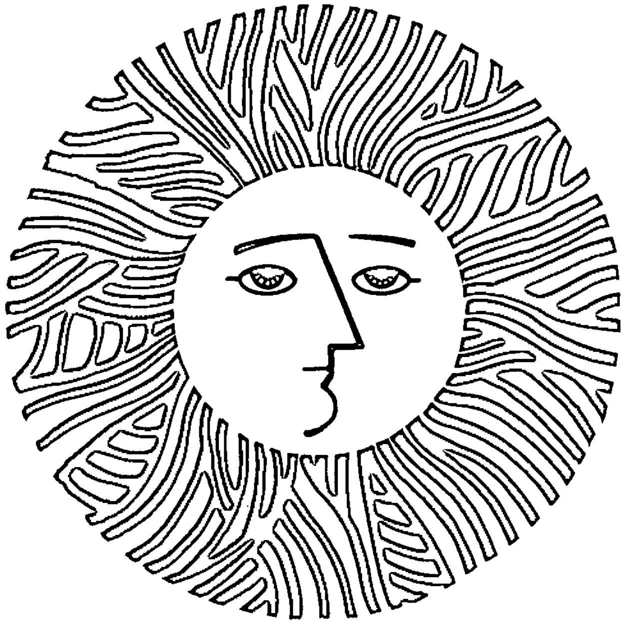

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November 6, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, Bonnie Jones, and Phyllis Fox

RE: Monthly Progress Report for October
Spent Shale as a Control Technology for Oil Shale
Retort Waters
LBID-308

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Analysis

This month we resumed development of an analytical protocol for quantitating oil and grease in retort water. We previously quantified oil and grease gravimetrically. This resulted in a number of problems including occluded water that was counted as oil and grease and nonreproducible results due to loss of volatiles during drying. It was decided to quantitate oil and grease spectrophotometrically to eliminate these problems, and work was suspended until an infrared spectrophotometer could be acquired and setup. The work reported on here involves the usual separation of oil and grease by reverse-phase chromatographic columns followed by spectrophotometric quantitation. This change in quantitation procedure resulted in a few minor changes in the previously reported separation method, including the substitution of carbon tetrachloride (CCl_4) for methylene chloride (CH_2Cl_2 has a C-H bond which is measured in the new quantitation procedure while CCl_4 does not have such a bond) and changes in drying procedure.

The recovery of oil by partitioning onto a reverse-phase chromatographic cartridge was demonstrated in a "clean" water system by emulsifying a small quantity of mineral oil in Milli-Q water. The water and oil were emulsified by vigorously shaking the two liquid phases in a separatory funnel. The phases were then allowed to separate, and 25 mL of the aqueous phase was withdrawn and passed through an activated reverse-phase chromatographic cartridge. The cartridge was eluted using the protocol outlined in the December 1979 monthly report, except that carbon tetrachloride (CCl_4)

was substituted for methylene chloride (CH_2Cl_2). The eluates were pooled in an Erlenmeyer flask and taken to dryness by passing a continuous stream of air over the liquids at room temperature. The residue was then quantitatively transferred and brought to volume in a 25-mL volumetric flask with several portions of CCl_4.

The CCl_4 solutions were than quantitatively analyzed for oil by using an infrared spectrophotometer. The percentage of transmission at 2920 cm^{-1} (representing absorbance due to C-H stretching) was measured through an SiO_2 cell (1-cm pathlength). A standard curve was obtained by analyzing a series of geometric dilutions of a working standard of mineral oil in CCl_4. The resulting peak at 2920 cm^{-1}, within the scan from 3200 to 2800 cm^{-1}, was measured using a peak height:baseline transmittance ratio technique.

The quantity of oil recovered from the emulsified samples ranged from 45 to 60 mg/L. This result has given us an excellent indication that this methodology may be appropriate for quantitating oil and grease in wastewater samples. This has also encouraged us to begin a comparison study of the partition-gravimetric and the reverse-phase chromatography methods. This study will be done in a "clean" system before applying this analytical protocol to retort water.

TASK 4: RAW AND SPENT SHALE STUDIES

During the month of October, we completed three continuous flow columns using 16-25 mesh Colony raw shale and 150-ton retort water. The first of the three columns completed our study of the effects of raw shale particle size and surface loading rates on absorbance, DOC, DIC, COD, and alkalinity. This column was operated at 0.1 gpm/f^2 in an upflow mode. The results, when compared to a similar column operated at 0.5 gpm/f^2, indicate that the reduction in absorbance, DOC, DIC, COD, and alkalinity was not effected by surface loading rate. Further examination of the data obtained from previous column runs (60-80 mesh raw shale) showed that the removal of alkalinity may depend on the surface loading rate for the smaller-sized shale. From the results obtained, it appears that removal of compounds that absorb at 450 nm is solely a function of the particle size.

The last two column runs were attempts at what we called "activation" of the raw shale; this "activation" step was accomplished by the use of a water-miscible organic solvent to soften and swell the kerogen. The columns were packed with 16-25 mesh Colony raw shale and 150-ton retort water was passed through the column at a surface loading rate of 0.1 gpm/f^2. Since the organic solvents would contribute chemical interferences to most of the measurements previously used (e.g., DOC, COD), it was decided that absorbance would be the only parameter monitored.

The first column was "activated" by soaking the shale in methanol for 16 hours. After draining the methanol, retort water was passed through the column in an upflow mode. The resulting plot of absorbance vs. effluent volume was identical to that for the unactivated raw shale. This indicated that if activation had been successful, it was not effective in improving the retention/partitioning characteristics of the column. Alternatively, activation had not been achieved.

The second column involved regeneration of the previously used raw shale by soaking in methanol, followed by rinsing in CH_2Cl_2 to remove sorbed organic solutes. The raw shale was then soaked in methanol and rinsed in deionized water to remove the organic solvents. The results of this column run, when plotted as absorbance units vs. time, were identical to those of the previously "activated" and unactivated columns operated under similar conditions. This indicated that the raw shale columns were not improved by this scheme.

The solvents that were selected for this study may not have been appropriate because kerogen is a relatively insoluble organic material. Solvents such as phenol or ethylene diamine may be more appropriate for "activating" the raw shale since other investigators have demonstrated that these solvents are capable of solubilizing the kerogen for oil recovery by solvent extraction.

TASK 5: SYSTEM STUDIES

Biological Oxidation of Retort Water

The protein assay and nephelometer described in the September monthly report were used in the toxicity studies we initiated this month. We studied the effects of retort water on cell protein yield in cultures that had reached stationary phase. Increasing volumes of retort water were added to baffled Erlenmeyer flasks and were diluted with distilled water to replicate constant volumes (30 mL). Several nutrient supplements, including phosphate, were also added. The flasks were than inoculated with a culture that had been acclimated to grow on 50% retort water media. They were than incubated at 30°C on a gyratory water bath shaker, and growth, as indicated by turbidity, was constantly monitored. When the turbidity values stabilized, the cultures were assumed to be in stationary phase and samples were removed for protein assays.

The initial results have been extremely ambiguous since only three experiments were completed this month. The results indicated that there was a trend toward decreasing protein yield with increasing concentrations of retort water; however, these yields were not reproducible. A possible explanation for these results was that the inoculum had been acclimated to a 50% concentration of retort water, which was in the middle of the range of concentrations for the experimental flasks. We also found that the pH of the batch cultures increased during incubation; the supplemental phosphate buffer was incapable of maintaining a constant pH in the culture flasks. We currently are trying to differentiate and resolve the problems of inoculum acclimation, innate retort water toxicity, and pH toxicity.

The dynamics of microbial growth in and substrate removal from retort water were investigated with a batch culture. Three liters of a 50% Oxy-6 retort water medium was inoculated with acclimated seed to initiate the experiment. The parameters of turbidity, absorbance (450 nm), pH, and concentrations of protein, COD, and DOC, were monitored throughout the study.

The microbial populations grew exponentially (as indicated by turbidity and protein concentration) after a short lag phase. The growth then ceased; the standing biomass decreased and reached a steady-state plateau (stationary phase) which was lower than the maximum concentration achieved. There was a concomitant decrease in growth substrates, as measured by soluble COD (SCOD) and DOC, and these values did not change upon cessation of microbial growth. Initial SCOD and DOC concentrations were reduced 51% and 54%, respectively, and continued monitoring (for five days) showed no further reduction. The pH, which was initially lowered to a value of 7 had increased to a value of 9 when microbial growth ceased. Addition of phosphate salts and phosphoric acid lowered the pH to a value of 7. However, this supplement did not stimulate growth or further the removal of solutes.

Turbidity proved to a good predictor of protein content and was valuable in this experiment as a facile, nondestructive reflection of biomass concentration. The DOC and COD values indicated only a limited degree of treatment. Investigations will continue in an attempt to determine the factors that are limiting microbial growth and substrate removal in retort water.

Steam Stripping

Operating data for the pilot-scale continuous flow and the bench steam stripper units were evaluated. Results from twelve successful runs of the pilot stripper suggest that a steam-to-water ratio of 0.4 is necessary for removals of ammonia and carbon dioxide above 90%. Eight runs were made with synthetic gas condensate and two each were made with Occidental gas condensate and retort water. This ratio is likely to be reduced by stripper design improvements, particularily with respect to column packing and control of steam flow. Recoveries of ammonia and carbon dioxide in effluent and brine were 75% of those in the influent.

Data from the bench-scale batch units provide an indication of the maximum attainable efficiency of continuous flow strippers, where mass transfer is not limiting. Results suggest that a steam-to-water ratio of 0.1 could attain up to 90% removal of ammonia, 99% removal of carbon dioxide, and 10% removal of acetic acid, the latter being a surrogate for organics in the waste. Even in a optimally designed continuous-flow stripper, attainable efficiencies would probably be lower due to mass transfer limitations.

These preliminary data and operating experience will be used to design a new steam stripper which will be used to develop design data.

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