Title
MONTHLY PROGRESS REPORT FOR APRILuSPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATERS

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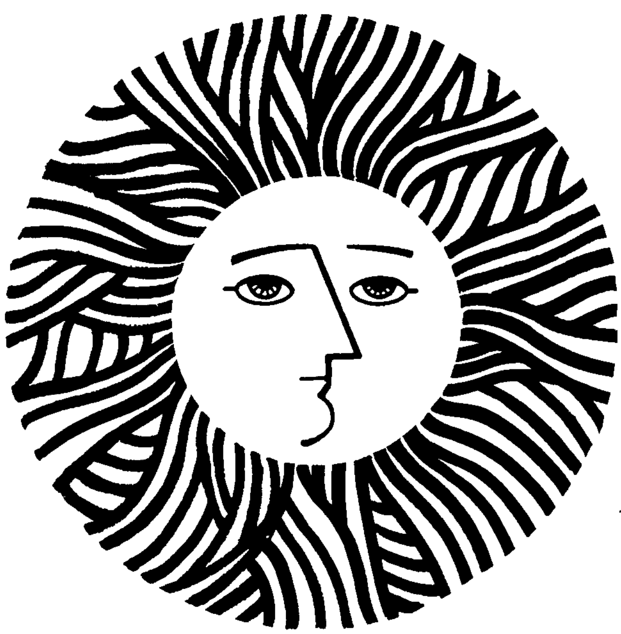

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May 13, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox

RE: Monthly Progress Report for April
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-203

PRESENTATIONS AND PUBLICATIONS

The paper "Potential Uses of Spent Shale in the Treatment of Oil Shale Retort Waters" by J. P. Fox, D. E. Jackson, and R. H. Sakaji, was presented at the Thirteenth Oil Shale Symposium, Golden, Colorado, April 18, 1980.

TASK 1. ANALYTICAL METHODS DEVELOPMENT

COD Test

The problem in ferrous ammonium sulfate (FAS) standardization (see March report) could not be traced to a known source of error. However, repeated titrations of the undigested dichromate solution used to standardize the FAS showed that, while the FAS titrant volumes differed by 0.48 ml, the relative standard deviation was 0.7%. The data indicated that the normality of the FAS can be satisfactorily determined for the purpose of standardizing the FAS reagent for the COD test.

A study on the digestion time required to achieve a maximum COD value for a sample of retort water demonstrated that two hours may be required to fully oxidize those materials that could exert a COD.

The reproducibility of the COD test was checked by using a potassium phthalate standard. Various volumes of phthalate standard solution were added to a series of COD flasks. The results of this test showed that the COD increased linearly with increasing volumes of phthalate ($r^2=1.00$) and the values were calculated to be 97% of theoretical. The y-intercept of this standard curve was negative. The actual value was 3.2% below the theoretical zero value, which is not an appreciable error. This indicated that the COD test was accurate and reproducible for the phthalate standard solution.

The phthalate standard was then used to fortify retort water by a method of standard additions to check the recovery of phthalate and reproducibility of the COD test for retort water. Various volumes of phthalate standard were added to COD flasks containing equal volumes of retort water. The data from these experiments should indicate the reproducibility of the COD test since standard addition should produce a linearly increasing response in COD parallel to the line derived by phthalate alone. The least squares equation of the standard additions data showed that the lines derived from the standards and standard addition with retort water were not parallel since the slope for the standard additions curve was 9.5% less. The 9.5% change in slope results in decreasing recoveries of phthalate for increasing concentrations of phthalate in retort water. The maximum inhibition was 4.1%. This data could indicate that the COD of phthalate in retort water may be inhibited by an insignificant but constant percentage.

The reproducibility of the COD of retort water C-18 effluents will be tested next month. As mentioned in the March report, the C-18 Sep Pak will be used to fractionate retort water samples to determine the accuracy of the COD test by comparison with organic carbon values. In addition, the reproducibility of the carbon analyzer will also be determined.

Protein Assay

We are continuing to investigate the dye binding protein assay which will be used as a direct measure of biomass. From initial studies it appears that the dye binding assay, using coomassie brilliant blue as outlined in the March report, can be used for retort water to distinguish abiotic particulates from microbial growth by quantitating the latter. This month we checked and modified analytical procedures that were leading to erratic results and, in addition, assayed cultures of bacteria for protein.

In order to determine if filterable substances and abiotic particulates in retort water interfere with the dye binding assay, a culture of microorganisms was filtered through a series of two polycarbonate membrane filters. The membranes were separated after filtration and each was assayed for protein. The second membrane gave no interference in the assay. This experiment did not clearly demonstrate that abiotic particulates do not interfere with dye binding because abiotic particulates might be present on the first membrane and interfere with the dye binding of protein in the digest from the first membrane.

We will attempt to assay a membrane with both biotic and abiotic particulates present, but without alkali digestion. Color response from this test could indicate extracellular materials or abiotic particulate interference.

In addition to the qualitative work completed this month some quantitative work has been finished. Culture flasks with S-55 retort water and various microbial seeds have been assayed for protein production. All the results showed the presence of protein in the culture flasks indicating that this assay may provide us with an excellent means of quantitating microbial growth. In addition to the aforementioned assays, three samples from the batch study (see Task 5) were assayed for protein and suspended solids. The initial results indicate that there is a positive correlation between suspended solids and protein. These results will be summarized after completion of the batch study.

Next month we will attempt to demonstrate the correlation between suspended solids and protein production. Furthermore, this analytical tool will be used to assay enrichment cultures for microbial growth to determine the limiting growth factors that may be encountered in the biological treatability studies.

TASK 4. SPENT SHALE STUDIES

An alternative method of spent shale treatment, slurry addition, was tried on 150-ton retort water using L-2 (<230 and 18-25 mesh) and Lurgi (<230 mesh) spent shale. This set of experiments was conducted in the manner briefly outlined in the March report. Beakers of retort water were placed on a jar testing apparatus with a single paddle in each beaker. A premeasured quantity of spent shale was added to the retort water while it was stirred at 100 RPM. This process of rapid mixing created the shale-water slurry and promoted good initial shale-water contact. After one minute the speed of the paddles was reduced to 40 RPM and mixing continued for an additional 15 minutes. Upon completion of the mixing process the jars were allowed to stand for one hour to allow the liquid and solid to separate by sedimentation under quiescent conditions. Samples for dissolved organic and inorganic carbon were drawn from below the surface of the supernatant fluid at the end of this period.

The initial data from the experiment that used L-2 (<230 mesh) spent shale and 150-ton retort water demonstrated that a ratio greater than 1 g of spent shale to 1 ml of retort water will be required to achieve greater than 90% removal of the dissolved inorganic carbon and to elevate the pH above 10.0. The experiment also demonstrated that dosages of 0.75 g of spent shale to 1 ml of retort water and 0.50 mg of spent shale to 1 ml of retort water are capable of removing 83% and 73% of the dissolved inorganic carbon content of retort water, respectively. These same respective dosages are capable of elevating the pH of retort water to 9.8 and 9.6, well above the pK value for ammonia-ammonium ion equilibrium. This clearly demonstrates that spent shale could be added to retort water to remove inorganic carbon by mixing in an open basin.

The limiting factor to this type of chemical treatment will be the design of a sedimentation basin to separate the water and solids. The quantity of spent shale that is required for a dosage of 1 mg spent shale to 1 ml of retort water occupies 86% of the shale-retort water mixture volume after one hour of settling. Dosages of 0.75 mg spent shale to 1 ml of retort water and 0.50 mg spent shale to 1 ml of retort water occupy 80% and 65% of the settled volume after one hour of settling. The large volume occupied by the solids will mean a substantial solids handling problem may develop. The high volume of solids means that settled solids will have to be removed quickly to prevent buildup of solid material and short circuiting that would result in poor solids separation allowing solids carryover.

The solids handling problem is the major obstacle in this type of application. If dissolved inorganic carbon removal and pH elevation become the primary objectives of this application then this treatment process could be used to provide some economic relief to the cost of using lime alone to remove the inorganic carbon and elevate the pH. The use of a combination of spent shale and lime might provide the most economical solution to chemical treatment.

Jar tests using L-2 (18-25 mesh) and Lurgi spent shales were completed late in the month and the test data are now being summarized. It appears that the large volume of solids is the major problem in this type of application. Solids handling may be the limiting factor in using spent shale by this method of application.

TASK 5. SYSTEM STUDIES

As a result of the ambiguous data collected from the CSTR experiments, we initiated, late in April, a batch experiment to determine the biological treatability of retort water, using lime-treated, ammonia-stripped 150-ton retort water. Biological growth will be quantitated by suspended solids, protein analysis, and COD removal. There will be no attempt to control the pH of the reactor in order to duplicate operating condition of the CSTR.

We will continue to monitor the COD until the COD increases or the suspended solids decrease (death phase). When this occurs, we are planning to add carbon sources to stimulate further growth. Regrowth would indicate that carbon had become limiting in the retort water. A lack of increase in suspended solids or growth after carbon amendment will indicate that some other factor is limiting or inhibiting further growth. If regrowth does not occur we will adjust the pH of the reactor if necessary to determine if this has any effect on regrowth. Once again, if no regrowth occurs, a phosphate magnesium supplement will be added to determine if growth in the aerator is limited by these nutrients.

Using this batch experiment and the enrichment cultures outlined in previous reports we should be able to determine:

1. Whether biological treatment is feasible.
2. If biological growth is limited by micro or macro nutrients.
3. If biological growth is limited by the presence of toxic compounds.
4. If the organics present in retort water are recalcitrant to microbial degradation.

Answers to these questions will provide us with the necessary preliminary information to enable us to operate an activated sludge unit and to provide the microorganisms with an optimal environment for growth. Placing the microoganisms in the proper environment will allow us to develop the necessary design criteria for an activated sludge treatment unit.

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