Title

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

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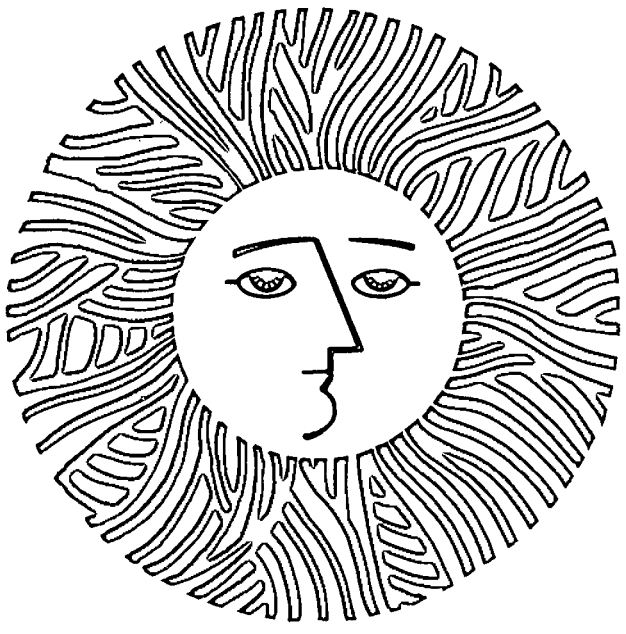

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June 13, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox

RE: Monthly Progress Report for May
Spent Shale as a Control Technology for Oil Shale
Retort Waters
LBID-235

TASK 1: ANALYTICAL METHODS DEVELOPMENT

COD Test

We are continuing to study the applicability and accuracy of the standard COD (chemical oxygen demand) test. As mentioned in previous monthly reports, the purpose of this exercise is to estimate the accuracy of the COD test for determining the quantity of organic matter present in retort water and, therefore, its applicability as a monitoring tool.

Experiments to determine the reproducibility of the COD test when used on C-18 Sep Pak effluent were conducted during May. Four COD runs were conducted using the same three C-18 cartridges for sample preparation. Between runs, the cartridges were cleaned and air dried prior to preparing the next sample. These four runs demonstrated that COD values for the C-18 effluents were reproducible (coefficients of variation (CV) <3 percent). Furthermore, the CV for COD means from the three cartridges for a given run did not exceed 3 percent. Between-run variability was greater. There was a significant variation in results between the first two experimental runs. As a result of this variation, greater care was taken in sample preparation for the last two runs. Samples for runs three and four were passed through the C-18 Sep Pak very slowly and, as a result, the variation between the runs was no longer significant. The data from these runs indicate that the cartridges, if properly used, will give reproducible results

for repetitive uses. The cartridges can therefore be used to demonstrate the accuracy of the COD test.

Carbon Analysis

In conjunction with the COD study, a carbon reproducibility study was conducted. The study indicated that total carbon (TC), total organic carbon (TOC), total dissolved carbon (TDC), and dissolved organic carbon (DOC) concentrations could be determined with a high degree of reproducibility; the coefficient of variation did not exceed 4 percent for any parameter. The results of this study also showed that there was a significant difference between the TOC and DOC values. The difference between means was 155 mg/L (4.5 percent of total). If the carbon present in the 155 mg/L difference between TOC and DOC were oxidizable there should be an equivalent change in the COD. A previous study showed that by the simple operation of filtration through a 0.45 µm mixed cellulose acetate filter, the organic carbon could be reduced but, that the COD of the water was not significantly altered. This suggests that the carbon removed by filtration is not oxidizable.

These experiments indicate that the COD test may be limited in its applicability for estimating the organic content of retort water. We feel that we are now able to proceed with the experimental design to demonstrate the inadequacies of the COD test.

Protein Assay

We are continuing to use the protein assay to assess biological growth in retort water. Several modifications of the standard assay have been made. In order to avoid the nonlinear standard curve mentioned in last month's report the protein standards are made up fresh daily in acid solution to maintain a constant pH in all samples throughout the experiment.

Since the quantities of protein produced in 10-mL samples of enrichment cultures may be rather limited, the limit of detection was decreased to 10 µg protein/100 µL by adding a 10-µg protein/100 µL standard to the samples. The response

of the standard curve was linear, and we are now able to detect smaller quantities of protein. Experimental results also indicated that neutralization of the caustic digestion solution was necessary to prevent nonlinear results.

Comparison of results from an experiment which compared digested samples to undigested samples showed that removal of suspended solids from 5- and 10-mL samples of enrichment cultures contained no detectable quantities of protein when left undigested. However, the suspended solids from a 20-mL sample of enrichment culture, when left undigested, give a response which is about 40 percent of the protein found in a similar sample which has been digested. A small quantity of extracellular products or easily ruptured cells could explain the partial response. The results do indicate the need for digestion prior to protein assay and that there is no interference produced by other suspended matter in the retort water. This gives us a positive indication that we are truly seeing growth in our cultures.

TASK 4. SPENT SHALE STUDIES

The spent shale slurry experiments initiated last month were completed this month. The results of dry feeding and mixing the L-2 (18-35 mesh) and Lurgi (<230 mesh) spent shales with 150-ton retort water to create a slurry were completed and reduced for interpretation. Combining the results of last month's initial experiment using L-2 spent shale (<230 mesh) with the results of this month's experiments showed that as much as 90 percent of the dissolved inorganic carbon (DIC) could be removed by adding this type of spent shale. In addition, the pH of the retort water could be elevated to 10.1, about 2.4 pH units above its starting value. The results of the tests showed that a major portion of the pH elevation was achieved during initial contact and mixing, with the balance occurring during the settling of the shale.

The experiment pointed out that the limiting factor in initiating a continuous-flow system of this type will be the

solids/liquid separation and solids handling. Maximum pH elevation and DIC removal could only be obtained with very high doses of spent shale; 100 g L-2 spent shale (<230 mesh)/100 mL 150-ton retort water; 75 g L-2 spent shale (18-25 mesh)/100 mL 150-ton retort water; and 85 g Lurgi spent shale (<230 mesh)/100 mL 150-ton retort water. Each of the aforementioned doses removed the following percentages of DIC: 90, 55, and 50 percent, respectively. The resulting pH values of 150-ton retort water after settling were 10.06, 9.31, and 9.28 respectively. If spent shale is used in this manner, the large quantities of spent shale that are present in the retort water will pose a serious solids handling problem.

During the sedimentation phase of the jar tests the height of the interface was measured as it settled in the graduated beaker under quiescent conditions. The settling curves that were derived from this data are typical for waters of high suspended solids concentration. That is, there is no discrete particle settling but only hindered settling due to the compaction and inter-particle contact of the spent shale. The lack of slope in the settling curves also indicates that the settling that is occurring is typical of the compression region of a settling curve.

The results of these studies would seem to indicate that application of this type of operation will be limited to the use of smaller quantities of spent shale. Sedimentation basin design for liquid-solid separation is based on the quantity of area required for free settling to occur. This area need is calculated on the rate of settling of the interface between the zone of discrete settling and zone settling, where the particles begin to form a blanket. In order to prevent short circuiting and solids carryover, it is necessary to maintain a blanket of solids by withdrawing a given quantity of solids from the compression region within the clarifier. The high solids concentration and large quantity of spent shale that would be present in the compression zone could pose a serious solids handling problem. This should not rule out the use of spent shale to treat the

water because it may still be possible to use the spent shale in smaller quantities supplemented by lime to chemically treat the retort water. The resulting solids could then be used in grouting and the chemically altered water could be treated further.

In addition to the coagulation studies we are currently trying to repeat our continuous column experiments. The short life of the first column may have been due to either exhaustion of the spent shale or coating of the spent shale by tarry substances present in retort water. In order to extend the life of the column we will attempt to run the column as a filtration bed. The media or spent shale will be used to filter out particulate matter within the bed. Removal of the tarry and particulate substances by filtration early in the bed should prolong the life of the bed by preventing coating of the spent shale in the latter part of bed allowing more DIC removal. The filtration of colloidal substances will be aided by a commercial cationic polymer.

The first column attempt failed due to physical problems; the side sampling ports leaked and the pump was not discharging a constant volume of water. At the writing of this report, a second attempt at column operation is under way. If no problems are encountered, the results will be reported next month.

TASK 5. SYSTEM STUDIES

Enrichment Study

After a short delay to develop the protein assay, we have reinitiated the enrichment studies. The protein assay developed over the last two months will be used to assess biological growth in the reactors. Protein production in an enrichment culture confirms that turbidity is caused by microorganisms.

An initial set of enrichment cultures was initiated using S-55 retort water in combination with a phosphate (P_i) supplement and an additional carbon source (fatty acids). The results showed an increase in protein and suspended solids production,

above the level yielded by retort water alone, with P_i addition, fatty acid addition, and P_i + fatty acid addition. The quantity of suspended solids and protein produced increased in that respective order. While growth had occurred, we could not determine the limiting factor. The results were too ambiguous for interpretation. The data indicated that the organics present could have been refractory, P_i could have been limiting, or toxic compounds could have been present.

In order to ascertain the growth limiting factor, a toxicity investigation was initiated to determine the dilution of retort water required for optimum growth. Various portions of S-55 retort water were inoculated with microorganisms and brought to a constant volume with distilled water. The cultures were incubated for a period of four days prior to assaying for protein. The normalized yield of protein (mg protein/mL retort water) showed a decrease in protein production with increasing quantities of retort water. This indicates that toxic compounds present in the retort water are inhibiting growth, since the smaller quantities of retort water yielded a larger normalized protein production. The results of this initial experiment are inconclusive because the quantity of P_i per flask remained constant but the retort water concentrations (i.e., carbon) varied. This means that the low yields of protein at high retort water concentrations may have been caused by P_i limitation. Nutrient limitation could be eliminated by adding the same quantity of retort water per flask.

During one of the runs, we tried correlating suspended solids and protein production. The membrane filters were tared prior to filtration. Following capture of the suspended solids, the membranes were dried at 103°C and weighed for suspended solids prior to assaying for protein. The results indicated a positive correlation between protein and suspended solids that showed a slight deviation at the high suspended solids values.

The results to date show that microbial growth does take place. Our work will continue to correlate protein production with increasing suspended solids production and increasing turbidity. In addition, we will try to correlate growth with

substrate removal (i.e., COD or organic carbon). We will continue to use the enrichment cultures to determine some of the difficulties in operating a CSTR.

The CSTR for aerobic oxidation studies has been built. The unit consists of four 4-L cylindrical reactors, 5 in. I.D., set up in series. Each reactor has a set of paddles to promote mixing and an air stone to provide O_2 transfer. We will begin CSTR studies as soon as our enrichment studies are complete and the Occidental retort water from LETC arrives.

Correlation of Microbial Growth and COD

We studied the aerobic oxidation of 150-ton retort water in a batch reactor to investigate the phenomenon of COD production that had been observed in the CSTR's. The soluble COD (SCOD), suspended solids, and pH were monitored daily for 21 days. Samples of the reactor fluid were also analyzed for protein. The correlation between the protein increase and production of suspended solids verified that the turbidity was caused by microbial growth.

The reactor fluid was prepared by treating 150-ton retort water with CaO until a pH value greater than 10 was achieved. Aeration for a 24-hr period decreased the ammonia concentration to about 2500 mg/L NH_3-N. The retort water was then neutralized with phosphoric acid, which also presumably ensured a non-limiting phosphorus source. Following neutralization, the retort water was placed in a 3-L Erlenmeyer, inoculated with a bacterial culture from the existing CSTR, and aerated by a magnetic stir bar and house compressed air.

The following were observed from this experiment. The increase in suspended solids (SS) was similar to the exponential growth exhibited by bacteria. An initial lag phase (SS=20 mg/L) was followed by exponential growth (doubling time of 4 hours), and then a brief stationary phase (SS=200 mg/L). After 3 days, another period of growth ensued that was peculiar in its arithmetic increase to an SS value of 350 mg/L at 4 days. These two periods of growth separated by a stationary phase are

indicative of diautic growth (i.e., sequential utilization of substrates) or sequential growth of different bacterial populations. The SS fluctuated between 300 and 400 mg/L for about 10 days, followed by a steady decline to 200 mg/L for 7 days.

The dramatic increases in SCOD seen in the CSTR's were not observed in the batch reactor. During the initial exponential growth phase, there was a parallel increase in SCOD but the SCOD began a slow decrease soon after. Aerobic oxidation and aeration only achieved a maximum 20 percent removal of the SCOD.

To determine if stationary phase was reached because of carbon limitation (i.e., only refractory carbon remained), additional carbon (fatty acids) was added to the culture about 5 days after reaching the stationary phase. This increased the level of SCOD in the container, but no increase in suspended solids was noted. This could indicate that the organisms were using the carbon source for maintenance only, or that they were nonviable.

Additional supplements of P_i and M_g^{+2} were added with little effect. The data from this portion of the experiment does not indicate anything significant. The ambiguous results may be an indication that the culture had entered endogenous respiration and death phase. The addition of carbon, P_i, and Mg^{+2} was insufficient to revive the culture. If the nutrient supplements are added earlier in the studies, then perhaps some effect of their addition may be observed.

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