Title

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

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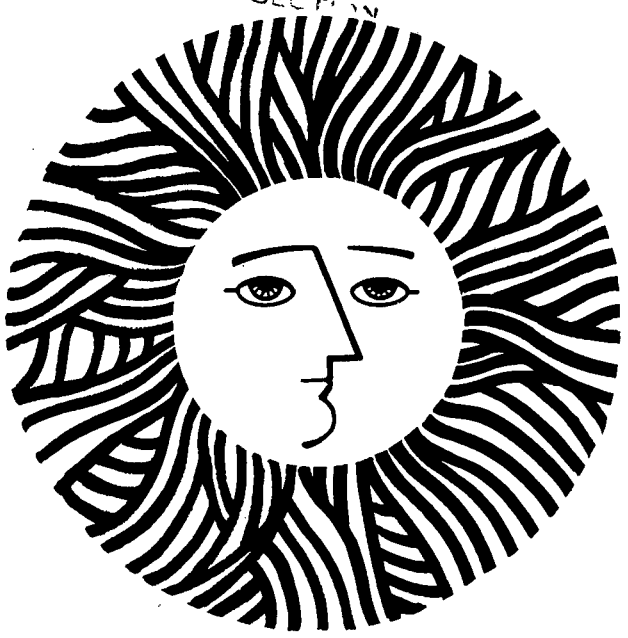

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September 11, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox

RE: Monthly Progress Report for August
Spent Shale as a Control Technology for Oil Shale
Retort Waters
LBID-287

TASK 1. ANALYTICAL METHODS DEVELOPMENT

COD Test

We are continuing experiments to demonstrate the feasibility of using C-18 Sep Paks to fractionate retort water samples. Experiments this month showed that the C-18 cartridges could be repeatedly used, if properly cleaned after each use. In addition, our studies have shown that the ability to fractionate a retort water sample is not dependent on the flow rate through the cartridge.

C-18 cartridges were activated by successively passing 5 mL methanol and 20 mL deionized water through the cartridge. A sample of retort water was then passed through the cartridge at 1 mL/min using a Sage 355 syringe pump to maintain a constant flow. Effluent samples were collected during a predetermined interval. These intervals correspond to the apparent equilibrium portion of the COD profile determined from last month's studies. Each cartridge was then cleaned by reversing the flow and successively washing with 5 mL each of methanol, methylene chloride, and tetrahydrofuran. The process of activation, sample preparation, and cleaning was repeated 10 times, using three single cartridges. The average COD values of the collected samples fell within a 5% relative standard deviation, indicating that the cartridges could be reused with proper cleaning.

The data obtained from this experiment also demonstrated that overnight drying of the cartridges is not required for reuse. The first six sample runs were performed after the cartridges had dried overnight. However, this drying time was eliminated between runs 7 and 8, and 9 and 10, with no change in the effluent COD values. We concluded that overnight drying of the cartridges was not required, i.e., with proper reactivation there was no residual chemically oxidizable material on the Sep Paks.

Upon completion of the reuse study, we attempted to demonstrate that variation in flow rate would not significantly affect fractionation of the sample. Flow rates of 20, 10, 5, 2.5, and 0.5 mL/min were each used to fractionate 15-mL samples of Oxy-6 retort water. Effluent fractions of 1.5 mL were collected and analyzed for COD. The cartridges were then cleaned and reused. The results showed that flow rates up to 20 mL/min could be used to fractionate the samples without altering the profile plot of COD versus effluent volume.

The results suggest that the C-18 cartridges can be used in a manner similar to preparative liquid chromatography (LC). As in LC, the standardized fractionation procedures should yield highly reproducible profiles for any given retort water. This means that we will continue with our work to demonstrate the possible problems associated with the COD test.

Protein Assay

Work on the BioRad protein assay continued with the completion of experiments initiated in July. The experiments this month further demonstrated that a 10-min alkaline digestion at 100°C was sufficient for yielding maximum protein from cells that had been concentrated on polycarbonate membrane filters. Additional data show that digestion periods of 30 minutes or longer result in breakdown of the filters and significant color interference at A(595).

During the course of these experiments, we uncovered several analytical problems that have yet to be resolved. As a result of these problems, we have begun an investigation of the Lowry protein assay.

Some basic problems associated with any assay for whole cell protein include (i) obtaining representative subsamples of the culture because of cell flocculation, (ii) loss of cells during sampling because of sorption to pipette tips and surfaces of membrane filter holders, (iii) cell lysis during washing of the membrane, and (iv) membrane retention of interfering substances from the extracellular fluid. A major problem with the dye-binding assay was that of erratic spectrophotometric readings. This was caused by the presence of particulate matter, which is an idiosyncracy of the dye-binding assay. These particulates make the use of a micro-flow-through cuvette impossible.

Our adaption of the Lowry assay for use with whole cells, in a sample matrix with considerable color interference, has been successful. Although the Lowry assay has a higher limit of detection for protein than the BioRad assay, procedural stipulations allow the use of a much smaller sample size. This saves considerable time during the filtration step. Another major advantage of the Lowry assay is that it can be performed in a single tube. The major disadvantage is that retort water color interferes with the Lowry assay at volumes as small as 1 µL. This means that the membrane used to collect the cells from the retort water must be thoroughly rinsed to ensure that all residual extracellular fluid has been removed. A minor disadvantage of the Lowry assay is the inability to use polycarbonate membrane filters because of their content of free phenolics. This problem was eliminated by the use of Teflon membranes. The assay is accomplished by filtering a small volume (i.e., 0.5 mL) of culture through a 0.4 µm pore diameter Teflon filter and digesting the retained cells in a Pyrex screw cap (Teflon-lined) test tube for 10 minutes at 100°C in 0.5 mL of 1 N NaOH. After digestion, 0.5 mL of deionized water is added to the digest followed by addition of the $CuSO_4$/Na-tartrate/Folin reagent. The color is allowed to develop for 30 minutes and the absorbalance is read at 750 nm.

Even after the filter is rinsed with phosphate buffer to remove extracellular fluid, certain abiotic materials that are removed from retort water by the membrane impart considerable color interference. This problem has been tentatively solved by rinsing the filter with methanol to remove these tar-like materials.

TASK 4. RAW AND SPENT SHALE STUDIES

During our studies on analytical methodologies, we have found the C-18 Sep Pak to be efficient at partitioning and retaining large quantities of organic material from retort water. The effluent from these reverse-phase cartridges is greatly reduced in color and odor. Dr. Daughton suggested in February, 1980, that the principle of reverse-phase chromatography could be incorporated into the development of a wastewater treatment process. Dr. Daughton hypothesized that the use of raw shale in a continuous flow column may be analogous to using a reverse-phase packing material such as contained in a C-18 Sep Pak (octadecyl silyl groups covalently bonded to surface silanol groups of the silica particles). These immobilized aliphatic coatings serve to partition hydrophobic materials from the retort water. Oil

shale is essentially an inorganic matrix that contains kerogen, a highly complex insoluble organic polymer, which can be viewed as analogous to the hydrophobic carbon coverage of the reverse-phase chromatographic packing.

Experiments were conducted to investigate the use of raw shale in the treatment of oil shale retort water. Three continuous-flow columns using two different size fractions of raw shale from the Colony mine were run at a surface loading rate of 0.1 gal/min/ft^2. These experiments indicate that raw shale columns remove about 25% of the organic carbon, about 60% of the inorganic carbon, and decrease the pH. These effects are maintained through about 1.5 pore volumes.

The first column run used 16-25 mesh shale. The organic carbon was reduced about 25% and the pH was lowered from 8.82 to 8.45 for about 1.5 pore volumes. Color was significantly reudced, suggesting the use of absorbance to continuously monitor column effluent. Experiments indicated that the influent/effluent differential absorbance at 450 nm was greatest, and thus, this wavelength was selected for future use.

The second column used 60-80 mesh shale. We encountered several technical problems during this run. Degassing of the retort water at the pump head caused partial blockage of the influent line, resulting in flow fluctuations between 0.4 to 2.0 mL/min. The nonsteady flow made data from this column run difficult to interpret. However, it was obvious that the removal of compounds that absorb at 450 nm was maintained for an extended period of time. In addition, we observed the same decrease in pH. The data from this run indicated that organic carbon and absorbance at 450 nm were reduced by 18% and 68%, respectively.

Degassing at the pump was resolved and a constant loading rate was maintained during the third column run. The organic carbon was reduced by 20% and the inorganic carbon by 56% throughout 1.5 pore volumes. The effluent absorbance at 450 nm was initially decreased by 68% and dropped to 22% after 3.5 pore volumes had passed through the column. This indicated the continued removal of a select class of compounds. A decrease in effluent pH was also noted.

Preliminary HPLC reverse-phase separation of column effluent samples showed that the compounds removed by the raw shale were probably the same as those removed by the C-18 Sep Paks. The chromatograms of filtered retort water, filtered column effluent (early and late), and C-18 Sep Pak effluent showed that the compounds removed were non-hydrophilic. These results also suggest that certain compounds are removed beyond the exhaustion point of

the column.

TASK 5. SYSTEM STUDIES

The pilot-scale steam stripper described in the July monthly report was built and tested using synthetic retort water. Three-hundred gallons each of Occidental gas condensate and retort water were received and analyses completed for solids, N forms, and other water quality parameters.

MISCELLANEOUS

Rick Sakaji attended an ACS course on liquid chromatography on August 24 in Las Vegas, Nevada. Phyllis Fox presented the paper, "Water Management Strategies: Issues and Priorities" at the Vail Oil Shale Symposium on August 13, and the paper, "Water-Related Impacts of Oil Shale Processing at the ACS Symposium in Las Vegas on August 26, 1980.

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