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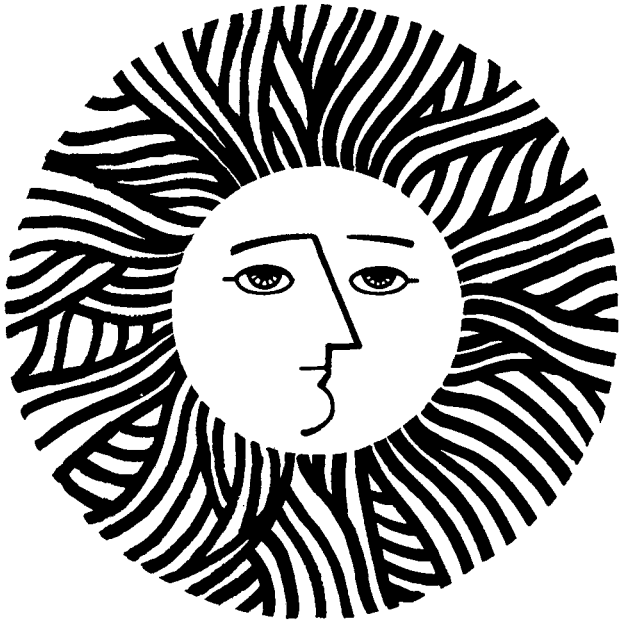

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LAWRENCE BERKELEY LABORATORY
Room: 128 Bldg.: 70 Ext.: 6698

April 9, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox

RE: Monthly Progress Report for March
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-193

## TASK 1. ANALYTICAL METHODS DEVELOPED

### Protein Assay

Quantitation of microbial growth on retort water is necessary for studying biological treatment processes and for performing enrichment experiments. Unfortunately, retort water has several characteristics that preclude any facile measurement.

The concentration of microbial biomass in a liquid culture is commonly measured by determination of at least one of the following:

- Dry cell mass can be measured by membrane filtration. However, the endogenous levels of filterable nonbiological particulates in retort water give high and nonreproducible background levels.
- Turbidity can be used if it is standardized to a parameter such as cell mass.

Nonbiological particulates interfere with turbidity measured by nephelometric or absorbance techniques. Furthermore, the highly chromophoric character of retort water prevents direct absorbance measurements, and the dark color of the particulates and colloidal matter gives a negative interference with scattered light measurements.

- Protein is a good direct measure of biomass. Whole cells can be digested to free their protein, but the endogenous color of retort water interferes with colorimetric methods. Alternatively, the cells can be separated from the culture medium prior to digestion.

From these considerations, we decided to investigate protein determination as a biomass indicator. There are five major methods

for protein assay: total protein nitrogen, biuret, Lowry, amino acid analysis (e.g. ninhydrin), and dye-binding. Total nitrogen and amino acid analyses are very time consuming. The Lowry method is very sensitive, but prone to many interferences. The biuret and dye-binding procedures have relatively high detection limits, but they are simple to perform. We have decided to investigate the latter two, beginning with the dye-binding method.

The most common dye-binding method uses Coomassie Brilliant Blue G-250 whose $A_{max}$ shifts from 465 nm to 595 nm upon binding to protein. Standard curves for 20 µg to 100 µg of bovine serum albumin per assay were found to be linear ($r^2 = 0.98$). Adoption of the method to retort water involves filtration of a measured volume of culture media through a polycarbonate membrane (0.4 µm pore diam.). The suspended solids captured on the filter are digested by boiling in alkali. The digest is neutralized and assayed using the dye-binding assay.

Polycarbonate membranes were found to produce little interference when submitted to digestion and dye-binding. In contrast, Millipore cellulose acetate membranes yielded considerable quantities of products that gave positive interference with the dye-binding. A major problem with this procedure is interference by alkali. This problem was eliminated by neutralization of the digest before assaying.

Further experiments will be designed to determine if filterable substances in retort water interfere with the dye-binding. A major problem with this objective will be in separating absorbance response from microbial cells (if present) from that of abiotic particulates.

COD Test

Experiments were initiated last month to determine the accuracy, reproducibility, and applicability of the COD test as a performance parameter for biological treatment. In biological treatment studies, BOD or COD is used as a measure of the oxidizable carbon in the influent and effluent. Organic carbon is not a suitable measure of oxidizable carbon because it is independent

of oxidation state of the waste. Our previous studies had indicated that COD was not a suitable performance parameter because the COD was observed to increase across the aeration basin of a laboratory-scale aerobic digester and during autoclaving of the samples. These results suggested that there are compounds present in retort waters that are not oxidized by potassium dichromate during the standard COD test. This month, we conducted some simple experiments to determine whether if there were classes of compounds that were not oxidized by the COD test.

Retort water was initially fractionated into two classes of compounds (hydrophobic and hydrophilic) by passing it through a reverse-phase C-18 Sep Pak (Waters and Assoc.). The C-18 Sep Paks were activated by successive elution with 10 mL of methanol and two additional 10-mL portions of deionized water. A 10-mL sample of retort water was then fractionated using the activated Sep Pak. The ratios of COD to organic carbon in the influent and effluent were determined using standard analytical procedures. If a class of compounds with no COD is preferentially distributed into one of these fractions, then the ratio of COD to organic carbon in the influent would be different from that in the effluent.

Initial replicate samples of the column effluent showed a wide variation in COD values. This prompted us to suspect residual methanol from Sep Pak activation or the leaching of material from the Sep Pak (which exerts a COD). Deoxionized water was used in place of retort water to check for background interference in the analysis. In addition, both activated and unactivated C-18 Sep Paks were checked for COD interference. The resulting data scatter could not be interpreted. However, it did prompt us to investigate the relative error inherent in the digestion and sample preparation steps of the COD procedure. Two investigators titrated undigested and digested blanks. The undigested blanks, used to normalize the ferrous ammonium sulfate (FAS) titrant, had a higher standard deviation in mL

of FAS required to titrate the standard (±0.52 mL and ±0.46 mL) than did the digested blanks (±0.13 mL and ±0.11 mL). Once again the discrepancy in the values could not be explained.

Samples of retort water analyzed for COD showed that the COD test is very reproducible (S.D. = ±0.11 mL FAS required to titrate sample). However, when a standard potassium phthalate solution is added to the retort water sample there is a wide variability in the recovery of added total theoretical COD (75-95%). The variation is greater than can be explained by inherent error.

Next month will be spent investigating the accuracy and reproducibility of the COD test on standard potassium phthalate samples, retort water, and retort water fortified with potassium phthalate. In addition, we will attempt to trace the problem in the FAS standardization.

The results to date demonstrate that the COD test is reproducible, but the accuracy and applicability of the test for the retort water samples are not known.

TASK 4. SPENT SHALE COLUMN STUDIES

The data gathered in February's study of a fixed bed of spent shale showed that spent shale could be used to remove inorganic carbon (IOC) and elevate the pH of retort water. However, the L-2 spent shale had a limited capacity to effect these changes, and unlike granular activated carbon, spent shale may not be amenable to regeneration. Thus, an alternative method of applying spent shale was developed and experiments were designed to test it. The new method uses a slurry contact method that employs flocculation, coagulation, and sedimentation to promote good shale-water contact and solid-liquid separation. Pulverized spent shale, added to the wastewater, would create a slurry that could be mixed (flocculated) to ensure good shale-water contact and to maximize the limited treatment capacity of the spent shale. The resulting suspension could be separated by sedimentation.

The scheme will be tested by adding pulverized and graded spent shale to beakers of retort water. These batches will be

rapidly mixed, flocculated, and settled to simulate the coagulation, flocculation, and sedimentation processes. The batch tests will be conducted using L-2 spent shale and 150-ton retort water. Dosage requirements for inorganic carbon (IOC) removal and pH elevation along with solid-liquid separation data will be developed to assess the viability of such an approach. If the initial studies with L-2 shale are successful we will proceed to evaluate Lurgi and TOSCO II spent shales.

TASK 5. SYSTEMS STUDY

The enrichment culture experiments, initiated last month, and the other unit treatment process studies have been delayed pending the outcome of our experiments to select suitable performance parameters, e.g., COD, oil and grease, and cell biomass. Our studies have shown that standard analytical methods may be inadequate.

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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