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

October 8, 1980

TO: Charles Grua

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

RE: Monthly Progress Report for September
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-300

TASK 1. ANALYTICAL METHODS DEVELOPMENTS

Organic Carbon Analyses

The Coulometrics carbon analyzer was delivered in mid September. One week was spent assembling the analyzer and running standards to determine optimum operating conditions for carbon analyses. Initial studies with standard carbon samples indicate that the instrument's background noise is about 1 ppm/min, and the typical sample analysis is completed in 5 min. Standard curves generated from dilutions of potassium acid phthalate were linear (r^2=0.99) and reproducible.

Protein Assay

Continued investigations of the Lowry protein assay were directed toward refining the filtration (cell harvest) and digestion steps (cellular protein liberation) of the assay. The chemical and physical interferences have been minimized by using Teflon membrane filters (0.2 μm pores) to separate the cells from the extracellular fluid. Chromophoric abiotic interferences (both particulate and solubilized residue) are removed by washing the filters with methanol after cell harvest. Pigmented material that has been sorbed by the cell is only partially eliminated. Teflon filters are required in order to avoid the chemical and physical interferences, generated during digestion, of membranes made from cellulose esters, polycarbonate, and glass fiber. These membranes release phenols, silicates, and particulates, all of which interfere with the Lowry assay.

The protein assay has been developed as a simple procedure. An accurately measured volume of culture is filtered through a prewetted Teflon membrane. The membrane is rinsed with phosphate buffer followed by

1 ml of methanol. The membrane is pushed to the bottom of a screw-capped Pyrex culture tube with a glass rod, which remains inside. The glass rod serves to position the membrane into the tube and to hold it under the volume of alkali. This is necessitated by the hydrophobicity of the Teflon. The tube is sealed with a Teflon-lined cap and heated at 100°C for 10 min in a fluidized sand bath. The digest, membrane, and glass rod remain in the tube to which the Lowry reagents are added. Absorbance is measured at 750 nm.

COD Test

The purpose of our COD studies has been to determine how accurate COD is as an estimator of total organic matter in retort waters. When COD is used on a routine basis, the chemically oxidizable organic material is assumed to be synonymous with total organic material. However, the presence of nitrogenous heterocyclics and aromatic hydrocarbons, which are not fully oxidized by the COD test, gives reason to doubt the applicability of the COD test as an estimator of organic material that could be oxidized via other means (viz., bio-oxidation).

Since COD results give the quantity of dichromate required to oxidize solutes, and because this is presumably a reflection of total organic solute, the ratio of COD to OC should be constant for a given sample of wastewater, regardless of how the sample has been treated. However, if non-COD yielding compounds could be physically separated from the remainder of the organic material, there should be a shift in the COD-to-OC ratio. By the use of an appropriate separation process, the presence of non-COD yielding compounds in retort water could be detected by a decrease in the COD-to-OC ratio.

The major drawback in this investigation has been the necessity of using filtered samples, in order to facilitate sample handling and to eliminate subsampling problems by the carbon analyzer injection syringe. Therefore, the measures of COD and OC were really soluble COD and dissolved OC.

We attempted to separate the non-COD yielding compounds from the remainder by the use of a reverse-phase chromatography cartridge: a C-18 Sep Pak. We hypothesized that the hydrophobic materials, which would also include most of the non-COD yielding compounds, would be partitioned onto

the cartridge and would effectively be separated from the other solutes. The value for COD:OC in the effluent would therefore be higher for the effluent than for the influent. The initial results of this experimental work indicated that the ratio of COD to OC remained constant in the influent and effluent of the C-18 cartridge. The consistency of the ratio was maintained even when the fractionated effluent was collected in small increments. These results indicate that COD and OC analyses for retort water consistently respond to the same solutes.

A shortcoming of this experiment is possibly in the use of filtered samples. Hydrophobic material present in the water may be sorbed to membrane surfaces or particulates and thereby be excluded during analysis of filtrate. Another problem is the question of whether the carbon analyzer determines all forms of carbon present in retort water. This is of particular concern because of the accumulation of black residue in the combustion furnace.

The significance of these preliminary results is that soluble COD can possibly be used as an estimator to reflect the amount of organic matter present in retort waters.

Turbidity Measurements

It is imperative to have a quick nondestructive method for quantitating growth of microbial cultures. In order to assess effects such as limiting nutrients, toxicity, and carbon availability, it is necessary to determine the point at which the cultures reach stationary phase. Microbiological investigations have traditionally used spectrophotometric measurements of cell density as a means of facile indirect quantitation of biomass concentration. However, as with many colorimetric tests, the intense coloration of retort water interferes with this measurement. As a result, we have begun to investigate the use of a DRT-100 turbidimeter (HF instruments). Unlike nephelometers, which only measure scattered light, the HF turbidimeters measures both scattered and transmitted light, thus eliminating the problem of absorbance due to color. We are beginning to standardize the operation of this instrument and to investigate the possibility of using serial dilutions for turbidimetric measurements.

TASK 4. RAW AND SPENT SHALE STUDIES

Studies continued to investigate the use of raw shale in the treatment of retort water. Two columns of raw shale from the Colony mine were operated in an upflow mode using 150-ton retort water. The surface loading rate and shale particle size were changed between runs to determine the most effective operating conditions.

The first column used 60-80 mesh raw shale and was operated at a surface loading rate of 0.5 gpm/ft^2. The results showed that absorbance (450 nm) was initially reduced by 68%. This reduction dropped to 20% by the fifth pore volume and to 12% by the ninth pore volume. The quantity of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) removed was small, being 16% and 13%, respectively. These reductions decreased to 9% by the second pore volume.

A comparison between this column and a similar column operated at a lower surface loading rate (0.1 gpm/ft^2) which was reported last month, showed that the reduction in absorbance is independent of the surface loading rate. The initial reduction in absorbance at 450 nm for both the columns was the same. However, the removals of DOC and DIC were significantly lower in the column operated at the higher surface loading rate.

The second column was operated at 0.5 gpm/ft^2 using 16-25 mesh raw shale. The initial reduction in absorbance (450 nm) was 51%, which decreased to 15% by the second pore volume and 4% by the ninth pore volume. The DOC reduction was not sustained and dropped from an initial removal of 18% to 2% during the first pore volume.

Comparison between these two column runs is possible since both columns were operated at 0.5 gpm/ft^2. The major difference between the columns was the size of the packing material (16-25 mesh vs. 60-80 mesh). It is apparent that the ability to reduce absorbance is dependent on the shale particle size. Initial reductions in absorbance were greater and were sustained for longer periods of time when smaller raw shale particles were used. Both columns initially reduced the effluent DOC concentrations by similar amounts. The data scatter for later samples precludes any further comparisons. The smaller mesh shale reduced the DOC concentration but the larger mesh did not.

The most important parameter, which has not been investigated, is the

effect of kerogen "activation" on removal of organic solutes from retort water. Activation analogous to that in reverse phase chromatography could possibly be accomplished by organic solvents that swell and soften kerogen. This will be investigated in the future.

TASK 5. SYSTEM STUDIES

Batch and continuous flow steam stripper units were operated to determine removals of NH_3, CO_2, and organics from synthetic gas condensate and retort water and from Occcidental gas condensate. Removals in batch experiments with synthetic waters were sufficiently high (90%) to establish process characteristics over the anticipated working range and will be used to calculate the Henry's Law constant and, subsequently, the theoretical steam-water ratio for complete stripping of each constituent in tall columns. Operation of continuous flow units with synthetic waste at high steam-water ratios confirmed 90% removals of NH_3 and CO_2. Most runs were conducted at steam-water ratios of 0.25 and below. Preliminary data evaluation indicates removals of NH_3, CO_2, and acetic acid (a surrogate organic) ranging up to 60%, 80% and 50% respectively. Operation of continuous flow units with Occidental gas condensate was upset by clogging of process condensers, possibly by ammonium carbonate, although some runs were completed, achieving about 50% removal of NH_3 and CO_2; sample analyses and data reduction for DOC are yet in progress.

MISCELLANEOUS

B. Jones, K. Yu, G. Langlois, R. Sakaji, and C. Daughton spent a week in the Colorado-Utah region visiting several oil shale mining and retorting operations. Site visits to Anvil Points (Paraho), Colony (TOSCO-Exxon), Tracts C-a (Rio Blanco) and C-b (Cathedral Bluffs), Logan Wash (Occidental), and Geokinetics proved to be interesting and educational. The site visits provided the members of the group with an overview of the problems associated with mining and production of synthetic fuels from oil shale.

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