Title
SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATERS

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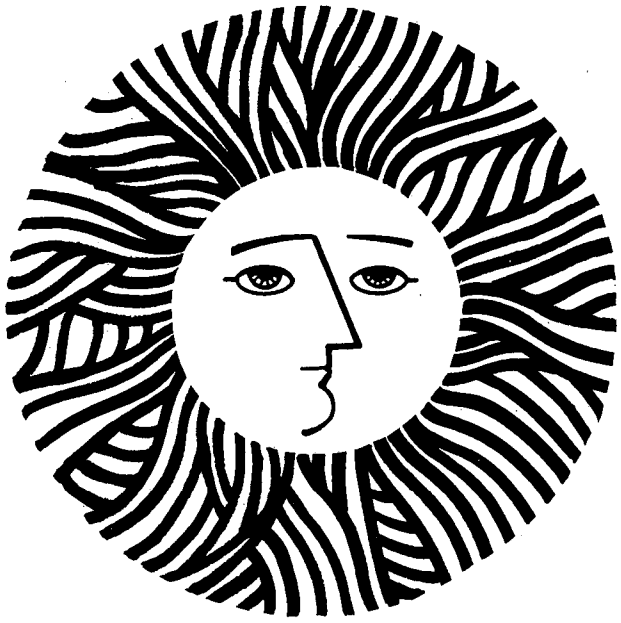

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February 9, 1981

TO: Charles Grua

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

RE: Monthly Progress Report for January
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-365

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

The purpose of developing a new analytical protocol to measure oil was to design a rapid and facile method for quantitating the broad class of organic compounds commonly referred to as "oil and grease." Oil and grease in wastewater streams produces unsightly films that can interfere with biological processes, inhibit mass transfer operations, and cause general maintenance problems. The quantitative methodology we are proposing involves the partitioning and retention of hydrophobic materials (oil and grease) from a relatively weak solvent (water) by a reverse-phase chromatographic cartridge (C-18 Sep Pak). The partitioned materials are then removed from the cartridge by elution with a relatively strong solvent (Freon). The eluate can be cleaned further by passage through a normal phase (silica) Sep Pak which retains materials that have "polar" characteristics, such as nitrogenous heterocyclic compounds. The eluate would then contain only true hydrophobic materials. The eluate from this process is then quantitatively assayed for oil and grease by infrared spectroscopy.

This new analytical protocol for oil and grease analysis was first proposed in the December 1979 monthly report and has since undergone modification. Experimentation this past month has involved the validation of the following analytical procedure (i.e., cartridge activation, sample preparation, drying, and quantitation). The C-18 Sep Paks are "activated" or "prewetted" by passing a 5-mL portion of methanol, followed by 20 mL of Milli-Q water to remove any residual methanol. A known quantity

of aqueous sample is then passed through a C-18 Sep Pak in order to effect the partitioning of the hydrophobic compounds. All liquids are pushed through the cartridge with a gas-tight syringe. The C-18 Sep Paks are then lyophilized for 2.5 h to remove the residual water. This obviates the need for solvent switch over -- i.e., the need for methanol which is soluble in both water and Freon. The C-18 Sep Pak is then eluted with 6 mL of Freon, and the eluate is passed through a silica (Si) Sep Pak which is connected in series to the C-18 Sep Pak. The final eluate containing the hydrophobic compounds is collected in a volumetric flask. (If the eluate is not first passed through the Si Sep Pak, it may contain fats, soaps, fatty acids, and other less hydrophobic species, in addition to oil.) The eluate is then brought to volume with Freon, and the oil is quantitated by infrared spectroscopy.

The first attempt to validate this method was by quantitatively creating an oil-water emulsion with mineral oil and Milli-Q water. The instability of the emulsion made it impossible to representatively subsample. As a result, we attempted to validate the protocol by quantitatively adding mineral oil to "activated" C-18 Sep Paks, followed by passing 50 mL of Milli-Q water through the cartridge. The water sample would contain a theoretical concentration of oil calculated from the mass of oil applied to the cartridge divided by the volume of water. The C-18 Sep Paks were then lyophilized, eluted, and spectrophotometrically assayed for oil. Recoveries of mineral oil ranged from 89 to 110%. The variability resulted from problems with the gravimetric determination of oil added to the cartridges. We had no access to a semi-micro balance. This experiment was repeated, and the recoveries were 90-101% of the added mineral oil. The reverse-phase partition technique for oil quantitation was used to determine the quantity of oil present in unfiltered Oxy-6 retort water. Three 10-mL samples of unfiltered Oxy-6 retort water were analyzed for oil content. The sample absorbances gave oil concentrations which were determined by interpolation from a curve generated by mineral oil standards. From these results, we found that Oxy-6 retort water has 131 mg/L of oil (as mineral oil) compared to the 260 mg/L reported in LETC's characterization of this retort water prior to formation of the composite sample.

Protocol validation is not yet complete; several questions must be addressed. Among them is the question of efficiency of the C-18 partitioning, especially with respect to retort water, and recovery of oil from fortified samples.

Protein Assay

The protein assay was validated as a method of quantitating cellular biomass, by using the cell culture from the second long-term batch experiment. Serial dilutions of the batch culture were analyzed for suspended solids (Standard Methods), dry mass (solids captured on a 0.4 μm polycarbonate membrane), absorbance (500 and 660 nm vs. filtrate), turbidity, and protein concentration. The linearity of the protein data (r^2 = 0.985) for the serial dilutions of cell culture suggests that the protein assay is a better measure of biomass than either of the gravimetric assays, both of which showed some deviation from linearity. Optical density, measured as absorbance, was more linear than the turbidity measurements which followed an exponential curve for the dilutions. This suggested that optical density should be followed, if practical; its major disadvantage is that the colored nature of the retort water requires that the absorbance values for each sample be measured against the sample's filtrate.

These results duplicate the results from a previous protein validation experiment. This indicates that the method is both accurate and reproducible. The methodology and validation results of the protein assay will be available (manuscript in preparation).

Ammonia Determination

The appropriateness of the distillation acidimetric-titration method of ammonia determination, as outlined in Standard Methods, was checked by the method of standard addition for Oxy-6 gas condensate. The recovery of ammonia from spiked blanks was 94%. This recovery was decreased to 85-91% for samples of gas condensate spiked with standard ammonia solution. This preliminary analytical work is being conducted as part of the steam stripping project. The steam stripping study will investigate

the use of steam to remove volatile organic compounds and inorganic gases from gas condensate and retort water.

Amines are recognized as an interference with this method because they distill over with volatile ammonia and are acidimetrically titrated with ammonia. The use of an ammonia probe may not rectify this problem because the probe is also sensitive to the presence of amines in the distillate. Additionally, the functioning of the gas permeable membrane in the probe is interfered with by the presence of surfactants, which increase the membrane permeability to compounds other than ammonia and amines.

TASK 4. SPENT AND RAW SHALE COLUMN STUDIES

Batch Isotherm Studies

TOSCO II spent shale (column runs #21 and #23) significantly reduced the dissolved organic carbon (DOC) and color in both 150-ton and Oxy-6 retort waters. As a result, a more detailed examination of the sorptive capacity of TOSCO II spent shale has begun. A series of batch studies has been initiated to derive the breakthrough curve for the combination of TOSCO II spent shale and Oxy-6 retort water. Results of the isotherm studies can then be compared with the data from previous continuous-flow experiments and applied to the modeling and design of future spent shale columns.

Batch experiment #3 was begun on 1.7.81 to determine equilibria times for Oxy-6 retort water and 25-120 mesh TOSCO II spent shale (effective particle size = 0.15 mm) and for Oxy-6 retort water and 12-40 mesh Calgon granular activated carbon (GAC, effective particle size = 0.55-0.65 mm). Time of equilibrium was defined as the point at which the DOC concentration in the liquid phase remained constant. Twelve sample sets were prepared for each adsorbent; each set contained a pair of vials. One series of vials contained equivalent masses of adsorbent, while the other paired series contained twice the mass. A constant volume of retort water was added to each vial. For each of the twelve sampling times, a blank containing only retort water was also sampled. The vials were agitated on a wrist-action shaker and at each of the twelve selected time intervals, a sample set was removed, filtered, diluted, and analyzed

for the concentration of DOC remaining in solution (expressed as Ci/Co, where Ci=DOC in solution at a given time interval and Co=DOC in solution at time zero). After 30 minutes, Ci/Co was 0.29 for GAC and 0.89 for spent shale. After 111 hours, Ci/Co for the GAC and spent shale were 0.19 and 0.72, respectively. The minimal adsorption of DOC by the spent shale was caused by insufficient sample agitation. The extremely rapid adsorption of 70% of the DOC by GAC means that a higher ratio of retort water to adsorbent would be required for accurate study. The experiment was terminated after 111 hours because of these operational problems.

On 1.20.81, batch experiment #4 was initiated using a higher solvent to adsorbent ratio for GAC and incorporating several modifications to improve sample mixing. After 30 minutes, Ci/Co was 0.33 for GAC and 0.79 for TOSCO II spent shale. Following 168 hours of agitation, Ci/Co had stabilized at 0.28 for the GAC while Ci/Co for the spent shale was declining slowly from a value of 0.56. This experiment was still in progress at the time of this writing; the final results will be presented at a later date.

TASK 5. SYSTEM STUDIES

Biological Oxidation Studies

Phosphate limitation. As mentioned in the December monthly report, researchers have assumed that inorganic orthophosphate (Pi) is a limiting nutrient in retort waters. Our previous work has shown that as little as 0.1 mM Pi was required for maximum growth on retort water. This experiment was repeated this month using lower concentrations of Pi to determine the minimum level of Pi required for maximum production of biomass. In order to demonstrate this, batch cultures were grown to stationary phase with varying quantities of Pi (0-0.1 mM). The cultures were then assayed for protein content. Graphs of protein concentration versus Pi concentration give the yield curves. Although the replicates of the protein assay were widely scattered (filtration problems), the data indicate that increasing the Pi supplement from 0.0 to 0.1 mM Pi linearly increases the quantity of protein that is produced in a culture.

Biological oxidation of spent shale column effluent. Effluent of Oxy-6 retort water from the TOSCO II spent shale column was inoculated with an acclimated culture to determine the effects of spent shale pretreatment on the biological treatment of retort water. Parallel cultures of untreated Oxy-6 retort water (i.e., column influent) were run as controls. The batch cultures of both the spent shale column effluent and the control had the same turbidities and protein concentrations at stationary phase, but the specific yield (i.e., mg of protein per mg of DOC removed) was higher in the culture containing the spent shale effluent. This suggests that the spent shale removed some of the refractory or toxic compounds. The two processes may remove different classes of compounds, giving a complementary or additive effect. A total decrease of 80% of the DOC was accomplished by the series of spent shale and biological oxidation processes. This is the highest reduction of DOC ever accomplished for retort water without the use of heat or chemicals.

Steam Stripping

Bench-scale batch experiments are being conducted to evaluate hot gas stripping as an alternative to steam stripping of shale oil wastewater. Preliminary design of a pressurized steam stripper unit (that might be later modified to hot gas stripping) was initiated.

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