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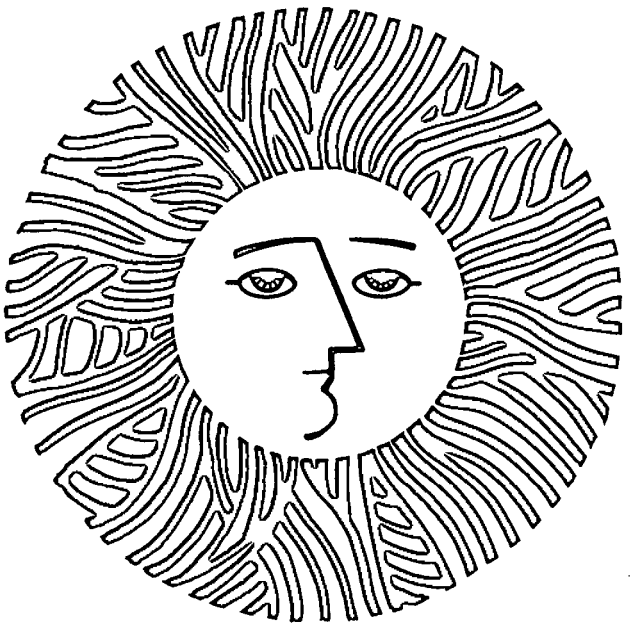

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December 8, 1980

TO: Charles Grua

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

RE: Monthly Progress Report for November
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-319

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

Our first experiment to compare the partition-gravimetric method (Standard Method) for oil and grease analysis with the reverse-phase chromatographic method was partially successful. In order to make a valid comparison between the standard method and the reverse-phase chromatographic method, the non-polar eluting solvent was changed from carbon tetrachloride to Freon (1,1,2-trichloro 2,2,1-trifluoroethane). Freon poses less of a health and safety hazard and is the solvent of choice for the partition-gravimetric method in the 14th edition of Standard Methods.

An oil/water emulsion was prepared by mixing a small quantity of mineral oil in a relatively large volume of Milli-Q water with a magnetic mixer and overhead beater. The resultant mixture was allowed to separate before the lower aqueous layer was siphoned off for analysis.

The results of the analyses demonstrated that the procedure which was used to emulsify the oil and water was inadequate. There was no detectable oil present in any of the samples as determined by either the partition-gravimetric or reverse-phase chromatographic methods.

The purpose behind the development of the reverse-phase chromatographic method of oil and grease analysis has been to drastically decrease the quantity of time required to partition organic compounds into an organic solvent, to decrease the volume of subsample required, and to decrease the loss of volatile compounds while the solvent was being

separated from the oil. The infrared (IR) scans of the eluate from the reverse-phase chromatographic cartridges had a significant background of C-H stretch in the 2920 cm^{-1} region.

This background was believed to be the result of incomplete solvent evaporation that left a methanol-water residue that eluted with the organic solvent. The methanol was redissolved with the oil in Freon and the resultant mixture registered a C-H stretch at 2920 cm^{-1}. The methanol is required for mobile-phase switchover. This means that an alternative to using the methanol would require that the cartridge containing the oil be dried before eluting with the strong organic solvent. Air-drying the cartridge prior to solvent elution is not a workable solution because of the time required to drive off the water. However, lyophilization or acetone azeotrope distillation may provide a solution to our problem.

Protein Assay

Nylon filters are a new type of membrane filter that has just been marketed. We conducted an investigation to determine if these membranes could be used, in the protein assay, in lieu of the more expensive Teflon filters. There was a significant decrease in color, apparently because of sorption of the reduced phosphomolybdate complex, when standard bovine albumin was assayed with the nylon filters. This indicates that the nylon filters cannot be used in our modified Lowry protein assay. We now routinely employ our protein assay. It is more reproducible and reliable than either suspended solids or turbidity.

TASK 4. SPENT AND RAW SHALE COLUMNS

Columns of raw and spent shale were operated in series under continuous upflow conditions at 0.1 gpm/f^2. The upstream column was filled with TOSCO II spent shale and was followed by a column of Colony raw shale. The TOSCO II spent shale had an effective particle size of 0.140 mm and the Colony raw shale was 16-25 mesh (1.19 - 0.707 mm). Water from Laramie Energy Technology Center's 150-ton retort was used in this run so it could be compared to those from previous L-2 spent shale columns and Colony raw shale columns. Effluent samples from both the raw and

spent shale columns were analyzed for dissolved organic (DOC) and inorganic (DIC) carbon, absorbance (450 nm), and pH.

The most important observation from the experiment was the quantity of color that was removed by the spent shale column. Color in the initial effluent from the column was reduced by 60%; this value increased to 69% as the first pore volume was leaving the column. This reduction in color decreased to 41% by the third pore volume, but the spent shale continued to remove 31% of the color after the 12th pore volume. The reduction in color corresponds to an initial effluent DOC reduction of 36% which increased to 41% before the first volume had completely exited the column. The DOC reduction was only 16% by the end of the third pore volume and 7% by the end of the twelfth pore volume. It appears that a third of the color is removed by the spent shale column and that the coloration in the water is due to a small fraction of the organic carbon.

The spent shale reduced the influent DIC by 95% in the initial effluent. The column was unable to remove any DIC by the end of the third pore volume. This removal of DIC was more limited than the L-2 spent shale column. This is consistent with previous batch studies.

The raw shale column did not perform as anticipated from the results of previous experiments. The DOC concentration in the initial effluent was reduced only 26% and by the time the second pore volume had completely passed through the column, DOC was no longer effectively removed. This corresponded to a 9% reduction in color which did not last past the exit of the second pore volume. The capacity of the raw shale column seemed to be reduced from the results of previous studies. In addition, the raw shale column did not remove any DIC.

Comparison of the data from the TOSCO II spent shale column with previous column studies reveals that:

1) TOSCO II spent shale removed a larger quantity of color for a greater period of time than in any previous spent or raw shale column experiment.

2) The removal of DOC was also greater and lasted for a longer period of time than in any previous column experiment.

3) The TOSCO II shale, in contrast to the raw shale, also reduced the DIC concentration. However it was not as effective as L-2 spent shale.

TASK 5. SYSTEM STUDIES

Biological Oxidation

The batch culture experiment (50% Oxy-6 retort water medium, inoculated with acclimated seed), described in October's monthly report, was continued in order to investigate some of the possible factors that limit microbial growth and organic solute removal. After microbial growth had reached stationary phase, there was no further reduction of organic solutes, as indicated by soluble chemical oxygen demand (SCOD) and dissolved organic carbon (DOC).

To demonstrate that carbon was limiting growth, easily degraded carbon sources were added to the culture medium. Two successive additions of two carboxylic acids (25 mM as C of sodium acetate and 25 mM as C of disodium succinate) stimulated growth, as quantitated by turbidity and protein measurements. These observations tend to confirm the suspicion that microbial metabolism in retort water was restricted to utilizing a fraction of easily degraded organic compounds.

The addition of the carboxylic acids resulted in an immediate increase in substrate concentration as measured by SCOD and DOC. These concentrations were reduced by microbial activity and the DOC concentration was reduced to the pre-addition value. However, the SCOD values were reduced to values below the pre-addition concentrations. There are three possible explanations for these observations:

1) Inorganic compounds that yield a SCOD are utilized by the microbial community during growth phase.

2) Organic solutes are being polymerized (polymerized compounds are often only partially oxidized during dichromate digestion) by extracellular enzymes secreted by the active microbial community.

3) Organic compounds are partially oxidized but not degraded by the microbial community yielding compounds of higher oxidative states which would have lower SCOD values.

It was postulated that "analog enrichment," the addition of a degradable compound of a structure similar to that of a non-degradable solute present in the medium, could stimulate the population to utilize the recalcitrant portion of the solutes. Phenol was added twice (10 mM as C and

50 mM as C) to the retort water medium. The results from the first addition were inconclusive and the second addition of phenol proved to be toxic to the microbial community. This experiment will be repeated to study the effect of "analog enrichment" on organic solute removal.

A batch experiment to demonstrate that carboxylic acids are the primary source of carbon that supports bacterial growth in retort water was initiated this month. Acidification induces the precipitation of material in retort water samples. Some of this precipitate may be elemental sulfur, but another portion may be organic acids. Treatment by acidification and filtration could remove what might be the easily degraded fraction of organic compounds.

Samples of retort water were acidified to pH 4.4 to allow precipitate formation, before separating the precipitate from the liquid by filtration. Batch cultures, containing either unaltered or acidified retort water (diluted 1:1 with deionized water), were inoculated with an acclimated seed. The cultures were incubated at 30^{o}C and allowed to reach stationary phase, as measured by turbidity, before samples were taken for protein, SCOD, and DOC analysis.

Results of nephelometric and protein analyses showed that the growth in acid-treated media was not significantly different from that of the control. The concentrations of DOC in the acidified retort water and in the unaltered retort water cultures were equal, indicating that filtration of acidified retort water did not remove a significant portion of the organic compounds. Therefore, the growth results should not have varied markedly between the two batch cultures. This experiment will be repeated using a better means for identifying the removal of organics compounds other than DOC. If the removal of organic compounds can be increased, then the difference between the cultures, as quantitated by cell yield, will be greatly accentuated.

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