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## ENERGY & ENVIRONMENT DIVISION

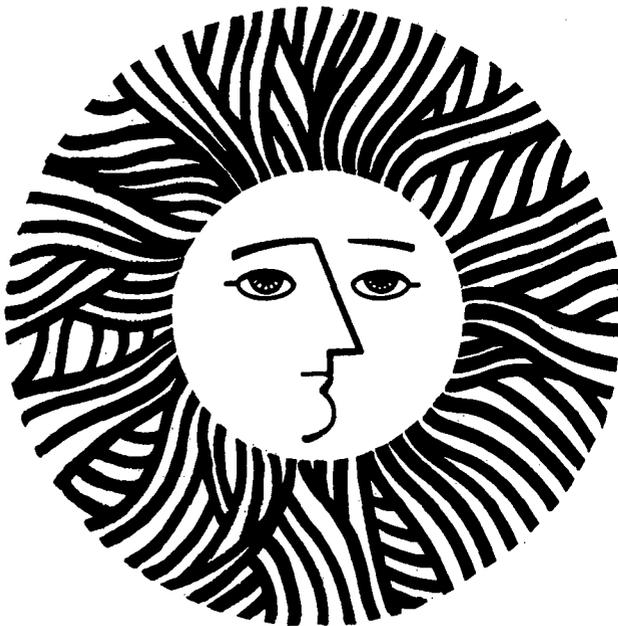
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January 5, 1981

TO: Charles Grua  
FROM: Richard Sakaji, Christian Daughton, Bonnie Jones, and Phyllis Fox  
RE: Monthly Progress Report for December  
Spent Shale as a Control Technology for Oil Shale Retort Waters  
LBID-332

PRESENTATION

B. Jones and C. Daughton presented an invited paper, "Removal of Contaminative Constituents from Retort Water: Difficulties with Bio-treatment and Potential Applicability of Raw and Processed Shales" (B. M. Jones, R. H. Sakaji, J. P. Fox, and C. G. Daughton) at the EPA/DOE Oil Shale Wastewater Treatability Workshop, December 2-3, 1980, Denver, Colorado. A copy of this paper is enclosed.

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

Experimental work this month has partially resolved the problem of drying the reverse phase C-18 Sep Paks after passage of the aqueous sample. The proposed drying step will eliminate the need for methanol mobile-phase switchover. Drying the reverse phase cartridges will allow us to elute the retained oil or hydrophobic material by direct application of a strong solvent (Freon); this gives a greatly simplified method.

The two drying techniques that were tried were acetone azeotropic distillation and lyophilization. Data collected from the initial experimentation showed that lyophilization may be the best drying technique of for this analytical procedure.

Azeotropic distillation involved placing a small quantity (100 uL) of acetone in a C-18 Sep Pak after the sample had been passed through the cartridge. When a vacuum is applied to the cartridge, the evaporation of water is enhanced by formation of the azeotrope (acetone-water). This speeds the removal of water from the C-18 cartridge. Unfortunately, infrared (IR) scans of "sample" blanks prepared in this manner indicated

the presence of an organic compound that absorbed in the critical  $2920\text{ cm}^{-1}$  region of the IR spectrum. This means that if drying is incomplete, there will be a significant residue of organic material which can interfere with the direct quantitation of oily material present in the sample.

Lyophilization (i.e., freeze drying) involves placing a frozen C-18 cartridge under a vacuum where the water is removed by sublimation below  $0^{\circ}\text{C}$ . This prevents the forced expulsion of water and the evaporation of the less volatile oils when the vacuum is applied directly to the cartridge. Cartridges are frozen by immersion in a MeOH-dry ice bath for 30 s. Immediately after freezing, a vacuum is applied to the cartridges until they dry (as measured by following the mass of water lost, from a blank cartridge). Although there are still procedural problems with lyophilization, the initial data from the experiments indicate that this drying method may be the most applicable for our purpose. IR scans of the sample blanks indicated that there was no background organic interference in the eluates from sample blanks. In addition, there were no visible traces of water in the Freon eluate, indicating that the technique effectively dries the cartridges.

As a result of experiments conducted this month, we are in the final stages of developing the procedure for this analytical technique. Validation of this analytical method, however, may be difficult. Work during this coming month will improve the drying procedure and begin method validation.

#### Validation of the COD Test

The chemical oxygen demand (COD) test is not capable of fully oxidizing nitrogenous heterocyclic compounds (e.g. pyridine, quinoline). This means that COD may not adequately quantitate the presence of organic carbon that is available for utilization as substrate by microorganisms. We have initiated experiments to study the problem of inadequate dichromate oxidation. Samples of water and retort water were spiked with known quantities of an organic compound. In this way, theoretical recoveries of organic carbon and COD could be calculated and compared to the actual recoveries.

The first compound to be studied was quinoline, a nitrogenous heterocyclic organic compound. The COD test oxidized 86% of the standard addition in both the retort water and water samples. In contrast, 103% of the organic carbon was recovered in the DOC (dissolved organic carbon) analysis of the spiked deionized water sample. The results of the standard addition to retort water are still pending. These results indicate that COD values may not adequately quantitate the presence of certain organic compounds that are present in retort water.

#### TASK 4. SPENT AND RAW SHALE COLUMN STUDIES

We have begun to examine the effects of TOSCO II spent shale on Oxy-6 retort water because both are waste products from potentially viable commercial processes. Two continuous-flow spent shale column experiments were conducted this month. In both column experiments, TOSCO II shale and Oxy-6 were used in the 1" i.d. Lucite columns; Oxy-6 retort water was passed through the column at a surface loading rate of 0.1 gpm/ft<sup>2</sup>.

The first column experiment, using TOSCO II spent shale (<25 mesh) and Oxy-6 retort water, was unsuccessful because colloidal spent shale particles clogged the column effluent screens, causing abnormal pressure and flow fluctuations in the column. Consequently, this experiment was aborted before completion.

The second column experiment used -25 +120 mesh TOSCO II spent shale to avoid the problems with screen clogging encountered in the previous experiment. This column experiment successfully demonstrated that:

- 1) The column initially removed 68% of the color (as measured by absorbance at 450 nm). This removal gradually decreased to 45% by the fifth pore volume and 15% by the 12th pore volume. After 44 pore volumes had passed through the bed, the color removal was still above 5%.
- 2) DOC removal initially reached a maximum value of 44% as the first bed volume began exiting the column. This reduction of DOC fell to 36% by the second pore volume and reached exhaustion (less than 5% removal) by the 10th pore volume.
- 3) Initial dissolved inorganic carbon (DIC) removal was 98% of the influent value. DIC removal was reduced to 40% by the third pore volume and the column was exhausted by the 10th pore volume.

4) The pH of the retort water fell from 8.9 to 7.1 during the first four pore volumes and slowly returned to the influent value by the 16th pore volume.

The data from a previous study using TOSCO II spent shale and retort water from run S-13 of LETC's 150-ton retort and the data from the TOSCO II spent shale and Oxy-6 retort water experiment are being reduced so that the results of the two studies can be compared. This comparison should demonstrate the ability of TOSCO II spent shale to treat different types of retort water and show the effects of different retort waters on the performance of spent shale columns.

#### TASK 5. SYSTEM STUDIES

##### Biological Oxidation

Determination of phosphate limitation. Several investigators have assumed that phosphate may be a limiting nutrient in the biological oxidation of retort water. In order to correct this assumed deficiency phosphoric acid has been used to control the pH. Such massive additions of a nutrient made it impossible to tell whether phosphate was indeed limiting.

A major facet of our investigation of biological oxidation of retort water has been the determination of the factors that critically affect microbial growth in retort water. Using batch cultures containing 50% Oxy-6 retort water, we have begun to investigate the possibility of phosphate limitation.

Results of the initial studies indicated that growth (as quantitated by protein) was markedly increased by the addition of phosphate to 0.1 mM concentration. Increase in growth was positively correlated to an increase in substrate removal as measured by both SCOD (soluble COD) and DOC. Increasing the phosphate supplement above 0.1 mM phosphate did not affect the production of more biomass nor enhance substrate removal. This indicates that the failure of microbial degradation of the remaining organic species in retort water has not been caused by phosphate limitation.

Effect of analog enrichment. It has been proposed that microbial growth in retort water occurs at the expense of an easily degradable organic fraction but the remaining portion of organic material is recalcitrant to

microbial degradation (see enclosed paper). Analog enrichment, the addition of a degradable compound of a molecular structure similar to that of a recalcitrant solute present in the medium, may enable the microbial community to oxidize a portion of the remaining refractory organic material.

The batch culture experiment (50% Oxy-6 retort water medium, 50% de-ionized water, inoculated with acclimated seed), reported in the October and November monthly reports, was repeated (with pH control using sulfuric acid) to investigate the effect of "analog enrichment" on microbial growth and organic solute removal.

Microbial growth (quantitated by turbidity and protein concentration) in the retort water medium reached a maximum in 2.8 days, declined slightly, and then remained constant. Concomitant with microbial growth, organic solute concentration was decreased by 50% as DOC and 52% as SCOD (soluble COD). There was no further reduction in organic solute content once growth ceased. As was observed in the first experiment, the addition of two easily degraded carboxylic acids (25 mM as C of sodium acetate and 25 mM as C of disodium succinate) stimulated growth. In contrast to the results from the previous batch experiment, however, the DOC and SCOD values did not drop below the pre-addition value.

The addition of phenol (20 mM as C), an inducer of oxygenases, stimulated a small, delayed, growth response. Subsequent to this microbial growth, the organic solute values returned approximately to pre-addition levels. There was an apparent modification of the medium; the "specific COD" (the ratio of SCOD and DOC) was reduced to 3.05 from a pre-phenol-addition value of 3.25. This indicates that the organic compounds remaining in solution may have become more oxidized than the compounds present before the phenol addition.

Quinoline, a nitrogenous heterocyclic compound, was then introduced, but the results were inconclusive because of the small amount of substance that was added. A second quinoline addition (30 mM as C) was reflected by an increase in organic solute concentration. The subsequent removal of solute (15% SCOD and 12% DOC) was not accompanied by a change in protein concentration. It is unclear whether the solute was removed through microbial action, or was simply stripped from solution by aeration.

EPA/DOE Oil Shale Wastewater Treatability Workshop  
December 2-3, 1980, Denver, Colorado

Removal of Contaminative Constituents from Retort Water:  
Difficulties with Biotreatment and Potential Applicability  
of Raw and Processed Shales

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Introduction

What constitutes treatment? This apparently simple question must be addressed before evaluating any treatment scheme for retort water. Wastewater treatment can be defined as the removal of volatile or non-volatile organic or inorganic contaminants from an aqueous effluent. These substances can have associated properties of color, odor, toxicity, oxygen demand, flammability, or corrosiveness. While the concept of treatment may be straightforward, the quantitation of treatment can be difficult. This problem is exacerbated by the complex and variable nature of retort waters. Therefore, the issues to be addressed are: what properties are appropriate to monitor for establishing the degree of treatment and what analytical methodology is compatible with the sample matrix.

In situ oil shale processing generates two major aqueous waste streams: gas condensate and retort water. Water from combustion, mineral dehydration, steam input, and often, groundwater intrusion, is collected with the shale oil during retorting. Retort waters have characteristic organoleptic properties (e.g., color and odor) and notably high concentrations of organic and inorganic components which include ammonia, carbonates, aliphatics such as carboxylic acids, and organonitrogen compounds. All of these characteristics vary in relative and

absolute values even among samples of a given retort water. In addition, different commercial processes can yield markedly dissimilar retort waters. Even after homogeneous retort water samples have been obtained (1), it is difficult to subsample representatively because of sedimentation of suspended solids and partitioning of hydrophobic solutes. The complex chemical nature and heterogeneity of retort waters can confound treatment monitoring. Individual contaminative substances may not be good indicators of treatment efficacy and certain chemical classes are not particularly conducive to quantitative measurement.

We have developed and applied some traditional and novel methods for the treatment of water from in situ retorting. Problems such as limited microbial growth and incomplete organic solute removal are inherent with the application of biological treatment. We have also investigated the feasibility of raw and processed shales to effect inorganic and organic constituent removal.

#### Biological Treatment

Biological treatment is a conventional method for upgrading wastewater; it converts soluble organic species into solid material that can sediment (i.e., flocculated microbial cells). This scheme fails, however, when (i) the cells do not settle, (ii) the components of the medium are toxic to microorganisms, or (iii) the microbial community cannot degrade the organic solutes.

Retort water can easily support luxuriant microbial growth. Biological treatment would, therefore, appear to be a promising approach for organic solute removal. Bench-scale experimental results, however, have never upheld this initial optimism. We have never observed the color and odor of retort water to disappear; indeed, the color of lime pre-treated retort water was reduced, but it became more intense during biotreatment. Many problems with biological treatment were elucidated by these initial studies. The control of pH has been a continuing problem; pretreatment may be required to remove soluble and insoluble carbonate

alkalinity. Bacterial flocculation has been insufficient. Most importantly, we have never observed soluble chemical oxygen demand (SCOD) or dissolved organic carbon (DOC) concentrations to be reduced by more than fifty-five percent.

Retort water can be modelled by assuming that the organic solute composition consists of two fractions: (i) an easily degradable fraction of carboxylic acids, and (ii) a recalcitrant fraction which includes polynuclear aromatics and nitrogenous heterocyclics. Initial growth in this model water would be quite rapid, but it would cease when the easily utilized carbon source had been depleted. Further growth and concomitant solute removal would be limited by the absence of usable carbon or of organisms with competent enzyme systems. This model serves to explain the commonly observed phenomenon of microbial growth in retort water: abundant initial microbial proliferation with the depletion of SCOD and DOC, followed by cessation of growth and retention of a large fraction of the original organic solutes.

This model can explain the results from batch culture experiments (50% concentrations of Oxy-6 retort water) in which we have followed the dynamics of growth and substrate removal. After initial exponential microbial growth, quantitated by protein concentration (2), stationary phase ensued and the rate of removal of organic solutes decreased to zero. The organic solute concentration was reduced only to fifty percent of the initial value; it then remained constant and further (diauxic) growth was not observed. During stationary phase, the addition of an easily degradable carbon source (i.e., carboxylic acids) consistently resulted in dramatic regrowth of the microbial community. This rapid increase in microbial density was undoubtedly at the expense of the supplemental carbon source. These results demonstrated that carbon was limiting bacterial growth. The remaining organic solute fraction was refractory to the microbial community. Further growth was not limited by toxicity; however, a necessary trace element or cofactor, even if present, may be unavailable to the cells because of ligand sequestering (e.g., by nitrogenous heterocyclics).

We have quantitated organic solute concentration as SCOD and DOC. Either of these parameters yields different, but limited, information about organic solute concentration. We believe that SCOD and DOC, when monitored in tandem, merge into a valuable concept for assessing the quality and quantity of soluble organic compounds (3). We have defined the ratio of SCOD to DOC as "specific-COD"; it is a measure of the overall oxidative state of organic matter, when the values are corrected for inorganic species. Methane and formic acid represent two extremes with specific-COD values of 5.33 and 1.33, respectively. In the carbon amendment experiment, the specific-COD value prior to carboxylic acid addition was higher than the value after the microbial community had degraded the supplementary carbon source (3.8 vs. 3.5). The SCOD concentration was reduced compared to pre-addition levels, but, most importantly, the DOC concentration remained the same. There are two possible explanations: (i) refractory organic solutes were partially oxidized but not mineralized after the carboxylic acid addition (e.g., via cometabolism), thereby yielding a lower COD per carbon content, or (ii) organic solutes were enzymatically converted to polymers that yield lower than theoretical COD values. We must emphasize that evaluation of either SCOD or DOC alone would have given misinformation about any further degree of treatment that may have been achieved.

From this work, we believe that further biological treatment experiments with raw retort water will yield little usable information. Initial solute reduction cannot be equated with the remaining SCOD or DOC in terms of ease or efficacy of removal. Equivalent values for either SCOD or for DOC do not necessarily reflect equivalent molecular species. Future research should use "spent" retort water (i.e., water freed of the easily degradable solute fraction by microbial pretreatment) in order to investigate the problems with microbial growth on the biorefractory compounds. The possibility of inducing sequential cometabolic alterations of the refractory species, perhaps by means of "analog enrichment", should be seriously considered.

## Raw and Processed Shales

Disposal and leachate problems indicate that processed shales may present a tremendous liability for commercial oil shale operations. Therefore, the possibility of beneficial uses of waste products should not be overlooked. Use of a co-generated waste, such as processed shale, as a treatment agent for retort water is appealing especially because processed shale must be wetted prior to disposal and both wastes are plentiful on-site.

Batch (4) and continuous flow column studies have demonstrated that processed shales can reduce the concentrations of DOC or dissolved inorganic carbon (DIC), as well as decrease color and odor. Processed shales are diverse because of the raw shale source and retorting process. Shales that have been completely burned are better for DIC removal (in continuous flow packed columns: 99% initially, 50% after two void volumes) and pH elevation.

Processed shales with more carbon residue have greater capacities to remove the DOC from retort water, but are not efficient for DIC removal. We have hypothesized that the residual carbon in the shale matrix retains constituents of retort water in a manner analogous to reverse-phase chromatography (5,6). Our studies on analytical methodology have shown that reverse-phase chromatographic packing materials are efficient at partitioning and retaining large quantities of dissolved materials from retort water, especially those associated with odor and color. If the residual carbon in processed shale is able to partition hydrophobic solutes from the water, then the abundant kerogen in raw shale should be even more efficient for DOC removal (5,6).

Results from initial continuous flow column experiments have demonstrated that raw shale can remove color and odor from retort water. Initial reductions of DOC have been 18 to 25 percent through one void volume, while color (as measured by absorbance at 450 nm) was reduced by 68 percent. Color and odor are associated with nitrogenous heterocyclics. Since this is one of the classes that is refractory to bio-oxidation, raw shale and biological treatments may be

complementary processes. If raw shale were analogous to reverse-phase chromatographic packing material, then the kerogen will require "wetting" or "activation" by an water-miscible organic solvent in order to effect partitioning of organic solutes. We are planning to investigate the "activation" of kerogen.

#### Conclusion

Retort waters are dissimilar because of the source of raw shale, the industrial retorting process, and differences in product collection systems. Furthermore, heterogeneity within a waste stream can result from changing conditions during a retorting operation. The waters produced are difficult to treat by conventional methods because of their assemblage of contaminative constituents and associated physical properties. Any scheme developed to treat retort water must be compatible with the many types of retort water that will be produced, and capable of removing the wildly varying relative and absolute quantities of problematic compounds and exotic xenobiotics.

#### References

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- (2) Daughton, C.G.; Jones, B.M.; Sakaji, R.H.; Yu, K. "Oil Shale Wasterwater Treatment Monitoring: Determination of Biomass as Protein", manuscript in preparation.
- (3) Daughton, C.G.; Jones, B.M. (unpublished data).
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