Title

MONTHLY PROGRESS REPORT FOR MAY. SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATERS

Authors

Sakaji, R.
Jones, B.
Daughton, C.

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

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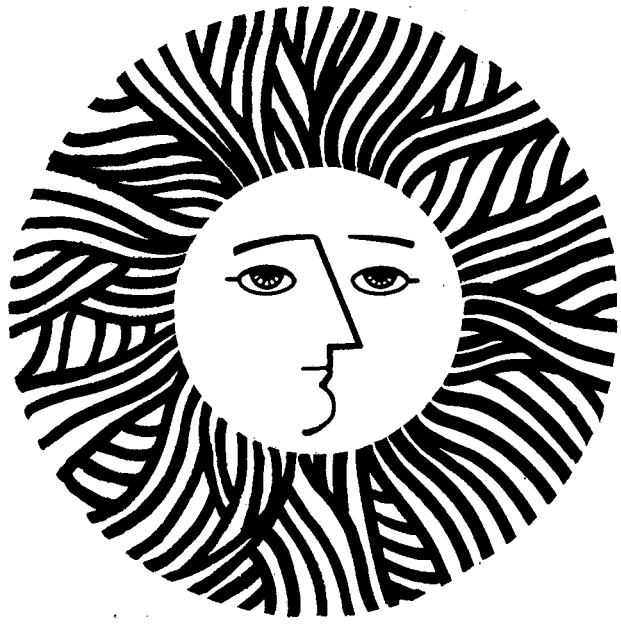

DISCLAIMER

June 3, 1981

TO: Charles Grua

FROM: Richard Sakaji and Bonnie Jones; Christian Daughton (SERL)

RE: Monthly Progress Report for May
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-408

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Oil and Grease Determination

The reverse-phase chromatographic/infrared spectrophotometric determination for oil and grease was introduced in the December 1979 monthly report. Since that time, the protocol has undergone a considerable amount of refinement and has evolved into a valuable analytical tool. Both oil and grease (fats, soaps, fatty acids, and other less hydrophobic species, in addition to oil) and aliphatic oil can be quantitated in retort water by this method. We foresee using this procedure in our research as a routine monitoring device.

An investigation to determine aliphatic oil concentration of Oxy-6 retort water revealed that our reverse-phase chromatographic/infrared spectrophotometric method was very reproducible (rsd = 4.7%, n = 10). The aliphatic oil concentration for Oxy-6 retort water, determined in this experiment, was higher in comparison with previous results. As monitored in sequential experiments, this high value of 46.6 mg/L continually decreased to 25.3 mg/L. This decrease in concentration was thought to result from de-emulsification of the sample that led to nonhomogeneity from stratification and from partitioning of hydrophobic species onto container walls during storage.

We previously reported difficulty with the quantitation of the oil and grease fraction because of a severe baseline shift in the infrared (IR) spectrum (3200-2800 cm^{-1}). When an oil and grease sample from Oxy-6 retort water was scanned from 4000-2800 cm^{-1} it became apparent that this "baseline shift" represented a wide band of IR absorbance from other compounds in the "grease" fraction of retort water. The absorbance yielded by the asymmetric methylene C-H stretch (2930 cm^{-1}) was added upon these other absorbance

peaks. Dilution of the oil and grease samples reduced these other aborbance peaks and allowed for accurate quantitation of the hydrocarbon content. We have found that the oil and grease concentration of the stored sample of Oxy-6 retort water decreased from 405 to 313 mg/L during the two week period previously mentioned. For any one subsample, however, the oil and grease results were reproducible (rsd = 6.9%, n = 8).

We feel that the oil and grease and aliphatic oil values assigned to Oxy-6 retort water should be expressed as a range because of the sensitivity of retort water to handling and storage conditions. A given subsample of retort water can be accurately characterized. In terms of determining the success of a treatment process, information regarding a change in concentration is most critical.

Our oil and grease protocol involves the partitioning of wastewater IR-absorbing solutes into a C-18 cartridge, lyophilization, and direct elution of the retained solutes with IR-transparent solvent. The eluate does not undergo the Si cartridge clean-up step. We have found that after application of a sample to a C-18 cartridge, 400 µL of sample remain in the pores of the packing material. Any non-partitioned, but occluded solutes, containing C-H bonds, that are in this 400 µL fraction will be mistakenly quantitated as oil and grease. If small sample sizes are used, this occluded volume of unfractionated sample will introduce significant error. To correct this problem, the 400 µL of retort water should be replaced with 400 µL of water free of IR-absorbing compounds prior to lyophilization. The effects of two types of washes (deionized water and 1% NaCl solution) on solute recovery were investigated (Table I). Both types of wash removed IR-absorbing material from the C-18 cartridges, mainly from the grease fraction. The unresolved question is whether the wash step removed solutes that had partitioned into the C-18, as well as the occluded, unfractionated water. Upon the conclusion of these investigations, we feel that the development of the oil and grease methods will be completed.

Validation of the reverse-phase chromatographic/IR spectrophotometric method has proved to be a difficult task. Fortification/recovery studies using water samples spiked with oil may not be possible because oil and water do not mix. Without the aid of surfactants, it is impossible to homogeneously spike and recover oil from a mixture. We obtained a sample of Soluble Oil (DO batch #029640) from Lubricating Specialties Company, an ARCO subsidiary. Initial attempts to quantitatively recover soluble oil spikes from solution were not successful; only 21% of the aliphatic oil was recovered from a

soluble oil solution (24.5 mg/L as mineral oil). Standard additions of soluble oil to retort water did not yield any measureable change in aliphatic oil concentration. We were unable to obtain proprietary information regarding the surfactant or oil concentrations or compositions of DO Soluble Oil. We therefore cannot judge accurately the results of the validation experiments. We cannot overemphasize the fact that the liquid-liquid partitioning method (Standard Methods, 14th ed.) also suffers from the inability to be realistically validated. Any oil spike easily transfers into the organic phase during "extraction" because it was not truly dissolved or emulsified in the aqueous phase.

TASK 5. SYSTEM STUDIES

Biological Oxidation

Our research has demonstrated that only fifty percent of the dissolved organic carbon in Oxy-6 retort water is biodegradable. Previous attempts to classify this fraction of retort water have been unsuccessful. This month we have shown that most of the biodegradable compounds are characterized by being more hydrophilic than the compounds of the recalcitrant fraction.

We have verified that C-18 cartridges can separate the constituents in retort water into polar and nonpolar fractions. Fifty percent of the dissolved organic material in Oxy-6 retort water is polar, and 50 percent is nonpolar, according to dissolved organic carbon (DOC) and chemical oxygen demand (COD) determinations on the two fractions. Each of these fractions was used as culture media. We have hypothesized that the biodegradable portion of retort water consists of fatty acids; dissociated short-chain fatty acids are not retained by the C-18 cartridge and would appear in the polar fraction. We, therefore, expected microbial growth to be predominantly in the polar fraction of retort water. Indeed, the polar fraction supported excellent growth. Further inspection of the data, however, showed that the microorganisms removed only 63% of the organic material from this fraction. In contrast, there was significantly less growth in the nonpolar fraction; microbial activity eliminated only 24% of the organic material from the nonpolar fraction. This represented a total carbon removal of 43% versus 55% in the unfractionated control. Explanations for this discrepancy include:

1. Nonbiodegradable compounds appeared in the polar fraction and biodegradable compounds, such as long chain fatty acids, were retained by the C-18 cartridge and were eluted along with the

nonpolar fraction.

2. A micronutrient required for complete microbial growth on the polar fraction was retained in the non-polar fraction, e.g., trace metals may have been chelated by nitrogenous heterocycles and sequestered in the nonpolar fraction.
3. Organic compounds in the nonpolar fraction may actually be polar compounds from the 400 μL of unpartitioned retort water that was occluded in the C-18 cartridge.
4. The catabolism of certain constituents in unfractionated retort water may be a cometabolic process that requires compounds from both fractions. When these compounds were separated into two fractions, cometabolism was no longer possible.

This experiment will be repeated with better control of the fractionating process. We will exclude the 400 μL of occluded retort water from the nonpolar fraction.

Combined Biological Oxidation/Spent Shale Treatment

Batch sorbent experiments (reported in March and April) indicated that a complementary relationship may exist between the spent shale and biological treatment processes. We also have observed enhanced removal of dissolved organic carbon (DOC) that may be attributed to an interaction between the sorbent and microorganisms. Two experiments were conducted this month to investigate this possibility.

Batch experiment #7 was conducted on TOSCO II spent shale (60-80 mesh) and biologically treated (spent) retort water (i.e., sorbent/solute). This spent medium consisted of 50% Oxy-6 retort water that was supplemented with phosphate and had undergone extensive biological oxidation. We have found from our previous studies that biological treatment consistently eliminates about 50% of the DOC from retort water, even with a highly acclimated inoculum. After this initial microbial growth and solute removal, however, further growth and DOC reduction ceases.

An apparent sorption equilibrium was attained, in batch experiment #7, after 1 hour of gyratory agitation ($C_i/C_o = 0.674$). After 16 hours, however, the DOC concentration began to drop below the "equilibrium" concentration ($C_i/C_o = 0.587$ after 24 hours). Furthermore, this auxillary DOC removal continued through 168 hours ($C_i/C_o = 0.327$). We have observed this same pattern in all previous spent shale/Oxy-6 retort water equilibrium batch experiments. We had hypothesized that microbial activity was responsible for

the enhanced DOC removal. The present results indicated that a synergistic removal process was accomplished by the combination of spent shale and microbial activity. Possible explanations for this phenomenon include: (1) alteration of the composition of the spent medium by sorption of toxic components onto or leaching of microbial growth factors from the spent shale, and (2) concentration onto the shale surface of the remaining organic constituents that may have been present in individual concentrations well below the affinity constants of the requisite enzymes.

On the basis of these results, a preliminary investigation was conducted to determine if the addition of small quantities of sorbent to batch biological cultures could increase the overall DOC reduction. Powdered activated carbon (PAC, I.C.I. 12-40 mesh), Colony raw shale (60-80 mesh), or TOSCO II spent shale (60-80 mesh) were added to flasks that contained either raw or spent Oxy-6 retort water. These mixtures were inoculated with acclimated bacteria, and samples were taken for DOC analysis at 1 hour to determine the DOC reduction mediated by sorption, and at 48 hours to determine total DOC reduction (i.e., sorption plus biological). The results from the inoculated raw retort water/sorbent mixtures (Table II) include:

1. DOC reduction as a result of biological activity alone (i.e., no sorbent addition) was 47 percent.
2. The DOC concentration of raw retort water was reduced 62% in the PAC mixture. This was 5% more than the sum of individual reductions by PAC sorption (10%) and bio-oxidation (47%).
3. The DOC of the raw shale/ retort water mixture was not reduced by sorption, but the total DOC reduction (52%) was 5% greater than that attributable to biological treatment alone.
4. The spent shale/retort water mixture reduced the DOC by 59 percent. This was 6% greater than the sum of the sorptive and biological reductions (6% and 47%, respectively).

These results indicated that 5 to 6 percent of the DOC reduction was attributable to synergistic effects between sorbent and raw retort water.

The results from inoculated mixtures of spent retort water/sorbent (Table II) indicated that:

1. The DOC concentration did not change in the inoculated flasks of spent retort water (i.e., no sorbent addition). This simply verifies that the "soft" fraction of the retort water was totally degraded.
2. The inoculated spent media/PAC combination reduced the DOC by 21 percent. Sorption by the PAC accounted for only a 3% reduction.

Biotreatment alone did not effect any DOC removal. Therefore, an interaction between biological and PAC treatment must have been responsible for the additional 18% reduction of DOC.

3. Raw shale reduced the DOC concentration of spent retort water by 3 percent. Sorption appeared to be responsible for the entire reduction.
4. The total DOC reduction for the spent medium/spent shale combination was 17%. Sorption reduced the DOC by 10%, so that 7% of the total DOC reduction was attributable to synergistic effects between biological and spent shale treatment.

The addition of PAC to spent retort water gave more enhanced removal of DOC than did its addition to raw retort water. In contrast, spent shale seemed to enhance the DOC removal from raw and spent retort water equally. We cannot determine from these data whether the sorbents removed classes of solutes complementary to those removed by biooxidation.

Table I

Effect of C-18 Cartridge Wash on
Apparent Oil and Grease Recoveries from Oxy-6 Retort Water

wash	oil and grease (mg/L)	mg/L reduction	oil (mg/L)	mg/L reduction
no wash	312.8	--	25.3	--
deionized water	257.0	56	20.9	4.4
1% NaCl solution	158.3	155	21.3	4.0

Table II

Percentage DOC Removal from 50% Oxy-6 Retort Water
by Combined Biological/Sorbent Treatment

Sorbent added to medium	% DOC Removal from Inoculated Medium					
	Raw Retort Water			Spent Retort Water		
	total	sorption	enhancement[4]	total	sorption	enhancement
none (control)	47	na[5]	na	nil	na	na
PAC[1]	62	10	+5	21	3	+18
raw shale[2]	52	nil	+5	3	3	nil
spent shale[3]	59	6	+6	17	10	+7

[1] powdered activated carbon, 12-40 mesh (1.3 mg/mL)
[2] Colony raw shale, 60-80 mesh (25 mg/mL)
[3] TOSCO II spent shale, 60-80 mesh (100 mg/mL)
[4] total % removal minus removals from biooxidation (i.e., control) and from sorption
[5] not applicable

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720