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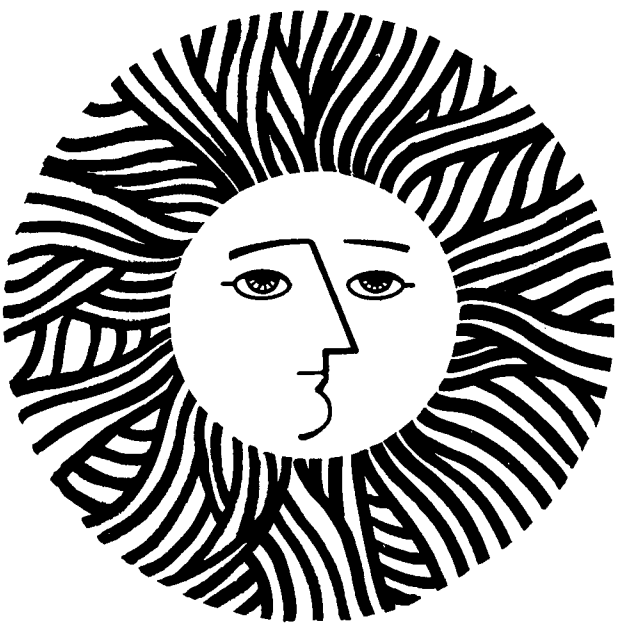

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LAWRENCE BERKELEY LABORATORY
Room: 128 Bldg.: 70 Ext.: 6698

March 9, 1981

TO: Charles Grua

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

RE: Monthly Progress Report for February
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-372

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Chemical Oxygen Demand

We utilize the soluble chemical oxygen demand (SCOD) test to monitor the degree of treatment achieved in retort water. The titrimetric-COD method (Standard Methods) produces fairly accurate and reproducible results. It is, however, cumbersome because it requires: (i) long analysis time (3-4 samples per hour), (ii) large quantities of expensive reagents (silver and mercury salts), (iii) large sample volumes, (iv) extensive laboratory bench space, and (v) disposal of significant quantities of hazardous waste. These disadvantages have lead us to an investigation of the more convenient "micro-COD" method.

The "micro-COD" method, developed by Jirka and Carter (Anal. Chem. 1975, 47, 1397-1402), eliminates many of the disadvantages of the titrimetric-COD method. The "micro-COD" test is a scaled-down version of the titrimetric-COD method. The analysis is performed in screw-cap test tubes allowing for great reduction in all the reagent requirements and associated waste. The main difference between the two methods is that the "micro-COD" method quantitates COD spectrophotometrically. This is done by quantitating the appearance of Cr(III) or the disappearance of Cr(VI) after sample oxidation. If the production of Cr(III) is determined, the sensitivity is greatly improved over the titrimetric procedure; this determination also avoids the accurate addition of dichromate.

We have encountered several problems with adapting the "micro-COD" method to our sample matrix and laboratory equipment. Following the requisite 150°C digestion period, a mercuric-ion precipitate formed in the

digest and inside the micro flow-through spectrophotometric cell during quantitation. Experiments have shown that the formation of the precipitate is prevented by slowly cooling the sample tubes in a warm water bath. The precipitate seemed to result only when the mercury and silver salts were both present.

The viscous digest necessitated the use of cuvettes instead of the micro flow-through cell for the colorimetric determination of COD. This is an awkward procedure that requires handling a concentrated acid mixture. We are trying to adapt the micro flow-through cell to the viscous digest to facilitate the use of the "micro-COD" method as a routine analytical procedure.

Oil and Grease Determination

We began experimentation to validate the analytical protocol for oil and grease outlined in the January 1981 monthly report. The first experiment was to determine the retention efficiency and capacity of the C-18 Sep Paks. During the course of spectrophotometrically analyzing these samples, we found a significant background contamination present in the blanks. This background was traced to the use of new Sep Paks. Previous experimentation had incorporated reused Sep Paks that were repeatedly "cleaned" with an organic solvent. In addition, previous recovery studies required that the eluate from these cartridges be diluted tenfold prior to analysis; this step diluted out most of the background interference. The high background level may explain the excessively high recoveries of oil reported last month. Experimentation this month demonstrated that this background can be significantly reduced by pre-washing the Sep Paks with a small quantity of organic solvent such as Freon.

The recovery experiments outlined in last month's research report were repeated incorporating the Freon pre-wash for both the C-18 and Silica Sep Paks. Gravimetrically quantitated masses of oil were added to C-18 Sep Paks. The Sep Paks were then lyophilized and eluted following our normal protocol. The recoveries of oil were 91.5, 93.5, 99.8, and 112%. The high recovery in the one sample was probably due to an error in placement of the fortification oil in the cartridge. While some background was still present, the pre-washing with Freon significantly reduced the problem. As a result, we decided to use the protocol to test the retention capacity of the C-18 Sep Paks.

No evidence of exceeding the retention capacity of the cartridges was noted in this experiment. Various quantities of Oxy-6 retort water were passed through C-18 Sep Paks. A total of six samples was run with the maximum quantity of retort water for a single cartridge being 30 mL. After lyophilization and elution, the oil concentration of the Oxy-6 retort water was determined for each cartridge. A reduction in the concentrations of oil with increasing sample volumes would indicate that the retention capacity of the cartridge had been exceeded. This was not noted in any of our samples. The quantity of hydrocarbon oil present in the Oxy-6 retort water was less than 25 mg/L as mineral oil. This was significantly less than the 131 mg/L reported last month, probably resulting from the background levels we detected this month.

The protocol that we have developed for quantitating oil and grease is actually a measure of true hydrocarbon oil and is therefore analogous to the hydrocarbon oil measurement outlined in Standard Methods. The use of the C-18 Sep Paks without benefit of the Silica Sep Pak cleanup is analogous to the oil and grease measurement in Standard Methods. Attempts to quantitate the organic compounds present in retort water as "oil and grease" have been unsuccessful because the eluate from the C-18 cartridges is highly colored and causes a significant baseline shift, which makes spectrophotometric quantitation impossible. Attempts to elute hydrophilic compounds from the retained mixture on the C-18 Sep Paks have not eluted all of the colored species. Colored materials are retained by the Silica Sep Paks and therefore cause no problem with true oil determination. Unless this baseline shift is eliminated, it will make comparison between the standard method for "oil and grease" analysis and our protocol very difficult.

TASK 4. RAW AND SPENT SHALE STUDIES

Spent Shale Isotherm Studies

Batch experiment #4 was begun on 1.20.81 and completed on 2.19.81. The purpose of this experiment was to determine the equilibration time required for the process of sorption of dissolved organic carbon (DOC) from retort water onto TOSCO II spent shale or granular activated carbon (GAC).

Two adsorbent-to-liquid ratios were used for both Calgon F-400 GAC and TOSCO II spent shale with Oxy-6 retort water. The ratios of GAC to retort water were 0.5 g and 1.0 g to 6.0 mL and the ratios of spent shale to retort water were 1.0 g and 3.0 g to 4.0 mL. At twelve selected times throughout the 720 hours study, a sample set was removed. The solids were removed by

membrane filtration, and the filtrate was diluted and analyzed for DOC concentration. The fraction of DOC remaining was expressed as Ci/Co, where Ci = DOC in solution and Co = DOC in solution at time zero.

As noted in last month's report, after 30 minutes, Ci/Co was 0.33 for the low ratio of GAC and 0.79 for the high ratio of TOSCO II spent shale. After 3 hours, Ci/Co for the low ratio of GAC to retort water reached equilibrium at a value of 0.28. Data for the low ratio of spent shale to retort water were discarded because of microbial contamination, and the possibility of biological reduction of DOC during the long incubation time could not be eliminated. The high ratio of GAC to retort water reached equilibrium within the first hour (Ci/Co = 0.24), while equilibrium for the high ratio of spent shale to retort water was reached after 250 hours (Ci/Co = 0.53).

The low ratio of GAC to retort water had an adsorptive capacity at equilibrium of 23.2 mg DOC/g GAC. The high ratio of GAC to retort water had an adsorptive capacity at equilibrum of 24.7 mg DOC/g GAC. The high ratio of spent shale to retort water had an adsorptive capacity at equilibrium of 1.7 mg DOC/g shale. The sorption results are summarized in Table 1.

Table 1. Sorption studies.

sorbent	g sorbent/mL retort water	Ci/Co at equilibrium	adsorptive capacity mg DOC/g sorbent
GAC	0.17	0.24	24.7
	0.083	0.28	23.2
Shale	0.75	0.53	1.7

TASK 5. SYSTEM STUDIES

Biological Oxidation Studies

We continued our investigation into the possibility of enhancing organic solute removal by means of sequential spent shale and biological treatment. The third pore volume effluent of the Oxy-6-TOSCO II spent shale column was used as a culture medium. Control cultures were grown on 50% raw Oxy-6 retort water. This experiment attempted to compare the biotreatability of the third pore volume effluent with that of the first pore volume effluent.

The specific growth yield (mg of protein per mg of carbon removed) on the shale-treated water was 10% higher than that for the control culture. The removal of organic substrate as DOC and SCOD from the spent shale column effluent culture was 56 and 58%, respectively. The control culture achieved similar reductions (56 and 51%, respectively). Therefore, an overall reduction of approximately 65% of the organic solute concentration was accomplished by this sequential treatment scheme.

The specific growth yield obtained on the third pore volume effluent was approximately equal to the first pore volume effluent, and both were greater than the specific growth yield from the raw retort water control culture. This indicated that the spent shale treatment may be removing substances from the first few pore volumes of spent shale treated retort water that are toxic or inhibitory to the microbial community. The biological removal of organic solutes was identical for both the third pore volume and control cultures. This suggested that the capacity of the spent shale to remove biorefractory compounds from retort water may have been exhausted by the third pore volume effluent.

STEAM STRIPPING PROJECT (C. Daughton, P. Fox, B. Jones, F. Pearson, and R. Sakaji)

Ammonia Determination

The precision of the distillation acidimetric-titration method for quantitating ammonia in Oxy-6 gas condensate was determined. Samples of Oxy-6 gas condensate were analyzed and the results indicated that this method was reproducible (rsd = 1.44%). The possibility that alkaline compounds (e.g., amines) codistill with the ammonia and interfere with the accuracy of the determination, however, still remains. Further objections to this procedure include: (i) the limited number of samples that can be analyzed at one time and (ii) the time-consuming, cumbersome nature of the protocol (20 minutes per sample).

An accurate, rapid method of quantitating ammonia is essential for the large number of samples that will be generated by the steam stripping project. We are interested in adapting one of the colorimetric methods of ammonia determination for use with gas condensate. These methods have low detection limits, thereby necessitating the dilution of samples. Fortunately, this dilution process may also serve to eliminate the interference of the

endogenous chromophoric compounds of gas condensate and retort water that would ordinarily preclude the application of a colorimetric method.

Batch Ammonia Air-Stripping

We have conducted preliminary batch investigations to demonstrate the efficacy of air-stripping of ammonia and organic material from Oxy-6 gas condensate. Gas condensate (1.5 liters) was heated to 95°C and the liquid was sparged using house compressed air (500 mL/min) for periods ranging from two to five hours. This batch bench-scale treatment scheme achieved a maximum removal of 98% of the ammonia, 55% of the COD, and 62% of the DOC after four hours of operation. A semi-log plot of C/Co (C = concentration at time t; Co = initial concentration) vs. time for the ammonia data yielded a straight line. This suggested that ammonia removal from this sample matrix could be described by the first order equation: $dc/dt = K_L a(C-Cs)$. The overall mass transfer coefficient, $K_L a$, is determined from the slope of the observed line. This same semi-log plot (C/Co vs. time) for organic solute removal yielded a curve with two distinct slopes. The steep initial slope indicated that a portion of the organic material was easily stripped. The lesser slope showed that little organic solute removal was accomplished with further stripping. Further, an increase in the specific COD (SCOD/DOC) from 3.31 to 3.86 during the stripping operation indicated that the more oxidized organic material was removed by this stripping operation. Air-stripping has the advantage of producing low volumes of overhead. This process is a viable option of ammonia and some organic compounds from gas condensate.

Steam Stripper Design

Further design details are being developed for the fabrication of the steam stripper. This includes the design of the steam generator, with a control system to adequately regulate the production of steam, and sampling ports. The choice and installation of appropriate monitoring equipment is being discussed and researched. We hope to begin operation of the steam stripper in mid-June.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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