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

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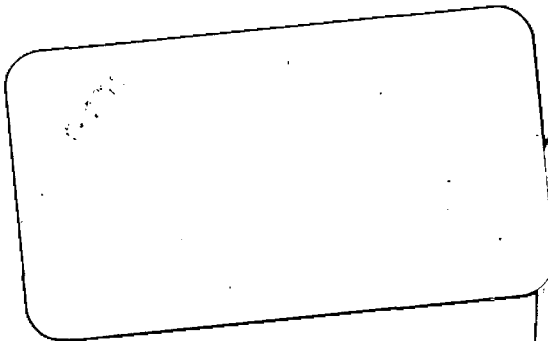
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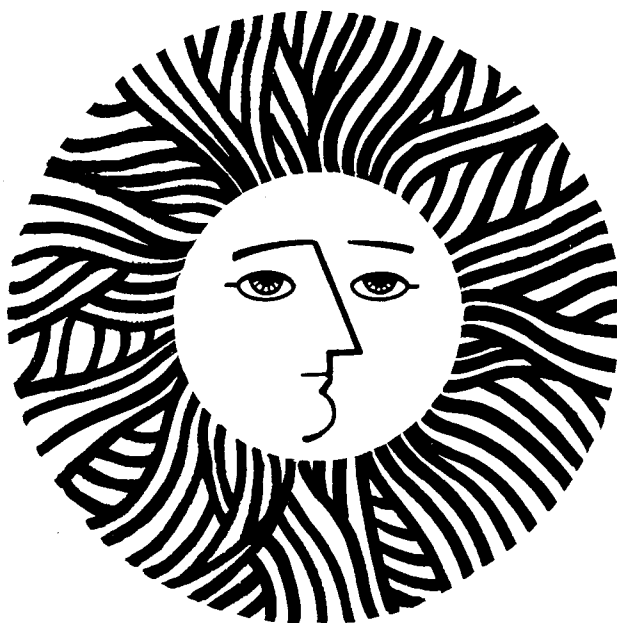
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January 8, 1980

TO: Charles Grua

FROM: Phyllis Fox

RE: December Monthly Progress Report for Spent Shale as a
Control Technology for Oil Shale Retort Waters
LBID-158

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Development of an alternate method of oil and grease analysis continued. This new method is being developed to circumvent some of the problems noted with standard methods and to accelerate the analytical procedure. In the new method, oil and grease is determined by passing a known quantity of sample through a reverse-phase C-18 column (C-18 Sep Pak). This column removes the non-polar fraction (neutral hydrocarbons or the oil and grease fraction) and passes the polar fraction which is discarded. The column is eluted with CH_2Cl_2 after mobile phase switch-over with methanol, and the eluate is dried, taken up in a solvent and cleaned up by passing it through a Si Sep Pak. The Si column removes any residual polar material from the C-18 eluate and passes the nonpolar fraction which is collected, dried, and weighed. This month, the elution efficiency, breakthrough characteristics, and suitable solvents for the Si Sep Pak were investigated.

A study of the elution efficiency of the Si Sep Paks, using CH_2Cl_2 as the eluent, was conducted. A 30-mg oil sample was dissolved in 10 ml of CH_2Cl_2 and the solvent was passed through the Sep Pak and collected. The Sep Pak was then eluted with three fresh 10 ml aliquots of CH_2Cl_2 and each eluate was collected separately in a tared pan. The solvent was evaporated from the samples and the residue was weighed. The data show that a single elution with 10 ml of CH_2Cl_2 was sufficient to recover 97% of the total mass that could be eluted with CH_2Cl_2 .

Breakthrough studies were initiated to determine the sorptive capacity of the Si Sep Pak. Oil samples of various weights were dissolved in CH_2Cl_2 . The aqueous effluent and the eluate from one rinsing with 10 ml of CH_2Cl_2 were combined and evaporated to dryness. There was no evidence that the sorptive capacity of the column had been exceeded up to 130 mg oil. The data indicated that 71% of the oil was recovered in the nonpolar fraction, i.e., the fraction that is passed by the Si Sep Pak.

The use of different organic solvents with the Si Sep Pak was investigated. As expected, the partitioning between polar and nonpolar fractions was dependent on the organic solvent used. The recovery percentage of oil and grease increased as the polarity of the solvent increased, in agreement with the eluotropic series. The percentage mass recovered was greatest for CH_2Cl_2 , followed by benzene, freon, hexane, and petroleum ether.

The initial results of these studies indicate that Si Sep Paks will serve an important function in sample preparation for oil and grease analysis and indicate that liquid chromatography or spectrophotometric methods may be used to obtain valuable data on the composition of oil and grease.

TASK 4. CONTINUOUS COLUMN STUDIES

A 1 inch by 36 inch long lucite column described last month was used in a preliminary column experiment this month to test analytical methods and the column setup. This experiment used 135 g of 18 to 40 mesh L-2 spent shale (from a steam-combustion run of LLL's 6000-kg retort) and 150-ton retort water. The L-2 shale was selected for this column run because data from previous batch studies indicated that it was effective at reducing inorganic carbon concentrations and elevating the pH of retort water. The column was operated in a downflow configuration at a surface loading rate of 1 gpm/ft^2 (20.65 ml/min) for a total of 21 min (3 pore volumes).

The alkalinity, COD, and pH were measured in the column effluent. This preliminary experiment indicated that the alkalinity was reduced through three pore volumes while the pH

elevation lasted through only one pore volume. No reduction in COD was observed.

Additional column experiments will be conducted next month. Effluent will be analyzed for pH, alkalinity, ammonia, volatile acids, COD, inorganic carbon, and conductivity. The resulting data will be used to evaluate the use of spent shale columns for the treatment of retort waters. Experiments will be initiated to investigate the use of a slurry of spent shale for treating retort waters.

TASK 5. SYSTEM STUDIES

The collaborative program with LETC to develop a compositing plan for LETC's five 800-gallon samples of Occidental Retort-6 process water was completed. We analyzed two of the five samples for alkalinity, conductivity, pH, ammonia, oxides of nitrogen, COD, and Na (Table 1) and used calculation procedures to check the reliability of the chemical analyses supplied by LETC. These investigations revealed that one of the five samples was chemically different from the other four. We, therefore, recommended that this sample be discarded and that the remaining four be directly composited. The statistical procedure proposed by LETC for compositing should not be used because the samples were not drawn at random from the same population, the magnitude of the parameters depend on retort operating conditions, and many of the water quality parameters are interdependent. These investigations also revealed that there is a chemical interference in the nitrate method used by LETC, and we recommended the use of Devarda's alloy method to measure nitrate. A composite of this Occidental retort water should be available by March 1 for use in the system studies.

The two batch activated sludge reactors were fed 100% retort water through the month. The effluent COD and mixed liquor suspended solids showed large fluctuations, and the reactors failed by the end of the month. We believe that reactor operation resulted in this failure; the 25% v/v load once a day over-stressed the microbial population. This problem has been eliminated by transferring the reactor contents to continuous flow reactors.

Table 1. Comparison of LBL and LETC-supplied analyses of two samples of unfiltered Occidental product water collected from Logan Wash, Colorado experimental retort #6 by Dr. D. S. Farrier.

Parameter	SAMPLE ES-79-049 (4/11/79)			SAMPLE 79(OXY 6)02W-01 (1/11/79)		
	LBL Analyses		LETC	LBL Analyses		LETC
	Replicate #1	Replicate #2	Analysis	Replicate #1	Replicate #2	Analysis
pH	9.21	9.13	9.33	8.13	8.38	8.48
Alkalinity (as CaCO ₃)	5,630	7,310	7,400	6,900	7,100	4,280
COD (mg/l)	6,920	7,380	14,000	4,200	5,100	12,500
Ammonia (mg/l as NH ₃ -N)	960	980	770 ^d	1,880	1,950	1,235 ^d
Total Dissolved Solids	11,300	12,000	8,620	710	740	490
Conductivity (µmhos/cm)	13,300	9,300	14,000	3,700	8,000	12,000
Oxides of Nitrogen (mg/l as NO ₃ -N)	28 ^a	0.0	1,100	49 ^a	0.0	120
Sodium (mg/l)	3560±62 ^b	3625 ^c	3,400	87±6 ^b	70 ^c	60

^a May be due to residual ammonia left in condenser following NH₃ analysis by Devarda's alloy reduction method (Standard Methods, 1975). Correct value is believed to be 0.0 mg/l.

^b Triplicates by calibration curve method.

^c Single analysis by standard additions.

^d Reported by LETC as NH₃. Converted to NH₃-N (multiply NH₃ by .82) for this tabulation.

One of these new reactors is being fed retort water and the other, retort water supplemented with glucose and a trace metal solution to eliminate nutritional deficiencies.

The continuous flow reactor system has been in operation for 1.5 months. The effluent from this reactor was analyzed for total soluble COD, and it was fractionated to determine polar and nonpolar COD. The results of these analyses indicate that the reactor is removing 20% of the total soluble COD and 49% of the polar COD. Since about 50% of the soluble COD is polar, the reactor is removing primarily polar organics.

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