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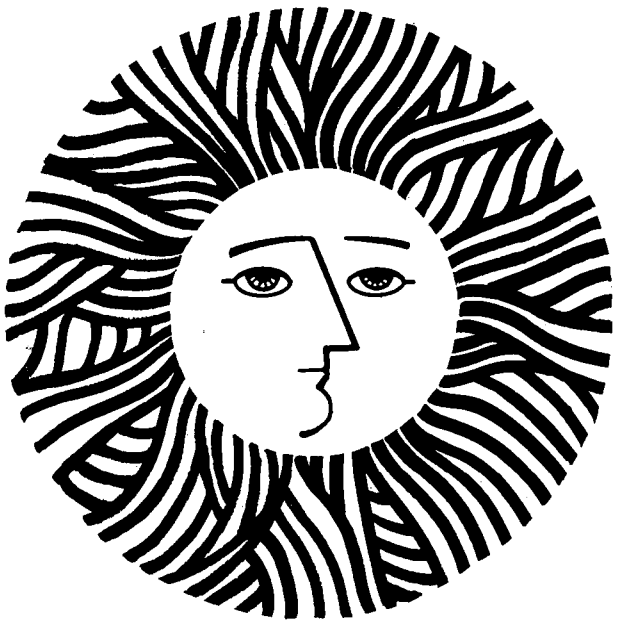

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9 December 1981

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RE: Monthly Progress Report for November
Oil Shale Waste Treatment: Fundamental Approaches
LBID-459

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Restructuring of Project

Review of literature from various sources as part of the problem definition milestone of the Uncontrolled Air Emissions of Volatiles task was still in progress this month. We had also begun some mass transfer calculations to determine by desk analysis, if possible, the quantities of volatiles that may be released from disposal piles. This work has now been discontinued at the request of DOE headquarters. Our research direction is now consolidated into waste treatment research. This is reflected in the new project title and in the new task designations.

TASK 1. ANALYTICAL METHODOLOGY

Organic Nitrogen Determination

Oil shale process waters are characteristically malodorous and intensely colored. We believe that the compounds largely responsible for these properties are the same compounds that are refractory to biodegradation -- i.e., nitrogenous heterocycles. Reported organic nitrogen values for a range of waters, however, have been variable (35 - 5000 ppm). One reason for this inconsistency may be the inherent limitations of the Kjeldahl method, the commonly applied wet-digestion analytical technique for organic nitrogen determination. The nitrogen from many nitrogenous compounds is not

stoichiometrically recovered, especially from those containing N-N and N-O bonds (see the introduction to the method in Standard Methods). Other workers have demonstrated that the temperature and length of digestion are critical for stoichiometric recoveries of nitrogen from the Kjeldahl procedure. The reproducible and quantitative determination of organic nitrogen in oil shale process waters is imperative for elucidating the mechanisms that inhibit the microbial alteration of the recalcitrant fraction of retort water.

A variation of the Kjeldahl method (using selenized Hengar granules, No. 2 Kelpak, and 20 mL sulfuric acid) was evaluated for recovery of organic nitrogen from an amino acid (glycine) and a nitrogen heterocycle (4-aminoantipyrine). Standard solutions of each substance with N-concentrations of 200, 2000, and 5000 mg/L were predistilled (to eliminate free ammonia) and digested to release organic nitrogen as ammonia; the ammonia in the digestate was distilled and quantitated by titration. Recoveries at each concentration were, respectively: glycine-N, 108, 98.7, and 99.1%; 4-aminoantipyrine-N, 77.0, 76.3, and 76.5%. Since 4-aminoantipyrine contains two N atoms in a pyrazole ring and one amino group, the recovery values presumably reflect either incomplete digestion, or the loss of nitrogen from the digestate.

We also determined free ammonia and organic nitrogen concentrations in four different oil shale process waters of two sample sizes (1.5 and 15 mL). For all samples, the organic nitrogen values from the high volume samples were significantly lower than from the low volume samples. This disparity of values from different sample sizes may reflect the inaccuracy inherent in the dispensing of very small titrant volumes, inappropriate technique, or exhaustion of the digestion reagents leading to incomplete digestion of the larger samples. In a subsequent experiment, an autotitrator was employed and great care was taken with the distillation technique. The determined N values were not affected by sample size; organic nitrogen values of Oxy-6 retort water from five different sample sizes (1 to 20 mL) were very reproducible (mean = 180.2 mg/L, rsd = 2.52%).

We are investigating the recovery of organic nitrogen from a pyrolysis/chemiluminescence total-nitrogen analyzer. Preliminary results have been encouraging; organic nitrogen recoveries from oil shale process waters have been up to 74 per cent higher than from the Kjeldahl digestion method. Further investigation will be necessary to evaluate the instrument and validate the results.

If it were assumed that the Kjeldahl organic nitrogen of Oxy-6 retort water (180 mg/L) was present solely as pyrazole ($C_3H_4N_2$), then 230 mg/L of carbon would be associated with the nitrogen. In Oxy-6 retort water, we have routinely found that approximately 1400 mg/L of dissolved organic carbon (DOC) is refractory to biooxidation. This hypothetical nitrogenous heterocycle would account for 16% of the recalcitrant carbon. If the organic nitrogen value from the pyrolysis/chemiluminescence analyzer is accurate and the same assumptions are made, then 64% (890 mg/L) of the remaining DOC could be associated with organically-bound nitrogen. These calculations are purely hypothetical, but they serve to demonstrate that most of the refractory organic carbon could be composed of nitrogen heterocycles, especially since most of these compounds would have carbon to nitrogen molar ratios greater than 3:2. The importance of accurately quantitating the organic-nitrogen fraction and of knowing the distribution of the nitrogen-bearing species cannot be overemphasized.

Ammonia Determination

Experimental results for recovery of ammonia from fortified raw and spent Oxy-6 retort water by using Weatherburn's method have been excellent. We obtained recoveries from 93 to 110 percent of the added ammonium sulfate. The standard curves for Weatherburn's method in the 10 to 100 mg/L ammonia-N range (quantitated at 633 nm), however, have not been as linear as those obtained at higher ranges (quantitated at 520 nm).

TASK 2. BIOLOGICAL TREATMENT OF PROCESS WATERS

The NBS fermentor was brought on-line for the production of biologically-spent retort water. The fermentor is capable of producing two to five liters of spent media per week. Microbial reduction of the DOC concentration in Oxy-6 retort water was slightly less than the amount removed in shake flasks (44 - 46% vs. 48 - 50%). The agitation and aeration of the fermentor has been observed, however, to effectively strip ammonia from the water (96% reduction).

Nitrogenous Heterocycles

Many researchers have observed that acclimated microbial cultures only can mineralize approximately half of the organic carbon in Oxy-6 retort water. We have proposed a treatment scheme (outlined in DOE Invention Case #IB-417, "Enhanced Bacterial Degradation of Recalcitrant Heterocycles in Synfuel Process Wastewaters", by C.G. Daughton; June 1981 Monthly Report

Enclosure) that may promote the biological mineralization of the remaining recalcitrant organic solutes. The documented protocol details the selective enrichment for microorganisms capable of using nitrogenous heterocycles as sole nitrogen sources. Pursuant to the ideas presented in this disclosure, we have initiated two enrichment experiments to investigate the possibility of derepression of N-abstraction enzymes by removing ammonia from spent Oxy-6 retort water.

The nitrogen-heterocycles of biologically-spent retort water, when separated from the inherently high ammonia content by ammonia stripping, reverse-phase partitioning, or sorption, may serve as excellent substrates for N-abstraction enzyme induction. Ammonia-stripped Oxy-6 retort water, the partitioned solutes from C-18 chromatographic packing material, and the solutes sorbed to powdered activated carbon were inoculated with mixed liquor suspended solids from a sewage treatment plant (15% dryweather flow from industrial contributors), soil particles, and an aqueous sample from a petroleum-wastewater treatment lagoon. These enrichment cultures are being maintained and will be evaluated for microbial growth and for the ability of the induced microbial community to further degrade organic compounds of spent retort water.

TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

Steam Stripping Studies

Two more pressure tests of the steam stripper were run and testing was begun on the steam generation system. As reported in the October monthly report, the city water system was used to pressurize the steam stripper for two hours. The continual pressure fluctuations of the city water system seemed to be a good simulation of stresses that may be encountered during actual operation. Both pressure tests were succcessful and no leaks were detected at a maximum pressure of 80 psi.

The raw wastewater preheater was filled with distilled water and pressure-tested. The first test revealed a small leak around one of the plugs in the bottom of the reactor. The safety pressure-relief valve was also tested; the valve met specifications by opening when the pressure reached 75 psi. No leaks were found after repair of the preheater. The unit was pressurized overnight and no substantial leaks developed.

The wiring of the control panel was completed. We began to test the steam generation system and to check the digital temperature readout probes (RTD). The steam generator required two hours to reach operating temperature. The flash evaporation system and steam drier both appeared to be

in good operating condition, but the tests could not by completed because of inaccurate RTD readouts. We have contacted the manufacturer for instructions on recalibration of the RTD's.

TASK 4. INTEGRATION OF TREATMENT UNITS

Ozone/UV Pretreatment Combined with Biooxidation

We have hypothesized that the apparent inability of ozonation and UV irradiation to alter the biorefractory organic compounds in spent retort water may have resulted from the rapid consumption of ozone by the excessive ammonia concentrations of retort water. In a third ozonation/UV irradiation experiment, ammonia-stripped spent retort water, from which microbial cells had been removed, was sequentially exposed to ozonation (60 min), ozonation in conjunction with UV radiation (30 min), and UV radiation alone (60 min). Ozone was metered to one liter of sample at 226 mg/L/h, and a 450W medium pressure mercury-vapor quartz lamp was the UV source. Time-course samples were diluted (1 in 2), inoculated with a microbial culture acclimated for growth on raw Oxy-6 retort water, and incubated for 72 hours. Dissolved organic carbon concentrations for each step are presented in Table I.

The results indicated that the removal of ammonia may have allowed for the alteration of recalcitrant solutes in spent Oxy-6 retort water by ozone and UV radiation. Approximately 244 mg DOC per L of raw retort water were made available for further microbial mineralization by ozonation/UV irradiation. Each of these samples was reinoculated with a retort-water acclimated microbial culture dervied from a petroleum wastewater treatment lagoon. This microbial culture was able to mineralize a larger portion of carbon that had been ozonated, but the overall DOC removal was not significantly improved (Fig. 1). The additive effect of this biological-physicochemical-biological sequence of treatments was an overall DOC removal of 56 per cent; this compared unfavorably with sorbent/biooxidation experiments in which we have shown that spent shale in combination with biological treatment removed up to 80 per cent of the organic carbon.

TASK 5. RETORT ABANDONMENT FINAL REPORT

Dewatering calculations were completed for a 60-year operation scenario at Tract C-b. New field permeability data for tract C-b have been received from Occidental Oil Shale, Inc. We will enter these in the model to see if they change the results substantially. The conditions reached by the

60-year operation will be used as the initial conditions for various re-invasion scenarios. For the base case of no control technology, retort permeability will be taken as 10,000 times greater than the undisturbed Mahogany zone. Permeabilities based upon experimental data will be used for grouted retorts. Curtain grouting around a block of retorts will be simulated by reducing the connected area of adjacent nodes on either side of the proposed curtain; this has the effect of reducing the horizontal permeability through the curtain by the same factor as the area reduction. We are now reviewing the literature to determine what a realistic factor of reduction would be.

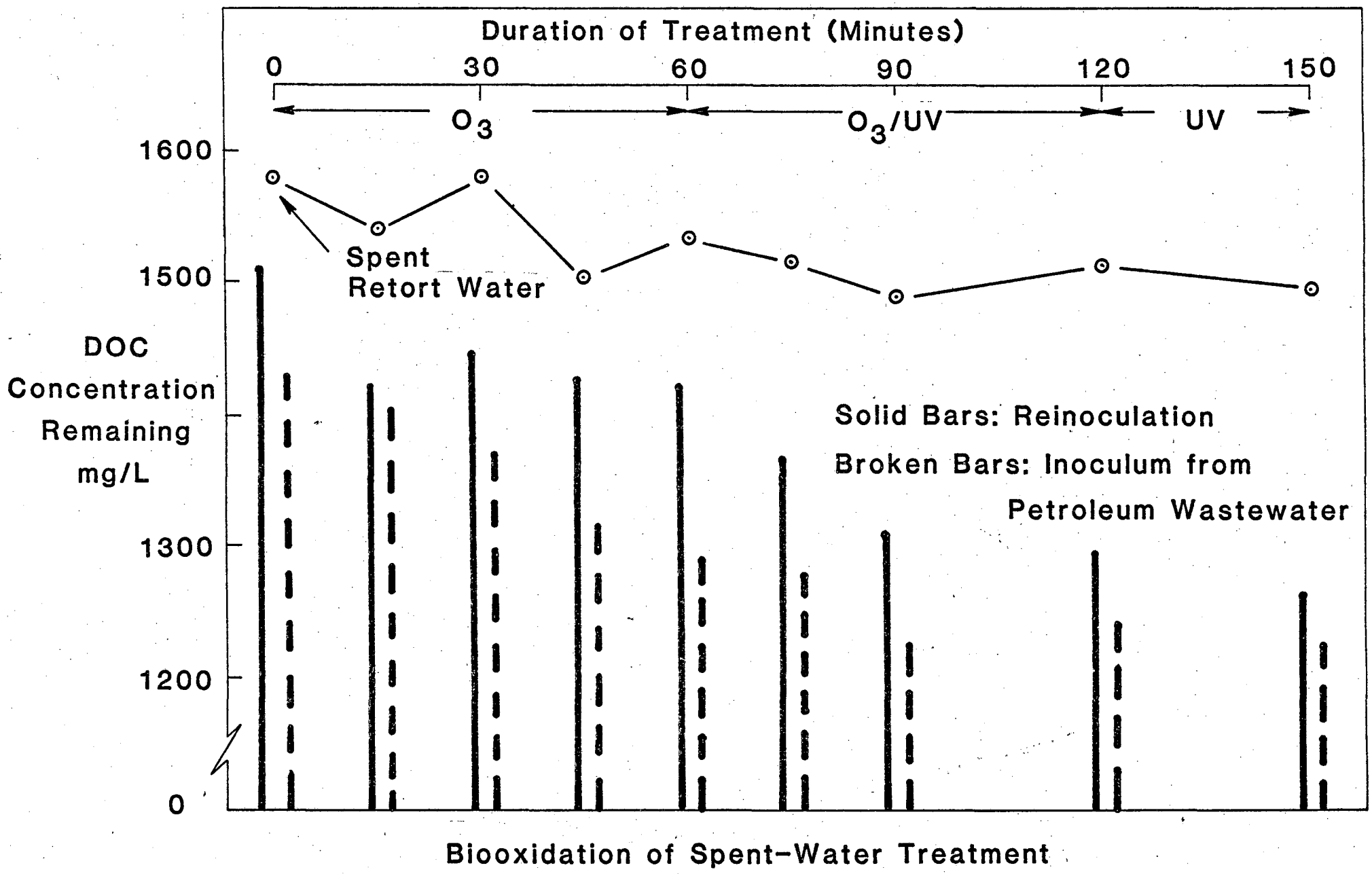
Miscellaneous

The Lawrence Berkeley Laboratory will be officially closed from December 17, 1981 to January 3, 1982. All personnel are required to take leave during this period. Only necessary maintenance-oriented work will be performed.

Table I. Organic Carbon Removal from Oxy-6 Retort Water by Ozone/UV Combined with Biological Treatment

sequential step #	treatment	mg carbon remaining per unit volume of raw retort water	cumulative % removed per unit volume of raw retort water
0	none (raw retort water)	2808	-
1	biooxidation	1581	44
NA	biooxidation (reinoculated control)	(1512)	(46)
2	ozone (60 minutes)	1534	45
3	ozone/UV (30 minutes)	1487	47
4	UV (60 minutes)	1494	47
5	biooxidation (after step 4)	1268	55
6	biooxidation (reinoculation of step 5 with petroleum waste)	1226	56

Figure1: Biologically Spent Oxy-6 Retort Water Treated by O_3/UV Followed by Re-oxidation with Two Inocula Types



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