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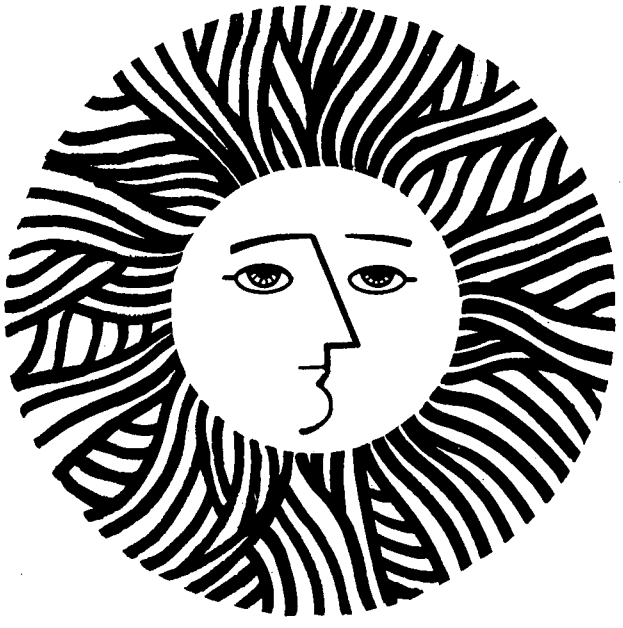

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4 February 1982

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RE: Monthly Progress Report for January

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TASK 1. ANALYTICAL METHODOLOGY

Sulfide Determination

Preliminary experiments with an Orion solid-state sulfide electrode have indicated that it may be suitable for determination of sulfide ion in process waters. The sulfide concentration of a wastewater sample from a LLNL simulated retort was determined from the inflection point of the mV/titrant response curve derived while titrating with lead perchlorate. This analytical procedure yielded a sulfide concentration of 6.7 mM (rsd = 5.5%, n = 5).

TASK 2. BIOLOGICAL TREATMENT OF PROCESS WATERS

Enrichment Studies

Enrichment studies were begun to select for a microorganisms that are enzymatically competent to degrade the refractory organic solutes in Oxy-6 retort water. We have postulated that this recalcitrant material is

predominantly nitrogen heterocycles. As described previously (June 1981), easily available inorganic nitrogen, such as ammonia, may repress the enzymes capable of degrading the nitrogen heterocycles. Reducing the ammonia concentration may permit derepression of nitrogen abstraction enzyme systems and possible degradation of the heterocyclic rings. Each enrichment culture was supplemented with 0.81 mM magnesium and 0.01 mM iron. Five sources of inocula were used: (1) oil refinery waste lagoon water, (2) activated sludge from the City of Richmond municipal wastewater treatment plant, (3) soil from an area of eroding asphalt, (4) a mixture of pooled inocula from all three sources, and (5) original Oxy-6 microbial culture enriched on raw retort water. Retort water was supplied as the sole source of carbon and nitrogen, as the sole source of carbon with a 2.5 mM nitrogen addition $(NH_4)_2SO_4$, and as the sole source of nitrogen with a 62.5 mM carbon supplement (sodium acetate/disodium succinate).

In the first set of experimental flasks, the ammonia was stripped (< 50 mg/L ammonia remaining) from Oxy-6 retort water that had already undergone extensive biological oxidation (spent retort water). Fifteen enrichment cultures were established; five sources of inocula were exposed to the three nutrient conditions.

The second set of experimental cultures contained refractory organic solutes from spent water sorbed to either C-18 chromatographic stationary phase or powdered activated carbon (ICI, Type HDC). These sorbents were then suspended in a buffered solution containing the same supplemental nutrients as above; the sorbed organic solutes served as the sole carbon source for the pooled inocula. The resulting microbial culture was transferred into homologous spent retort water media for quantitation of DOC removal. As outlined in the patent application (enclosed June 1981), concentrating the biorefractory organic solutes on a solid sorbent may raise the effective concentration of these compounds above the requisite enzyme affinity values.

A third set of flasks used the pooled inocula and the following untreated oil shale process waters as sole nitrogen and carbon sources: Oxy-6 retort water, Oxy-6 gas condensate, 150-ton (from LETC's 150-ton retort, run 13), T.V., S-55, Omega-9, and Geokinetics.

The second, third, and seventh transfers of these cultures into fresh homologous media were monitored for DOC reduction over 96 hours. The results for the Oxy-6 spent retort water cultures (experimental culture sets 1 & 2) are presented in Table I.

The DOC reductions in the other raw wastewaters are expressed as the percentage of DOC removed from 50% raw wastewater (Table II).

From the first set of cultures, the bacteria exposed to the sole carbon and nitrogen and sole carbon treatments of spent media were capable of removing equivalent cumulative amounts of DOC from raw retort water (54-56% and 52-55%, respectively). Cultures in the sole nitrogen treatments appeared to be capable of utilizing only the supplemental carbon, suggesting that nitrogen may have been the limiting nutrient in these cultures. The bacterial cultures derived from activated sludge mineralized a larger portion of the recalcitrant solutes in spent media than either the refinery lagoon or soil inoculum, as indicated by DOC reduction. The DOC removals from the cultures derived from the pooled inocula were similar to those of the activated sludge inoculum; this indicated that the three sources were each removing the same fraction of organic compounds from spent media. In addition, the original Oxy-6 retort water culture failed to extensively mineralize the solutes in the spent retort water, regardless of the nutrient conditions. The total reduction of DOC (49-51%) was less than those achieved with the new inocula. The microbial cultures enriched on solutes sorbed to C-18 and PAC (2nd experimental set) exhibited DOC removals from spent medium similar to those of the other inocula.

Without extensive controls, the reduction in DOC from the other inoculated process waters could not be attributed solely to biodegradation; other routes of DOC reduction include biosorption and volatilization. Of all the retort waters inoculated with the pooled inocula, 150-ton appeared to be the most difficult to treat, exhibiting only an 11% decrease in DOC (176 mg/L). A slight reduction in Oxy-6 gas condensate was achieved (33%, or 120 mg/L), although we have observed similar removals for gas condensate through volatilization. The pooled inocula removed 49% of the DOC from raw Oxy-6 retort water, this was equivalent to the removals obtained with our existing primary Oxy-6 culture. We will continue to search for inocula sources and continue to pursue the strategy of selective enrichment.

TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

Steam Stripper

Several test runs of the steam generation system were performed. The maximum rate of steam generation was approximately 18 lbs. per hour. Several problems were encountered during operation. The heating element in the steam

drier failed. The cause of this failure was probably because the element was designed for submerged applications. A replacement element which is compatible with operation in a wet steam atmosphere will be required. It is uncertain whether other problems that have been encountered were attributable to the inoperable steam drier.

Excessive condensation in the bottoms collector (2 to 3 times the volume of condensate in the overheads) was observed. Various approaches to this problem are being considered. Heat losses from the bottoms collector and from the lower part of the reactor may be involved. Heating and insulation of these parts may alleviate this problem. Entrapment of air (noncondensable gas) is a possible cause of inadequate overheads condensation. Filling the overheads condenser with water and draining it during startup is a possible way of creating a vacuum and excluding air from the system; this would improve the flow of steam into the condenser. An attempt to improve operation by evacuating the whole system prior to operation was unsuccessful.

Steady-state proved difficult to obtain during the first runs. After a certain volume of water was collected in the bottoms, the temperature of the system fell rapidly. Cautious periodic draining of the bottoms were required to avoid depressurizing and cooling the system.

During the heavy rains of January, the pilot plant area at SEEHRL was flooded. Flood waters of 1.5 feet damaged the recirculation pump on the flash evaporation system. Several other motors were flooded, and five days were spent dismantling, drying, and testing them.

TASK 5. RETORT ABANDONMENT FINAL REPORT

Numerical Modeling of Groundwater Flow Regimes

We are repeating the dewatering calculations which were done last year by Mohsen et al., in order to establish the initial conditions for re-invasion of groundwater. In these calculations we have adjusted the input data to reflect better data that have become available in the past year. In the original work, all materials were modeled as isotropic media for long-term simulations. It now appears that modeling them as anisotropic media (a more realistic assumption) reduces the effect on drawdown under nearby surface streams during the life of the project, compared to the earlier results.

We have discovered that, for anisotropic media, the model TRUST gives erroneous results in the initial 10-day portion of the problem. Errors are due to over-estimating the vertical conductivity. This has only a minor

effect on the long term simulations, but we are now working to identify and rectify this apparent bug in the program.

Effect of Fluidizer on Grout Permeability

The second series of grouts that were tested (arbitrarily designated series R) contained only spent shale, 0 or 10 per cent fly ash, and 0.25 per cent of either of two lignosulfonate fluidizers, CZ-503 or -512. Examination of the cured grouts by scanning electron microscopy has not revealed the mechanism of increased strength or reduced permeability associated with the use of fluidizer CZ-503 compared to CZ-512 (strength and permeability data were presented in the monthly report for July, 1981). Inquiry to the maufacturer, Crown-Zellerbach, revealed that the difference between these two products is that 512 has been desugared and 503 has not. Removal of the sugars makes 512 a more effective fluidizer simply because some inert ingredients (i.e. sugars) have been removed. While this does not cause of low permeability, this information will help pre-select the best candidates for screening lignosulfonate fluidizers for spent shale grouts.

Report Preparation

Preparation of the final reports on grout development for retort abandonment and on alternative strategies for retort abandonment is now in progress. This month we drafted sections detailing the experimental methods.

ADMINISTRATION

Preparation of the annual reports for the Energy and Environment Division at Lawrence Berkeley Laboratory has begun.

Table I. Removal of Oxy-6 Retort Water Solutes by Bacterial Enrichment Cultures

Source of Inoculum -nutrient conditions	% DOC Removed: Transfers[1] 2	3	7	mean[2]	cumulative removals from raw retort water[3]
Primary Removal					
Original Oxy-6 Culture	49	48	45	47	47
Secondary Removal					
Refinery Waste					
-C&N[4]	12	11	15	13	54
-C[5]	12	15	11	13	55
-N[6]	5	9	8	7	51
Activated Sludge					
-C&N	17	14	13	15	55
-C	17	16	15	16	56
-N	0	0	2	1	48
Soil					
-C&N	12	11	8	10	52
-C	12	13	13	13	54
-N	0	0	5	2	49
Pooled					
-C&N	NA[7]	17	16	17	56
-C	NA	19	12	16	56
-N	NA	0	5	3	50
Original Oxy-6 Culture					
-C&N	NA	NA	8	8	49
-C	NA	NA	13	13	51
-N	NA	NA	0	0	47
Pooled (C-18)[8]					
-C&N	NA	9	12	11	51
-C	NA	14	18	16	54
-N	NA	6	9	8	50
Pooled (PAC)[9]					
-C&N	NA	16	12	14	53
-C	NA	15	13	14	54
-N	NA	10	4	7	50

1 number of culture transfers (passages)
2 mean DOC removal from three sets of data
3 total percentage removal from primary and secondary treatments compared with raw retort water
4 spent retort water served as sole carbon and nitrogen sources
5 spent retort water served as sole carbon source
6 spent retort water served as sole nitrogen source; DOC of supplemental carbon subtracted from total DOC removed
7 not analyzed
8 microbial inoculum from pooled sources, enriched on solutes sorbed to C-18 packing material
9 microbial inoculum from pooled sources, enriched on solutes sorbed to PAC

Table II. DOC Removed from Oil Shale Process Waters by Bacteria Enriched on Spent Oxy-6 Retort Water[1]

Process Water	% DOC Removed	DOC Removed (mg/L)
Oxy-6 retort water	49	702
Oxy-6 gas condensate	33	117
150-ton	11	176
T.V.	18	250
S-55	36	406
Omega-9	32	132
Geokinetics	30	247

1 pooled inocula sources from refinery waste lagoon, activated sludge, and soil

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