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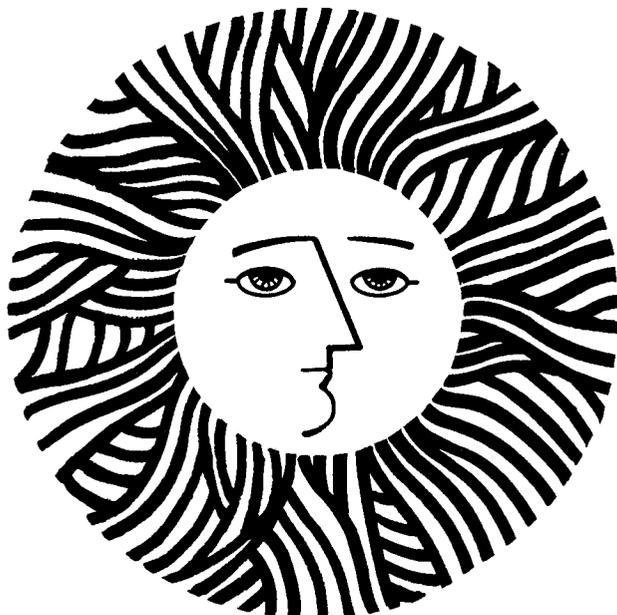
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8 October 1982

TO: Art Hartstein

FROM: Peter Persoff, Richard H. Sakaji, and Jerome F. Thomas

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RE: Monthly Progress Report for September
Oil Shale Waste Treatment: Fundamental Approaches
LBID-630

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TASK 1. ANALYTICAL METHODOLOGY

Ammonia Nitrogen Determinations

Two methods for determination of ammonia-N were compared: distillation-titration and phenate colorimetric (Weatherburn's method). The two methods are described in detail in "Quantitation of Ammonia in Oil Shale Process Wastewaters", J. Cantor, B.M. Jones, R.H. Sakaji, and C.G. Daughton (LBID-465). Nine process wastewaters and a composite wastewater were analyzed by each method. Ten replicates of each sample were analyzed by the phenate method and, because of equipment limitations, five by the titrimetric method.

The results of the analyses are shown in Table I. No significant difference was found between filtered and unfiltered waters analyzed by the phenate method. The comparison study, therefore, was conducted using unfiltered waters. The phenate method appeared to be more precise, with relative standard deviations (rsd's) of 1.5 percent or less for unfiltered samples, while the titrimetric method gave rsd's of 4.7 percent or less. The

two methods generally agreed within 8 percent, except for two samples (150-Ton and TV), which were the only samples for which the phenate method gave lower values.

Carbon Analysis

Sample handling problems were encountered in the determination of dissolved organic carbon (DOC) in steam stripper overheads samples. The large concentrations of inorganic carbon in the samples caused foaming and bumping during acidification, which is required to liberate inorganic carbon as CO₂ gas; the total carbon that remains after sparging is an estimate (direct) of DOC. To avoid this difficulty in future analyses, total dissolved carbon (TDC) and dissolved inorganic carbon (DIC) will be measured directly and DOC determined by difference, as described in "Coulometric Quantitation of Carbon in Oil Shale Process Wastewaters via UV-Persulfate or High-Temperature Oxidation", by G.W. Langlois, B.M. Jones, R.H. Sakaji, and C.G. Daughton (LBID-561; 1982).

A sample of the material that crystallized in the overheads condenser sight glass during the steam stripper run was dried, weighed, and dissolved in ASTM Type 1 water. The solution was analyzed for ammonia, DOC, and DIC. It was found to contain by weight 0.3 percent organic carbon (considered negligible), 14.5 percent inorganic carbon, and 17.7 percent ammonia nitrogen. This strongly suggests ammonium bicarbonate, which contains 15.19 percent carbon and 17.72 percent nitrogen by weight. IR spectroscopy of the solid in a KBr pellet was inconclusive.

Sulfide Determination

Sulfide determinations on samples used for the steam stripper run showed that sulfide was absent from the feed water. This corroborates the finding of Wallace et al. (14th Oil Shale Symposium Proceedings, 1981) that sulfide in process wastewaters is not stable in storage.

TASK 2. BIOLOGICAL TREATMENT OF PROCESS WATERS

Biodegradation/Volatilization Studies

Nine oil shale process wastewaters and a composite water were subjected to biooxidation in shake-flask cultures. The wastewaters were Oxy-6 gas condensate, Rio Blanco Sour water, and Oxy-6, 150-Ton, TV, S-55, Omega-9, Geokinetics, and Paraho retort waters; a composite water contained equal

volumes of these nine process waters. Each wastewater was diluted with an equal volume of a phosphate buffer (pH 7.2) that contained magnesium and ferrous ions. Each medium (40 mL) received 0.1 mL of inoculum from a culture that had been acclimated either on the homologous wastewater or on the composite water for six weeks before the start of the experiment; these acclimated enrichment cultures were passed at one-week intervals. Biological treatment was done in screw-capped Erlenmeyer flasks to minimize anticipated losses of DOC by volatilization; to ensure aerobic conditions, the flasks were opened for 5 minutes every 48 hours. Control treatments for each water included HgCl_2 to inhibit biological growth; these were used to estimate losses of DOC into the static head space. In addition, a parallel experiment was run where each water was inhibited with HgCl_2 but not sealed; a cotton wool plug was used to allow more extensive volatilization of compounds to the atmosphere while minimizing evaporation of water. After 120 hours in a water-bath shaker at 30 °C, the waters were filtered (0.45- μm pore diameter polycarbonate membrane) and the hydrophilic (HpF) and lipophilic (LpF) DOC were measured on the filtrates. Results of the analyses were compared with time zero values (Table II) after correction for dilution (i.e., normalized to values for raw undiluted waters).

For the inhibited controls, all losses of DOC were assumed to result from volatilization. DOC losses from the media in capped Erlenmeyers ranged from nil to 274 mg/L. These differences probably result from the various compositions of the waters. The DOC loss from each of the parallel uncapped (cotton-plugged) Erlenmeyers was greater.

The amount of DOC that was biodegraded was calculated as the total loss of DOC during the experiment minus that lost by volatilization in the capped Erlenmeyer; it therefore represents a lower estimate of the removal by biodegradation (i.e., some of the compounds that volatilized from the inhibited controls may have been biooxidized in the noninhibited treatments).

Biooxidation was greater for each water when the inoculum had been acclimated on the homologous water. The highest absolute removals of DOC by biooxidation occurred in the composite water (1392 mg-C/L) and in Oxy-6 retort water (1384 mg-C/L); the percentage of total DOC removed by the Oxy-6 retort water culture (49 percent) was equivalent to that usually obtained for this water. The percentage removals of DOC were lowest for Oxy-6 gas condensate (8.9%), TV (2.6%), and Paraho retort (nil) waters. Oxy-6 gas condensate also contained the lowest percent concentration of HpF-DOC (15.9%). The extraordinarily high concentrations of DOC and ammonia may have been

responsible for the low DOC removals from Paraho retort water. This is supported by the results for the composite water where DOC removal (1392 mg/L) was not only greater than the average for the nine waters (440 mg/L), but greater than that for any other water; apparently, dilution of the Paraho DOC in the composite water allowed for more biooxidation. The loss of DOC from the composite water by volatilization was 84 and 298 mg/L from the capped and uncapped flasks, respectively. These compare well with the average losses from the nine waters: 87 and 277 mg/L, respectively. Likewise, the initial total- and HpF-DOC values for the composite water compared with the averages of the nine waters: 6046 and 4184 mg/L versus 6397 and 4998 mg/L, respectively.

The amount of DOC biooxidized was closely correlated with the quantity of HpF-DOC removed (Fig. 1), supporting the hypothesis that compounds in this fraction are more easily biodegraded than the compounds of the lipophilic fraction. The amount of DOC biooxidized was greater than the quantity of DOC in HpF for Rio Blanco and Geokinetics waters, although a portion of the HpF remained after biological treatment; this suggested that a small portion of the LpF may be more easily degraded than the remaining HpF. In addition, the remaining HpF may have been newly derived from incomplete biooxidation of compounds that were previously in the LpF. Only Paraho retort water did not fit this correlation. Since Paraho had the highest percentage of DOC residing in the HpF (90.5%), it should be the most amenable to biotreatment.

The degree of biooxidation achieved by these initial enrichment cultures was promising for several process waters. The enrichment process will be repeated on more dilute media for process waters exhibiting insignificant biological removals of DOC; for example, Paraho retort water should exhibit significant reductions in DOC when its ammonia concentration (24,338 mg-N/L) is reduced to non-toxic levels. We anticipate that the percentage of DOC in HpF will eventually be a useful predictor of biotreatability.

TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

Steam Stripping

The steam stripper was run using a composite of retort waters from several runs of Lawrence Livermore Laboratory's small simulated in-situ retort. With a low steam-to-feed ratio of approximately 1:10, the volumes of overheads and bottoms collected after a 30-minute run were 0.75 and 10.27 L, respectively. The calculated feed volume (10.8 L) was in slight excess of the

volume collected in the bottoms. Calculated mass balances indicated recoveries for ammonia, DOC, and DIC of 106, 106, and 66 percent, respectively. Removals, calculated as percent of mass removed from feed, of ammonia, DOC, and DIC were 41, 17, and 85 percent, respectively.

The headspace in the overheads condenser contains a significant volume of noncondensed steam. At low steam flows this can represent a large mass of steam that is not accounted for during the collection of the condensed overheads immediately after a run. This loss artificially decreases the steam flow rate and prevents an accurate accounting of the flow streams into and out of the packed bed. Precipitation of a crystalline material (believed to be ammonium bicarbonate) in the sight glass of the overheads condenser also introduced error into the mass balance calculations (see Carbon Analysis in this report). Although ammonia was apparently sequestered in the sight glass as ammonium bicarbonate, recovery of 106 percent was calculated without considering this material. This may have partly resulted from accumulation of ammonia in the condenser headspace during the 12-minute interval between introduction of the feed water and the draining of the collection vessels, which marks the start of the run. Design modifications to reduce these problems are being considered.

TASK 5. RETORT ABANDONMENT FINAL REPORT

The final version of the report which includes all review comments received is in preparation.

Miscellaneous

P. Persoff attended the Fourth Briefing on Oil Shale Technology at Lawrence Livermore National Laboratory, Sept. 22-23.

Samples of Oxy-6 retort water that were treated by UV-ozonation as reported at the Fifteenth Oil Shale Symposium have been supplied to M. Conditt, University of Colorado, Boulder.

Table I. Comparison of Colorimetric and Titrimetric Ammonia Methods

Process Water	Titrimetric ¹ (unfiltered)		Colorimetric ¹ (filtered)		Colorimetric ¹ (unfiltered)		Colorimetric: Titrimetric	unfiltered: filtered
	mean	rsd (%) ²	mean	rsd (%) ³	mean	rsd (%) ³	(% diff) ⁴	(% diff) ⁵
Paraho	24,338	1.8	23,750	0.7	24,655	0.7	1.3	3.7
150-ton	11,925	4.7	11,180	1.1	10,516	1.1	-13.4	-6.3
Oxy-6 GC	6,709	1.1	6,933	1.0	6,994	0.7	4.1	0.9
Composite	6,079	1.5	-----	---	6,276	0.8	3.1	na
S-55	4,006	1.8	4,005	2.0	4,188	1.5	4.4	4.4
Omega-9	3,365	0.9	3,551	4.9	3,638	1.4	7.5	2.4
TV	2,324	1.6	2,346	6.9	2,097 ⁶	1.4	-10.8	-11.9
Geokinetics	1,503	3.2	1,505	1.8	1,589	0.6	5.4	5.3
Oxy-6 RW	1,022	4.5	1,136	0.9	1,117	0.9	8.5	-1.7
Rio Blanco Sour	969	4.6	1,032	1.1	1,061	1.1	8.7	2.7
mean ⁷	<u>6,240</u>				<u>6,206</u>			

¹ mg/L NH₃-N

² n=5 for each sample

³ n=10 for each sample

⁴ [(colorimetric unfiltered mean) - (titrimetric mean)]/(colorimetric unfiltered mean)

⁵ [(colorimetric unfiltered mean) - (colorimetric filtered mean)]/(colorimetric unfiltered mean)

⁶ analysis by second operator

⁷ mean for nine waters, excluding composite

Table II. Removal of Total- and HpF-DOC (mg/L) from Oil Shale Process Wastewaters by Biodegradation and Volatilization

process water	initial DOC			DOC biodegraded ¹				volatilized ²	
	total	HpF	(%) ³	total	(%) ⁴	HpF	(%) ⁵	capped	uncapped
Composite	6046	4184	69.2	1392	23.0	1542	36.9	84	298
Oxy-6 RW	2800	1583	56.5	1384	49.4	1162	73.4	0	130
150-Ton	3434	1429	41.6	902	26.3	614	43.0	0	180
S-55	2364	1048	44.3	728	30.8	516	49.2	222	524
Geokinetics	1692	542	32.0	566	33.5	254	46.9	0	222
Omega-9	870	346	39.8	167	19.2	123	35.5	65	126
TV	2986	1411	47.2	76	2.6	220	15.6	126	514
Rio Blanco	212	62	29.2	74	34.9	20	32.3	22	68
Oxy-6 GC	752	120	15.9	67	8.9	25	20.8	72	158
Paraho	42460	38440	90.5	nil	nil	365	90.9	274	570

¹ culture volumes of 40 mL in 250-mL screw-cap Pyrex Erlenmeyer flasks; values corrected for volatilization from capped controls

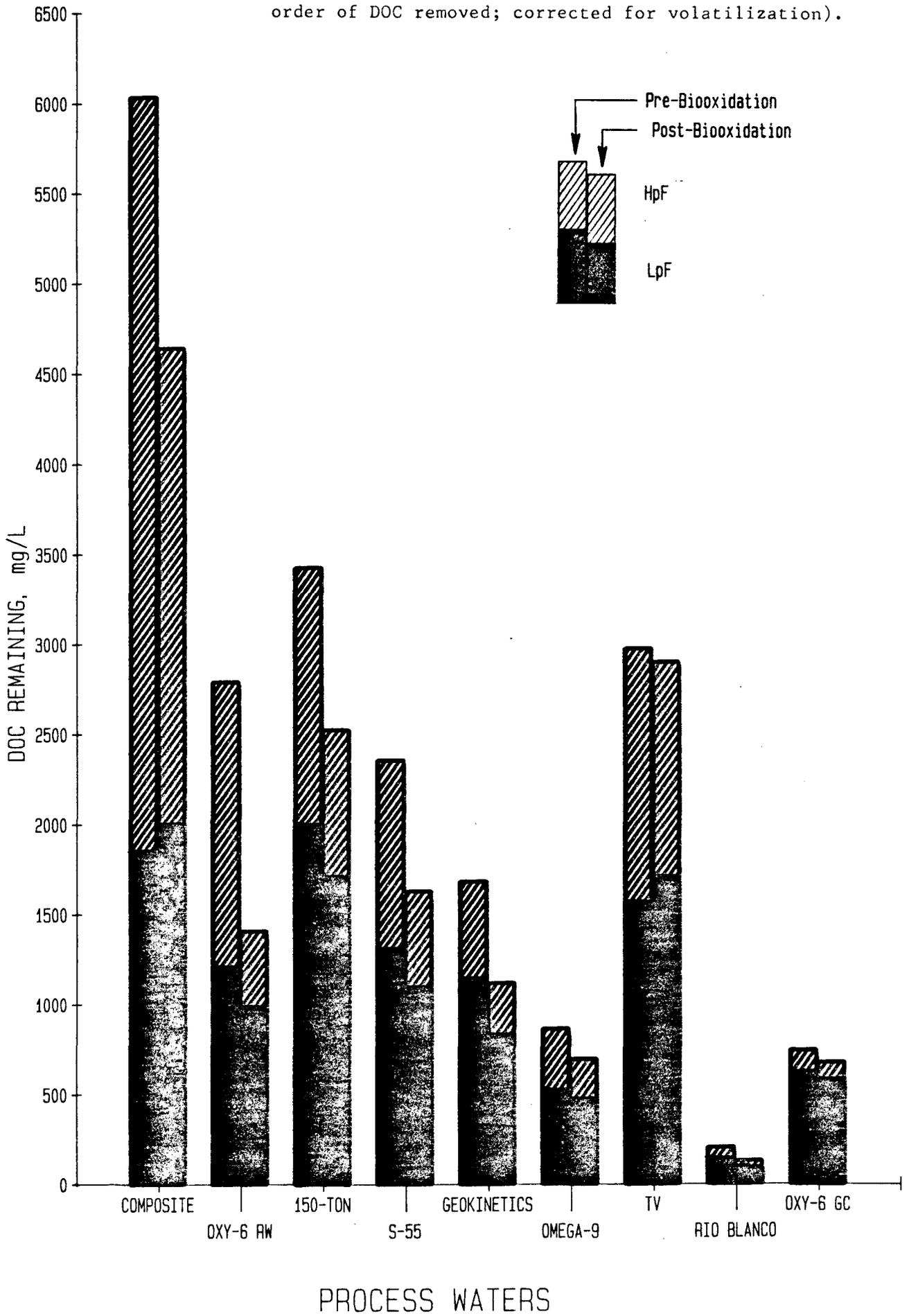
² HgCl₂-inhibited cultures; head-space in capped Erlenmeyers (controls) was 235 cm³; uncapped samples used cotton wool plugs to allow headspace exchange while minimizing water evaporation

³ HpF as percentage of initial total DOC

⁴ percentage of initial total DOC biodegraded

⁵ percentage of initial HpF that was biodegraded

Figure 1. Biooxidation of Oil Shale Process Waters Diluted 50 Percent (Values normalized to undiluted waters; ranked in decreasing order of DOC removed; corrected for volatilization).



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