

LBID-432
UC 91



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

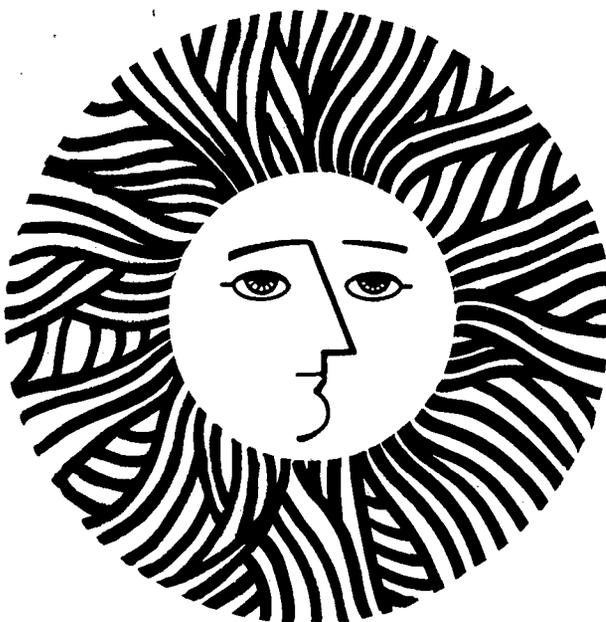
RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 26 1981

LIBRARY AND
DOCUMENTS SECTION

For Reference

Not to be taken from this room



LBID-432
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

July 31, 1981

TO: Charles Grua

FROM: Richard H. Sakaji, Bonnie M. Jones, and Jerome F. Thomas;
Christian G. Daughton (SEEHRL)

RE: Monthly Progress Report for July
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-432

ANNOUNCEMENTS

Professor Jerome F. Thomas, Chairman of the Department of Sanitary Engineering, U.C. Berkeley, has been appointed Principal Investigator of the Oil Shale Wastewater Treatability Project.

To more accurately reflect the nature of SERL'S research, the name change to the Sanitary Engineering and Environmental Health Research Laboratory (SEEHRL) has been recently approved.

TASK 1. ANALYTICAL METHODS DEVELOPMENT

Protocol Development

We have developed and modified several protocols to provide continuity and to standardize the application of analytical methods to oil shale process waters. These protocols include:

1. Jones, B.M.; Sakaji, R.H.; Daughton, C.G.
"Standardized Titrimetric COD Protocol", LBL Oil Shale Wastewater Treatability Project, 12 January 1981.
2. Yu, K.; Jones, B.M.; Sakaji, R.H.; Daughton, C.G.
"Protein Assay Protocol", LBL-SERL Oil Shale Wastewater Treatability Project, 24 April 1981.
3. Cantor, J.; Jones, B.M.; Sakaji, R.H.; Daughton, C.G.
"Distillation Titration Ammonia Protocol", LBL-SEEHRL Oil Shale Wastewater Treatability Project, 27 July 1981.

We will use the documentation of these laboratory procedures to aid in the preparation of publication of these methods. Copies of these protocols are enclosed with this month's report.

TASK 4. SPENT AND RAW SHALE STUDIES

Batch Isotherm Studies

We conducted a batch equilibrium experiment (#8) using fractionated Oxy-6 retort water and TOSCO II spent shale. The polar and nonpolar organic solutes were separated by reverse-phase partitioning and the retained fraction was eluted, the organic solvent was removed, and the solutes were redissolved in ASTM Type I water. A 48-hour sorptive equilibrium study was conducted using each solute fraction in combination with TOSCO II spent shale. This experiment was designed to elucidate whether spent shale preferentially sorbs polar or nonpolar organic compounds. The following results were obtained:

1. Of the dissolved organic carbon (DOC) in unfractionated Oxy-6 retort water, 43 per cent was nonpolar.
2. The organic solutes in the nonpolar fraction reached sorptive equilibrium with spent shale within 8 hours; approximately 49 per cent of the nonpolar DOC was sorbed by the spent shale at equilibrium. The amount of carbon removed from the nonpolar fraction was equivalent to the amount of carbon removed from raw Oxy-6 retort water by Tosco II spent shale in previous batch equilibrium experiments.
3. The sorption of polar organic solutes was minimal; only 3 to 4 per cent of the polar DOC was sorbed by spent shale after 8 hours. Another 4 per cent of the DOC was removed between 24 and 48 hours, but this may have been a result of data scatter.

These results indicate that Tosco II spent shale preferentially sorbs nonpolar organic compounds from Oxy-6 retort water and has a very low sorptive affinity for the easily biodegradable polar constituents. This is fortuitous because we have found from our biological treatment studies that the majority of the recalcitrant species resides in the nonpolar fraction. These findings verify our hypothesis that spent shale and biological oxidation are complementary processes for the treatment of oil shale retort water.

TASK 5. SYSTEM STUDIES

Biological Oxidation Studies

As documented in a previous monthly report (May 1981), we have determined that the major portion of the biodegradable material is contained in the polar fraction of Oxy-6 retort water. Since the results from the initial experiment were somewhat ambiguous, we repeated the experiment three times incorporating

better control of the reverse-phase fractionation and a nutrient supplement. The results from these experiments (Table I) confirmed the trends noted in the previous experiment:

1. The polar fraction contained two to three times the biodegradable organic carbon of the nonpolar fraction.
2. A portion of the retained organic material was easily degraded.

These results supported our hypothesis that microbial growth occurred exclusively at the expense of fatty acids in retort water. Since ionized short-chain fatty acids would be associated with the polar fraction and long-chain fatty acids with the nonpolar fraction, both fractions indeed should have supported microbial growth.

The reverse-phase fractionation of retort water would be expected to efficiently separate all inorganic nitrogen species from the nonpolar fraction. Microbial growth with the nonpolar solutes supplied as a sole carbon and energy source would rapidly become nitrogen limited if the cells were unable to use nitrogenous heterocycles as sole nitrogen sources. An exogenous nitrogen source could enhance the DOC removal if the N-heterocycles were not usable, or alternatively, it could suppress removal by repression of heterocycle-specific enzymes. In experiments II, III, and IV, therefore, portions of the nonpolar fraction were supplemented with nitrogen in the form of ammonia. In experiment II, the DOC removal was enhanced by a nitrogen supplement of 2.5 mM NH_4Cl (39% vs. 31%), but the results from the subsequent experiments were ambiguous.

The results from subsequent experiments also indicated that the fractionation procedure may have removed, via irreversible sorption, components that otherwise would have inhibited microbial growth in retort water. In experiments II and IV, the DOC removals from the recombined fractions and from the sum of the polar and nonpolar fractions were increased compared with the unfractionated control culture. In addition, the per cent reductions in DOC were not consistent in these three experiments. The absolute organic solute reduction from the recombined fractions in experiment IV (1029 mg/L) was the greatest we have observed for biotreatment alone.

Investigations of the mineralization of the organic solutes in the two fractions will continue in an effort to understand the limitation of microbial growth in retort water. We plan to use the retained solutes, which presumably include N-heterocycles, as substrates for the induction of nitrogen-abstracting enzymes in our N-heterocycle degradation experiments.

Combined Biological Oxidation/Spent Shale Treatment

We repeated the combined biological/sorbent treatment studies (batch experiment #4) using two dosages of each sorbent. Sorbent was added directly to a shake flask containing an inoculated sample of 50% Oxy-6 retort water. The sorbent additions consisted of low and high dosages of TOSCO II spent shale (100 mg/mL and 500 mg/mL) and I.C.I. powdered activated carbon (PAC) (1.3 mg/mL and 6.6 mg/mL). The results and conclusions from this investigation (Table II) include:

1. DOC removal was not enhanced for either dosage of PAC or for the low dosage of spent shale. The reduction of DOC could be accounted for by the summation of DOC removals from sorption and biooxidation in all three cases.
2. In contrast, the total reduction of DOC for the high dosage of spent shale was 74 per cent; this was 8% more DOC removal than could be accounted for by the addition of sorptive (16%) and biological (50%) DOC removals.

Although we observed a slight enhancement of DOC removal for the high dosage of spent shale to retort water, we did not observe the pronounced enhancement of DOC removal that was reported in earlier experiments. As mentioned previously (Monthly Report, June 1981), the nonreproducibility of enhanced DOC removal may be caused by variability of the microbial inoculum. We plan to continue investigating the interaction of spent shale and biooxidation.

Table I
Bacterial Removal of DOC from Oxy-6 Retort Water
Fractionated by Reverse-Phase Separation in Four Experiments

<u>Fraction¹</u>	<u>Dissolved Organic Carbon Concentration (mg/L)</u>							
	<u>I²</u>		<u>II³</u>		<u>III⁴</u>		<u>IV⁴</u>	
	<u>initial</u>	<u>Δ⁵</u>	<u>initial</u>	<u>Δ</u>	<u>initial</u>	<u>Δ</u>	<u>initial</u>	<u>Δ</u>
control (unfractionated)	1575 1.00 ⁶	865 55 ⁷	1496 1.00	656 44	1471 1.00	838 57	1432 1.00	817 61
polar	752 0.48	455 63	746 0.50	513 69	835 0.57	642 77	819 0.57	643 79
nonpolar	807 0.51	199 24	646 0.43	200 31	NR ⁸	NR	NR	NR
nonpolar + N ⁹	NR	NR	646 0.43	256 39	657 0.45	208 32	632 0.44	314 50
recombined polar + nonpolar	NR	NR	1408 0.94	777 55	1516 1.03	842 56	1427 1.00	1029 72

¹ each control and fraction of Oxy-6 retort water was diluted 50% prior to inoculation

² recycled reverse-phase cartridge was not rinsed before elution

³ recycled reverse-phase cartridge was rinsed with 2 mL ASTM Type I water; rinse discarded

⁴ new reverse-phase cartridge was rinsed with 2 mL ASTM Type I water; rinse pooled with polar fraction

⁵ DOC removed by biooxidation

⁶ portion of DOC in fraction compared with initial unfractionated DOC

⁷ % of DOC removed by biooxidation compared with initial DOC

⁸ experiment not run

⁹ supplemented with 2.5 mM ammonium chloride

Table II
Per Cent DOC Removal from 50% Oxy-6 Retort Water
by Combined Biological/Sorbent Treatment

% DOC Removal from Inoculated Retort Water

<u>sorbent</u>	<u>total</u>	<u>sorption</u>	<u>enhancement</u> ¹
none (control)	50 ² (737) ³	na ⁴	na
PAC ⁵			
1.3 mg/mL	63 (917)	11 (167)	1 (13)
6.6 mg/mL	85 (1238)	36 (527)	0
spent shale ⁶			
100 mg/mL	57 (832)	10 (151)	0
500 mg/mL	74 (1086)	16 (234)	8 (140)

¹ total % removal minus % removal from biooxidation (i.e., 50%) plus % removal from sorption

² per cent reduction from raw 50% Oxy-6 retort water (initial DOC = 1460 mg/L)

³ DOC (mg/L) removed

⁴ not applicable

⁵ powdered activated carbon (I.C.I.), 12-40 mesh

⁶ TOSCO II spent shale, 60-80 mesh

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.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720