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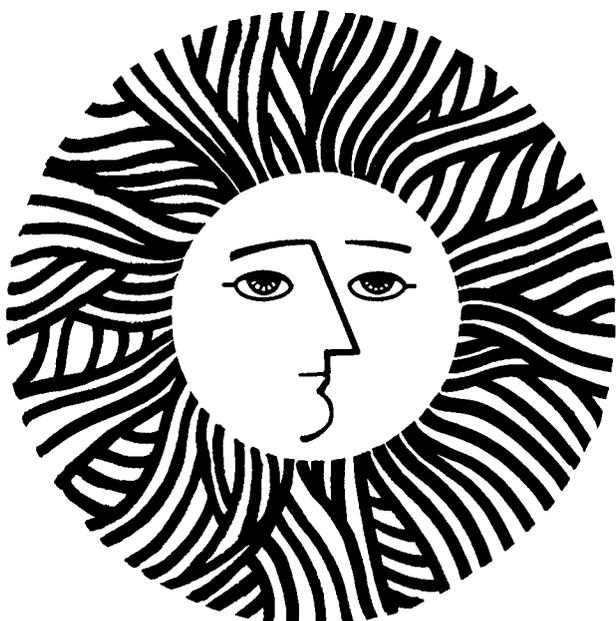
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2 August 1982

TO: Art Hartstein

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

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RE: Monthly Progress Report for July
Oil Shale Waste Treatment: Fundamental Approaches
LBID-591

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A review of our research was presented to Art Hartstein on 13 July 1982. The LBL-SEEHRL Oil Shale Project hosted representatives from Los Alamos National Laboratory, Battelle Pacific Northwest Laboratories, Laramie Energy Technology Center, University of Colorado, Colorado State University, and Lawrence Livermore National Laboratory for project reviews and the DOE-EV Solid Waste Management Workshop organized by Ralph Franklin on 14 July 1982.

TASK 1. ANALYTICAL METHODOLOGY

Organic Nitrogen Determination

The evaluation of the pyrochemiluminescent nitrogen analyzer (model 703C, Antek Instruments, Houston, TX) for the determination of inorganic and organic nitrogen species in oil shale retort water continued after the instrument was returned from the manufacturer following minor warranty repair. Preliminary results using pyrochemiluminescence for the detection of organic nitrogen compounds in Oxy-6 retort water yielded remarkable concordance when compared with results from wet chemical methods of determination.

We have postulated (May 1982 Monthly Report) that the majority of the organic nitrogen-bearing compounds reside in the lipophilic fraction (LpF) and that reverse-phase fractionation ("Rapid Fractionation of Oil Shale

Wastewaters by Reverse-Phase Separation", C.G. Daughton, B.M. Jones, and R.H. Sakaji, LBID-485; enclosure with February 1982 Monthly Report) may present a very easy and rapid means of separating organic from inorganic nitrogen species for purposes of quantitating these two classes. To investigate this hypothesis, Oxy-6 retort water was separated into LpF and HpF. The raw water and each fraction were distilled ("Quantitation of Ammonia in Oil Shale Process Wastewaters", J. Cantor, B.M. Jones, R.H. Sakaji, and C.G. Daughton, LBID-465; enclosure with December 1982 Monthly Report), digested following a variation of the Kjeldahl method (using selenized Hengar granules, No. 2 Kelpak, and 20 mL sulfuric acid), and redistilled. The two types of distillates were quantitated by both titration and pyrochemiluminescence. Total nitrogen content of raw Oxy-6 retort water and the two reverse-phase fractions were determined by pyrochemiluminescence. There appeared to be excellent agreement between the two methods of detection (Table I).

Ideally, the sum of distillable and organic nitrogen should equal total nitrogen. For the three samples analyzed by pyrochemiluminescence, the recovery of total nitrogen exceeded the sum of the fractions. This may have been the result of incomplete digestion of nitrogen-containing organic compounds by the modified Kjeldahl procedure compared with the combustion step utilized by the pyrochemiluminescent method. Offgassing of ammonia during the fractionation procedure for the HpF sample could contribute to the lack of mass balance for that sample. Loss of volatile, nontitratable nitrogen-bearing organic compounds during the distillation step could also account for the apparent incongruity.

For each of the five columns of data, the amount of nitrogen determined in the HpF and LpF should equal the nitrogen recovered from the unfractionated sample for each treatment. Except for total nitrogen determined by pyrochemiluminescence, the nitrogen in the unfractionated samples is greater than the sum of the nitrogen in the two fractions. Loss of ammonia during fractionation may account for this difference in the distillable nitrogen samples. Organic nitrogen compounds irreversibly retained by the packing material during fractionation could contribute to low recoveries from the organic nitrogen samples.

The HpF of Oxy-6 retort water appeared to contain the majority of the distillable nitrogen as determined by either method of detection. According to the wet chemical method of determination, the LpF was a poor indicator of organic nitrogen. Nitrogen determinations by pyrochemiluminescence, however, contradicted these results. Additional study is required to evaluate the

fractionation procedure as a facile means of separating the two classes of nitrogen in retort water.

TASK 2. BIOLOGICAL TREATMENT OF PROCESS WATERS

Municipal activated sludge, herbicide-exposed soil, and bacteria acclimated for growth on Oxy-6 retort water were used as sources of inocula in an attempt to develop acclimated microbial communities for each of nine oil shale process waters (Oxy-6 gas condensate, Rio Blanco sour water, and Oxy-6, T.V., 150-Ton, S-55, Omega-9, Geokinetics, and Paraho retort waters) and in a composite wastewater composed of equal volumes of each of these nine process waters.

Enrichment media were prepared by diluting 15 mL of each wastewater with 5.0 mL of phosphate buffer, 9.5 mL of ASTM Type I water, and 0.5 mL of a trace nutrient solution (0.72 mM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 99.7 mM $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Each enrichment culture will be transferred weekly to homologous medium and after three to four transfers, the cultures will be monitored for dissolved organic carbon (DOC) removal (after appropriate corrections for volatilization).

TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

Steam Stripper

There were several objectives to the initial testing program of the LBL-SEEHRL steam stripper. One of the primary objectives was to determine if the steam stripper could function as designed and constructed. The separation of o-nitrophenol and methylene blue, in last month's experiments, demonstrated that the steam stripper was functioning. The volatile o-nitrophenol was stripped from the influent wastewater while the nonvolatile methylene blue was not. The analytical results, however, indicated that there were still operational problems that must be addressed.

In an attempt to resolve the operational problems, we completed two test runs with a composite sample of process water that was blended from several wastewaters from LLNL's small retort. The composite sample contained large quantities of the components of interest, i.e., DOC, dissolved inorganic carbon (DIC), S^{2-} , and NH_3 . The results from these two runs were quite encouraging. Removals of dissolved gases, carbon dioxide (as DIC), NH_3 , and H_2S (as S^{2-}), were greater than 94%. There were discrepancies, however, in some of the mass balances. The total recoveries from both the overheads and bottoms were: NH_3 (97.0-99.6%), DOC (96.7-103.2%), DIC (72.0-81.2%), and S^{2-} (65.0%). The poor recoveries of CO_2 and H_2S were attributed to incomplete capture of the gases during condensation. The CO_2 and H_2S ,

being noncondensable, sparingly soluble gases, apparently were not as efficiently swept out and condensed with the steam as was the ammonia. The difficulties with attaining a mass balance around the steam stripper will be addressed in subsequent experimental runs.

During both experimental runs, a substantial portion (10 to 40 percent) of the wastewater feed was recovered in the overheads condenser. This may have resulted from an excessive temperature differential between the feed and the packed bed, which would cause evaporation of the wastewater with subsequent condensation in the overheads. Physical carryover of wastewater droplets from the influent stream into the overheads condenser by the gas stream may also account for these results.

Gas sampling equipment was assembled and connected to the top of the steam stripper bed to monitor steady-state operation. This will enable the quantitation of gases in the exit gas stream during operation with minimal disruption of the closed system.

Experimental runs of the steam stripper conducted to date used unrealistically high steam to liquid ratios. The reduction of this ratio to more commercially feasible values will be a priority of future work. To accomplish this reduction in ratio, the operating conditions of the steam stripper will have to be modified, or the design of the system may have to be slightly altered. These problems will be addressed in upcoming experimental work.

Work has begun on preparation of an operation manual for the steam stripper.

TASK 5. RETORT ABANDONMENT FINAL REPORT

A draft of "Control Technology for In-Situ Oil Shale Retorts" (LBL-14468) by P. Persoff and J.P. Fox has been distributed for peer review. The final version will be prepared and submitted to DOE after reviewer suggestions and comments are incorporated.

Table I. Comparison of Titrimetric vs. Pyrochemiluminescent Methods of Nitrogen Detection in Oxy-6 Retort Water

	<u>Distillable N¹(mM)</u>		<u>Organic N²(mM)</u>		<u>Total N (mM)</u>
	<u>I³</u>	<u>II⁴</u>	<u>I³</u>	<u>II⁴</u>	<u>II⁴</u>
unfractionated	75	75	12	15	96
HpF	69	70	4	0	87
LpF	1	0	5	6	9

¹distillation following procedure in LBID-465

²digestion by modified Kjeldahl method

³titrimetric determination (endpoint was pH 5.4)

⁴pyrochemiluminescent detection

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.

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