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## ENERGY & ENVIRONMENT DIVISION

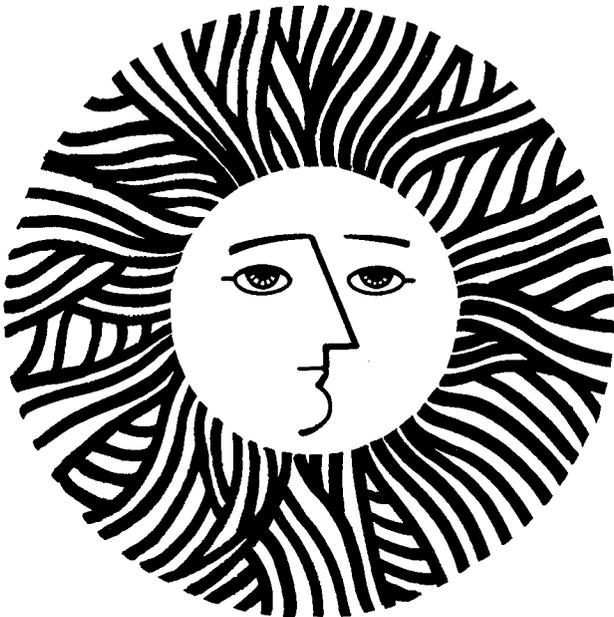
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4 June 1982

TO: Art Hartstein

FROM: Bonnie M. Jones, Peter Persoff, Richard H. Sakaji, and Jerome F. Thomas  
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RE: Monthly Progress Report for May  
Oil Shale Waste Treatment: Fundamental Approaches  
LBID-552

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#### MILESTONES

Enclosed under separate cover is the report entitled "Ozonation and UV Radiation: Effect on Oil Shale Wastewater Biorefractory Organic Solutes" (LBID-549) by B.M. Jones, G.W. Langlois, R.H. Sakaji, and C.G. Daughton.

#### TASK 1. ANALYTICAL METHODOLOGY

Wet chemical methods (i.e., Kjeldahl) for the accurate determination of organic nitrogen in concentrated wastewater samples are fraught with difficulties. The analysis is often tedious, time-consuming, and hazardous to perform; in addition, incomplete recovery from a range of organic nitrogen species limits the applicability of these methods. To circumvent these problems, we have begun to evaluate a pyrochemiluminescent nitrogen analyzer (model 703 C, Antek Instruments, Houston, TX) for the determination of organic nitrogen in oil shale process waters.

Nitrogen species in a nitrogen-free solvent are converted to nitric oxide (NO) by oxidative pyrolysis in a pure oxygen environment at approximately 1000 °C. The resultant NO is contacted with ozone and a metastable nitrogen

dioxide molecule is produced. The excited  $\text{NO}_2$  molecules relax to a stable state and emit photons, which are spectrophotometrically detected; the amplified output can be directly correlated to nitrogen concentration. Since this method of detection responds to most forms of nitrogen, we are developing a method for the rapid determination of organic nitrogen in the presence of high concentration of inorganic nitrogen. The reverse-phase fractionation procedure ("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) can be used to separate nearly all of the organic nitrogen species, which reside in the lipophilic fraction (LpF), from the inorganic nitrogen compounds (esp. ammonia). The LpF can be eluted with an organic solvent and can be injected directly into the nitrogen analyzer.

The response to pyridine standards (ranging from 1.2 mM to 123.0 mM) in ASTM Type I water was increasingly nonlinear for the more concentrated samples. We are investigating the problem of curvilinear response.

Preliminary analyses of nitrogen in Oxy-6 retort water yielded excellent results compared with the values obtained by the colorimetric phenate method for ammonia determination ("Quantitation of Ammonia in Oil Shale Process Wastewaters" by J. Cantor, B.M. Jones, R.H. Sakaji, and C.G. Daughton, LBID-465; enclosure with December 1981 Monthly Report) and by the Kjeldahl method. The nitrogen content of the hydrophilic fraction (HpF) of Oxy-6 retort water was essentially identical to the ammonia value obtained by the colorimetric phenate method (i.e., 77.2 mM vs. 78.6 mM). In addition, the organic nitrogen content of the LpF was similar to preliminary values obtained from Kjeldahl determinations on Oxy-6 retort water (8.4 mM vs. 12.9 mM). Nitrogen analyses will be a major emphasis of our planned work. Therefore, the validation of this instrument for use with oil shale retort waters and the development of a method for organic nitrogen will be a primary objective.

## TASK 2. BIOLOGICAL TREATMENT OF PROCESS WATERS

An experiment was designed to elucidate the specificities of bacterial enzymes for three related nitrogen heterocycles. Mixed bacterial communities acclimated to one of three methyl-substituted pyridines were added to solutions containing one of the other two methyl-substituted pyridines (e.g., 2-methylpyridine culture was the inoculum for 2,6-dimethylpyridine and for 2,4,6-trimethylpyridine). The UV-absorbance of each compound was followed and compared with the absorbance of control cultures to which  $\text{HgCl}_2$  was added.

It appeared that the enzymes responsible for altering the compounds and cleaving the heterocyclic rings of 2-methylpyridine and 2,6-dimethylpyridine were interchangeable. The only other observable trend was that the more highly substituted the compound, the more difficult it was to degrade.

### TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

The steam stripper was operated in countercurrent mode using distilled water as the feed stream. Introduction of preheated feed water did not appear to disrupt the operation of the stripper, but we presume that heat loss from the lines decreased the temperature of the feed stream to below the value preset on the RTD controller. Since we cannot yet measure the actual emergent feed water temperature, the setting was kept at a temperature equivalent to the temperature in the bottoms collector to prevent flashing of the feed water at its entry point. The feed water accumulated in the bottoms collector as expected. Variable operating conditions prevented precise measurements and comparisons between the runs.

The stripping column and the tee at the top of the column were wrapped with heating tape to offset heat losses. The effectiveness of the heating tapes will be tested next month.

To obtain more precise operational control, the voltage to the steam drier was regulated with a variable transformer (April 1982 Monthly report). Adjustment of the voltage output on the transformer decreased the temperature oscillations in the system. Control of the system temperature was also improved by relocating the overheads condenser RTD from the tee directly above the column to the tee directly above the overheads condenser. In spite of these improvements, the temperature increased consistently throughout operation. This was thought to result from the time required to heat the large thermal mass of the stainless-steel vessels to a stable temperature and from interference among the RTD controllers.

The on-off cycling of each RTD controller was found to interrupt the cycles of the other controllers; this crosstalk prevents effective temperature control of the steam stripper. Some minor wiring errors were corrected, but this did not eliminate the interference. In addition, increasing the size of the filter capacitors across the relays did not decrease the high-frequency interference.

Self-draining manometers, electronic pressure transducers, and Bourdon-tube gages were investigated for measuring steam pressure. A Bourdon-tube gage attached to tubes filled with a fixed volume of water appeared to be the simplest and most cost effective method for pressure measurement.

In spite of the operational problems, a preliminary evaluation of the overall operation of the steam stripper was attempted by adding two distinctly colored dyes, methylene blue and p-nitrophenol, to acidic feed water. Methylene blue, a charged, high-molecular weight chromophore, was predicted to remain in the liquid phase and to be recovered in the bottoms collector. In contrast, p-nitrophenol, low-molecular weight compound that is uncharged in acid solutions, was expected to partition to the gas phase. None of the methylene blue appeared in the overheads condenser and some stripping of the p-nitrophenol was observed. The majority of the phenol, however, remained with the liquid phase. The ortho isomer of nitrophenol will be used in the future because o-nitrophenol is more easily steam distilled. These results demonstrated that the feed water was not being physically carried from the column to the overheads condenser and that separation processes were occurring in the column.

#### TASK 5. RETORT ABANDONMENT FINAL REPORT

A draft of the final report for the retort abandonment project was completed, changes from internal reviewers are being incorporated, and preparation for distribution to external review has been initiated. Reviewer comments will be incorporated, and a final version of the report will be prepared next month.

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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