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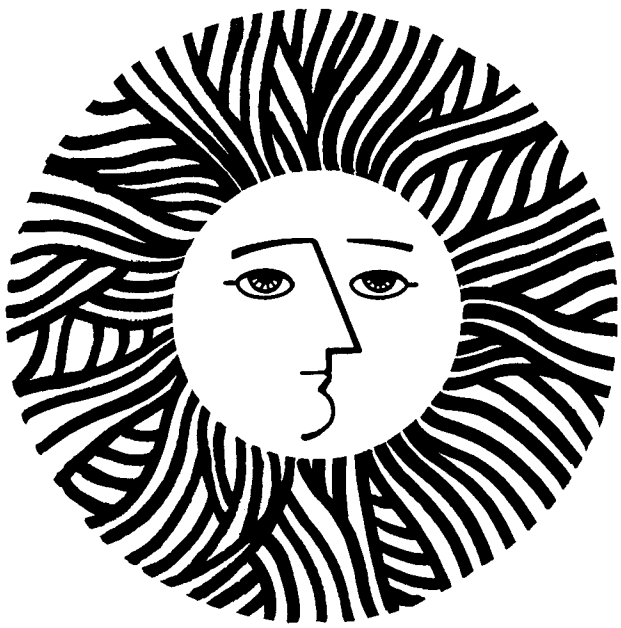

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30 April 1982

TO: Art Hartstein

FROM: Bonnie M. Jones, Peter Persoff, Richard H. Sakaji, and Jerome F. Thomas
Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, California 94720
and
Christian G. Daughton
Sanitary Engineering and Environmental Health Research Laboratory
University of California, Berkeley
Richmond, California 94804

RE: Monthly Progress Report for April
Oil Shale Waste Treatment: Fundamental Approaches
LBID-540

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PRESENTATIONS

C.G. Daughton presented a talk "Fundamental Approaches to Oil Shale Wastewater Treatment" at the DOE Oil Shale Chemistry Meeting, Lawrence Berkeley Laboratory, 1 April 1982, and a review of the LBL Oil Shale Program to the Lawrence Berkeley Laboratory Energy and Environment Review Committee, 15 April 1982. An informal review of the project was given to Arthur Hartstein on 31 March 1982.

B. Jones presented a paper, "Oil Shale Waste Treatment: Physico-Chemical Treatment Methods" (R.H. Sakaji, B.M. Jones, and C.G. Daughton), at the 15th Oil Shale Symposium, Golden, Colorado, 30 April 1982. A copy of the abstract is enclosed.

TASK 2. BIOLOGICAL TREATMENT OF PROCESS WATERS

Enrichment Studies

Selective enrichments on pure compounds were initiated for microbial populations capable of oxidizing nitrogenous heterocycles. The first set of enrichments was begun using alkyl-substituted pyridines. Each of the model compounds (2-methylpyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine, i.e., α-picoline, 2,6-lutidine, and 2,4,6-collidine, respectively) was diluted with basal salts medium to 2.14 mM

and the three experimental conditions under which each compound was used included:

(1) The substituted pyridine served as a sole source of nitrogen and carbon.

(2) The pyridine medium was supplemented with an easily degradable carbon source (67.5 mM carbon from equivalent amounts of acetic, propionic, butyric, and valeric acids). A small amount of nitrogen (0.4 mM NH_4Cl) was added to stimulate initial growth on the fatty acid carbon sources. The added nitrogen would quickly become limiting, and continued growth would necessitate utilization of the nitrogen contained within the heterocycle.

(3) An uninoculated control contained the substituted pyridine in basal salt medium.

The microbial inocula were derived from a combination of acclimated cultures that originated from (1) soil that had been conditioned with retort water in the field, (2) domestic compost, (3) a pooled inoculum from previous enrichment studies on spent media, and (4) a culture grown on 100% Oxy-6 retort water in a bench-scale fermentor.

Each shake flask will be monitored for substrate loss and cell growth by following the maximum UV absorbances and peak shifts in the UV scans of each model compound and by individual cell counts. Cultures established on the pure compounds will be used as an inoculum source for further enrichment studies on retort water that has been subjected to extensive biological treatment (spent retort water).

TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

Steam Stripper

The startup procedure for operation of the steam stripper is being documented for an operations manual. We are currently focusing our attention on startup and operation of the steam generation system. The objective is to maintain a steady rate of steam generation over an extended period of time. Due to severe heat losses within the system we have not been able to obtain steady state conditions which would allow calibration of steam production rate. Although the results from tests this month were erratic, they were more promising than previous results; the ratio of steam collected in the overheads condenser to that condensed in the bottoms was much greater.

Transient operating conditions were traced partly to the steam drier and RTD controllers. A variable transformer was installed for the steam drier, since the drier was overrated for our application, this should decrease the temperature fluctuations caused by the on-off cycling of the steam drier. In addition, careful adjustment of the response bands on the RTD controllers may also correct some of the transient fluctuations; variable tranformers may be required, however, to minimize the transients.

The reactor column was packed by filling the column with water and gradually pouring the ceramic saddles through the top opening of the stainless-steel "tee" directly above the column. The column was filled to 75% capacity, and the packed bed was then flushed with water to remove ceramic dust. A sudden pressure drop in the overheads vessel during startup caused a 2-foot plug of packing material to be lifted to the top of the column. Several packing saddles fell into the overheads condenser and became lodged in the upper valve of the sampling bomb. A stainless-steel screen was installed in a vertical joint of the "tee" between the column and the overheads vessel to prevent any further incidents.

The feed preheater was tested by disconnecting the effluent tube from the column and pumping water at ambient temperature through the heater. Although the RTD controller was set for 90° C, the measured temperature was between 92 and 93° C; the effluent feed water temperature was 88° C. This suggests that improved control and data collection capabilities may be required.

TASK 5. RETORT ABANDONMENT FINAL REPORT

Numerical Modeling of Groundwater Re-Invasion

TRUST is designed to maintain model stability by refusing time steps that result in a head increase at any node which exceeds a preselected limit. For desaturated materials which are wetting (i.e., saturation is increasing), the change in head is calculated from the relationship between the degree of saturation (S) and the pressure head (h). For all materials, including the abandoned retorts, we used an assumed relationship between S and h which was based on observations of natural materials. This relationship is entered into the input data as a table of (h,S) data pairs. For h greater than 0, S equals 1. For h less than -18 m, S equals 0.2; that is 0.2 is the residual

saturation that cannot be drained from the material. For h less than -18 m, therefore, dS/dh equals 0 and dh/dS is infinite.

This led to a problem which had never been encountered before in simulating re-invasion of abandoned retorts. This resulted from the uniqueness of the situation being modeled. At the start of the model run, the top of the retorts are 100 m above the water table; therefore they are in the region where dh/dS equals 0 (the program substitutes a value of 10^{-12} m). In a very small time step (on the order of 100 sec) then, the small amount of water entering the retort is enough to cause a large increase in head at that node, exceeding the preselected limit.

For real materials, dS/dh is never zero for any h less than zero. Therefore we redefined the relationship between S and h so that dS/dh is greater than zero for all h less than zero. This allowed the model to take more reasonable time steps (on the order of 10,000 sec).

Final Report Preparation

The preparation of the final report draft on retort abandonment is in progress. Work this month has focused on reviewing data from various leaching studies to predict the groundwater quality effects of in-situ leaching, and on using the leaching kinetics model (developed at LBL by W.G. Hall) to determine the feasibility of intentional leaching as a control strategy.

Oil Shale Waste Treatment: Physico-Chemical Treatment Methods

R.H. Sakaji and B.M. Jones; Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

and

C.G. Daughton; University of California, Berkeley, Sanitary Engineering and Environmental Health Research Laboratory, Richmond, California 94804.

Physicochemical treatment methods for oil shale process wastewaters are often unsuccessful or infeasible because concentrations of organic and inorganic solutes necessitate the excessive use of chemicals or energy. We have focused our investigations of physicochemical methods on those that utilize (i) cogenerated wastes and materials (e.g., spent shale), (ii) environmental factors (e.g., UV radiation), and (iii) feasible conventional methods (e.g., steam stripping). Emphasis is placed on the evaluation of those methods that remove organic solutes that are complementary to those removed by biological treatment or enhance the performance of biological treatment.

Physical treatment methods will undoubtedly find use for the removal of characteristically high concentrations of dissolved ammonia. The petroleum industry commonly removes ammonia via steam stripping since the ready availability and high heat capacity of steam make it technically and economically attractive. We have designed a "pilot-scale" steam stripper that does not use a reboiler for steam generation. The stripper is a totally closed system with provision for steady-state operation and collection of overheads and bottoms. The stripping column is 16 feet (4.88 m) high, packed with 1/4" ceramic saddles, and designed for counter-current flow. Column length is dictated primarily by the requirement for ammonia removal, because carbon dioxide and sulfides also would be removed.

Certain spent shales and activated carbons can be used to sorb organic compounds from retort waters. Although sorption "isotherms" have indicated that that TOSCO II spent shale and activated carbon are inefficient for removing organic carbon from Oxy-6 retort water, the carbon that is removed by sorption belongs exclusively to the fraction that is recalcitrant to initial biodegradation. Sequential treatment by spent shale and biooxidation has effected better than 80% removal of DOC from Oxy-6 retort water. We had speculated that spent shale could perhaps be used like activated carbon to concentrate certain refractory compounds at a solid-liquid interface and thereby increase their accessibility to bacteria. Experiments have shown, however, the total removals resulted solely from normal biooxidation and from surface sorption, i.e., no synergistic enhancement of biodegradation could be demonstrated by the use of either sorbent.

The intensity of UV radiation at higher elevations could have profound effects on ponded retort waters. UV photolysis of organic solutes could produce more chromophoric compounds and exacerbate the recalcitrance of organic solutes by inducing their polymerization, or alternatively, environmental UV irradiation could provide an economical means of treatment for degrading normally recalicitrant compounds. Extensive treatment of (i) raw, (ii) biologically treated (spent), or (iii) ammonia-stripped, spent Oxy-6 retort water by sequential or simultaneous treatment with ozone and UV radiation effected only a 5% removal of DOC. More surprisingly, when these extensively treated waters were subjected to biological treatment, the removal of DOC was only slightly better than that from untreated controls; ozonation often increased the biorefractory nature of raw retort water.

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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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720