Title
MONTHLY PROGRESS REPORT. OIL SHALE WASTE TREATMENT: FUNDAMENTAL APPROACHES

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RE: Monthly Progress Report for June
Oil Shale Waste Treatment: Fundamental Approaches
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MILESTONES

Sent under separate cover is the report "Coulometric Quantitation of Carbon in Oil Shale Process Wastewaters via UV-Peroxydisulfate or High-Temperature Oxidation" (LBID-561) by G.W. Langlois, B.M. Jones, R.H. Sakaji, and C.G. Daughton.

Enclosed is the Summary of the draft report "Control Technology for In-Situ Oil Shale Retorts" (LBL-14468) by P. Persoff and J.P. Fox.

Enclosed is a preprint of the paper "Physicochemical Treatment Methods for Oil Shale Wastewater: Evaluation as Aids to Biooxidation" (LBL-14666) by B.M. Jones, R.H. Sakaji, and C.G. Daughton, which is to be published in the Fifteenth Oil Shale Symposium Proceedings, Gary, J.H., Ed., Colorado School of Mines Press, Golden, Colorado.

TASK 3. PHYSICOCHEMICAL TREATMENT OF PROCESS WATERS

Steam Stripper

The problems which had previously been experienced with unstable column temperatures have been resolved. The "crosstalk" among the relays was almost completely eliminated by installing RC (resistance-capacitance) filters across the terminals of the RTD controller relays, and across the microswitches operating the cumulative timers. As a result of these modifications, system stability has improved markedly; during a 2-hour run the overheads temperature was maintained within a range of ±0.2 degrees C. These small, regular fluctuations apparently result from the lag time between addition of coolant and detection of the resulting temperature change by the condenser RTD. This lag was reduced but not eliminated by relocating this RTD closer to the cooling coils. Attempts to eliminate the fluctuations by adjustment of the coolant addition rate and the controller bandwidth have been unsuccessful. It has not yet been determined if these fluctuations are affecting the performance of the steam stripper significantly. Various modifications of the cooling system control configuration are being considered.

The stripping column and upper tee were wrapped with heating tape in order to reduce condensation and maintain isothermal conditions in the column. Data accumulated since making this modification suggest that operating conditions have improved. The temperatures along the outside surface of the column have been kept constant by using thermocouples and variable transformers to control the heat tapes. This suggests that isothermal isothermal operating conditions are being approached.

Performance of the steam stripper was evaluated using ortho-nitrophenol and methylene blue as volatile and non-volatile compounds, respectively. During the initial attempt, the tee above the column (also the entry point of the preheated feed water to be stripped) was overheated, which caused the dye solution to vaporize and carry over into the overheads vessel. The overheating was caused by an erroneously low temperature reading which resulted from the feed water dripping onto the thermocouple in the tee above the column. Extending the feed water injection tube to a point below the thermocouple eliminated this problem. During the next run substantial separation of the compounds was achieved. According to spectrophotometric determinations, over 99% of the ortho-nitrophenol was found in the overheads, along with 29% of the methylene blue, indicating some blow-over of the feed water. Because of difficulties subsequently encountered in the quantitation of the dye mixture, a different nonstrippable dye will be sought for future tests.

TASK 5. RETORT ABANDONMENT FINAL REPORT

A draft of the final report on this project, "Control Technology for In-Situ Oil Shale Retorts", by P. Persoff and J.P. Fox (117 p.), has been completed and mailed to outside reviewers. A summary of the report is enclosed.

CONTROL TECHNOLOGY FOR IN-SITU OIL SHALE RETORTS

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SUMMARY

Modified in-situ (MIS) oil shale retorting would result in degradation of groundwater quality if reinvading groundwaters were to leach the in-situ retorted shale. The objective of this work was to quantify the problem of groundwater pollution and to evaluate technologies for its control. This was accomplished by a review of the literature of allied fields (oil shale mineralogy and leaching, cement chemistry, construction grouting, Piceance Basin geohydrology), by numerical modeling, by experimental studies, and by engineering assessments of individual control technologies.

Numerical simulation of dewatering and reinvasion for a typical location showed that reinvasion would take over 200 years. Leachate transport away from the abandoned retorts would not occur during this time. At completion of reinvasion, flow through the retorts would transport leached solutes in aquifers toward surface streams. Transport to surface streams would take 130 to 1450 years after completion of reinvasion, depending upon location.

Based on reported experimental studies using actual and simulated MIS spent shale, the leachate would be alkaline and contain high concentrations of TDS, B, F, Pb, Se, V, phenols, and organic nitrogen, compared to existing groundwater quality. Affected groundwaters would have essentially the same composition as the leachate, but the concentrations in surface waters would be reduced by dilution.

The severity and extent of groundwater impacts would depend upon site-specific and process specific factors. If local geohydrologic conditions are favorable, leachate transport could be reduced by low permeability of surrounding media.

The composition of leachate would also be affected by retort operating conditions. Review of the literature indicated that the most favorable conditions for leachate quality include retorting in an air-steam atmosphere, with combustion of char, no use of recycle gas, and long residence time at high temperature to promote the formation of the silicate minerals in the diopside-augite series. Although these operating conditions are favorable, they are not sufficient to reduce all leachate constituents to safe levels. That these conditions can be achieved uniformly throughout a retort also has not been demonstrated.

Backfilling abandoned retorts with a grout based on surface-retorted shale appeared to be a technically feasible method to reduce the transport of leachate substantially. Grouting would require 200 to 270 gallons of water per barrel of oil recovered by MIS retorting. Grouting retorts would

not reduce the concentration of solutes in leachate but would reduce the rate of its transport through aquifers and the effect on surface streams. Candidate grouts based on Lurgi spent shale were prepared and tested for permeability and structural properties. These grouts are non-Newtonian fluids, with yield strengths about 60 dyne/cm^2. Adequate fluidity is necessary to fill the entire retort from a small number of grout injection holes. This was achieved by inclusion of 0.25-percent lignosulfonate fluidizer in the grout. Addition of 10-percent fly ash or fly ash-gypsum cement increased the elastic modulus (stiffness) of the grout, but not sufficiently to allow the grouted retort to support the overburden and thus allow enhanced resource recovery. Permeability of grouts was measured by saturating the samples, placing them under confining pressure, and measuring the flow of water resulting from an applied hydraulic gradient against a back pressure. Permeability of the grouts tested varied with confining pressure; permeabilities in the range of 10^{-6} cm/sec were measured.

Another proposed control technology is to intentionally leach the retorts, and treat the leachate for re-use. This would require at least 60-120 gallons of water per barrel of oil recovered. This strategy would be effective for solutes which are mass-transfer-controlled, but not for solutes which are solubility-controlled. A mathematical model of mass-transfer-controlled leaching was verified for organic carbon. Some inorganic solutes, however, have been reported to be solubility-controlled, and the mechanism controlling concentrations of other inorganic solutes is not clear. Assuming that a treatment process for leachate can be demonstrated, it was found that treatment of 4 pore volumes of leachate appears to be adequate to reduce the concentration of total organic carbon in leachate to 10 percent of its initial value. Additional work is required to validate this technology for other solutes.

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