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OCTOBER MONTHLY PROGRESS REPORT - CONTROL TECHNOLOGY FOR IN SITU OIL SHALE RETORTS

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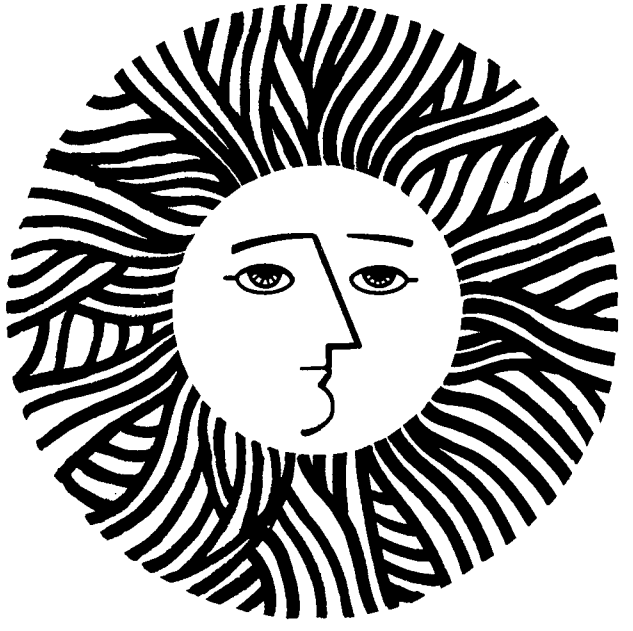

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LAWRENCE BERKELEY LABORATORY
Room: 128 Bldg.: 70 Ext.: 6698

November 8, 1979

TO: Charles Grua and Art Hartstein

FROM: Phyllis Fox and Peter Persoff

RE: October Monthly Progress Report
Control Technology for In Situ Oil Shale Retorts
LBID-134

Task 3. Evaluation of Barrier Options

Spent shale grout development. ASTM standard tests on Lurgi spent shale showed that it is not cementitious as received. During FY 1979, a series of experiments, in which $CaCO_3$ was added to Lurgi spent shale and the mixture calcined, showed that a true hydraulic cement containing C_3A and β-C_2S (active compounds in portland cement) could be produced. A 1:1 $CaCO_3$-spent shale ratio, held for one hour at 1000°C, produced a cement with a strength of 2660 psi (ASTM C109). During October 1979, two additional experiments to further improve the quality of cemement produced were in progress.

Addition of gypsum to calcined cement. C_3A ($3CaO \cdot Al_2O_3$) is one of the compounds formed by calcining Lurgi spent shale in the presence of $CaCO_3$. In portland cement, this compound hydrates almost instantly, causing a "flash set" or "false set", with no contribution to ultimate strength. In commercial practice this problem is dealt with by adding about 5% gypsum ($CaSO_4 \cdot 2H_2O$) to the ground clinker. This reacts preferentially with C_3A to form ettringite, ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$), which adds

strength to the hardened cement paste. Accordingly, the effect of addition of gypsum to Lurgi spent shale cements is being investigated. Mortar cubes for ASTM C109 strength measurements have been made and are curing. Strength measurements should be available next month.

Addition of Fe_2O_3 to raw mix. C_4AF ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) is an active compound of portland cement, which has not been detected in any of the hydraulic cements produced so far. Small amounts of Fe_2O_3 have been added to the spent shale-$CaCO_3$ mixture prior to calcining to see if C_4AF is produced, and whether significant improvement of the cement results. X-ray diffraction and strength measurements should be available next month.

Permeability measurements. Although Lurgi spent shale as received is not cementitious, a slurry of it could be injected into an abandoned retort to reduce permeability and provide some strength. In order to measure the results of such a treatment, simulated grouted cores were prepared. Simulated in situ spent shale (-3/8" + 1/4") from Lawrence Livermore Laboratory run L-2 (6000-kg retort) was packed into cylinders and pre-wetted. A grout consisting of 95 parts Lurgi spent shale, 5 parts portland cement, and 80 parts water was pumped into the L-2 spent shale matrix. Permeability measurements of this material showed that permeability decreased with time to about 20 millidarcy. It is interesting to note that assuming spherical particles of 3.5×10^{-6} m (the median particle diameter reported by Lurgi for this material) and 50% porosity, the Kozeny-Carman equation predicts a permeability of about 30 millidarcy. Thus the low permeability appears to result from the fine size of particles in the grout.

Strength requirements for grouted retorts. Rock mechanics calculations have been initiated to evaluate the strength and stiffness requirements for

a grouted in situ spent retort to minimize subsidence and allow retorting of previously intact pillars. Initial efforts have concentrated on obtaining the load/deformation and strength characteristics of intact and retorted oil shale. This information will be used in evaluating the pre- and post-retorting subsidence and structural integrity in the overlying strata. Preliminary calculations will be done using beam on elastic foundation theory, followed by finite element calculations.

Groundwater flow model.

The dewatering model described in the third quarterly report (LBID-040) has been set up. Several runs were made to compare the model results with the known Theis analytical solution. This was done to check for any errors in the input data of the model (30 x 20 element mesh). The model data plot matches the Theis solution for small values of time but shows instability for large time values. Further computer runs are being made to debug the program.

Task 5. Evaluation of Leaching Options

An equilibrium isotherm was developed to show the relationship between the concentration of Total Organic Carbon (TOC) existing at equilibrium in the solid and liquid phases in the spent shale leaching columns. Two separate long-term batch studies of seven shale and distilled water mixtures ranging from 1.5 to 0.1 gm of shale per ml of water were conducted for periods of 21 and 73 days. At the end of the respective time periods the mixtures were centrifuged and the TOC concentrations in the centrate determined. The corresponding equilibrium concentration of TOC in the shale for each mixture was then determined by subtracting the amount of TOC removed by the leachate from the organic carbon originally present in

the unleached shale. This latter quantity was determined by wet oxidation with chromic and other acids of finely ground shale from which the inorganic carbon had been removed with sulfurous acid. The procedure used is a standard method used to determine the organic carbon content of soils. An average TOC content of 1.7 percent by weight was found by this method. The resulting isotherm, obtained by plotting "q", the solid phase TOC concentration, against "C", the corresponding liquid phase TOC concentration, is essentially linear for leachate TOC concentrations of less than 40 mg/l. This linear relationship will simplify modeling and analysis of the leaching and solute transport problem considerably.

A change in the operation of the column leaching studies was instituted. Previously, flow in the columns was in the upward direction. A reservoir was provided at the bottom of the column to supply water across the entire cross-section of shale. It was discovered that the reservoir was acting as a trap for leachate. The incoming water, being lighter than leachate, would rise into the shale. A portion of the leachate already in the shale bed would then fall back into the reservoir instead of rising through the column as intended. This had two adverse effects. First, although net flow is upward, there are strong downward components of velocity. Second, the pool of water varies greatly in concentration of salts and TOC over the period of column operation. These effects violate assumptions used in the derivation of the leaching and transport model that the initial concentration of fluid entering the column is zero and that the velocity is uniform in the direction of flow. These observations were verified in an experiment in which water was passed downward through a column of spent shale. A much sharper concentration front was observed moving downward along the column

than was observed for a corresponding upflow experiment. A new column run was started using columns modified for downward flow.

During the past year considerable difficulty has been encountered in the measurement of TOC in the leachate from the batch and column studies in this study. A new Dohrmann Model DC-52A Total Carbon Analyzer was obtained by LBL. Leachate samples are now being analyzed by both the Dohrmann instrument and the Beckman 915A analyzer used previously. It is expected that both instruments will be used in the future to provide cross checking of results.

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