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SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATERS

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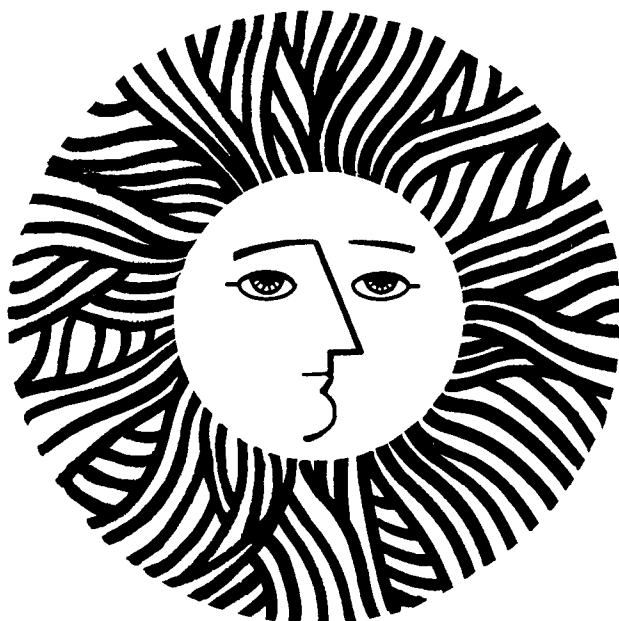
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February 12, 1980

TO: Charles Grua
FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox
RE: Monthly Progress Report for January
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-175

TASK I. ANALYTICAL METHODS DEVELOPED

The investigation into the proposed method for oil and grease analysis outlined in the last monthly report is continuing. We are trying to resolve problems that occur after the retort water sample is passed through the C-18 Sep Pak. The Sep Pak retains approximately 400 μ L of retort water which contains a high concentration of dissolved solids. This material is included when the oil and grease is subsequently determined gravimetrically. During mobile phase switchover, the residual water is swept out of the cartridge with the methanol. The methanol is combined with the methylene chloride eluate and then dried. The resulting residue contains not only the sought-after hydrophobic materials, but also dissolved polar and inorganic solids from the 400 μ L of retained water.

The first experiment involved washing the C-18 Sep Pak, after sample application, with deionized water in an effort to flush the residual hydrophilic materials from the cartridge. This process swept a mass of 9.1 mg (59% of the total retained residue) from the column. Since the 400 μ L of retained water has a TDS concentration of 10,000 mg/L, the hydrophilic solids residue from the rinse should have been, at most, 4 mg. These results indicated that hydrophobic material was also swept from the column. Because of these findings, the water rinse step was abandoned.

As an alternative approach to removing the dissolved hydrophilic residue retained by the column, an attempt was made to selectively redissolve the oil in the dried organic eluate with methylene chloride. The methylene chloride solution was then passed through a Si Sep Pak and the effluent was pooled with a methylene chloride rinse, dried, and

the residue weighed. The residue was hydrophobic material (aliphatic mineral oil).

The problem with the redissolving step is that the depth of the residue in the drying pan may prevent complete solvent-residue contact. This could result in low oil recovery. To increase the surface area on which the organic eluent from the C-18 column was dried, glass beads were placed in the pans. This increased the solvent-residue contact area. The pan and the glass beads were extracted with five 5-mL portions of methylene chloride. The initial results indicated that there was no apparent difference in the masses of oil extracted from the dried residues of pans with and without glass beads.

In addition to the residual hydrophilic solids problem, the hydrophobic sorptive capacity of the C-18 Sep Pak is also unknown. A retort water sample was passed through a series of four C-18 Sep Paks. Each Sep Pak was individually eluted. Residual mass was found in each eluate and the residue of the fourth Sep Pak approached the maximum theoretical mass of hydrophilic solids left by the water residue in the Sep Pak. This indicated that more than one C-18 Sep Pak in series might be required to sorb all of the organic matter present in retort water.

Disregarding the aforementioned problems, a set of retort water samples was run through the complete analytical procedure outlined in December's report. The results of this test indicated that the concentration of oil is only about 92 mg/L in the retort water from Occidental's Logan Wash Retort #6.

The problems with gravimetric analysis have become very apparent. The data we have gathered clearly indicate the need for a more specific means of detection. This could possibly be accomplished using an infrared spectrophotometer or an infrared detector with high-performance liquid chromatography. Future work will involve the pursuit of these analytical methods.

TASK 4: CONTINUOUS-FLOW COLUMN STUDIES

As a result of the initial column study that was conducted in December 1979, several analytical and procedural modifications have been made in preparation for the next continuous-flow column experiment. The experiment

will be conducted in the same 1-in. I.D. x 36-in. long plexiglass column using retort water from LETC's 150-ton simulated retort (Run #13) and L-2 spent shale as bed material.

Using a surface loading rate of 1.0 gpm/ft² (Q = 20.65 mL/min. for a 1-in. I.D. column), the first column study suggested that both breakthrough and exhaustion of the spent shale bed (noted by a decrease in pH of the column effluent) may occur within one bed volume. The high surface loading rate made it difficult to track the reaction front through the column, as samples for alkalinity analysis had to be drawn and titrated at two-minute intervals. As a result, the next column study will be conducted at the much lower surface loading rate of 0.01 gpm/ft² (Q = 2 mL/min. for a 1-in. I.D. column). This flow rate will result in a minimum residence time of 1.9 hr. for a column 1-in. in diameter x 36-in. long with a 50% void volume.

In addition to the lower surface loading rate, alterations will be made in the composition of the bed and the mode of flow through the bed. The composition of the column bed will be made more uniform by selecting 18-25 mesh shale (particle diameter of 0.7 to 1 mm). This will be done so that the results of later batch and surface area studies will be applicable to constructing a model spent shale column. Since there were no problems with flow restriction due to column plugging in the previous experiment that used 18-40 mesh shale, none are anticipated for this column run that will use larger-sized particles. The larger particles will also allow the columns to be filled and operated in upflow mode. At the low surface loading rate, no problems with bed fluidization are anticipated.

Total chemical oxygen demand (COD) and total alkalinity were used in the first column study as estimates of organic and inorganic carbon concentrations, respectively. However, the contribution of ammonia and carboxylic acids to alkalinity and the nonqualitative nature of the COD test resulted in ambiguous data. Therefore, the column effluent will be analyzed for organic carbon, inorganic carbon, carboxylic acids, and ammonia as well as pH, conductivity and alkalinity. Total alkalinity will be used to confirm, after correcting for ammonia and volatile acids, the inorganic carbon values obtained by the carbon analyzer (combustion-infrared analyses). The new methodology for oil and grease analysis will be

used to investigate the possible effect of spent shale on the oil and grease concentration of retort water.

TASK 5: SYSTEM STUDIES

The data from the continuous-flow activated sludge reactors that were fed 100% retort water are ambiguous. One of the major problems in this study appears to be growth in the feed lines and in the media reservoirs. As a result, we have not been able to achieve steady-state conditions in the reactors. A media preparation scheme is being developed that should eliminate biological growth in the reservoir. This will involve autoclaving the media to prevent biological degradation. In order to incorporate the autoclaving step in the media preparation scheme, we must ensure that the process of autoclaving does not significantly alter the retort water. We will attempt to demonstrate the effects of autoclaving by measuring the chemical oxygen demand of the retort water in autoclaved and nonautoclaved samples.

Since the results from the continuous flow studies have been so ambiguous, we have initiated a series of enrichment culture experiments in an attempt to clarify the problems we are encountering. The first enrichment culture is an attempt to establish a microbial community in retort water from LETC's 10-ton retort (S-55). The low ammonia concentration of the retort water will allow us to investigate biological degradation in a continuous-flow reactor, without pretreating the water to decrease the ammonia toxicity. Prior to setting up a continuous-flow reactor, samples of the S-55 retort water were placed in several Erlenmeyer flasks. The samples were inoculated with soil and activated sludge seeds before incubating at 27°C on a shaker (150 rpm). All samples showed signs of growth. Once the reactor is assembled, an inoculum from these enrichment cultures will be used to seed the reactor.

Enrichment culture experiments are being performed on the effluent from the continuous-flow reactor that is being fed CaO-treated retort water. Even though the results from this reactor have been ambiguous, the data indicate that there is a high COD residual in the effluent. This nonmetabolized portion of retort water could be the result of several possibilities such as:

- (1) Depletion or nonavailability of a nutrient required for growth
- (2) Accumulation of toxic metabolites
- (3) Presence of only biorefractory compounds
- (4) Fallibility of microbial community.

These possibilities seem very likely. An attempt to achieve growth on the centrifuged and filtered effluent of the reactor was unsuccessful. The enrichment studies will attempt to address the aforementioned possibilities and provide us with further insight into the problem of biological degradation.

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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