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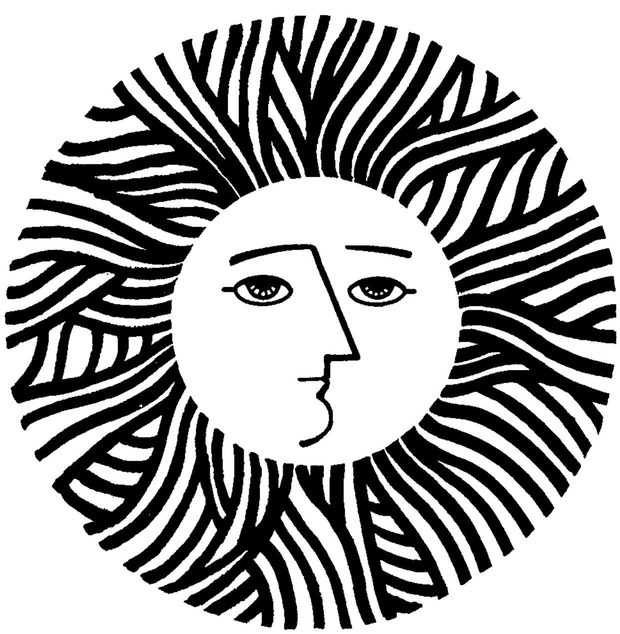


LAWRENCE BERKELEY LABORATORY
Room: 128 Bldg.: 70 Ext.: 6698

March 10, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox

RE: Monthly Progress Report for February
Spent Shale as a Control Technology for Oil Shale Retort Waters
LBID-186

TASK 1: ANALYTICAL METHODS DEVELOPMENT

The problems with oil quantitation have yet to be resolved. We have temporarily suspended research on this analytical method until the necessary instrumentation for quantitative analysis can be purchased and assembled. We are currently awaiting delivery of an infrared spectrophotometer and high performance liquid chromatograph (HPLC) for quantitative work. Use of this instrumentation has become a necessity because of the problems, noted in previous monthly reports, that are associated with quantitation by gravimetric analysis.

Studies on the reproducibility, accuracy, and applicability of the chemical oxygen demand (COD) test in characterizing retort water have been initiated. Verification of the suitability of chemical oxygen demand (COD) measurements for oil shale retort water is necessary before this test can be used to evaluate biological treatment performance. The ambiguous results previously obtained under the Task 5 system studies prompted this study. In that work, the COD increased during aerobic biological treatment. This led us to suspect that certain organic compounds, which were subsequently biologically altered, were not oxidized in the COD test.

TASK 4: CONTINUOUS FLOW COLUMN EXPERIMENTS

A second spent shale column was successfully completed during the first part of February. The 3 ft 1-in. ID Lucite column, packed with 18-25 mesh L-2 spent shale, was operated in an upflow mode at a surface loading rate of 0.1 gpm/ft^2. As in the December experiment, retort water from LETC's 150-ton retort (Run R-13) was treated by the spent shale column. The lower surface loading rate made sample collection easier, and the use of organic and inorganic carbon (OC and IOC) rather than alkalinity and COD produced more reliable data.

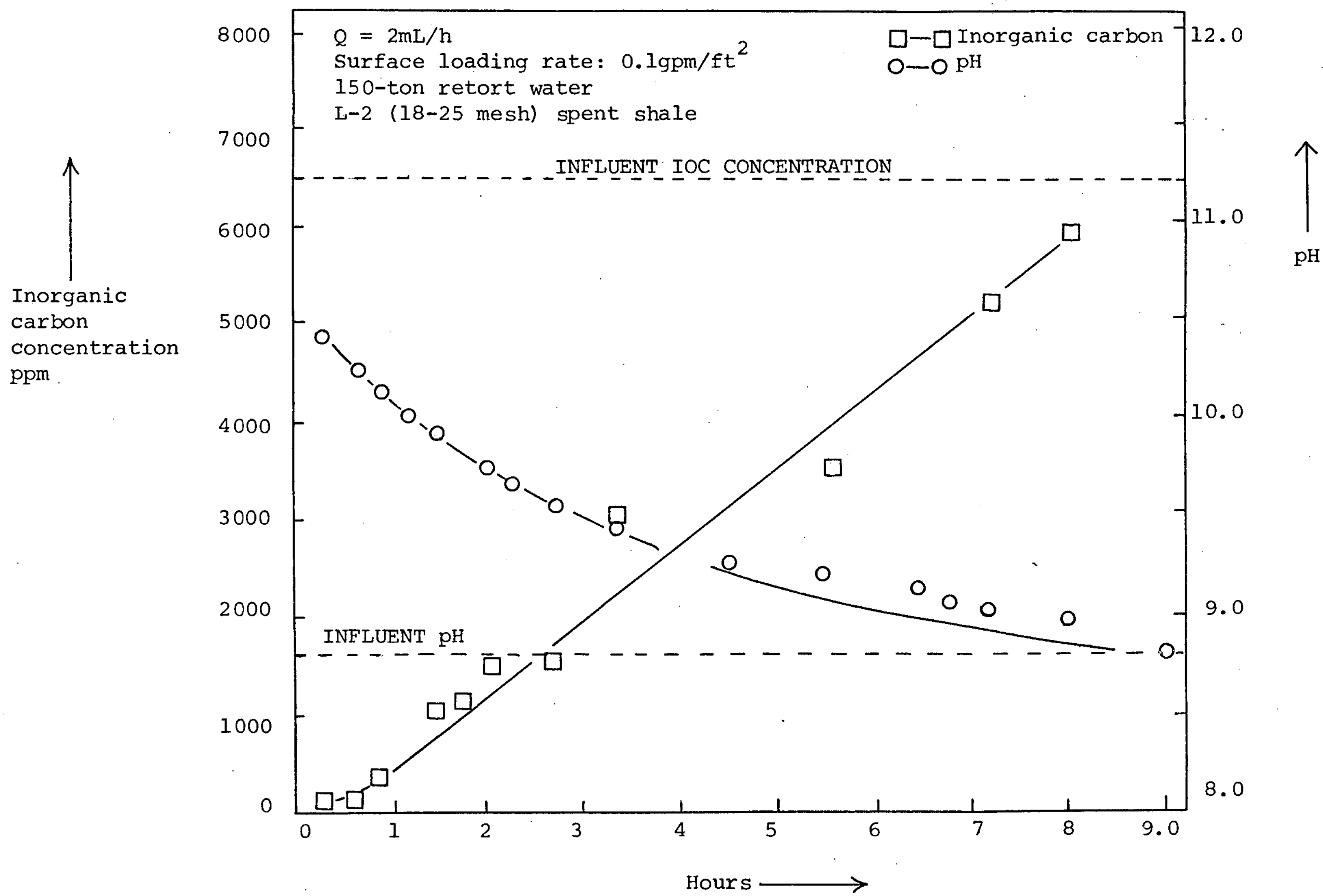
The IOC and pH of the column effluent as a function of time into the run is shown in Figure 1. The dashed lines show the initial IOC and pH. The spent shale column achieved an initial IOC reduction of 99 percent which was not sustained; after three void volumes had passed through the column, the IOC reduction dropped to 50 percent. Similarly, the pH elevation capability of the spent shale was short-lived. The pH of the retort water was increased from 8.8 in the column influent to 10.4 in the initial effluent; after three void volumes had passed through the column, the pH of the column effluent dropped to 9.4. Analyses of the column effluent indicated that no organic carbon and no saturated aliphatic oil material was removed by the spent shale column.

Head loss readings taken during the column run indicate that this will not be a significant factor in determining the operational life of the column. Head loss was less than 5 feet throughout the life of the column. The duration of column operation will be determined by its capacity to remove IOC and OC and by its ability to elevate the pH of the retort water.

The short duration of pH elevation and IOC removal in the specific shale-water combination studied suggests operational life may limit the use of fixed-bed columns in retort water treatment. Additional work with other spent shales and retort waters is required to further investigate this tentative conclusion. However, the treatment of retort water with a spent shale slurry may be feasible. The spent shale could be finely pulverized (not feasible in column operation due to fluidization problems) and well-mixed to ensure good shale-water contact, thus maximizing the treatment capacity of spent shale. Experiments are currently being designed to test the slurry concept.

Additional fixed-bed columns using different spent shales and retort waters will be run in future months. Arrangements were made this month with DEI to receive 40 pounds each of three separate spent shales from the Paraho retort. These spent shales were produced under different operating conditions and will provide valuable information on the effect of retorting conditions on spent shale treatment.

Figure 1. Effect of L-2 spent shale column on inorganic carbon concentration and pH of 150-ton retort water



TASK 5: SYSTEM STUDIES

As noted in the January monthly report, bacterial contamination of the feed reservoir had been a problem in the continuously stirred tank reactor (CSTR) biological studies. Autoclaving the media was our first attempt to alleviate the contamination problem. However, test results show that autoclaving the retort water significantly alters the COD without altering the organic carbon concentration. This finding is significant because it indicates that the measurement of COD may be inadequate to evaluate performance of biological reactors. Experiments are presently being designed to clarify the suitability of the COD test for evaluating biological treatment processes. If necessary, an alternative parameter will be developed. (Organic carbon is not suitable for performance of biological reactors as it is independent of the oxidation state of the waste.)

Previous biological treatability studies indicated that aerobic oxidation removed very little of the organic carbon in retort water. Therefore, enrichment studies have been initiated to develop a microbial population capable of biodegrading the organics in retort water. Low carbon removals by the microbial population could be due to the depletion or nonavailability of a nutrient, accumulation of toxic metabolites, presence of biorefractory compounds, or fallibility of the microbial community.

Preliminary studies were conducted this month to investigate some of these factors. The effluent from an operating two-stage aerobic reactor was filtered to remove cells, diluted, and used as a growth medium. This filtrate in various combinations with fatty acids and inorganic phosphate, was seeded with bacteria from the operating reactors, added to flasks, and incubated at 27°C for 24 or 96 hours. Experimental results were evaluated by visual inspection for turbidity (growth in the flasks) due to the lack of a suitable performance parameter for cell growth.

Regrowth, as evidenced by turbidity in the flasks, occurred after 24 hours in the flasks supplemented with fatty acids. There was no visual difference between flasks containing fatty acids only and fatty acids and inorganic phosphate. After 96 hours regrowth occurred in some of the flasks without fatty acids. The presence of phosphate did not visually affect the amount of regrowth in any of the flasks. Other flasks, treated identically, showed no growth in 96 hours. These results suggest that the low reduction of COD by the two-stage CSTR system studied here, is limited by the presence of biorefractory compounds rather than by toxicity or nutrient limitations. Quantification of the results and further studies of this nature will require the development of a protein assay to determine cell mass. Work has been initiated to develop such a method.

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