Title

MONTHLY PROGRESS REPORT FOR JULY: SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATERS

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August 12, 1980

TO: Charles Grua

FROM: Richard Sakaji, Christian Daughton, and Phyllis Fox

RE: Monthly Progress Report for July
Spent Shale as a Control Technology for Oil Shale
Retort Waters
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TASK 1. ANALYTICAL METHODS DEVELOPMENT

Knowledge of the accuracy, precision and applicability of analytical techniques that are used to assess the performance of retort water treatment processes is crucial for valid assessments. We are continuing to develop and validate the protein assay for quantitation of microbial growth in retort water and the use of C-18 cartridges to fractionate retort water and to demonstrate the applicability of the COD test to retort water.

COD Test

We had previously demonstrated that the COD test was reproducible for retort water (RSD < 5%). However, its accuracy, or ability to estimate theoretically oxidizable (i.e., total) organic matter, remains questionable because of the presence of classes of chemical compounds such as nitrogenous hetercyclics, which could be resistant to dichromate oxidation. Assuming that the determination of organic carbon (OC) via combustion and infrared detection is a better estimator, we plan to obtain OC:COD ratios for untreated raw retort water and for C-18 fractionated retort water. If the non-COD yielding compounds are selectively partitioned and retained by the C-18 stationary phase (or alternatively, selectively passed with the effluent), then a change in the OC:COD ratio will be apparent. Such a change would conclusively demonstrate the presence of non-COD-yielding compounds.

We have continued the investigation of C-18 Sep Pak cartridges for the fractionation experiments. The sorptive capacity of a C-18 cartridge for organic compounds will determine the volume of retort water that can be applied to obtain a uniform effluent. This value will also be required to determine the maximum sample size for oil and grease samples in our future studies.

Retort water samples vary qualitatively and quantitatively in organic carbon because of the various retorting processes and within-run variability. Therefore, we determined the profiles of COD versus milliliters of C-18 effluent for 150-ton (run #13), S-55, and Oxy-6 retort water. To ensure equilibrated partitioning processes within the C-18 cartridges, the samples were pumped at 1 ml/min through gas-tight syringes by a variable-speed precision syringe pump. Triplicate 20-ml samples were fractionated by methanol-wetted/water-rinsed cartridges. The initial 2 ml of effluent were collected in 1-ml portions. The subsequent 18-ml were collected in 0.75-ml portions.

A graph of COD versus effluent fraction volume for each water was characteristically different, but each water gave an initial increase in COD, followed by a plateau, and finally another increase (Figure 1). The initial increase in COD was presumedly caused by dilution of the 400 µl of retained water from activation of each cartridge and by the partial retention and subsequent elution of weakly-partitioned compounds. The latter possibility is evidenced by the migration of a brown band through each cartridge. The plateau area would correspond to the elution volume of an equilibrated partitioning process, representing constant leakage of poorly retained compounds and total retention of hydrophobic materials. The final increase in COD was caused by breakthrough of compounds that had been retained by the stationary phase.

Each water had a plateau area that corresponded to a different elution volume range. This would necessitate prior knowledge of the cartridge sorptive capacity for a given water in order to sample in this area of minimal COD change. However, an unforeseen result of this study was the ability to generate a "fingerprint profile" of COD versus effluent volume that was highly characteristic and reproducible for each water. This capability could possibly find utility in "typing" retort processes.

A surprising result was the necessity of pre-wetting each cartridge with methanol, followed by a water rinse. Without activation, essentially no retention of COD was found.

Experiments planned include determination of the effects of flow rate on COD/effluent profiles and the number of times that the cartridges can be reused. We can then proceed with the fractionation studies for demonstration of the applicability of the COD test to retort water.

Protein Assay

The measurement of cellular biomass is necessary for investigation of problems in biological treatment of retort water. Because of the intense and variable color, abiotic particulates and tarry materials of the retort water, the measurement of turbidity and suspended solids are not sufficient for estimation of cellular biomass.

Our investigation of the Bradford dye-binding protein assay for protein measurement has continued. Sufficient cellular material for the detection limit of the assay was obtained by the concentration of cells onto 47 mm x 0.4 μm pore diameter polycarbonate membrane filters. This step also separated the extracellular fluid from the cells, preventing interference from the colored retort water.

The cells that were collected on membranes required alkaline digestion (0.25 N NaOH) at 100°C to liberate their constituent proteins. Polycarbonate membranes only yielded interferences for the assay after 30-45 minutes of digestion. Membranes made from mixed cellulose esters gave substantial interference after limited digestion. We found that the digestion was mostly easily done in Teflon-lined screw-capped culture tubes placed in a fluidized sand bath. This is made easier to operate than a boiling water bath, and it has the great advantage of allowing refluxing inside the tubes since their tops remain at less than 50°C. The tubes must be sealed to prevent loss of the digestion mixture volume.

Replicate volumes of a bacterial culture were filtered and the membranes were digested for 0, 5, 10, 20, 30, 45, and 60 minutes. The protein assay gave a maximum absorbance between 10 and 20 minutes. The 0, 5, and 60 minute samples gave much lower values, presumably because of insufficient digestion and excessive protein denaturation, respectively.

A minor disadvantage of the dye-binding assay is the interference of alkalie, which necessitates neutralization of the digested samples prior to dye addition. We will therefore investigate the Lowry protein assay, which has the disadvantage of less sensitivity than the dye-binding assay when standardized against bovine serum albumin. A major disadvantage of the dye-binding assay is the particulate nature of the color complex, which causes erratic absorbance readings when the micro-flow-through cell is used in the spectrophotometer instead of the more cumbersome currettes.

An advantage of cell collection on membrane filters is the ability to estimate dry cell mass prior to digestion. Turbidity can also be correlated with protein concentration. This will allow us to non-destructively monitor growth in the planned enrichment culture experiments that will be started when the protein assays are developed.

TASK 5. SYSTEM STUDIES

Studies have been initiated to investigate steam stripping of gas condensate and retort water. A bench-scale unit (Figure 2) has been set up and is being used to determine the steam-to-water ratio from Henry's Law constant. Acidity dissociation constants were measured for ammonium and carbonic acid over the range 20 - 95°C to determine the conditions of temperature and pH required to simultaneously steam strip them. Above about 95°C, there exists such a pH range that widens with further increase in temperature, suggesting use of a pressurized superheated process. Design of such a stripper-condenser unit was completed (Figure 3) and fabrication initiated. Fabrication of an unpressurized stripper unit was completed for evaluation of process efficiency up to 100°C.

MISCELLANEOUS

Christian Daughton and Rick Sakaji attended the Colorado School of Mines Oil Shale course in Laramie, Wyoming from July 28 - July 30th. Two new research technicians were hired to replace graduate students who completed their studies.

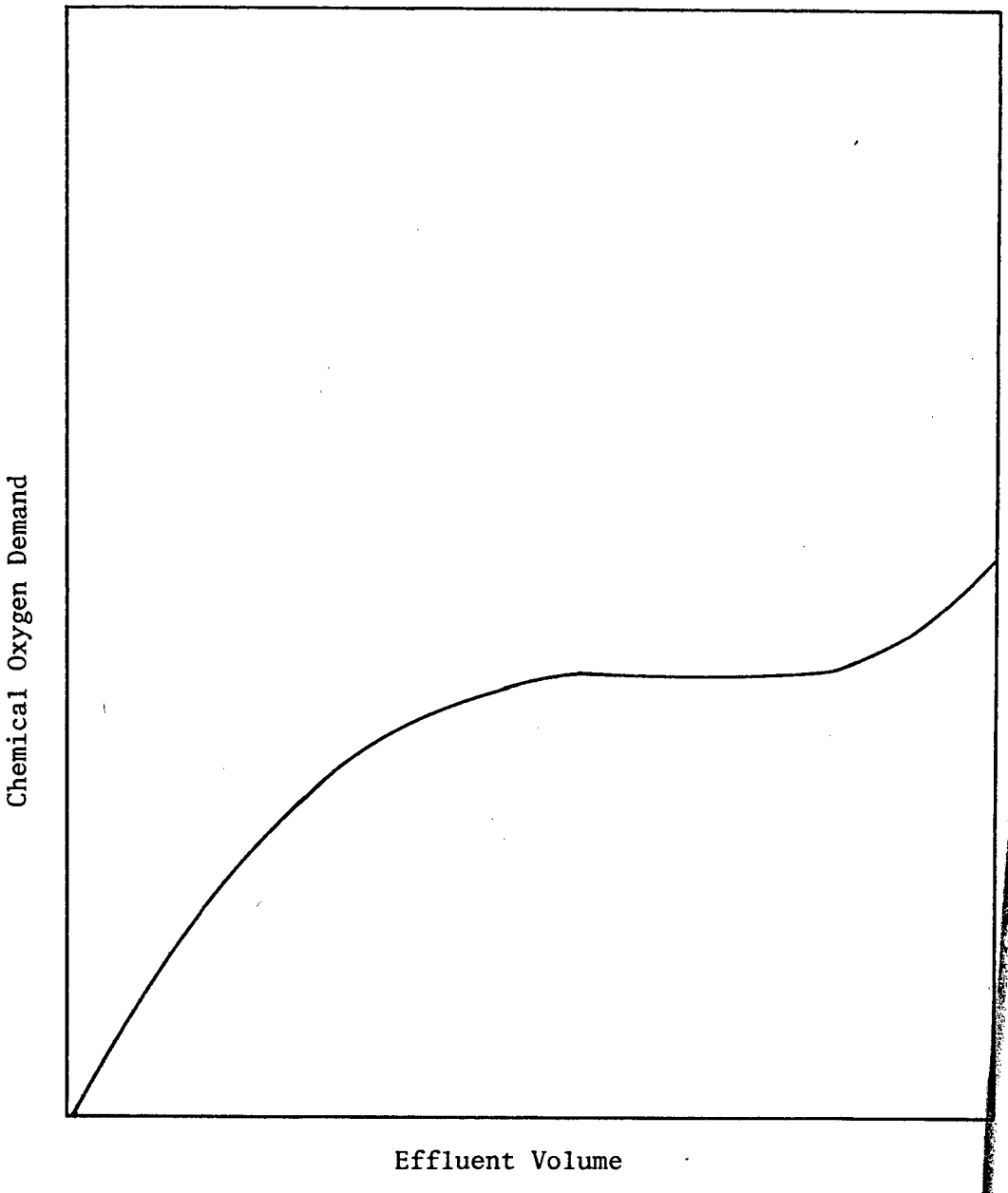

Figure 1. Generalized breakthrough curve for C-18 Sep Pak

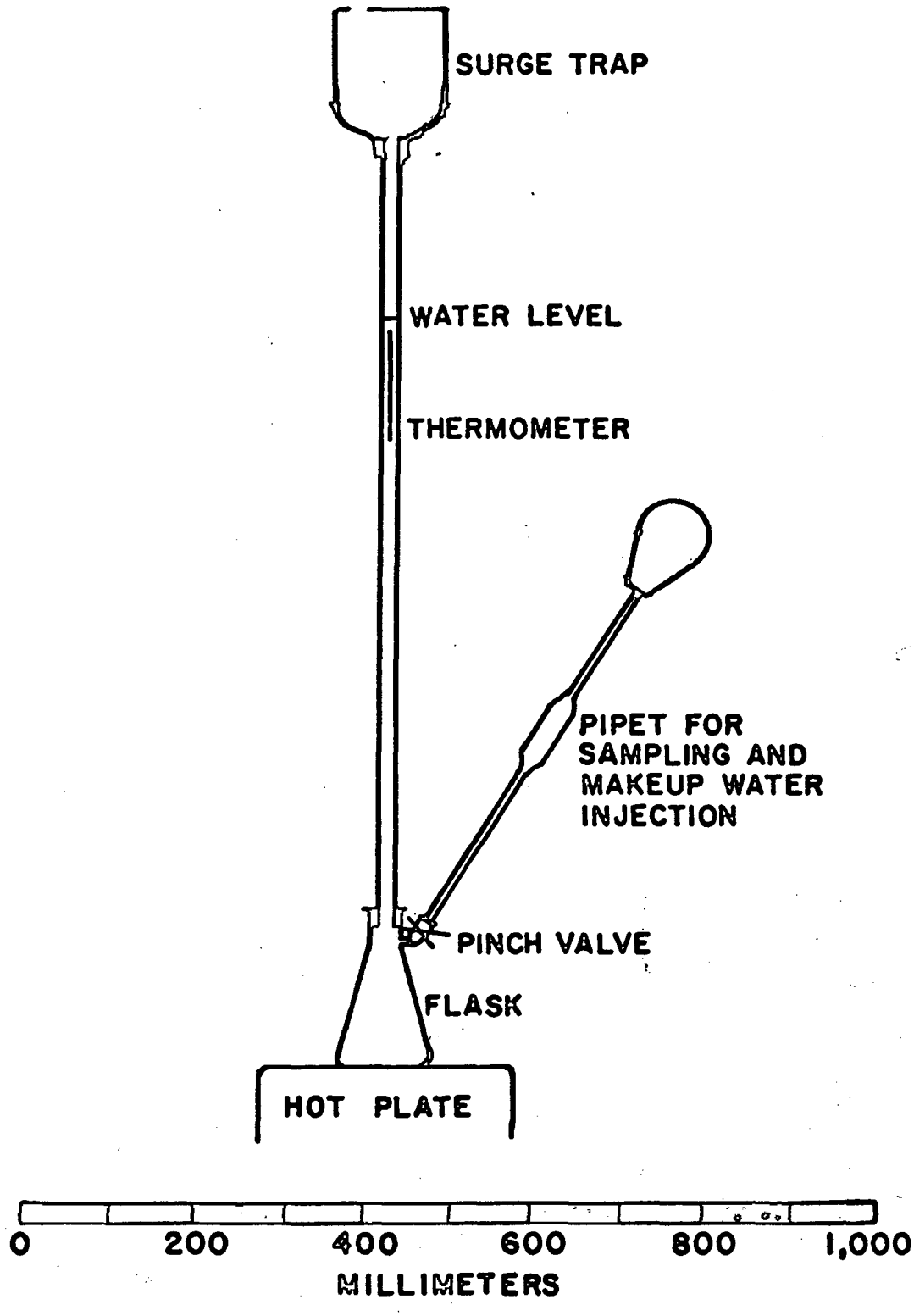

Figure 2. Bench-Scale Apparatus for Determination of Henry's Law Constant for Steam-Water Systems

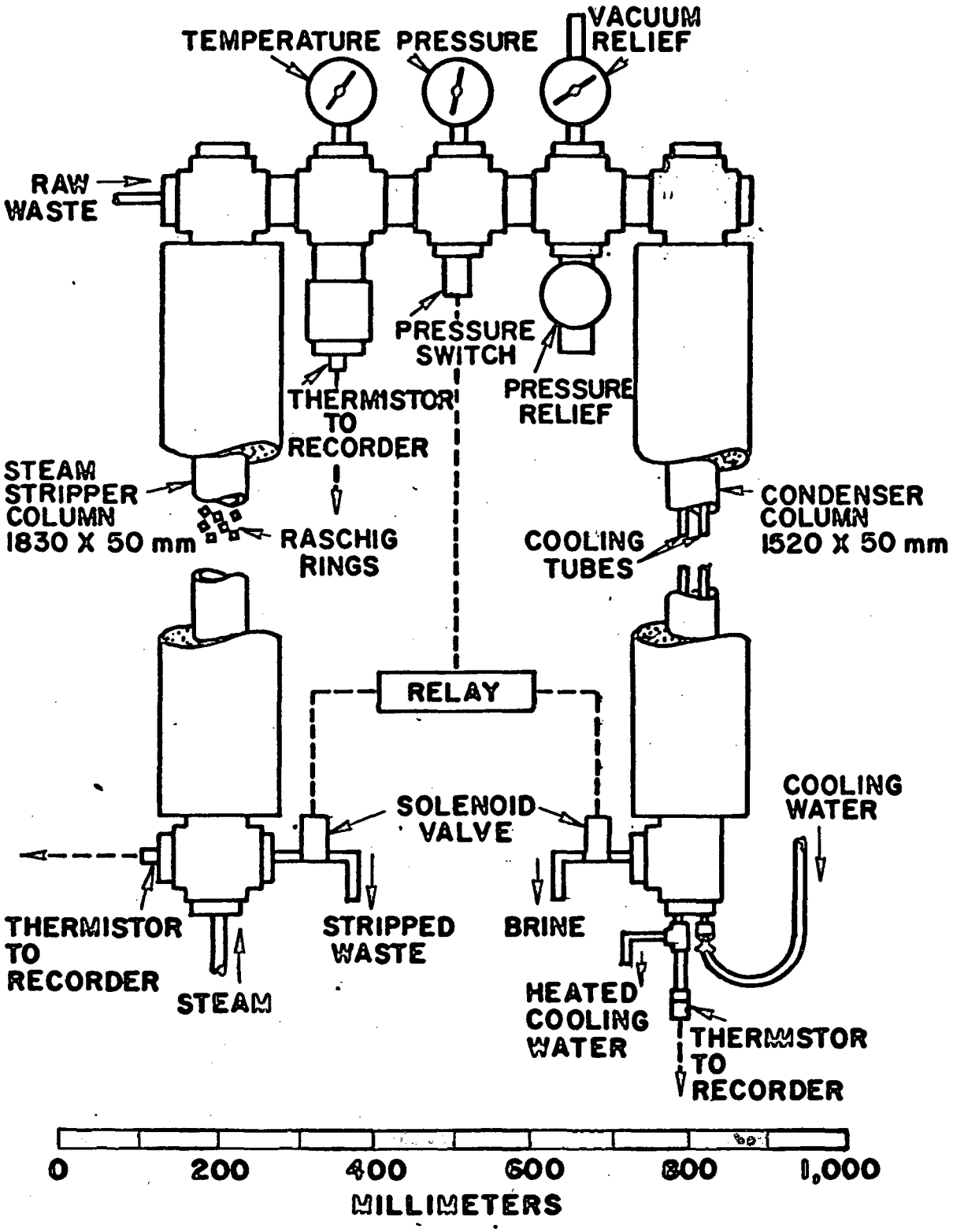

Figure 3. Pilot Scale Steam Stripper Apparatus, Capable of Operating at up to 100 psi and 160C.

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