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CHEMICALLY ASSISTED *IN SITU* RECOVERY OF OIL SHALE

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The Department of Chemical Engineering

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Boulder, Colorado.

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Reporting Period: April 1, 1991–June 30, 1991.

Objectives:

The objective of this work is to investigate, in the laboratory, the parameters associated with a chemically assisted *in situ* recovery procedure, using hydrogen chloride (HCl), carbon dioxide (CO_2), and steam (H_2O), to obtain data useful to develop a process more economic than existing processes and to report all findings.

Summary of Technical Progress:

This report covers the status of DOE project (Award Number DE-AC22-89BC14479; UCB Account Number 153-6529), specifically the milestone schedule status is reported. The research project supported is the investigation of a chemically assisted *in situ* oil shale extraction method, involving lower temperature and pressure than existing procedures, with the goal of developing an economically viable recovery method . The technical progress of the project is reported. The project status is that previously designed modifications to the project were completed. The Data Acquisition Processing board was installed and configured. Experiment #5 was run under previously-determined, optimal conditions. A few problems were found in the process design, and corrections were designed. A design for an on-line, real-time, gas-composition measuring device is being considered. The new epoxy performed satisfactorily.

The modifications to the original process were completed when the metal o-rings arrived. The process then was capable of running the reaction at the optimal conditions: 325 °C and 6 bar.

The Data Acquisition Processing (DAP) board, purchased from Microstar Laboratories, arrived and was installed. Because the DAP board has its own CPU, real-time operating system, and many on-board,ROM-based commands, set-up is extremely quick and easy. The DAP board has performed very well. There are only two deficiencies with the data logging and plotting software that was included with the DAP board purchase. First, plotted data that has scrolled off the computer screen can not be recovered and reviewed. Second, the program's disk logging function has no averaging capability. The later is a serious problem because of the amount of data generated during one experiment. Experiment #5, which run for 53 hours yet was cut short by at least 48 hours, generated over 5 Megabytes of data with the DAP board providing data averaged over 3 seconds. The DAP board can be programmed to average data over any time period, but it is necessary to be able to observe the process data at least every five seconds. Furthermore, computation of the amounts of gases flowed into the reactor gas chamber requires that the pressures be available (on disk) every second. A solution is to average over a period of time in which data is relatively constant. When data changes significantly, it is saved to disk along with the current time. Such a program is being written while ordered equipment is arriving.

Reaction #5 was run for 53 hours before breakthrough occurred. Breakthrough was indicated by a sharp pressure rise on the down-stream-side of the core, which was open to a 1.5 Liter collection vessel. Unfortunately coincident to breakthrough was the total failure of a Swagelok-to-Cajun-VCR adaptor union, forcing immediate shutdown before any enhanced oil recovery technique could be attempted. In spite of this, a small amount of oil was observed in the tubing on the core side of the reactor (which is physically beneath the core). The failure of the union cut short the experiment by about 40 hours. After breakthrough it was planned that the reactant gases would be flowed through the core for approximately 24 hours. Then steam flooding would be used to force the freed oil out of the core matrix for approximately 24 hours.

The failure of the union, made of SS316 stainless steel (which is rather immune to HCl attack even at 325 °C), is believed to have been triggered by the failure of a thermocouple (TC) that had its tip located within the fitting. The TC sheath is of SS304 type stainless steel, which is rather susceptible to HCl at 325 °C. The failure of the TC sheath released the contents of the TC to the reactor. The TC filler reacted with the reactant gases in a highly exothermic reaction. The local temperature extreme, which may have exceeded 1000 °C, greatly accelerated the attack of HCl on the fitting and subjected the fitting to thermal stresses much in excess of its capabilities. There are a number of indications to support the above conclusions. The primary is that shortly before the TC and union failed, the TC indicated a very swift rise in temperature, from approximately 200 °C (the steady average over 48 hours)[1], to above 600 °C linearly, to 1370 °C (DAP TC full scale) exponentially. The second indication is that failed TC is missing 5 cm of sheath from the tip, but the Chromel and Alumel TC wires remain intact (but not the TC junction). The use of SS304-sheathed TC's was a design flaw, and the TC's need to be replaced. Inconel-sheathed TC's have been ordered.

The second design flaw would severely limit the amount of shale oil freed by chemical reaction that can be removed from the reactor. There are two design modifications. The first is a large reduction in the internal diameter of the tubing that will carry the oil vertically from the bottom of the reactor up and out of the sand bath. A large diameter tubing would not be able to carry the liquid from a gas-liquid mixture vertically because the gas will bubble through the liquid. A small diameter tube will prevent this. The current tubing is 1/4 inch; it will be replaced with 1/8 inch tubing with 0.049 inch walls, giving an 0.027 inch ID.

The second design modification is the addition of a Pyrex glass cyclone that will separate shale oil from spent reaction gases. The cyclone will be placed as close to the reactor as possible to limit the possibility of oil clogging tubing. Pyrex will allow visual observation of the collected oil, yet will not require protection from the hot oil (as any polymer would).

A third problem was observed in the silicon rubber sealant. Silicon rubber sealant was used to seal the pipe threading used to join the Cajun VCR joint to both the top and bottom flanges of the reactor. After cool down, it was observed that what little of the silicon rubber at top flange remained

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[1]The union and TC tip were located approximately 20 cm above the fluidized-sand-bath's surface.

was brittle, while the silicon rubber on the bottom flange was intact and still flexible. It is concluded that silicon rubber sealant is able to handle high temperatures, but is quite susceptible to the reactant gas mixture at high temperature. The pipe fitting-to-Cajun VCR adaptor has been replaced by welding 1/4 inch tubing directly to the top flange.

Quarter summary: All modifications previously planned where completed and a reaction experiment was run. A couple design flaws were discovered, improvements were designed, and all parts are expected in the first week of July. Experiment #6 is expected to run the following Monday. Barring further mishap, experiments will be run one each week thereafter. The project is behind schedule , but the project is well positioned to make significant and considerable progress.

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