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DOE/BC/14479--T2

CHEMICALLY ASSISTED *IN SITU* RECOVERY OF OIL SHALE

DE-AC22-89BC14479

The Department of Chemical Engineering

The University of Colorado at Boulder

Boulder, Colorado.

Contract Date: September 5, 1989.

Anticipated Completion Date: September 4, 1991.

Government Award: $91,967.

Principle Investigator: W. Fred Ramirez.

Project Manager: W.D. Peters.

Reporting Period: October 1, 1991 - December 31, 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 the solutions to the problems discussed in the third quarter status, were found

to function satisfactorily. Future needs have been considered, and appropriate equipment and instrumentation changes have been designed.

Only one experiment was performed this quarter, with some improvement over the previous experiments. The increase in shale oil recovery followed directly from the changes discussed last quarter, but the improvement could have been larger with wider-spread implementation of the changes. Equipment was purchased to rectify the need, and will be installed shortly. Further, a minor change in the design was necessary to account for the brittleness of high temperature electrical resistance heating tapes.

The focus of the work this quarter has been on the development of computer software to enable the use of on-line parameter identification, the design of the instrumentation necessary to adequately observe the system, and the design of a continuous gas mixer to implement the experiment.

In order to identify the various parameters for the simulation model, it is necessary to know the gas concentrations within the gas chamber and exiting the reactor in real-time. Thus an on-line instrument is necessary to measure the concentrations of HCl and of H_2O or CO_2 on-line (the third may be estimated with an Equation of State (EOS) by assuming there are no other gases present). The first choice of instruments, gas chromatography, is not feasible. The design is based on gas-phase–absorption–near-infrared (IR) spectroscopy.

While a gas chromatograph would theoretically perform as required, in practise the damage caused to the thermal conductivity detector's (TCD) filaments by acid etching would be problematic and expensive at best. A TCD is necessary because the more commonly used flame-ionization detector (FID) is incapable of detecting either H_2O or CO_2. To further

complicate matters, any chemical means of striping out HCl would also strip out H_2O and CO_2.

The infrared spectroscopy method has been used to measure HCl concentrations to several parts per million[1,2] with a 100 mm optical path. All three gases have distinctive infrared absorptions. However, infrared sources and optics are expensive, and difficult to use. Fortunately, quantum effects allow the use of harmonic overtones of the specific infrared frequencies that are in the near-infrared domain. Near-infrared diode lasers are cheap, easy to control, and reliable and ordinary optics may be used. Figures 1, 2, and 3 show the near-IR spectrometer design.

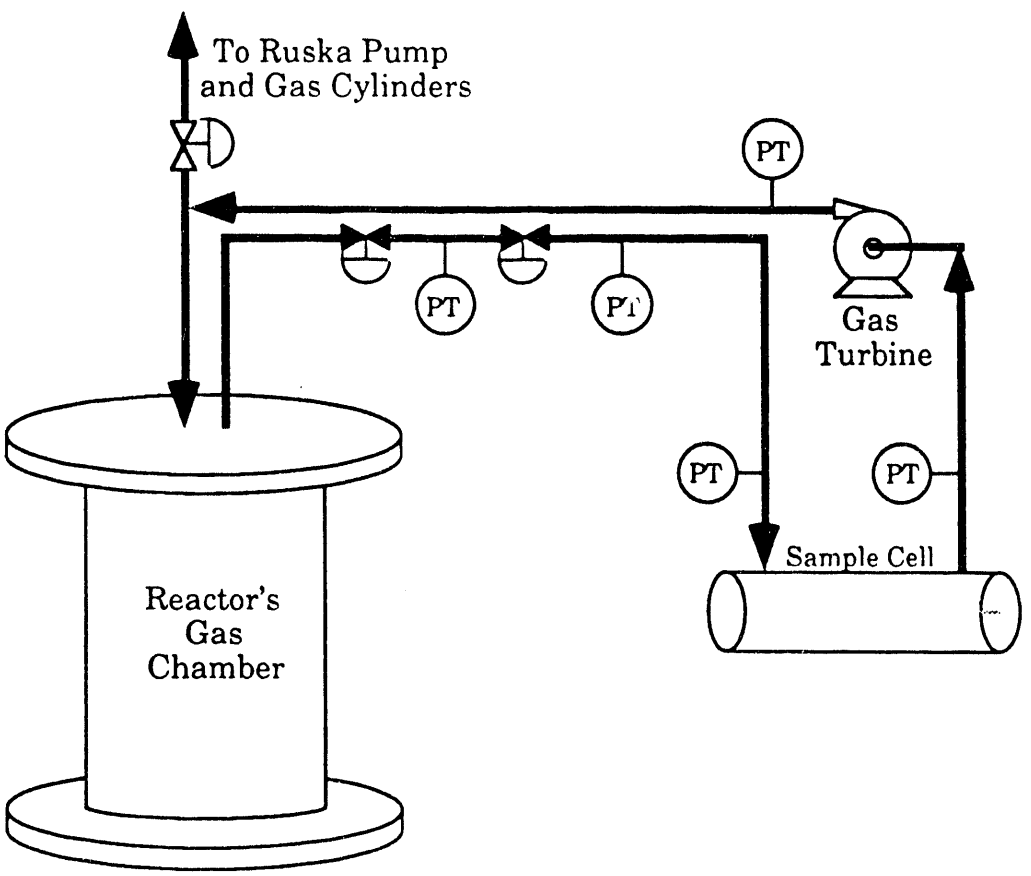

Figure 1. Sample Loop Diagram.

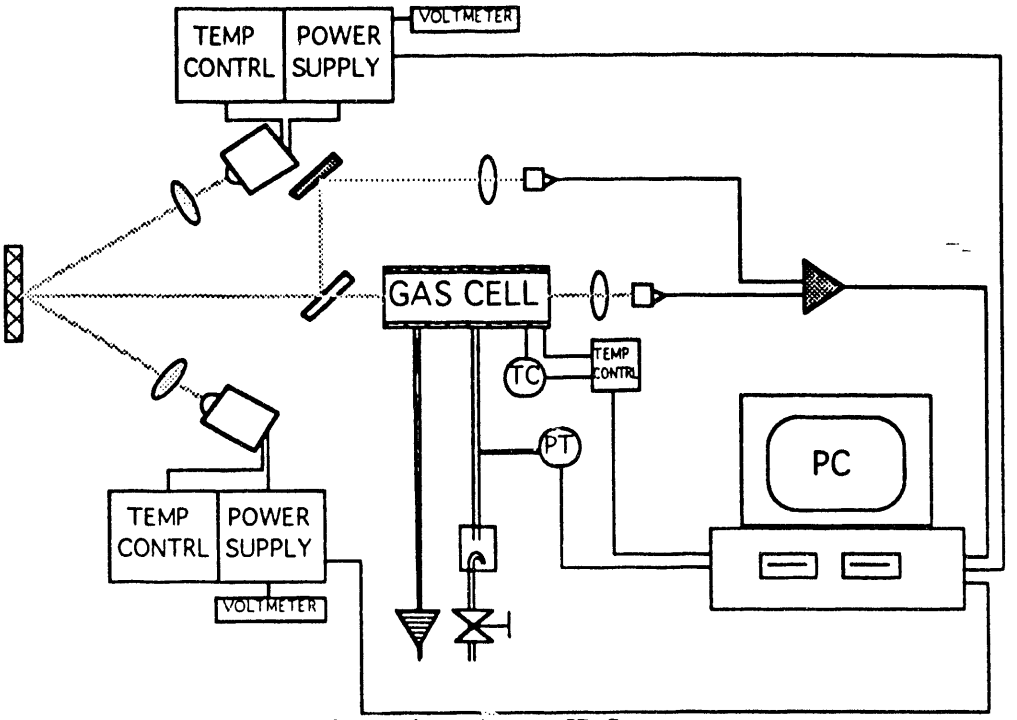

Figure 2. Design of near–IR Spectroscope.

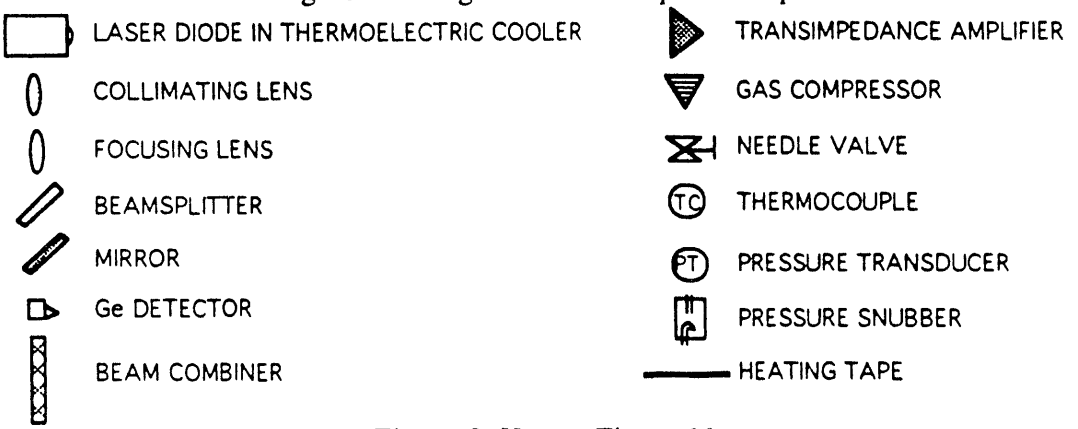

Figure 3. Key to Figure 11.

In order to quickly recover shale oil from the marlstone, the fissures within the marlstone will be used to facilitate reactive gases transport with convective flow instead of diffusive transport. Convective flow requires equipment to provide steady state flow and controlled mixing of HCl, H_2O, and CO_2. The equipment to achieve this has been designed, and is shown in Figure 4.

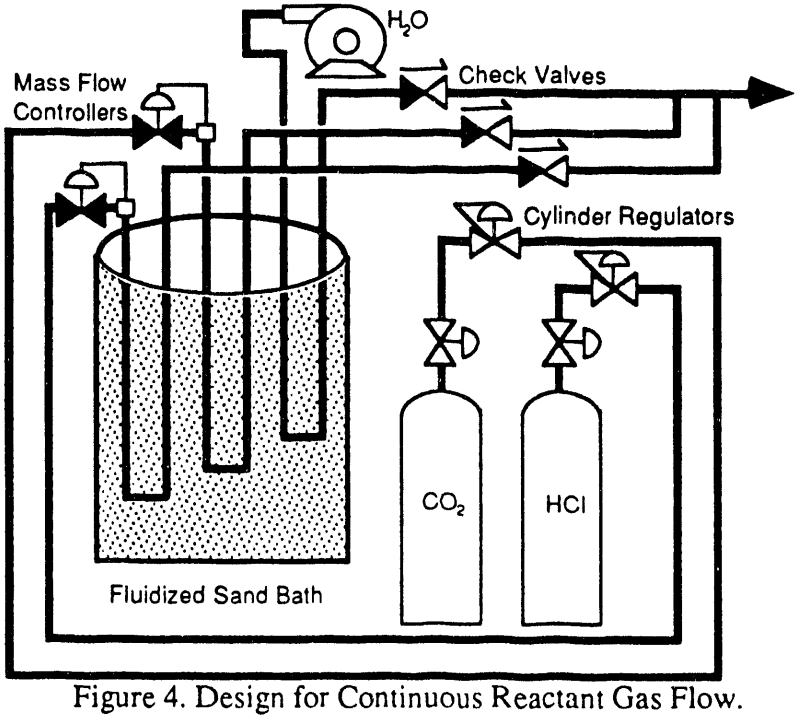

Figure 4. Design for Continuous Reactant Gas Flow.

Quarter summary: The project is behind schedule, but the project has been shown to be partially successful. Parts purchasing has begun for both continuous flow gas mixer and the near-IR spectrometer. The project is well positioned to make significant and considerable progress. In particular, experience with reacted oil shale is necessary to successfully recovery oil of reasonable viscosity—the project is now prepared and capable of reacting oil shale.

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[1]Alan C. Stanton and Joel A. Silver. *Measurements in the HCl 3←0 Band Using a Near-IR InGaAsP Diode Laser.* Applied Optics, **27**(24), 5009 (1988).

[2]Motoichi Ohtsu, Hiroki Kotani, and Haruo Tagawa. *Spectral Measurements of NH3 and H2O for Pollutant Gas Monitoring by 1.5 μm InGaAsP/InP Lasers.* Jpn. J. Appl. Phys. **22**, 1553 (1983).

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