

75

# **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, 1993.**

**Government Award: \$91,967.**

**Principal Investigator: W. Fred Ramirez.**

**Project Manager: Ernie Zuech.**

**Reporting Period: April 1, 1993 - June 30, 1993.**

## **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<sub>2</sub>), and steam (H<sub>2</sub>O), 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 progress is being made towards being able to run meaningful experiments.

**MASTER**

da

The manufacturer of the data acquisition processor (DAP) hardware released the first version of the DAP device driver for OS/2. After the submission of the previous Quarterly Report, it was discovered that the new version of the device driver required that the data acquisition software be updated and recompiled to be used with the new device driver. Unfortunately, the software library supplied with the the new device driver could not be used with compiler possessed by the researchers. After several months, the exact cause of the trouble was finally diagnosed. The manufacturer was contacted and a solution was devised.

The problem was that IBM's C Set/2 compiler has undergone significant alterations between the version possessed by the researchers and the version required by the software library. Specifically, the software library required a certain compiler function, which had been (slightly) renamed when the compiler was updated. Recompiling the software library for use with the new version of the compiler (after the manufacturer supplied the source code) fixed the function name mismatch. The base of the data acquisition program is now functional. The strip-chart style plotting routine of the data acquisition program is nearly functional.

Communication with Hewlett-Packard (HP) revealed that the thermal conductivity detector (TCD) installed in the gas chromatograph (GC) has platinum filaments, not tungsten filaments. Furthermore, a HP chemist asserted that the platinum filaments should resist any corrosion from the HCl present in the gas samples.

Professor John Falconer of the Department of Chemical Engineering at the University of Colorado-Boulder confirmed this when he stated that in the experience of his research group, small amounts of HCl do not cause corrosion of the platinum filaments. Professor Falconer was not able to confirm the

corrosion resistance of platinum filaments in face of higher concentrations (percents of HCl, which is what we use).

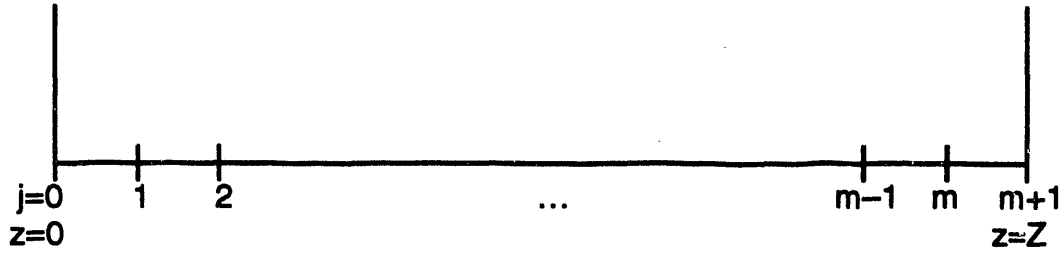
If the filaments do succumb to HCl corrosion, then nickel filaments are available for \$1200. The nickel filaments are reportedly even more corrosion resistant, but more expensive than the platinum filaments. Thus the GC with the TCD will suffice to monitor the gas concentrations within the gas chamber and in the exit stream. The near-infrared spectrometer previously designed and presented is thus unnecessary.

Before experiments may begin, the GC must be tested and calibrated. Then it needs to be installed into the experiment with a sample loop and sample valve. Because it is desirable to have the data acquisition hardware control the GC, the possibility of an actuated sample valve will be examined.

The graduate student is preparing for his comprehensive examination.

A recent literature search revealed that the pyrolysis reactions for modified *in situ* retorts (which are the most relevant to the chemically assisted *in situ* recovery method) are rate limited, instead of mass transport limited. Because the models previously developed by the researchers assumed that the reactions would be mass transport limited, it is necessary to modify the models.

The homogeneous breakthrough model previously derived and presented assumed that the reactions were diffusion limited. For finite differencing purposes, the one-dimensional diffusion problem is put onto a grid. The spatial variable is  $z$ , and the node index  $j$  runs from 0 to  $m+1$ .



The Stefan-Maxwell equation for ordinary diffusion of ideal gases is

$$\nabla x_i = \sum_{h=1}^{nc} \frac{1}{c D_{i,h}} (x_i N_h - x_h N_i)$$

where  $x_i$  is the mole fraction of component  $i$ ,  $N_i$  is the molar flux of component  $i$ ,  $c$  is the molar concentration of the gas mixture,  $D_{i,h}$  is the binary diffusivity of component  $i$  through component  $h$ , and  $nc$  is the number of components.

By discretizing the variables on to the grid, using the second order central difference formula for the first derivative, and assuming that the total molar concentration and the total molar flux of the gas mixture are both constant with respect to  $z$ , the Stefan-Maxwell equation becomes:

$$\frac{x_{i,j+1}^{(k)} - x_{i,j-1}^{(k)}}{2 \Delta z^{(k)}} = \sum_{h=1}^{nc} \frac{1}{c^{(k)} D_{i,h}} (x_{i,j}^{(k)} N_{h,j}^{(k)} - x_{h,j}^{(k)} N_{i,j}^{(k)}) \text{ for } j \in [1, \dots, m] \quad (1)$$

where  $x_{i,j}$  is the mole fraction of component  $i$  at node  $j$  (the superscript “(k)” indicates during time step  $k$ ),  $N_{i,j}$  is the molar flux of component  $i$  at node  $j$ .

Equation 1 is subject to two constraints:

$$\sum_{h=1}^{nc} x_{h,j}^{(k)} = 1 \quad (2)$$

$$\sum_{h=1}^{nc} N_{h,j}^{(k)} = N_t^{(k)} \quad (3)$$

The continuity equation in one dimension ( $z$ ) without any homogeneous reaction is:

### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

$$\frac{\partial c_i}{\partial t} = - \frac{\partial N_i}{\partial z}$$

where  $c_i$  is the molar concentration of component  $i$  and  $t$  is the temporal variable. By discretizing the continuity equation and using the implicit Euler equation, the above becomes:

$$x_{i,j}^{(k)} = x_{i,j}^{(k-1)} + \frac{\Delta t}{2c \Delta z} \left( N_{i,j+1}^{(k)} - N_{i,j-1}^{(k)} \right) \text{ for } j \in [1, \dots, m] \quad (4)$$

Equations 1–4 apply to the nodes where diffusion occurs. At the outside nodes ( $j=0$  and  $j=m+1$ ) special conditions apply. At  $j=0$ , the mole fractions are identical to the mole fractions of the gas mixture in the gas chamber,  $y_i$ .

$$x_{i,0}^{(k)} = y_i^{(k)} \quad (5)$$

subject to the constraint of Equation 2. Equation 1 is modified

$$\frac{x_{i,1}^{(k)} - x_{i,0}^{(k)}}{\Delta z^{(k)}} = \sum_{h=1}^{nc} \frac{1}{c^{(k)} D_{i,h}} \left( x_{i,0}^{(k)} N_{h,0}^{(k)} - x_{h,0}^{(k)} N_{i,0}^{(k)} \right) \quad (6)$$

subject to the constraint of Equation 3. The continuity equation is irrelevant here.

At the node  $j=m+1$ , the conditions are determined by the heterogeneous reaction kinetics. For simplicity, it is assumed that the reaction kinetics are first order with respect to the molar concentration of HCl at that node. Thus the molar fluxes at the node  $j=m+1$  are

$$N_{i,m+1}^{(k)} = - v_i k c x_{i=\text{HCl},m+1}^{(k)} \quad (7)$$

where  $k$  is the rate constant and  $v_i$  are the stoichiometric constants. The total molar flux is computed from Equation 7 (or is constrained by the below equation).

$$N_t^{(k)} = \sum_{h=1}^{nc} N_{h,m+1}^{(k)} = - k c x_{i=\text{HCl},m+1}^{(k)} \sum_{h=1}^{nc} v_h \quad (8)$$

Equation 1 is again modified

$$\frac{x_{i,m+1}^{(k)} - x_{i,m}^{(k)}}{\Delta z^{(k)}} = \sum_{h=1}^{nc} \frac{1}{c^{(k)} D_{i,h}} \left( x_{i,m+1}^{(k)} N_{h,m+1}^{(k)} - x_{h,m+1}^{(k)} N_{i,m+1}^{(k)} \right) \quad (9)$$

subject to Equation 2.

When Equations 1 and 4 are used only for  
 $i \in [1, \dots, nc-1]$

and Equations 2 and 3 are incorporated, then the system of non-linear equations (Equations 1–9) is well determined and solvable, provided values for  $\Delta z$ ,  $c$ ,  $y_i$ ,  $D_{i,h}$  and  $k$  are known *a priori*. Computed code to solve this system of non-linear equations has been implemented in FORTRAN on an IBM RS/6000. A meaningful summary of the results is as yet unavailable.

Quarter summary: The equipment will be ready as soon as the GC is ready, the pressure transducers are recalibrated, and the data acquisition software is complete.

**END**

**DATE  
FILMED**

**9 127 193**

