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PHYSICS OF OIL SHALES
A PROGRAM OF THEORETICAL AND EXPERIMENTAL STUDIES

Quarterly Progress Report
September 21, 1982-January 1, 1983
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QUARTERLY REPORT

Kinetic Scheme for Insitu
Electromagnetic Heating of Oil Shale

An abundance of models for modified insitu oil shale retorting have been developed in recent years; the most notable being those of Braun (1981) and Travis et al. (1982). These models require some sort of rubblizing to take place before retorting begins. Bridges et al. (1980) have recently reported on experimental results of RF heating of un-rubblized shale. Their results indicate that it is possible to perform true insitu retorting when an appropriate geometry of electromagnetic heating antennas are placed in the shale. As the shale heats the porosity increases, permitting the evolved gas of the pyrolysis to drive the oil to recovery wells. Experimental results indicate that large scale commercial retorting should be possible with this technique.

In this report we present the mathematical foundations of the physical processes for true insitu retorting by electromagnetic heating.

The modeling of insitu retorting via electromagnetic heating requires a mathematical formulation of the problem and empirical relations for such quantities as thermal conductivity, heat capacities, rate constants, permeabilities, and viscosities. The mathematical formulation consists of equations for conservation of species, saturations, capillary pressure, momentum and energy. These equations constitute a system of coupled non-linear partial differential equations which must be solved numerically. The empirical relations used for a description of the kinetics are primarily those described by Braun (1981) and Sresty (1982). The permeability relations are derived from the data of Sresty. Thermal conductivity and heat capacity data are primarily from Braun (1981) and Dubow et al. (1980). Viscosity data is extracted from the work of Christenson (1980).

The RF heating technique requiries very low temperatures for pyrolysis (300°C - 400°C); because of this low temperature the decomposition of carbonate minerals is very small and can be neglected in the model. Additionally, reactions of evolved carbon with evolved gases is also minimal [see Travis (1982)]. Combustion and cracking of oil vapors are also expected to be small.

We consider a system composed initially of organic and inorganic materials. The organics consist of kerogen, carbon and organic hydrogen; the inorganics consist of a bulk mineral component and bound water. As the shale is heated the kerogen and organic hydrogen yield gases and oil, some of the oil being gaseous the rest a liquid. Following Braun (1981) we assume for kerogen pyrolysis the following products:

$$
\begin{aligned}
&[1\text{Kg. Kerogen}] \rightarrow [f_1 \text{ Kg. carbon}] + [f_2 \text{ Kg. organic hydrogen}] \\
&+ [f_3 \text{ Kg. oil}] + [f_4 \text{ Kg. CO}] + [f_5 \text{ Kg. } CO_2] + [f_6 \text{ Kg. } H_2] \\
&+ [f_7 \text{ Kg. } CH_4] + [f_8 \text{ Kg. } CH_x] + [f_9 \text{ Kg. } H_2O]
\end{aligned}
$$

where CH_x are unknown gases and f_i are stochimetric coefficients ($\sum_{i=1}^{9} f_{(i)} = 1$).

$f_1 = .1664$
$f_2 = .0045$
$f_3 = .6585$
$f_4 = .0106$
$f_5 = .0390$
$f_6 = .0042$
$f_7 = .0189$
$f_8 = .0601$
$f_9 = .0378$

Additionally carbon is formed by coking, which is a function of heating rate and residence time of the oil in the shale. Organic hydrogen decomposes to form hydrogen gas. The equations which describe the mass balance of the organics are:

$$\frac{dU_{(K)}}{dt} = -K_{(K)}U_{(K)}, \quad U_{(K)}(t=0) = U_{(K)}^{0}$$

$$\frac{dU_{(H)}}{dt} = f_2 K_{(K)} U_{(K)} - K_{(H)} U_{(H)}, \quad U_{(H)}(t=0) = U_{(H)}^{0}$$

$$\frac{dU_{(C)}}{dt} = f_1 K_{(K)} U_{(K)} + \frac{.00365\, f_{21}\, f_3\, K_{(K)}\, U_{(K)}}{\sqrt{R_T}}, \quad U_{(C)}(t=0) = 0$$

where (K), (H), (C) denote kerogen, hydrogen and carbon. $U_{(i)}$ denotes densities of substances in Kg. per cubic meter of shale; $K_{(i)}$ are the rate coefficients;

$$K_{(K)} = 2.81 \times 10^{13} e^{-\frac{26390}{T}} \left(\frac{1}{\text{sec}}\right)$$

$$K_{(H)} = 10.7 e^{-\frac{10190}{T}} \left(\frac{1}{\text{sec}}\right)$$

R_T is the heating rate. The bound water is converted to gas according to:

$$\frac{dU_{(W)}}{dt} = -\frac{U_4^{\circ} R_T}{T_H - T_L}, \quad U_{(W)}(t=0) = U_{(W)}^{0}$$

where U_W° is the initial water density and T_H, T_L are constants. The inorganics are assumed to be unchanged by heating so that:

$$\frac{dU_{(Inorg)}}{dt} = 0$$

The porosity is a function of the densities of organics. Initially the porosity is zero. as chemical reactions take place the shale becomes porous. The porosity is defined by:

$$\phi = 1 - \frac{U(K) + U(H) + U(W) + U(C)}{(U^{\circ}_{(K)} + U^{\circ}_{(H)} + U^{\circ}_{(W)} + U^{\circ}_{(C)})}$$

where $U^{\circ}_{(i)}$ are initial values of respective densities. The permeability of the shale a product, $K_R K$, where, K_R, is the relative permeability the permeability, K, is a function of porosity which in turn is related to the temperature history. An empirical relationship is obtained from the data of Sresty (1982) to describe the evolution of the permeability with time.

The gaseous forms satisfy a bulk species equation:

$$\frac{\partial}{\partial t}(\phi S_g \rho_g) + \nabla \cdot (\rho_g \vec{V}_g) = \sum_{i=4}^{9} f_{(i)} U_{(K)} K_{(K)}$$

$$+ U_{(H)} K_{(H)} + \frac{U^{\circ}_4 R_T}{T_H - T_L} + \sum_{i=22}^{24} (.00365) f_{(i)} f_3 U_{(K)} K_{(K)} + f_3 X K_{(K)} U_{(K)}$$

In the above X denotes the fraction of oil evolved which is in gas gorm.

The series equation for the oil is:

$$\frac{\partial(\phi S_o \rho_o)}{\partial t} + \nabla \cdot (\rho_o \vec{v}_o) = (1-X) f_3 K_{(K)} U_{(K)} - .00365 f_2 f_3 K_{(K)} U_{(K)}$$

In the above S_g, S_o are saturations of gas and oil phase, $\vec{v}_g$, $\vec{v}_o$ are velocites and ρ_g, ρ_o are the densities. in KG. Per Cubic meter of gas and oil.

f_{21} = .7038

f_{22} = 0604

f_{23} = .1927

f_{24} = 0431

The total mass of the system is conserved in that the sum of all the species equations yields a bulk equation of continuity.

The momentum equation for turbulent flow in a porous media is the Forcheimer equation[4]

$$\vec{v}_{(i)} = \frac{-\frac{\bar{\bar{K}}_{(i)}}{\mu} \bullet \{\nabla \rho_{(i)} + \rho_{(i)} \vec{g}\}}{\{1 + \beta \rho_{(i)} \mid \bar{\bar{K}}_{(i)} \; \vec{v}_{(i)} \mid\}}$$

where (i) denotes gas or oil phase. In this equation $\frac{\bar{\bar{K}}}{\mu}$ is the mobility tensor, $\vec{g}$ is the gravity vector β is the turbulence factor Katz, (1956). This vector equation can be decoupled to components in $\hat{r}$ and $\hat{z}$ directions.

$$v_r = \frac{-\frac{K_r}{\mu} \frac{\partial \rho}{\partial r}}{\{1 + \beta\rho \left| \frac{\bar{\bar{K}} \cdot \vec{v}}{\mu} \right| \}}$$

$$v_z = \frac{-\frac{K_z}{\mu} \{\frac{\partial \rho}{\partial z} - \rho g\}}{\{1 + \beta\rho \left| \frac{\bar{\bar{K}} \cdot \vec{v}}{\mu} \right| \}}$$

where:

$$\left| \frac{\bar{\bar{K}} \cdot \vec{v}}{\mu} \right| = \frac{-1}{2\beta\rho} + \left\{ 1/4 \, \beta^2 \rho^2 + \left[\left(\left(\frac{K_r}{\mu} \right)^2 \frac{\partial \rho}{\partial r} \right)^2 + \left(\left(\frac{K_z}{\mu} \right)^2 \left(\frac{\partial \rho}{\partial z} - \rho g \right) \right)^2 \right]^{\frac{1}{2}} \right\}^{\frac{1}{2}}$$

The saturations S_g, S_o are related by:

$$S_g + S_o = 1$$

The equation of state is taken as:

$\rho_g = \frac{PM}{ZRT}$ where P is pressure, M is molecular weight R is the gas constant and T is temperature, Z is the compressability factor.

In addition a relationship between for capillary pressure is needed.

$$P_c = P_g - P_o$$

Consider now the energy balance for the gas-liquid-solid system. Some simplifying assumptions are necessary for the modeling. Since the electromagnetic heating is relatively constant over the region interest and since velocities are small and pore size is small it is a good assumption that the temperatures of gas, liquid, and solid are equal at any point in space. We can write a bulk energy balance Bird (1960).

$$C_{p_o} \frac{\partial}{\partial t}(\phi S_o \rho_o T) + C_{p_g} \frac{\partial}{\partial t}(\phi S_g \rho_g T) + V_{Inor} C_s \frac{\partial T}{\partial t}$$

$$+ C_W \frac{\partial}{\partial t}(V_W T) + C_K \frac{\partial}{\partial t}(V_K T) + C_H \frac{\partial}{\partial t}(V_H T) + C_{p_o} \nabla \cdot (\rho_o \vec{V}_o T)$$

$$+ C_{p_g} \nabla \cdot (\rho_g \vec{V}_g T) = \nabla \cdot ((\bar{\bar{\lambda}}_g + \bar{\bar{\lambda}}_o + \bar{\bar{\lambda}}_s + \bar{\bar{\lambda}}_W + \bar{\bar{\lambda}}_K + \bar{\bar{\lambda}}_H) \cdot \nabla T)$$

$$+ \frac{D}{Dt}[\phi(S_g \rho_g + S_o \rho_o)] + g(\vec{r}, t) + \sum_{i=1}^{N} \Delta H_{(i)}$$

Where N is the total number of chemical reactions considered and the ΔH_i are the corresponding enthalpies.

In the above $\bar{\bar{\lambda}}_{(i)}$ are thermal conductivity tensors $C_{p(i)}$ are specific heats. $\frac{D}{Dt}$ denotes' convective derivative, $g(\vec{r},t)$ is the electromagnetic source, $\Delta H_{(i)}$ are heats due to reactions.

The electromagnetic source term is related to the electric fields and the electrical conductivity (σ) by:

$$g(\vec{r},t) = \bar{E} \cdot \bar{J} = \sigma|\vec{E}|^2$$

We have twelve equations for the twelve unknowns S_g, S_o, P_g, P_o, T, $U_{(K)}$, $U_{(H)}$ $U_{(c)}$, $U_{(W)}$, V_g, V_o, g. These equations are to be solved similtaneously by an appropriate numerical technique. The detailed numerical studies will be carried out in the next quarter.

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