EFFECTS OF HYDROTHERMAL CHEMISTRY ON RESERVOIR EVOLUTION

Charles G. Sammis, Todd M. C. Li, and William F. Downs
Department of Geosciences
Pennsylvania State University
University Park, PA 16802

Although the corrosion and scaling problems associated with handling geothermal fluids are well known, the effects of hydrothermal reactions are often overlooked in geothermal reservoir modeling. Water-rock chemistry can be expected to affect the evolution of a reservoir in at least three ways: (a) the heats of reaction may contribute directly to the energy production, (b) the viscosity and thermodynamic properties of water are affected by the dissolved solids--this is especially important in two-phase regimes, and (c) the porosity and permeability change with time due to dissolving and precipitation as well as due to the volume change associated with alteration.

Chemical Energy

Table 1 summarizes the important hydrothermal reactions in a granitic source rock together with the heats of reaction and associated volume changes. Note that the available chemical energy is comparable to the thermal energy while the associated volume changes are an order of magnitude larger than those due to thermal contraction.

Table 1

IMPORTANT REACTIONS IN GRANITIC ROCK

(CHEMICAL REACTIONS TAKEN FROM HELGESON, 1969)

PROCESS	Heat released		Solid volume change per 100g of initial min $\Delta V_s(cm^3/100g)$
	per mole of initial min. ΔH(kcal/mole)	per 100g of initial min ΔH(kcal/100g)	
HYDROTHERMAL ALTERATION			
$2NaAlSi_3O_8(s)+2H^+ + H_2O \longrightarrow Al_2Si_2O_5(OH)_4(s)+4SiO_2(s)+2Na^+$ Low Albite → Kaolinite + α-quartz	11.21	4.27	-1.882
$3KAlSi_3O(s)+2H^+ \longrightarrow KAl_3Si_3O_{10}(OH)_2(s)+6SiO_2(s)+2K^+$ Microcline → muscovite + α-quartz	2.96	1.063	-5.907
DISSOLVING AND PRECIPITATION			
$SiO_2(s) + 2H_2O \longrightarrow H_4SiO_4(aq)$ α-quartz	-6.22	-10.352	-37.760
COOLING			
GRANITIC ROCK (300°C) → GRANITIC ROCK (65°C) (ρ_R = 2.65 g/cm^3, C_R = 0.25 cal/g°C, $\beta_R = 2.5 \times 10^{-5}$/°C)	-	5.875	-0.2217

Although significant chemical energy exists, it cannot always be extracted. One of the first questions we addressed (Morris, 1975; Morris and Sammis, 1975) was the delineation of reservoir conditions under which one could expect to extract significant chemical heat. For the case of dissolving-precipitation reactions, a comparison of thermal energy with chemical energy leads to a simple relation between solubility and heat of reaction for a given ratio of chemical to thermal energy extracted. Because the rate of dissolving is controlled by the solubility at the outlet temperature, the resulting relation is independent of all crack and flow parameters. In the case of quartz, the solubility at 300°C is too low for chemical heat to make a contribution - thermal energy is extracted far faster than chemical energy under all flow conditions.

In the case of alteration reactions, however, the reaction rate is not limited by solubility and, depending on the alteration rate, significant chemical energy may be extracted. Morris (1975) has delineated the combinations of flow parameters, crack parameters, heats of reaction and alteration rates for which chemical energy associated with the alteration may be extracted. One of the objectives of our experimental program is to determine alteration rates in typical reservoir rocks, and thus assess the importance of such reactions to the total thermal regime.

Numerical Model for Single-phase Flow Including Porosity and Permeability Changes

The changes in porosity and permeability associated with both dissolving and alteration reactions are easily incorporated into the standard finite difference schemes commonly used in numerical reservoir modeling. The molality of each important solute may be treated as a dependent variable to be found together with the temperature and velocity fields. In addition to the standard three equations for the conservation of mass, momentum, and energy, an equation may be written for the conservation of each solute species. Such an equation directly incorporates permeability changes associated with dissolving and precipitation. It requires, as an additional constitutive relation, the experimentally determined rate equation. Permeability changes associated with alteration reactions may be written explicitly in terms of the temperature, flow velocity, crack parameters, water chemistry, and appropriate alteration rate equation. This larger system of equations may be combined and solved using exactly the same numerical scheme employed by Harlow and Pracht (1972). Using their notation (variables are defined in Table 2), the energy balance equation is

$$\frac{\partial}{\partial t}\{[b_R\rho_R(1-\theta) + b_w\rho_w\theta]T\} + \vec{\nabla}\cdot\rho_w b_w\theta\vec{u}T = \vec{\nabla}\cdot[K_R(1-\theta)\vec{\nabla}T] + \rho_w b_w T_s S \qquad (1)$$

and the mass and momentum balance equations may be written in the form

$$\frac{\partial\theta}{\partial t} - \vec{\nabla}\cdot\left\{\frac{k\rho_0}{\mu}[\vec{\nabla}\phi + \vec{g}\beta_w(T-\langle T\rangle)]\right\} = S \qquad (2)$$

$$\vec{u}\theta = \frac{-k\rho_0}{\mu}[\vec{\nabla}\phi + \vec{g}\beta_w(T-\langle T\rangle)] \qquad (3)$$

The equation of state of water

$$\rho_w = \rho_0[1-\beta_w(T-T_0)] \qquad (4)$$

and a porosity-permeability relation

$$k = \left(\frac{4d_c{}^2}{5}\right)\left[\frac{\theta^3}{(1-\theta)^2}\right] \tag{5}$$

are also required. It also is important to include the temperature dependence of the viscosity of water

$$\mu = \frac{0.279}{T(°C)-3.8} \quad \left(\frac{gm}{cm\ sec}\right) \tag{6}$$

If we only consider the dissolution and precipitation of SiO_2

$$SiO_2\ (S) + 2H_2O \rightleftharpoons H_4SiO_4 \tag{7}$$

we can write two more balance equations: the conservation of SiO_2 during the reaction,

$$\frac{\partial}{\partial t}[W_R\rho_R(1-\theta)] + \frac{\partial}{\partial t}\left[\frac{m_{H_4SiO_4}\overline{M}_{SiO_2}}{10^3}\rho_w\theta\right]_R = 0 \tag{8}$$

and the mass balance for SiO_2 in solution

$$\frac{\partial}{\partial t}\left[\frac{m_{H_4SiO_4}\overline{M}_{SiO_2}}{10^3}\rho_w\theta\right] = \frac{\partial}{\partial t}\left[\frac{m_{H_4SiO_4}\overline{M}_{SiO_2}}{10^3}\rho_w\theta\right]_R - \vec{\nabla}\cdot\left[\frac{m_{H_4SiO_4}\overline{M}_{SiO_2}}{10^3}\rho_w\theta\vec{u}\right] + \rho_w M_s S \tag{9}$$

The subscript R indicates that we only consider the part of the subscripted expression which is due to the reaction. The time rate of change of molality $[\partial m/\partial t]_R$ is given in terms of experimentally determined rate constants, k_+ (for the forward dissolution reaction) and k_- (for the reverse precipitation reaction) by the rate equation

$$\left(\frac{\partial a_{H_4SiO_4}}{\partial t}\right)_{P,T,M} = \frac{A}{\rho_w V}\{k_+ a_{SiO_2} a^2_{H_2O} - k_- a_{H_4SiO_4}\} \tag{10}$$

If we assume a pure quartz-water system $a_{SiO_2}=a_{H_2O}=1$. The activity of H_4SiO_4 may be written in terms of the molality

$$a_{H_4SiO_4} = \frac{\gamma_{H_4SiO_4} m_{H_4SiO_4}}{\gamma^0_{H_4SiO_4} m^0_{H_4SiO_4}} \tag{11}$$

The reference state is chosen such that $\gamma^0=m^0=1$. If we also assume $\gamma_{H_4SiO_4}=1$ (true only for pure water) equation (10) may be written

$$\left[\left(\frac{\partial m_{H_4SiO_4}}{\partial t}\right)_{P,T,M}\right]_R = \frac{1}{\rho_w}\left(\frac{A}{V}\right)\left[k_+ - k_- m_{H_4SiO_4}\right] \tag{12}$$

In general we can write A/V=(Fracture Parameter)/θ where the fracture parameter can be readily found for simple assumed fracture geometries.

Following Harlow and Pracht (1972), these equations may be solved in the following sequential order: (a) the energy balance equation (1) (in finite difference form) is solved for T at the new time step using the values of θ, u, and T at the previous time step; (b) equations (8), (9), and (12) are used to find θ and m at the new time step; (c) equation (2) is solved for new values of ϕ; and (d) equation (3) is solved for new values of u. The procedure is then repeated for the next time step. We are currently working on such a solution procedure for simple reservoir configurations.

Kinetics of the Dissolution and Precipitation of SiO_2

In order to implement the above scheme, the rate constants k_+ and k_- must be known. These have been determined experimentally by measuring m as a function of time in the apparatus shown in Figure 1 (Barnes and Rimstidt, 1975)

$$k_+ = 2.03\ e^{-28.3/RT}\ \text{moles/cm}^2\text{sec}$$

$$k_- = 3.30\ e^{-22.5/RT}\ \text{moles/cm}^2\text{sec}$$

where the activation energies are in kcal/mole. The rate-constants are only weakly dependent on pressure and salinity of the solution. In the case of saline brines, the major effect on the kinetics of quartz dissolution is to lower a_{H_2O} in (10) (Lindsay and Liu, 1968) and slightly lower $\gamma_{H_4SiO_4}$ in (11).

References

Barnes, H.L., and J. D. Rimstidt, Control of Silica Scaling, in Geothermal Reservoir Engineering, ed. P. Kruger and H.J. Ramey, Jr., SGP-TR-12, Stanford University, 1975.

Harlow, F.H., and W.E. Pracht, A Theoretical Study of Geothermal Energy Extraction, J. Geophysical Research, 77, 7038-7048, 1972.

Helgeson, H.C., Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures, American Journal of Science, 267, 729-804, 1969.

Lindsay, W.T., Jr., and C.T. Liu, Vapor Pressure Lowering of Aqueous Solutions at Elevated Temperatures, U.S. Office of Saline Research and Development, Progress Report No. 347, 235 p., 1968.

Morris, J.R., A Preliminary Study of the Importance of Hydrothermal Reactions on the Temperature History of a Hot, Dry Rock Geothermal Reservoir, M.S. Thesis, Pennsylvania State University, 1975.

Morris, J.R., and C.G. Sammis, The Recovery of Chemical Energy from a Dry-Rock Geothermal Reservoir (abstr.), Trans. Am. Geophys. Union, 56, 1073, 1975.

Table 2 Summary of Notation

θ	porosity, open volume for water flow (per unit volume)
ρ_w	density of water, a function of temperature
ρ_R	density of rock
$\tilde{u}$	water velocity
S	source or sink of water from surface pipes (volume per unit volume per unit time)
p	water pressure
g	acceleration of gravity
μ	coefficient of water viscosity
k	permeability
b_R, b_w	specific heats of rock and water, respectively
T	temperature
$\langle T \rangle$	average water temperature at a given depth
T_0	reference temperature for thermal expansion
T_s	source or sink temperature
K_R	thermal conductivity of rock
ϕ	$(p-p_0)/\rho_0$ where p_0/ρ_0 is a function of depth only
d_c	measure of average crack spacing
β_w	volumetric expansion coefficient of water
m	molality
$\overline{M}$	molecular weight
W_R	grams quartz per gram of rock
a	activity
(A/V)	surface area per unit water volume, a function of fracture geometry
k_+	rate constant for the forward dissolving reaction
k_-	rate constant for the reverse precipitation reaction
γ	activity coefficient
M	mass

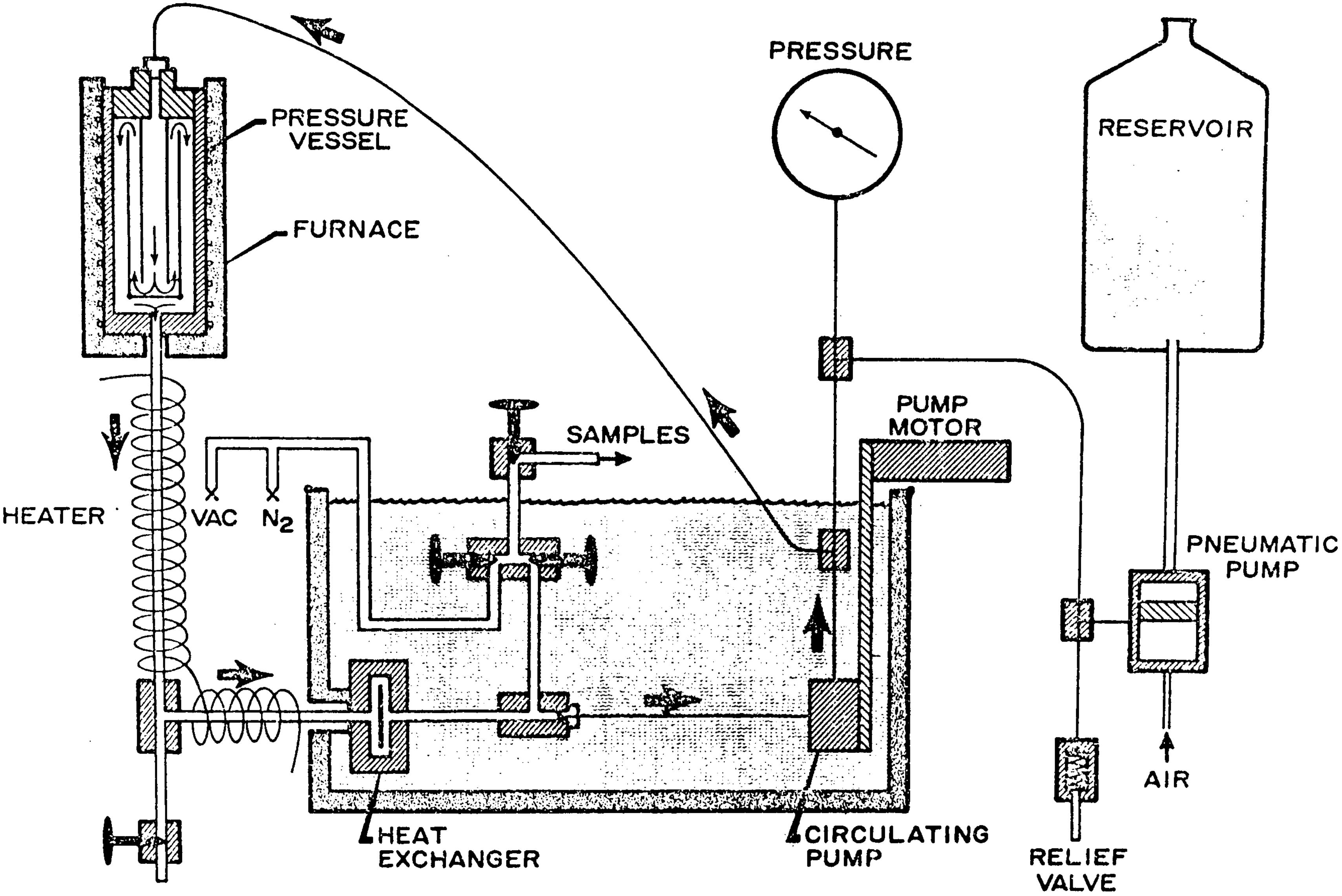
PRESSURE VESSEL
FURNACE
PRESSURE
RESERVOIR
PUMP MOTOR
SAMPLES
HEATER
VAC
N2
PNEUMATIC PUMP
AIR
HEAT EXCHANGER
CIRCULATING PUMP
RELIEF VALVE

Figure 1