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SOLUTION CHEMISTRY AND SCALING IN HOT DRY ROCK GEOTHERMAL SYSTEMS

by

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ABSTRACT

Field and Laboratory experiments have focused on measuring the kinetics and equilibria associated with the transport of minerals from granite to circulating aqueous solutions. Presently two wellbores drilled to a depth of approximately 10,000 ft in the Valles Caldera region of the New Mexico Jemez mountains permit closed-loop circulation of fluid through a hydraulically fractured granite geothermal reservoir containing rock at 200°C. Field measurements have dealt primarily with the buildup of dissolved and suspended material in water as it is circulated through the fractured region. Chemical treatment methods involving the selective dissolution of quartz (SiO_2), a major component of granite, with sodium carbonate solutions have been employed to increase the *in situ* permeability of the rock matrix. Laboratory measurements have concentrated on identifying the effects of temperature, pH and chemical additives on the solubility of granite samples taken from the two test wellbores. Promising results from these solubility experiments are tested in a laboratory-scale circulating system to examine kinetic parameters influencing rock dissolution and reprecipitation (scaling) under conditions that simulate the *in situ* reservoir and heat exchange environments.

INTRODUCTION AND SCOPE

Four main topics are discussed in this paper. A brief description of the Los Alamos Scientific Laboratory field program aimed at developing stimulation techniques for creating reservoirs and extracting energy from the hot dry rock geothermal resource is presented. This places proper perspective for the next section describing field and laboratory experiments which have examined dissolution mass transport between the hot reservoir rock and circulating aqueous working fluid solutions which are used to extract the heat. In the third section enhanced dissolution of reservoir rock using sodium carbonate (Na_2CO_3) solutions as a chemical stimulation method is discussed. The final section covers potential scaling problems for hot dry rock energy extraction systems.

HOT DRY ROCK PROJECT DESCRIPTION

One concept being pursued by the Los Alamos Scientific Laboratory (LASL) consists of creating a geothermal reservoir in hot Precambrian granite by hydraulic fracturing. Energy would be removed by circulating water over the surfaces of an $\sim$1-2 km^2 fracture using a two-hole, closed circulating loop connected to a surface heat exchange system.[1] Cold water under a high enough pressure to prevent vaporization would flow down one hole, enter the fractured region and circulate with buoyant forces helping to pump fluid up the second hole. Because water is not present in the hot reservoir rock in sufficient quantities to provide an indigenous source of fluid as is the case in a natural hydrothermal system, these stimulated reservoirs are referred to as "dry." Hot dry rock energy extraction technology provides a different set of crystallization/dissolution problems quite unique from those encountered in hydrothermal environments. The kinetics and equilibria associated with *in situ* granite-water interactions are important in determining how the fluid and rock composition of the system will vary over the 20-40 year lifetime of a geothermal power plant. This affects the heat exchange performance of both the reservoir and the surface plant. In particular, pressure drop, fluid circulation patterns, and fluid permeation losses, and fracture system stability itself will be influenced by the chemical dissolution and reprecipitation reactions occurring in the reservoir. Although no serious corrosion problems are anticipated from granitic crystalline rock environments, silica and/or carbonate scaling on heat exchange surfaces is quite probable.

LASL's current field efforts have involved a program of drilling into hot granite, fracturing it to create heat transfer surface area, and developing techniques and instrumentation to determine the *in situ* geometry of the fractured region. Energy extraction experiments (10 to 100 MW(thermal)) are planned to assess the fluid flow, heat transfer and geochemical characteristics of a HDR reservoir.

The field operation is situated on the western rim of the Valles Caldera, an extinct volcanic crater, which is located on the Jemez

Plateau of north-central New Mexico. Two deep boreholes have been drilled to form the circulation loop of a 10-20 MW(thermal) heat extraction experiment. One hole, GT-2, was drilled to a depth of 2928m (9606 ft) and hydraulically fractured through casing at a depth of 2800m (9200 ft). A second hole, EE-1, was directionally drilled to intersect the GT-2 target fracture. A downhole connection was made between EE-1 and GT-2 over depths ranging from 2800m (9200 ft) to 2900m (9600 ft). The equilibrium bottomhole temperature in both holes is approximately 200°C with a geothermal gradient of 50 to 60°C/km in the Precambrian section. The flow through the fractured region is characterized by a high impedance, too high to permit fluid circulation at rates of 1.14-2.28 x 10^{-3} m^3/min (300-600 gpm) required for extraction levels of 10 to 20 MW(thermal). Additional hydraulic fracturing out of the bottom section of EE-1 reduced the pressure drop but no direct, low impedance connection was made between the EE-1 and GT-2 fracture system. Subsequent distance ranging experiments revealed that accumulated wellbore gyroscopic and magnetic surveying errors caused the directionally drilled EE-1 hole to fall short of the GT-2 target fracture by about 10-13 m (30 to 40 ft). Consequently, the EE-1 fracture probably propagated with parallel orientation to the GT-2 vertical fracture due to the similarity of the *in situ* stress field. A schematic diagram depicting this situation is shown in Fig. 1.

Measured permeabilities by conventional drill stem and modified pressure-transient flow testing[2,3] in the Precambrian section ranged from 4 x 10^{-7} to 10^{-5} darcy with average values of 0.1 to 1 x 10^{-6} darcy for depths of 2700-3000m (9000-10 000 ft) in GT-2 and EE-1. These values agreed reasonably well with laboratory measurements on core specimens under steady state permeation flow conditions.[4] If the flow between EE-1 and GT-2 is controlled by the matrix permeability of the rock, the measured impedance of 1.09 x 10^{10} Pa-sec/m^3 ($\sim$100 psi/gpm) could easily be accounted for by flow through the 10m (30 ft) fracture separation.[2] Redrilling and chemical dissolution techniques are being considered to reduce this flow impedance to an acceptable value of 5.5 x 10^8 (Pa-sec/m^3 (5 psi/gpm) or less.

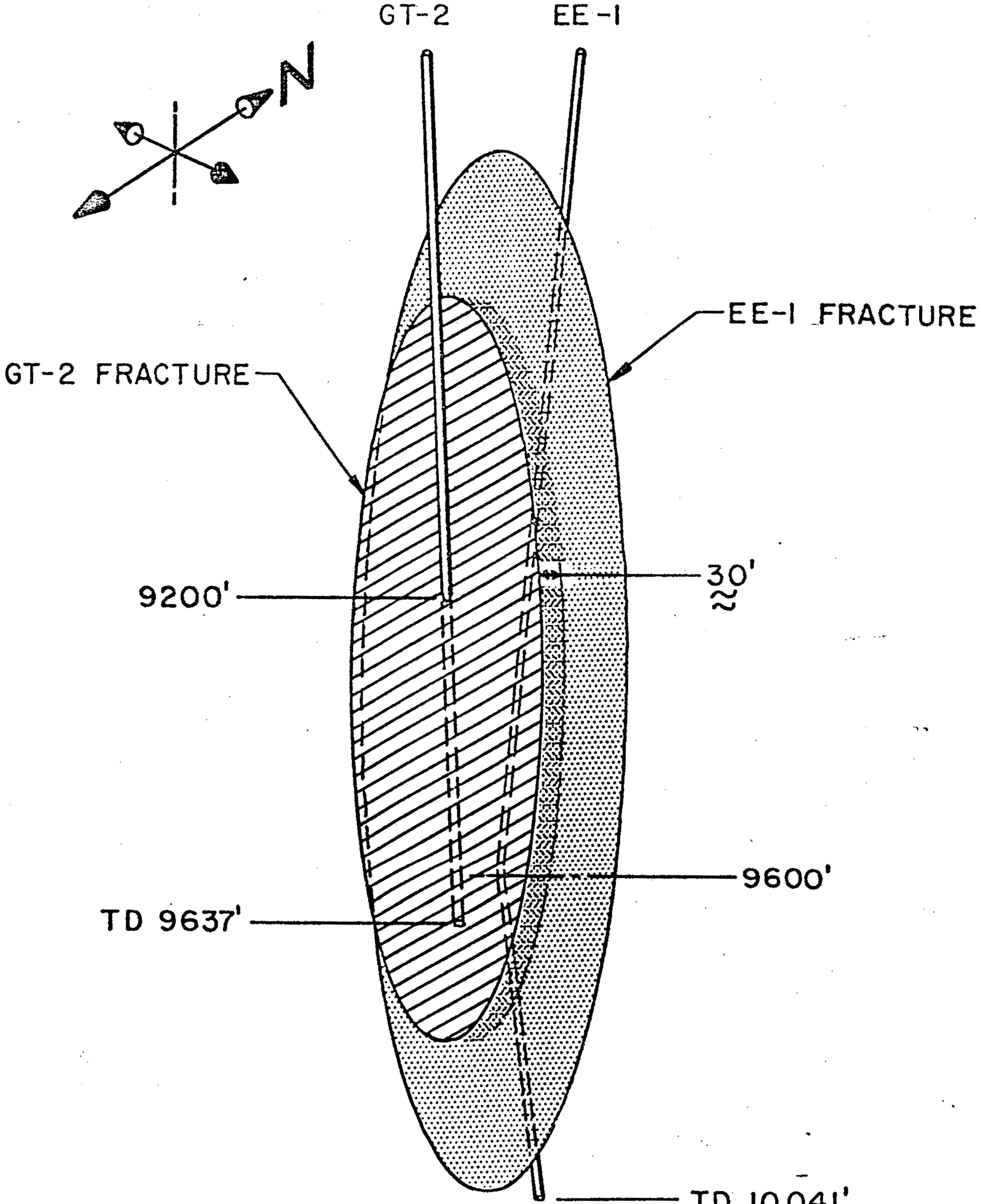

Fig. 1 Conceptual schematic diagram of the EE-1/GT-2 parallel fracture. Viewing direction is along the fracture edge. Wellbore angles of inclination are somewhat exaggerated. Depths shown in feet.

In the fractured region, the granitic rock penetrated is classified as a biotite granodiorite consisting of four main mineral components: quartz (SiO_2), plagioclase ($CaAl_2Si_2O_3$ - $NaAlSi_3O_8$), microcline or orthoclase ($KAlSi_3O_8$), and biotite [$K_2(Fe,Mg)_2(OH)_2(AlSi_3O_{10})$]. Table 1 gives compositions at two different depths in GT-2 and EE-1. As water or chemicals are circulated through the fractured region they will dissolve a fraction of the host minerals and may even cause the reprecipitation of mineral alteration products on exposed rock surfaces by hydrogeochemical interactions. The rates of these kinetic processes and their effect on system performance are being examined in an extensive laboratory and field effort being conducted at LASL.[2,4]

TABLE 1

BIOTITE GRANDODIORITE IN GT-2/EE-1[2,4]

Mineral	% by Volume $\sim$2615m ($\sim$8580 ft)	2900 m ($\sim$9515 ft)
Quartz (SiO_2)	29 ± 3	25 ± 3
Microcline ($KAlSi_3O_8$)	21 ± 3	15 ± 2
Plagioclase (32% $CaAl_2Si_2O_3$, 68% $NaAlSi_3O_8$)	34 ± 3	38 ± 3
Biotite [$(K_2(Fe, Mg)_2(OH)_2(AlSi_3O_{10})$]	11 ± 2	13 ± 2
Calcite ($CaCO_3$)	<0.5	$\leq$0.1
Epidote [$(Ca, Fe^{+3})Al_2Si_3O_{12}(OH)$]	1	3 ± 1
Sphene ($CaTiSiO_5$)	2 ± 1	2 ± 1

IN SITU RESERVOIR AND LABORATORY DISSOLUTION MEASUREMENTS

At least seven major parameters control the dissolution of reservoir rock:

1. rock composition and microstructure
2. inlet fluid composition

3. temperature
4. fluid velocity
5. residence time
6. rock surface area/fluid volume
7. pH

In the _in situ_ environment the rock composition and microstructure, temperature and rock surface area to fluid volume ratio are defined. Cores extracted from GT-2 and EE-1 provide some flexibility in studying individual mineral-water interactions but in the field one is forced to examine the gross rock matrix-water interactions. Fluid velocity and residence time can only be varied in a relative sense in the field because absolute values for porosity and fracture surface area are not known. Laboratory experiments conducted on core material have the advantage that all of the parametric effects listed above can be studied on an individual basis.

Field geochemical experiments to date have consisted of injecting fresh water into one borehole, circulating it through the EE-1/GT-2 fractured region and returning the fluid to the surface in the second borehole. Up to this time no water has been recirculated, but over 5.6×10^6 liters (1.5×10^6 gallons) have been injected with a large number of samples analyzed to determine inlet and outlet fluid composition. Typical results are given in Table 2 for the major cations and anions present in the injected and recovered water. Titration, selective ion electrodes, atomic absorption, and other spectrophotometric methods were used for analysis. Residence time distribution studies using a Na-fluorescein dye tracer technique have shown that flow in the EE-1/GT-2 fracture system is very dispersed around a mean system volume of ∿38 000 liters (10 000 gallons). The values given in Table 2 for water circulated through the reservoir correspond to a mean residence time of 14 hours. The total dissolved solids level increases from ∿400 ppm for the injected water to ∿1200 ppm for the returned water. The aqueous silica (SiO_2) concentration reaches a value approximately equal to the saturation concentration or solubility of quartz at 200°C.

Experiments using core material are conducted in three different ways:[2,4] (1) agitated teflon-lined autoclave batch systems with crushed

TABLE 2

HOT DRY ROCK GEOTHERMAL FLUID COMPOSITION

200°C

BIOTITE GRANODIORITE

9200-9600 ft

	Injected Water (ppm)	Water After ~14 hr Exposure in situ* (ppm)	Water After 24 hr Exposure Lab Core Samples (ppm)
SiO_2	42-50	220-260	180-220
Na	12-60	240-300	36
K	3-8	25-40	15
Ca	13-23	14-16	4
Mg	1-5	0.3	0.08-0.20
Fe	0.3-1.0	2-6	1.3-3.3
Al	<1	0.2-0.6	1.6-3.2
F	1	12-14	12
Cl	3-10	310-400	4-5
SO_4	10-20	80	<100
HCO_3	200-280	180	~150
CO_3	<10	~0	~0
S	~0	1-2	<1
PO_4	<0.1	0.2-0.5	~0.1

*After 1.5×10^6 gallons circulated.

core or drilled cuttings exposed to fluid under its vapor pressure at temperatures of interest up to 250°C, (2) flowing systems which expose crushed core or prepared slabs of core material to circulating fluid maintained at pressures of 10 to 69 MPa (1300 to 10 000 psi) at temperatures up to 300°C, and (3) permeation systems which use a pressure gradient to force fluid to penetrate through a core specimen maintained at a fixed confining pressure at temperatures up to 300°C. Results are shown in Table 2 for a 24 hr exposure of 1.0 g of 16 x 24 mesh (∿0.85 mm diameter) crushed core (9515 ft - see Table 1) material to 15 g of water at 200°C.

In comparing these laboratory measurements with the _in situ_ fluid composition, both SiO_2 concentrations approach the saturated quartz condition and imply a similar controlling mechanism of rock dissolution. The difference in SiO_2 concentrations for ∿14 versus 24 hr exposure is not significant in view of the uncertainties surrounding the value of exposed rock surface area in the _in situ_ environment versus the laboratory measuremens. pH values of 6.8 - 7.0 are observed for both field and laboratory fluids. However the much higher values for Cl, Na, Ca, and K observed in the field are possibly caused by the influence of indigenous pore fluid on circulating water contained in the fractured EE-1/GT-2 reservoir. A steady decline in the total dissolved solids (particularly Cl, Na, Ca, and K) level has been observed as more and more fresh water is circulated. This could be expected as the pore fluid source of dissolved salts is depleted. The agreement between laboratory and _in situ_ F concentrations suggests that the source of F is active dissolution of rock rather than from pore fluid.

CHEMICAL LEACHING FOR SELECTIVE DISSOLUTION

The use of chemicals to selectively dissolve rock in fractured oil or gas reservoirs to increase formation permeability or conductance is in practice today. In particular, acid treatment of carbonate formations is commonly used to increase oil and gas production. In an analogous fashion, the selective dissolution of silica might effectively be used to decrease the high flow impedance that presently characterizes the EE-1/GT-2 fracture system. Laboratory experiments conducted during the past year at LASL have demonstrated that dilute aqueous solutions (0.1 to 4.0 N) of sodium carbonate (Na_2CO_3) react with EE-1/GT-2 core specimens to dissolve SiO_2 primarily by attacking the quartz component of the granite.

The reaction is sufficiently irreversible to result in essentially stoichiometric conversion of crystalline silica ($SiO_{2(c)}$) into a soluble form. Na_2CO_3 acts to buffer the solution into the moderately basic region (∿pH=10) and thus provides an active source of hydroxide ions (OH^-) which can react with dissolved silicic acid $Si(OH)_4$ to form soluble metasilicates[5], thus increasing the effective solubility of silica.

$$CO_3^{2-} + H_2O = HCO_3 + OH^- \qquad (1)$$

$$SiO_{2(c)} + 2H_2O + nOH^- = Si(OH)_{4+n}^{-n} \qquad (2)$$

Both the rate and final saturation concentration achieved increase as the pH or OH^- concentration increases. Thus concentrated sodium hydroxide (NaOH) solutions would result in faster dissolution rates because of the higher OH^- concentration. However, using dilute $Na_2CO_{3(aq)}$ as the reactant to induce dissolution is advantageous for a first experiment in the EE-1/GT-2 system because the reaction rates are slow enough to permit control of the experiment and adequate interpretation of the results.

In order to optimize the design of a field experiment for carbonate leaching, a series of laboratory tests were performed to collect data on the reaction kinetics of Na_2CO_3 solutions on granite and on the fluid flow characteristics expected in the reservoir. In effect, we would like to control the location and extent of silica dissolution in the system. Reaction kinetic data tells us how fast silica dissolves as a function of time and fluid residence time data collected in the EE-1/GT-2 reservoir tells us how long the reacting fluid would be exposed to the reservoir rock. By combining this information we can select solution concentration and volumes for specified flow rates to insure that the carbonate will not be expended before it reaches the zone of high impedance.

Because the chemical dissolution reaction involves both liquid and solid phases, one would expect that the reaction rate, with surface kinetics controlling, would be proportional to the rock surface area to fluid volume ratio (a*). Gas absorption and mercury porosity measurements were used to estimate surface areas accessible to the fluid. Experiments were made using the agitated autoclave batch vessels described earlier. Kinetic runs at 200°C with 0.1 to 4.0 N Na_2CO_3 and pure water solutions were made on both core slabs and drill cuttings. For core slabs, $a^* = 55\ cm^2/90 cm^3 = 0.6\ cm^{-1}$ based on nominal area and liquid volume. For cuttings, 1 g of 16 x 24 mesh samples were used in 1.5 cm^3 of liquid, with a nominal $a^* = 2\ cm^{-1}$. Solution samples were taken at different exposure times up to 120 hr and analyzed for aqueous silica using atomic absorption and the silico-molybdate spectrophotometric method.[6] When core slabs were used sample weight losses were also determined. The time dependence of weight loss or aqueous solution concentration buildup was then used to determine dissolution rates. A simple model was fit to both weight loss and SiO_2 concentration rate data yielding the instantaneous dissolution rate R as a function of a* and the difference between the saturated SiO_2 concentration corresponding to the initial Na_2CO_3 concentration and the SiO_2 concentration at a particular time t:

$$R = \frac{d\left[SiO_{2(aq)}\right]}{dt} = \frac{-1}{V}\frac{dM}{dt} = k_d^* \, a^* \left[SiO_2{}^{sat}_{(aq)} - SiO_{2(aq)}\right] \qquad (3)$$

where

k_d^* = dissolution rate constant, cm/sec

a^* = accessable rock surface area to fluid volumeratio = S/V, cm^{-1}

$\left[SiO_2{}^{sat}_{(aq)}\right]$ = aqueous saturation concentration of silica, g/liter or ppm

$\left[SiO_{2(aq)}\right]$ = aqueous concentration of silica, g/liter or ppm

M = core slab mass, g

t = time

The rate constant k^*_d is determined empirically and depends on rock type, temperature, flow rate, and Schmidt number. The dissolution rate R is expressed as a rate of sample weight loss ($-dM/dt$) or as a rate of SiO_2 concentration increase ($d\left[SiO_{2(aq)}\right]/dt$). If we assume that essentially all of the sample weight loss is due to silica dissolving, then by using a simple material balance eq (3) can be rewritten:

$$\frac{dW}{dt} = k_d^* a^*(W^\infty - W) \tag{4}$$

where W = weight loss of sample at time t, grams

W^∞ = weight loss of sample as t → ∞ (or saturation), grams

Typical weight loss data collected by Charles[7] for EE-1/GT-2 granite core slabs are plotted in Fig. 2. The theoretical lines shown are obtained by integration of eq (4) using an appropriate value for $k_d^* a^*$ determined by plotting the initial rate ($t \rightarrow 0$) as a function of W^∞. Figure 3 shows initial dissolution rate for both core slabs and cuttings as a function of carbonate concentration. The non-linear concentration dependence shown is caused by the non-linear dependence of $\left[SiO_{2(aq)}^{sat}\right]$ on carbonate concentration (see Fig. 4). By using experimental values of initial rate for cuttings plotted as a function of $\left[SiO_{2(aq)}^{sat}\right]$ from Fig. 4, a linear relationship corresponding to eq (3) results as shown in Fig. 5. A similar relationship was determined for the core slab data.

An empirical treatment of the dependence of $\left[SiO_{2(aq)}^{sat}\right]$ and $[OH^-]$ on initial $[Na_2CO_{3(aq)}]^\circ$ was done to provide a method for understanding how OH^- participates in the dissolution mechanism. By using pH measurements to determine H^+ activity, OH^- activity could be estimated using the ion product for water and assuming that H_2O was at unit activity. Empirical equations relating $[OH^-]$ to $[Na_2CO_{3(aq)}]^\circ$ and $\left[SiO_{2(aq)}\right]$ to $[OH^-]$ were developed:

$$[OH^-] = 5.36 \times 10^{-3} \, (2[Na_2CO_3])^{0.38 \pm 0.03} \tag{5}$$

$$\left[SiO_{2\,(aq)}^{\;sat}\right] = 6.44 \times 10^{8} \, ([OH^-])^{1.75 \pm 0.27} \tag{6}$$

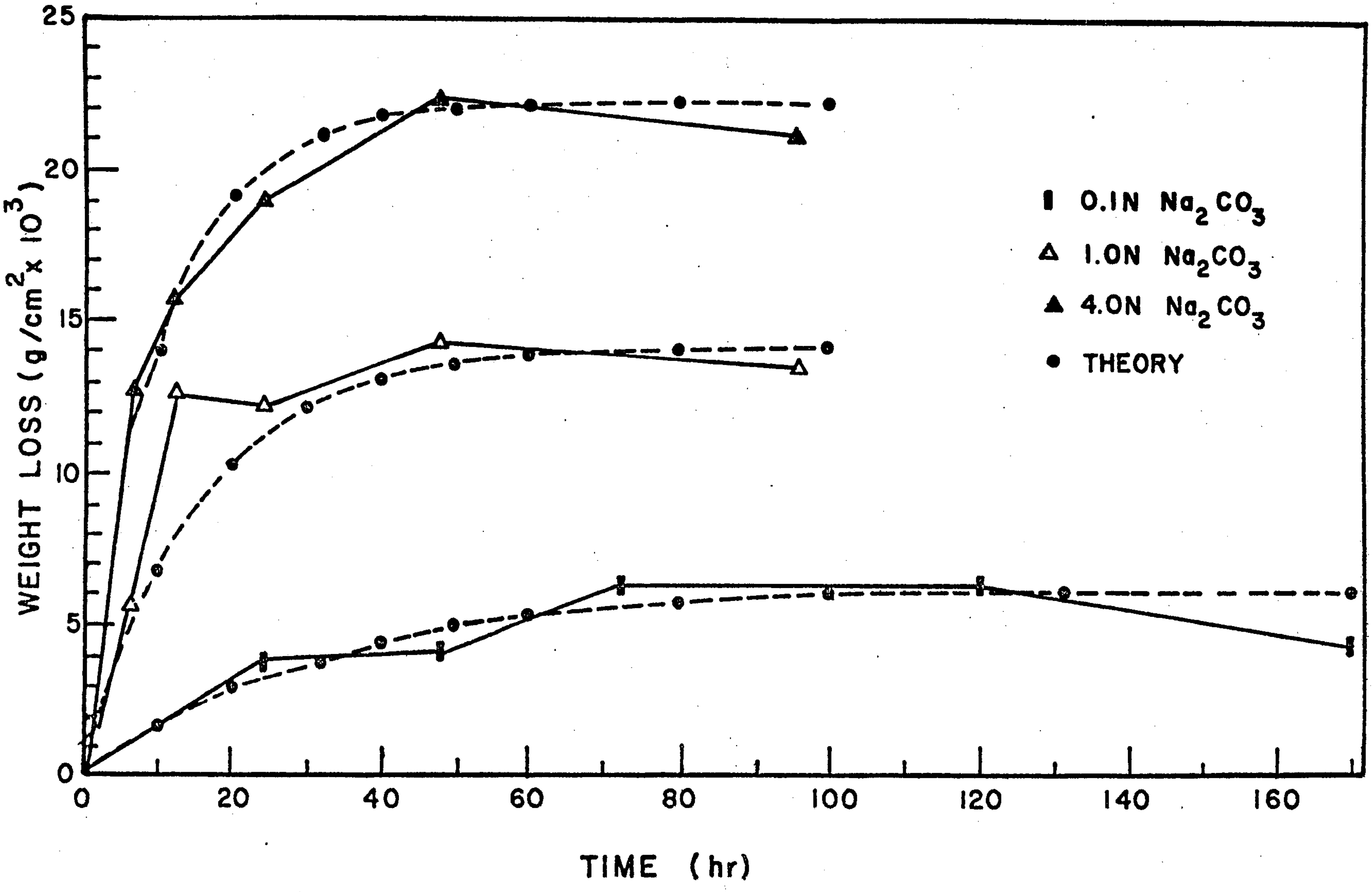

Fig. 2 Core slab weight loss at 200°C as grams per nominal surface area (cm^2) as a function of time for three difference sodium carbonate concentrations. A 55 cm^2 slab was used in 90 cm^3 of solution. The theoretical lines shown correspond to an integration of eq (4). (data taken by R. Charles[7]).

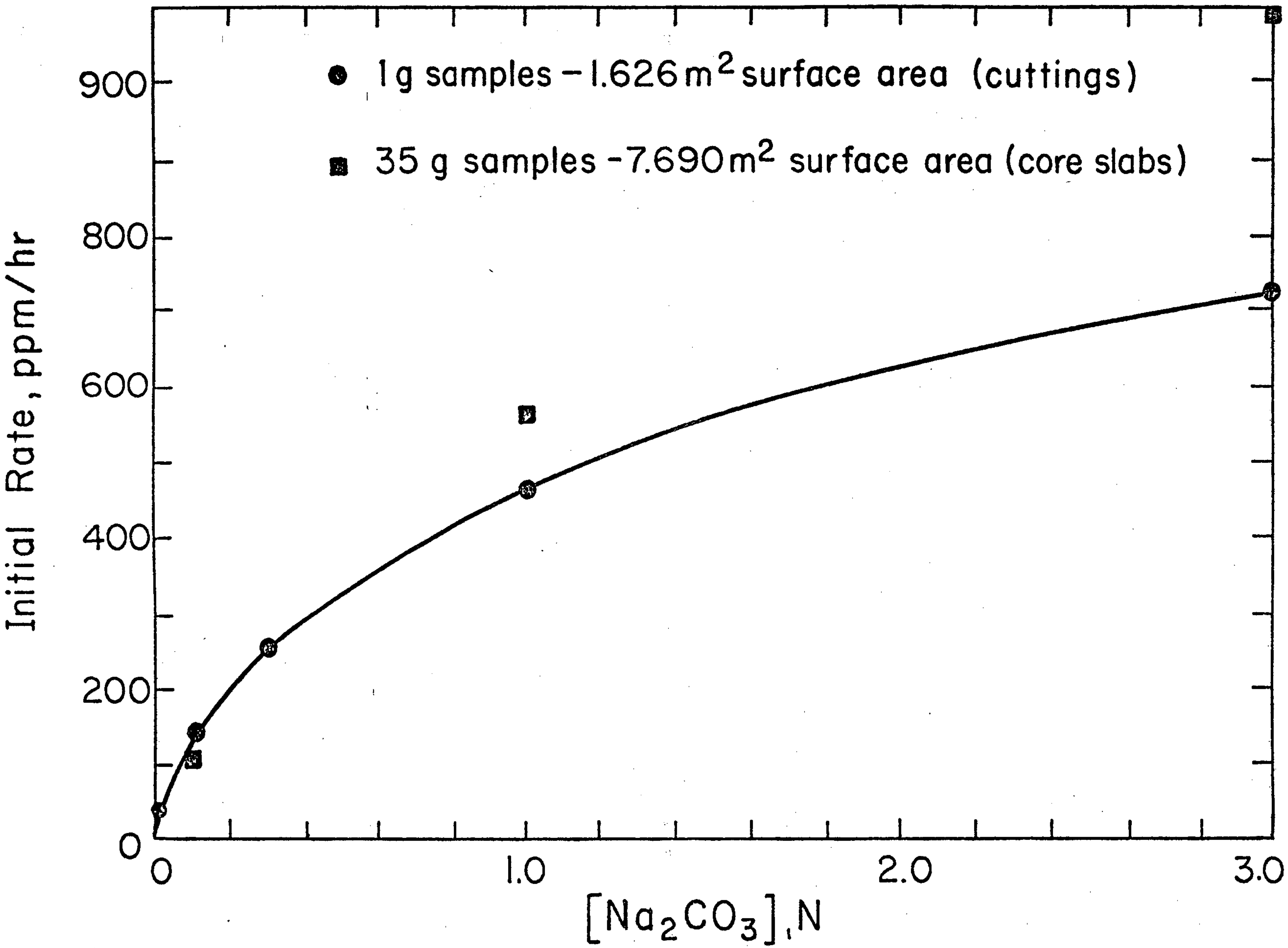

Fig. 3 Initial dissolution rate as a function of initial sodium carbonate concentration at 200°C. Accessible rock surface areas listed.

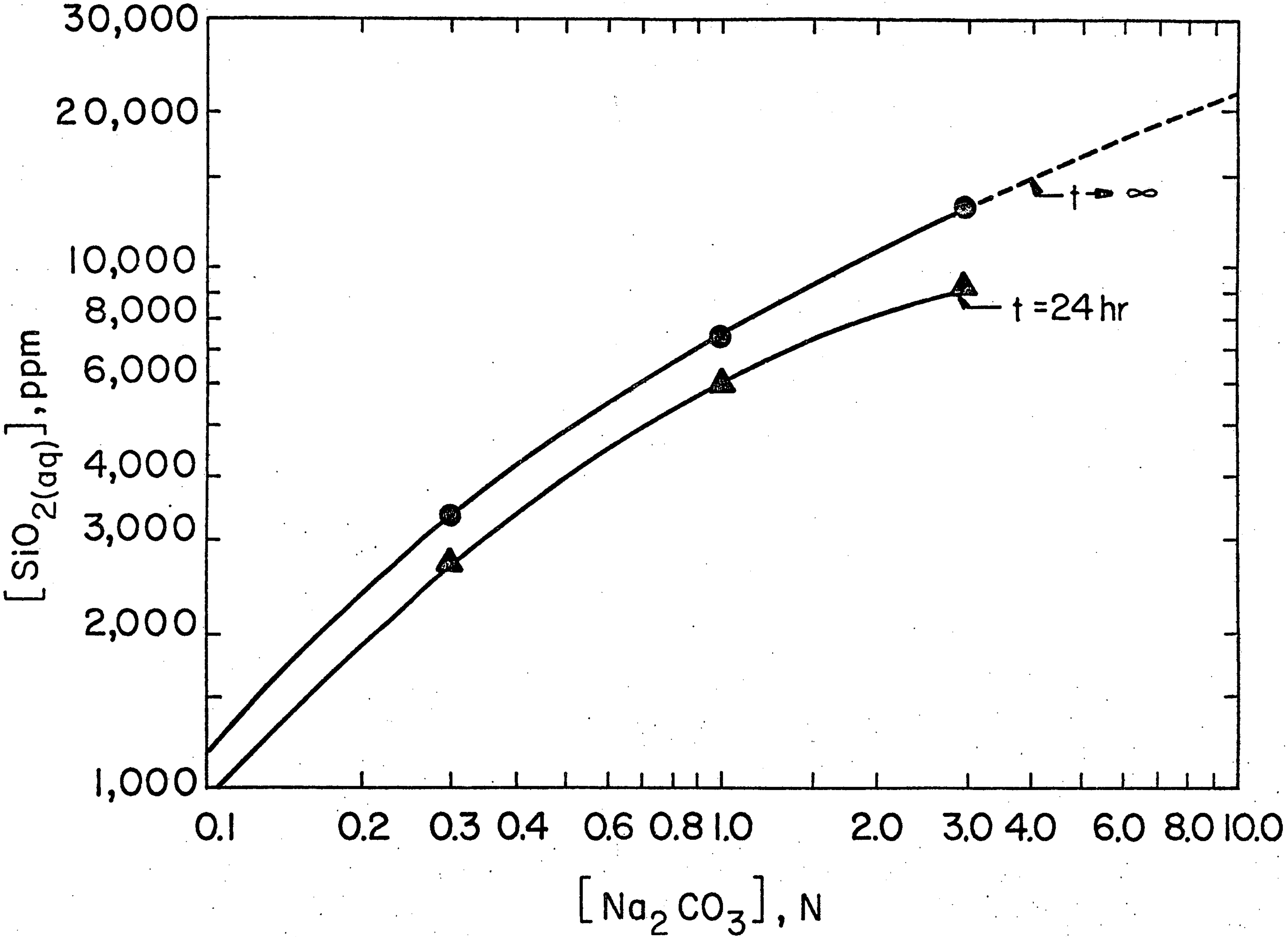

Fig. 4 Aqueous concentration as a function of initial sodium carbonate concentration.

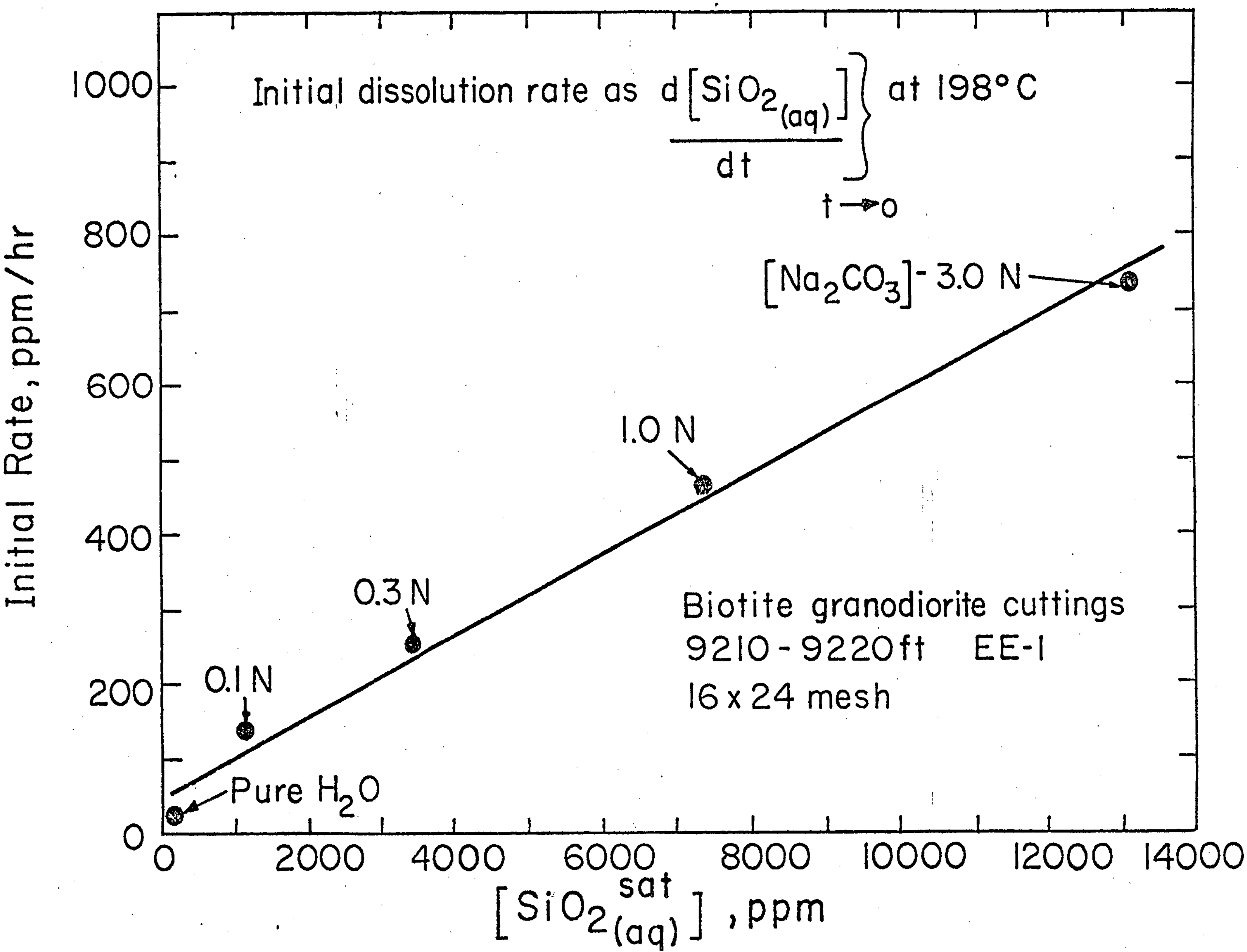

Fig. 5 Initial dissolution rate as a function of silica saturation concentration.

where all [ ] values are in gmoles/liter. Exponents are given to a 95% confidence level of accuracy. Before one can say how many OH^- ions are participating in the reaction, the effects of activity versus concentration need to be estimated.

SCALING IN HOT DRY ROCK SYSTEMS

Based on field and laboratory measurements, silica dissolves quite rapidly at temperatures $\geq$ 200°C reaching a quartz-limited saturation condition and thus provides the potential for a scaling problem in the heat exchange equipment associated with our hot dry rock energy extraction loop. As heat is removed, temperatures will decrease from 200°C to 40°C at which point the aqueous silica concentration is supersaturated with respect to all known forms of solid silica from crystalline quartz to amorphous silica gel.[5] The nucleation and growth kinetics of scale formation for fluids of this composition are virtually unknown. Consequently a combined laboratory and field program is underway to evaluate the magnitude of the problem. Air-cooled finned-tube heat exchange modules will be used in the 10-20 MW(thermal) field experiments and will be fully instrumentated to provide diagnostic information on the location and growth rates of scale. Laboratory experiments using high velocity (Reynolds numbers up to 50,000) circulation loops are underway to characterize the parametric dependence of scale nucleation and growth for simulated hot dry rock fluids. Particular attention will be given to the role of colloid formation and silica polymerization, substrate condition, and boundary layer hydrodynamics in influencing the kinetics of scale formation. Results of these experiments will be reported in a later paper.

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