Dissolution rate of powdered quartz in acid solution

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Abstract—The study reported in this paper concerns the role of salts in dissolution of powdered quartz. Kinetic dissolution experiment was carried out in acid media at 60 and 90°C to know the mechanism of acid alteration of rocks. The dissolution rate of silicon was accelerated by addition of such salts as sodium chloride and sodium sulfate in solution above about pH 2 but not affected below about pH 2. An accelerating effect of divalent sulfate ions was greater than that of monovalent chloride ions. Moreover, this effect became remarkably greater with increasing concentration of salts, increasing temperature and increasing pH value from 2 to 4.

INTRODUCTION

The studies on the dissolution rate of solid silica were summarized by ILER (1955). Dissolution of silica is one of the most important reactions in geochemical processes, such as weathering and alteration of rocks. In areas near active volcanoes rocks are often altered by action of acid thermal solution or gases. Geological and mineralogical investigations have been carried out by many investigators. For example, LOVERING (1957) reported the precise study on the alteration of volcanic ash at Valley of Ten Thousand Smokes. But much remains to be learned of the reaction of parent materials with chemically active fluids.

Acid thermal alteration of wall rocks at the earth's surface should be considered as the reaction in open systems. Moreover, the reaction of silicate with solution is generally slow. In such reactions the equilibrium will not be reached. Accordingly, in alteration the reaction rate will be more significant than the equilibrium relation between minerals and their environments, as pointed out by GARRELS (1958).

Alteration processes consist of decomposition and rearrangement of original materials in the hydrothermal solution. The initial step of the reaction is the decomposition of minerals or the breakdown of chemical bonding in minerals.

While the alteration reaction is complicated because of numerous variables, one of the most important factors is the chemical character of active solution. Then,

kinetic dissolution experiments on the decomposition of powdered quartz were carried out to examine the influence of the chemical character of active solutions. The study reported in this paper concerns mainly the role of salts in decomposition reaction of powdered quartz.

EXPERIMENTAL

As seen in Fig.1, only plastic equipments were used for this experiment to avoid contamination. A polyethylene bottle of 500ml fitted with a polyethylene condenser was placed in a constant temperature bath. The pH values and anion concentrations of leaching solutions were adjusted by addition of acid and salt solutions into distilled water. From 0.5 to 2g, but usually 1g of powdered quartz (150 ~ 200 mesh) was suspended in 300ml of the leaching solution, which was stirred continuously with a magnetic stirrer coated with polyethylene for 30hr. The pH values of the leaching solution were measured in the range from 60 to 90°C with a high temperature pH meter, while little differences were found in the pH values of the initial and final solutions in this experiment.

The dissolution rate of silicon was determined by periodically pipetting a 10ml aliquot from the bottle, by filtrating through a 0.45μ Millipore filter to remove powdered quartz and by chemically analyzing the filtrate, in which silicon was determined colorimetrically by the molybdenum blue method. The state of silicon dissolved in the solution will not be considered in the following discussion because it can not be known by this experiment.

Fig.1. Equipment for experiment

RESULTS AND DISCUSSION

Dissolution curve of silicon

The amounts of dissolved silicon at different times are shown in Figs.2 to 5. As seen in Fig.2, below about pH 1, i.e., in strongly acid solution the data gave curved lines which imply the gradual decrease in the dissolution rate of silicon with time. More distinctly curved lines were obtained at 90°C than at 60°C and in hydrochloric acid of pH 0.2 than of pH 1.1. The dissolution rate of silicon was not affected by the addition of salt in a strongly acid solution.

Fig.2. Concentration of dissolved Si in HCl at different times. pH 0.2 —●—, pH 1.1 —○—

Fig.3. Concentration of dissolved Si in HCl at different time. pH 2.1 —●—, pH 3.1 —○—, pH 4.2 —●—. (Data of pH 3.1 are plotted on the line of pH 4.2 at 60°C).

Fig.4. Concentration of dissolved Si in 0.5M Cl^- solution adjusted with HCl & NaCl at different times. pH 2.1 —○—, pH 3.2 —●—

Fig.5. Concentration of dissolved Si in 0.5M Cl^- solution adjusted with HCl & NaCl at different times.

In hydrochloric acid of about pH 2 to 4 the data gave nearly straight lines as seen in Fig.3. In the range of about pH 2 to 3 the dissolution rate was increased by the addition of sodium chloride though curved lines were not obtained as seen in Fig.4. As shown in Fig.5, at about pH 4 curved lines were obtained again with a remarkable increase in the dissolution rate by the addition of sodium chloride.

Approximate equation for dissolution rate of silicon

Figure 6 shows that the amount of dissolved silicon at any time was approximately proportional to the weight of powdered quartz suspended in the leaching solution. OKKERSE *et al.* (1961) reported the decrease in the surface area of silica gel due to the change in the surface texture after heating the gel in solutions of different pH values.

Assuming that the change in the surface of powdered quartz brought about the depression of the dissolution rate with time, we get curved lines shown in Figs.

2 and 5, and the following approximate equations:

$$m = K_1 S t + m_0$$

$$S = S_0(1 - K_2 t)$$

$$m - m_0 = K_1 S_0 t - K_1 K_2 S_0 t^2$$

where m and m_0 are the amounts of dissolved silicon at time t and zero, S and S_0 the surface area of powdered quartz at time t and zero, and K_1 and K_2 the rate constants for dissolution of silicon and for decrease in apparent surface area, respectively. The amounts of rapidly dissolved silicon at the initial stage is m_0 and appears as an intercept on the data plot. Therefore, m_0 was obtained from an intercept of the dissolution curve on the y-axis.

As the surface area of powdered quartz was not measured in this experiment, $K_1 S_0$, which represents the dissolution rate at time zero, will be used in the following discussion.

Fig.6. Concentration of dissolved Si at different times when powdered quartz of 0.5, 1.0 and 2.0g were suspended in HCl of pH 1.1 at 90°C.

Influence of pH, temperature and salts

Figure 7 shows $K_1 S_0$ in the solution of different chloride ion concentrations at different pH values at 90°C. ILER (1955) summarized that sodium chloride greatly accelerated the formation of soluble silica

Fig.7. Apparent rate at different pH values. Influence of Cl^- at 90°C.

Fig.8. Plot of apparent rate v. chloride concentration pH 3.5 —●—, pH 4 —○—

from colloidal silica. In this experiment the dissolution rate was accelerated above about pH 2 but not below about pH 2, with increasing concentration of chloride ions. Moreover, this figure shows that an accelerating effect by chloride ions becomes remarkably greater with increasing pH values from 2 to 4.

Figure 8 shows the approximately linear relation between the logarithm of K_1S_0 and the logarithm of chloride ion concentration. As seen in this figure, the increase in chloride ion concentration, the increase in pH value and the rise of temperature accelerated the dissolution rate of silicon.

Figures 9 and 10 show that the dissolution of silicon was catalyzed by sulfate ions as well as chloride ions and that the catalytic activity of divalent sulfate ions was higher than that of the monovalent chloride ions.

Fig.9. Apparent rate at different pH values.
Influence of SO_4^{2-} at 90°C .

Fig.10. Plot of apparent rate v. anion concentration at pH 3.5, $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$
—○—, $\text{HCl} + \text{NaCl}$ —●—.

As is generally known, water molecules tend to react as ligands with a number of cations and to form complexes. Since anions, such as chloride and sulfate ions which are abundant in the hydrothermal solution, are also ligands, it is reasonable to expect that they behave in much the same way as water molecules. In this way chloride and sulfate ions as catalysts promote undoubtedly the breakdown of chemical bonds in the original minerals, which might facilitate the rearrangement to more stable structures under the new conditions.

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