PROCEEDINGS, 49th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 12-14, 2024
SGP-TR-227

Interaction of Silica Glass Solubility and Metal Corrosion under Supercritical Condition

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Keywords: dissolution rate, corrosion rate, silica glass, iron plate, supercritical

ABSTRACT

The experiment to estimate the interaction of dissolution behavior of silica glass and iron plate corrosion under supercritical condition (400-500 degree C, 40-96MPa) was carried out. Firstly, the dissolution rate of silica glass increased with pressure and temperature. But in the case of same pressure (60MPa), the Si concentration of fluid was higher at lower temperature due to higher fluid density. Secondary, in the case of the test with iron, the silica dissolution rate increased. But Si concentration was almost same. Fe concentration is higher than the case without iron. And at the surface of iron plate, fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) are precipitated. Then the increasing of silica dissolution was due to consuming of aqueous silica to precipitate fayalite and this suggest that the metal casing has possibility influence the reservoir rock dissolution.

1. INTRODUCTION

Supercritical geothermal resources are found in higher temperature and pressure regions than those of traditional geothermal resources used for power generation. If these resources could be developed, they may increase the amount of geothermal power generated and reduce the CO_2 emissions from conventional energy resources. Therefore, investigation and research has been ongoing around the world, for example, the Kakkonda geothermal field in Japan, three regions in Iceland, including the Krafla and Reykjanes area where the Icelandic Deep Drilling Program (IDDP), the Rotokawa area in New Zealand, the Larderello area in Italy, and the Geysers area in the United States, as areas with especially high potentials for supercritical geothermal development (Reinsch et al., 2017).

Supercritical fluids have a density close to that of liquids and high dissolution ability, while retaining gas transport properties and compression ratio. Due to high compression ratio, the physical properties change significantly even with slight changes in temperature and pressure. This means that even small changes in temperature and pressure of geothermal fluids can significantly change their ability to dissolve rocks and transport solutes. Experiments on the reaction between rocks and water under supercritical conditions have been carried out, for example, by Kennedy (1950) and Morey et al. (1951). Furthermore, Fyfe et al. (1978) assumed that the equilibrium state of the system was an equilibrium between the elution of quartz into the solution and the precipitation from the solution and added kinetic considerations of mass loss and deposition.

The casing metal materials is expected to use in many cases for the extraction of geothermal energy. In the supercritical region, the dissolution of rocks will change by the influence of metal ions from material corrosion or scale precipitation on material.

Then we carried out the experiment of water-rock-material interaction at supercritical region. To simplify the experiment, the rock was represented by the main component, SiO_2, and the metal was pure iron. Here, a glass sample was used as the quartz. The glass sample has a higher solubility than quartz, so we thought it would be possible to see the effects of pressure and the presence of iron in a short term. In this study, we measured the weight loss rate of quartz glass, investigated its relationship with dissolved concentration, temperature and pressure dependence, and changes when iron was added, and investigated the possibility of adaptation to deep geothermal heat (Yanagisawa et al.,1997).

2. EXPERIMENT

There are several methods for measuring the dissolution of quartz in supercritical fluids, and Fournier (1982) broadly divided them into three types. (1) Obtained from the change in mass of quartz before and after the test. (2) Rapidly cool the reaction vessel and analyze the silica remaining in the solution after opening the vessel. (3) While maintaining the reaction vessel at high temperature and pressure, extract solution and analyze the silica. Then, this test was conducted using method (1), and the sample was further shaped into a plate.

The quartz glass used in the experiment is made of Sendai quartz, has a polished surface, and measures 20 x 10 x 1 mm^3 (weighs around 0.43 g). The pure iron is made by Showa Denko and has a purity of 99.99% or higher. After cutting it into 20 x 10 x 1 mm^3 (weighing around 1.4 g), it is polished to No. 400 with emery paper and polished with a HNO_3 + HF mixture. The mechanical layer was removed by chemical polishing. After that, it was washed again with acetone and dried for more than 24 hours before being tested. The mass of this test piece was measured with an accuracy of 0.01 mg using an electronic balance.

The test used a small self-contained autoclave with an internal capacity of 30 ml (height 100 mm, diameter 20 mm) connected to a pressure holding device as shown in Fig. 1. The autoclave's main body is SUS310S and the internal volume is 30ml. The pressure holding device of autoclave consists of pneumatic piston cylinder, regulator, valve and pressure gauge. The pressure was adjusted by a regulator after reaching the set temperature. Measurement errors were kept within ±2°C for temperature and ±0.5MPa for pressure. To avoid crevice corrosion due to direct contact between the sample and the inner wall of the autoclave, the sample was placed inside an alumina tube, and both quartz glass and pure iron were placed vertically. In addition, in a system where both were coexisting, the wide surfaces of the samples were made not to overlap.

EXPERIMENTAL

SiO_2 glass (STARTING MATERIAL)	
Purity	99.9%
Initial water	200 ppm
Size	10 X 20 X 1mm
CONDITIONS OF HYDRATION	
Temperatures	400,450 and 500℃
Pressures	40,60,80,96 MPa
Durations	6 to 144 hours
Solution	Pure Water
Volume	30ml

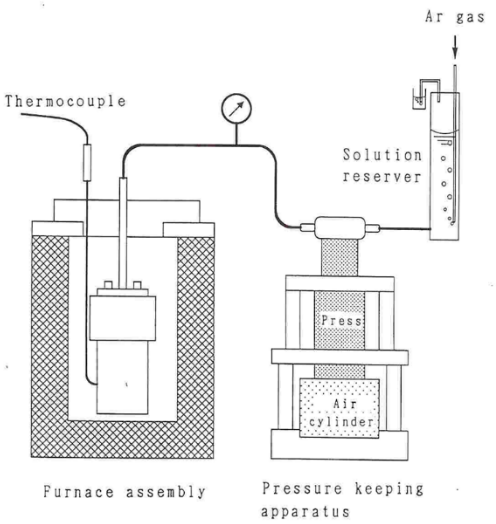

Figure 1: Test Condition and

The test was conducted at a temperature of 500°C, a pressure of 40-96MPa, and a time of 24-168 hours. The fluid used was pure water that had been degassed with argon gas in advance. After the test, the mass of the sample taken out from the autoclave was measured after drying. Regarding pure iron, corrosion products on the sample surface were observed using a scanning electron microscope (SEM) and then identified by X-ray diffraction. In addition, the Si and Fe concentrations of the solution after the test were measured by inductively coupled plasma (ICP) emission spectrometry. The amount of solution collected was approximately 28 ml, that is, the volume of the sample and the alumina tube was subtracted from the internal volume of the autoclave.

3. RESULTS

3.1 Test time and weight reduction of silica glass

Figure 2 shows the time dependence of the weight loss per unit area of silica glass at 60 and 80 MPa, 500°C. The weight loss is approximately proportional to test time, and this means the dissolution rate is constant until 168 hours.

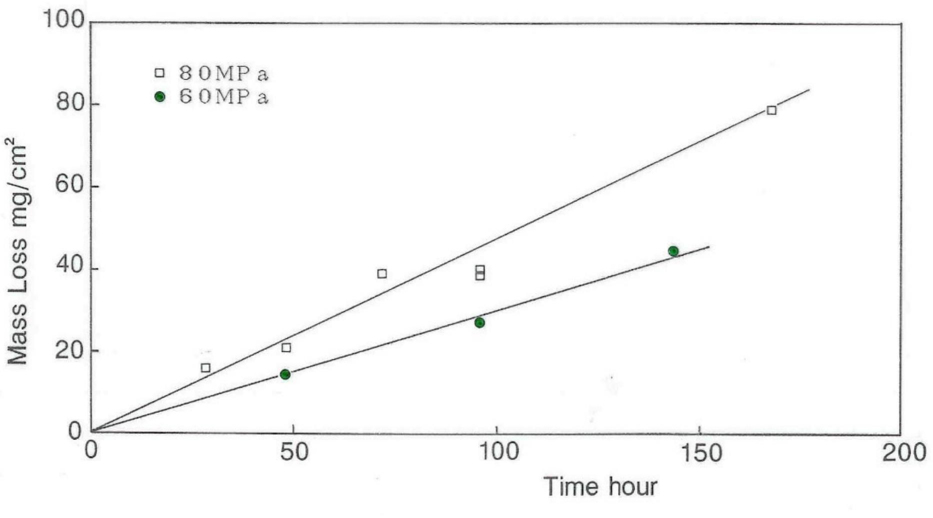

Figure 2: Mass Loss of Silica Glass versus Test time

3.2 Pressure dependence of mass reduction of silica glass

Figure 3 shows the relationship between the rate of weight loss rate per unit area of silica glass and pressure. In the range of 40-96 MPa, the weight loss rate showed an almost linear change and changed from 0.05 to 0.7 mg/(cm^2・h). Figure 4 shows the relationship between the Si concentration of the solution and the pressure, which also has an almost linear relationship with the pressure. The dissolution rate value in Fig. 3 is not directly proportional to the pressure and becomes 0 at about 35 MPa when extended to the lower pressure side. And the dissolution rate of quartz glass depends on pressure is that the amount of reaction increases as the Si concentration increases. In addition, the right side of Fig. 3 shows the value of the dissolution rate converted per year. At 96MPa, it reaches about 30mm per year.

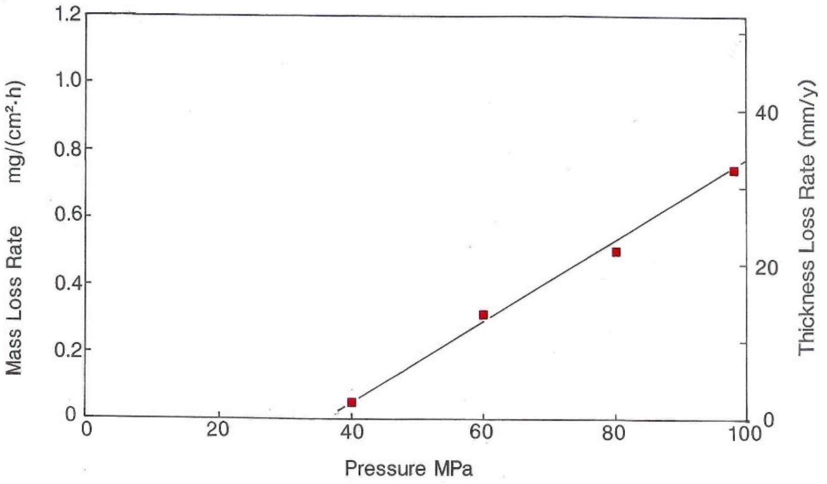

Figure 3: Mass Loss of Silica Glass versus pressure at 500 C

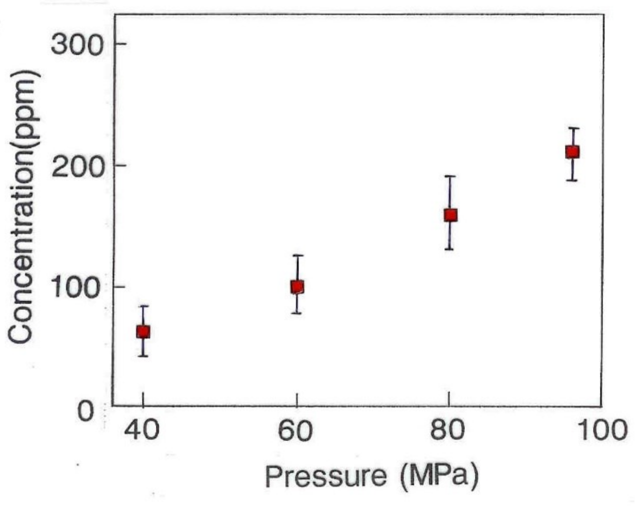

Figure 4: Si concentration versus pressure at 500C

3.3 Temperature dependence

Figure 5 shows the relationship between the melting rate of quartz glass and temperature from 400 to 500 °C at 60MPa. The dissolution rate increased with temperature. And Fig.6 shows the concentration of Si decreased with temperature as "retrograde solubility" by Fournier (1983).

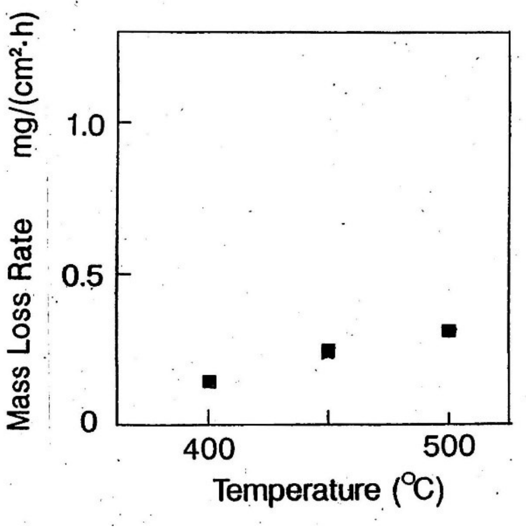

Figure 5: Mass Loss of Silica Glass versus temperature at 60MPa

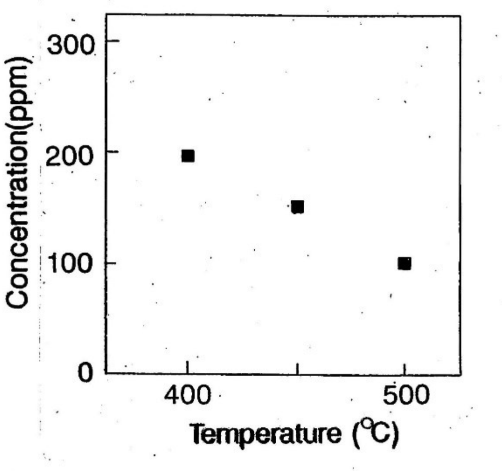

Figure 6: Si concentration versus temperature at60MPa

3.4 Dissolution of quartz glass when adding iron plate sample

Figure 7 shows the weight loss rate of quartz glass when a pure iron plate sample (20 x 10 x 1 mm) was added at 500°C compares with the case of quartz alone. The dissolution rate accelerated at all pressures compared to when using only quartz glass. It also showed a linear change in the range of 40-96 MPa. The slope of the straight line was as the same as that of the sample made only of quartz glass. The difference due to the addition of iron was about 0.2 mg/cm^2/hr, which corresponded to 10 mm/year.

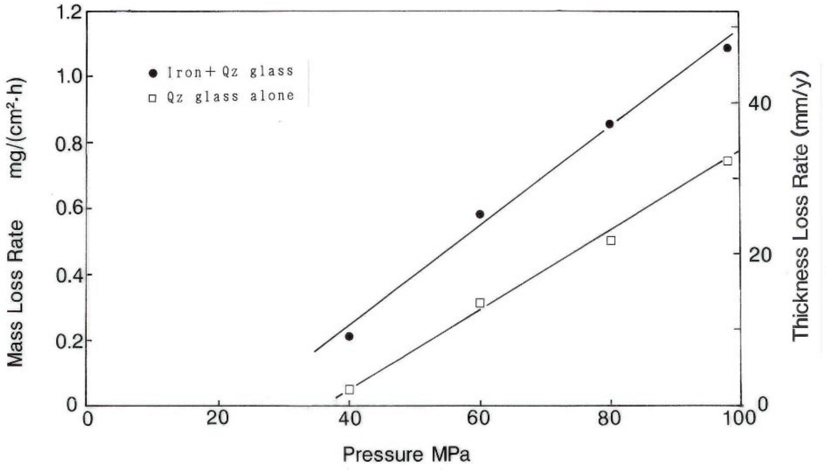

Figure 7: Mass Loss of Silica Glass versus pressure at 500 C

Table 1: Precipitated minerals on iron surface detected by X-ray diffraction. Double circle show the high strength of X-ray diffraction.

	500C, 60MPa			500C, 96hr			Iron plate Only
	48hr	96hr	144hr	40MPa	60MPa	80MPa	
Magnetite (Fe_3O_4)	◎	○	○	◎	○	○	○
Fayalite (Fe_2SiO_4)	○	○	◎	○	○	◎	
Cristobalite (SiO_2)			○			○	

Table 1 shows the identification results by X-ray diffraction of precipitated minerals on the iron plate surface. Besides the underlying iron, the peaks of magnetite (Fe_3O_4) and fayalite (Fe_2SiO_4) were detected. The X-ray diffraction strength of fayalite relative to magnetite becomes stronger as time passes and pressure increases as the mass of quartz glass decreases. At the same time, crystallization of cristobalite (SiO_2) was also observed. Here, the plate-like crystals seen in surface observation are magnetite and fayalite, and the spherical particles are cristobalite. In addition, when X-ray diffraction was performed on the substance attached to the alumina tube, a peak of goethite (FeO(OH)) was observed. There is also a possibility of the formation of an amorphous material consisting of Fe and Si.

Figure 8 shows the relationship between Fe concentration and pressure at 500 C in the case of test using only iron plate, iron plate plus quartz glass and only quartz glass. The difference of Fe concentration between the quartz glass + iron plate system test and the iron plate sample only test system became larger as the pressure increased. In the case of only the iron plate sample, Fe concentration show the peak value at 60 MPa and decreased on higher pressure region. And in the case of only quartz glass sample, Fe concentration value (4.6 ppm) is considered from the inner wall of the autoclave, but when a blank test was performed to check, and the Fe concentration was 2.3 ppm. Both values were increased compared to the value in pure water (0.05ppm) before the test.

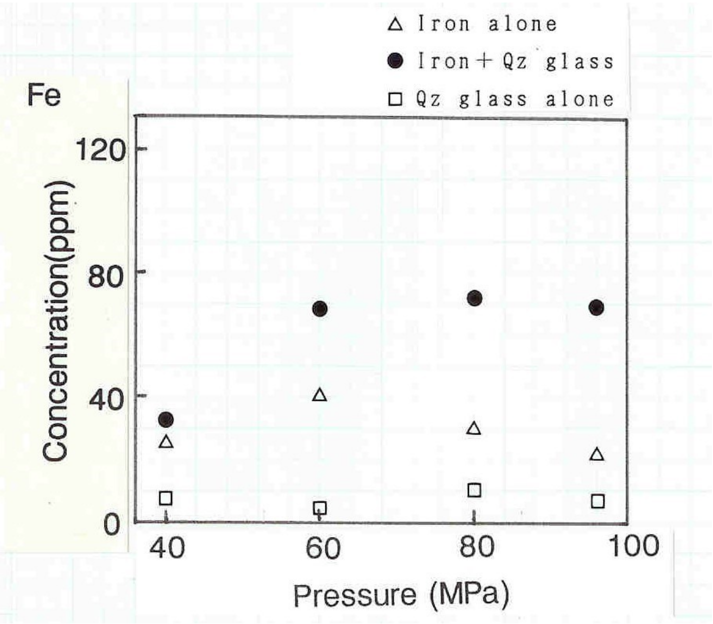

Figure 8: Fe concentration versus pressure at 500C

Figure 9 shows Si concentration dependence with time and pressure at 500°C with that of the quartz glass sample only, there was almost no difference from in the case of quartz glass and iron plate test. Al concentration originating from the alumina tube in the system had almost no difference depending on the presence or absence of iron, like Si, and the value was less than 10 ppm. There was also no difference in the ratio between the amount of quartz dissolved and the amount attached to alumina depending on the presence or absence of iron. It is considered that the increase in the amount of quartz glass dissolved by adding the iron plate is mainly due to the consumption of silica in the solution due to the formation of fayarite on the surface of the iron plate sample.

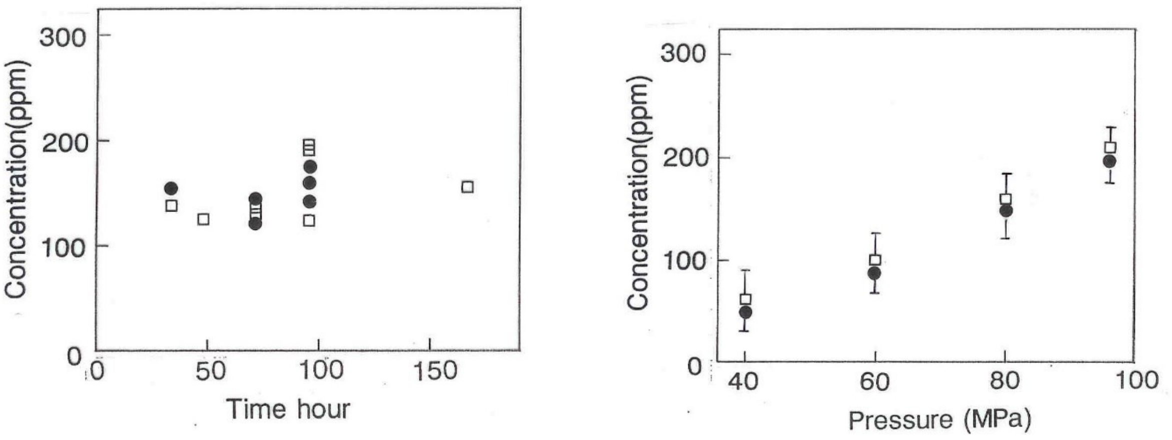

Figure 9: Si concentration versus time and pressure at 500C

3.6 Effects of the area of the iron plate sample and when using SUS304 plate

Figure 10 shows the weight loss of quartz glass change with the reaction area ratio of iron plate and quartz glass from 0 to 2. As the surface area of the iron plate increased, the amount of dissolved quartz glass increased linearly. This indicates that the amount of dissolved iron or the amount of deposited iron minerals on the surface corresponds to the amount of dissolved glass.

And Fig. 10 shows the case weight loss of quartz glass when SUS304 is used instead of iron plate and the value shown as open square symbol. The amount of glass was same as the case of only quartz glass used. In the case using SUS304, Ni and Cr oxides were formed on the surface, but iron oxides and silicate minerals were not detected. And Fe concentration in the solution using SUS304 was same as in the case of quartz alone.

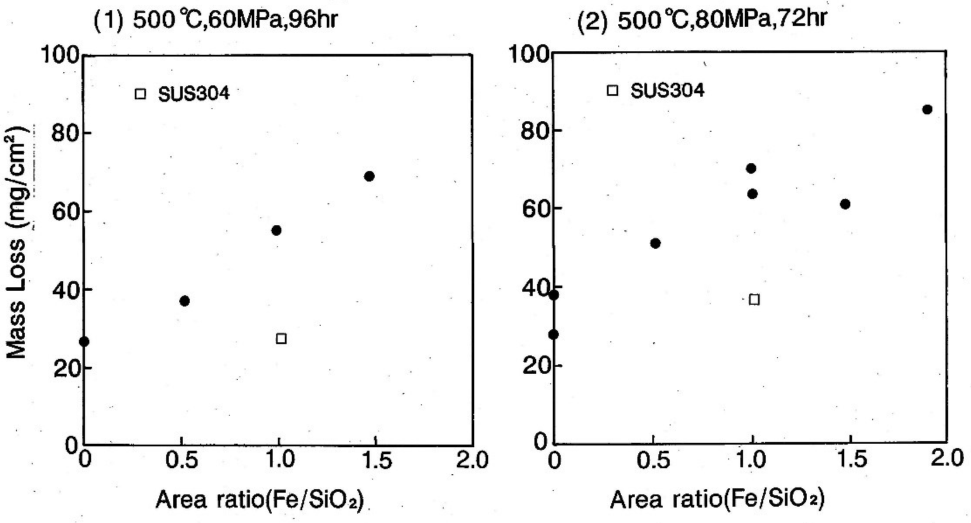

Figure 10: Mass Loss of Silica Glass versus area ratio

4. DISCUSSION

In this test system, quartz glass dissolved as silica ion in solution and precipitated as cristobalite or fayalite on iron plate. And silica deposition has been observed not only at temperature drop areas such as connections to pressure holding devices, but also on alumina tubes near quartz glass and on the outer walls of autoclaves.

And at supercritical condition, the fluidity of the fluid becomes faster, and the hydrated silica near the surface is transported faster and deposited in the autoclave. In this system, the movement of dissolved silica within the fluid was difficult as rate-determining process. Then, the melting of glass or the deposition of silica is thought to be rate-determining. If deposition of silica were rate-determining, the Si concentration should continue to rise during the measurement, but Si concentration was almost constant during test duration. This suggests that dissolution of quartz glass is rate-limiting process.

Table 2: Change of mass loss rate by temperature at constant density

Temperature (C)	Pressure (MPa)	Density (g/cm^3)	Mass Loss (Q) (mg/cm^2/hr)	LogQ	1000/T
450	60	0.476	0.27	-0.569	1.383
500	86	0.476	0.60	-0.222	1.294

In addition, based on the results of the dissolution test at 450°C, we attempted to calculate the activation energy at 450-500°C when the density is equal. Table 2 shows the dissolution rate, its logarithm, and the value of 1000 times the reciprocal of temperature. Here, R is the gas constant.

$$\varDelta \log Q = E \times \varDelta(1000/T)/2.303R \tag{1}$$

The activation energy was calculated to be approximately 75kJ/mo1. This value is close to the activation energy of dissolution reaction on the silica glass surface (60.9-64.9 kJ/mol (Rimstidt & Barnes (1980)). It is also closer than the activation energy of deposition (49.8 kJ/mol (Rimstidt & Barnes (1980)) and the activation energy of diffusion (16 to 21 kJ/mo1 (Lasaga (1984)). Then, the dissolution rate and its dependence on pressure are the result of reflecting the surface reaction, which is the rate-determining process. This is also shown by the relationship between the dissolution rate at 400-500°C and the concentration of Si in the solution.

And we discuss about the reaction rate for each experimental condition. Fyfe et al. (1978) treat the system as having reached an equilibrium between silica dissolution and deposition when the concentration of the solution remains constant several hours after the test. Here, if the dissolution rate constant is a, the deposition rate constant is b, and the concentration is x, then the change in the concentration of the solution is as follows:

$$dx/dt = a - bx \tag{2}$$

This formula converted as follows:

$$x = a/b[1-\exp(-bt)] \tag{3}$$

From this formula, b can be calculated from the time the concentration as reached a constant level, and a can be calculated from the equilibrium concentration x. In other words, if time to reach equilibrium was longer, the value of b becomes smaller. Fyfe et al. (1978) found that when the pressures are approximately equal, both a and b depend on the temperature. In the case of the pressure increases at same temperature, the concentration of the solution increases and the time to reach equilibrium increases, so b becomes smaller and a becomes larger.

In this experiment, due to the Si concentration of the solution was not measured at short test duration, b cannot be directly determined from equation (2). But the Si concentration is almost constant in the case from 24 to 168 hours test. Therefore, a/b can be calculated from Si concentration. Here, the dissolution rate of quartz glass is proportional to the above dissolution rate constant a. Then, it is possible to estimate the deposition rate constant b from the Si concentration and dissolution rate.

Figure 11 shows the pressure and temperature changes in the deposition rate constant b when the iron-free system is set to 1 at 500℃ and 60MPa. The figure also shows the dissolution rate constant a. According to the results, when the pressure increased, b also increased up to 60 MPa, and remained almost constant above than 60MPa. And the variation of b when the temperature changed was greater than the variation of a. This shows that the lower the temperature, the longer time is required for deposition, which corresponds to the experimental results.

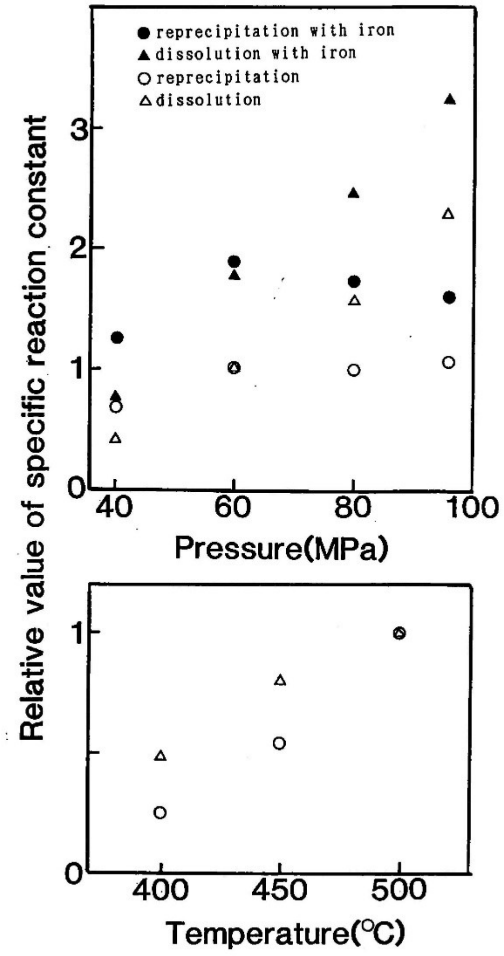

Figure 11: Relative value of specific reaction constant of dissolution and reprecipitation versus pressure and temperature. (Value at 500C , 60MPa and without iron is unit)

5. SUMMARY

(1) The dissolved weight of quartz glass dissolved was approximately proportional to the test time. The dissolution rate increases with the increase of pressure and temperature. At a pressure of 60 MPa, the Si concentration in the solution was higher at lower temperatures at 400-500°C, contrary to the dissolution rate.

The reason why the dissolution progresses continuously is the supercritical fluid has high fluidity and dissolved silica to precipitate at the periphery of autoclave at the same time. Then the activation energy for the dissolution rate was calculated approximately 75 kJ/mol. It suggests that the surface reaction in the silica glass is the rate-determining process in this system.

(2) When iron plate samples were added, the dissolution of quartz glass increased at 500°C and 40 to 96MPa. Fayalite precipitated on the surface of the iron plate sample. And Si concentration was same as the case of iron plate free system. Fayalite precipitation accelerated the dissolution of quartz glass. This corresponds that quartz glass dissolution increased with the surface area of the iron plate sample was increased. When SUS304 test plate was used instead of iron plate, the dissolution of quartz glass was same as without SUS304..

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