

## Research Article

# Corrosion Behavior of Simulated HLW Glass in the Presence of Magnesium Ion

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Received 13 May 2011; Accepted 5 July 2011

Academic Editor: Michael I. Ojovan

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Static leach tests were conducted for simulated HLW glass in  $MgCl_2$  solution for up to 92 days to investigate the dissolution mechanism of HLW glass under coastal repository condition. Under the condition that magnesium ion exists in leachate, the dissolution rate of the glass did not decrease with time during leaching, while the rate decreased when the magnesium ion depleted in the leachate. In addition, altered layer including magnesium and silica was observed at the surface of the glass after the leach tests. The present results imply that dissolution of the glass is accompanied with formation of magnesium silicate consuming silica, a glass network former. As a consequence, the glass dissolved with an initial high dissolution rate.

## 1. Introduction

For the performance assessment of high-level radioactive waste (HLW) glass to be disposed of in geological repositories, it is important to fully understand the corrosion of HLW glass by groundwater. The progress of glass dissolution has been understood as follows from extensive studies on HLW glass [1, 2]. The glass dissolution starts at an initial high dissolution rate called “forward rate” after contact with solution. As the contact time between the glass and the solution prolongs, the ion activities such as concentration of dissolved Si increases in the solution, and then the solution composition comes to near saturation for the glass. Under such near saturation conditions, the glass dissolves at a low rate called “steady state rate” which is also known as residual rate or final rate. Long-term corrosion of HLW glass is presumed to proceed at the steady state rate under stagnant groundwater likely to be in deep geological repository. It is also known for HLW glass that formation of minerals as a secondary phase such as zeolite assemblages of the analcime ( $NaAlSi_2O_6 \cdot H_2O$ ) type consumes dissolved silicon (Si) in solution and causes the dissolution rate to increase to as high as the initial high forward rate [2–4]. For performance assessment of HLW glass, it is therefore important to investigate

the influence of a secondary phase on the corrosion behavior of glass under repository conditions.

Under coastal repository condition, there is a possibility that relatively high amount of magnesium (Mg) ion is contained in groundwater. It is well known that several magnesium silicate minerals such as sepiolite [ $Mg_2Si_3O_6(OH)_4$ ], chlorite [ $Mg_5Al_2SiO_3O_{10}(OH)_8$ ] and saponite [ $(Ca,Na)_{0.33}Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ ] are thermodynamically stable in aqueous condition at below 100°C which is envisaged under repository condition. Formation of these minerals or other magnesium silicate minerals consumes dissolved Si at near the surface of glass.

Leach tests for simulated HLW glass have been conducted in solution in the presence of Mg [5–9]. Strachan [5] conducted static leach test using PNL76-68 glass, a borosilicate type simulated HLW glass developed in U.S.A, in brine solution containing KCl/ $MgCl_2$ / $NaCl$  at 70°C and 90°C, and no remarkable difference in dissolved glass was observed between brine solution and in deionized water (DIW). Grambow and Strachan [6] conducted similar tests using other types of simulated HLW glass, C31-3 and MCC76-68, in  $MgCl_2$  solution at 90°C, and observed the decrease in dissolution for MCC76-68 glass compared to that in DIW, while the amount of the dissolved glass in  $MgCl_2$

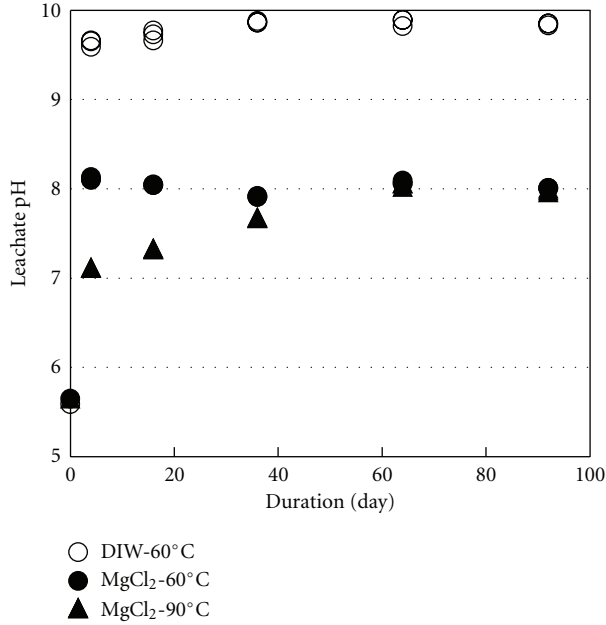


FIGURE 1: pH of the leachates versus time for DIW test and for MgCl<sub>2</sub> solution tests.

TABLE 1: A chemical composition of P0798 type simulated HLW glass.

Oxide	wt%	Oxide	wt%
Al <sub>2</sub> O <sub>3</sub>	5.00	Na <sub>2</sub> O	10.0
B <sub>2</sub> O <sub>3</sub>	14.2	Nd <sub>2</sub> O <sub>3</sub>	1.38
CaO	3.00	SiO <sub>2</sub>	46.6
CeO <sub>2</sub>	3.34	ZnO	3.00
Fe <sub>2</sub> O <sub>3</sub>	2.04	ZrO <sub>2</sub>	1.46
Li <sub>2</sub> O	3.00	Other	5.53
MoO <sub>3</sub>	1.45	Total	100

solution and in DIW was comparable for C31-3. In addition, Grambow noted that altered layer, suspected as sepiolite, formed in MgCl<sub>2</sub> solution had a potential to protect the glass from the dissolution [6]. These results may suggest that the effect of Mg on the glass corrosion depends on the composition of the glass.

In the present study, static leach tests were conducted for P0798 type simulated HLW glass in MgCl<sub>2</sub> solution for up to 92 days to investigate the dissolution mechanism of HLW glass under coastal repository conditions. The corrosion behavior of the glass is discussed focusing on both the formation of secondary phase and the characteristics of the leachate comparing with the glass corrosion in DIW.

## 2. Experimental

A P0798 type borosilicate glass, developed by Japan Atomic Energy Agency, was used as a specimen. The composition of the glass is shown in Table 1. Static leach tests were conducted

for powdered and finely polished coupon glass samples under the atmospheric condition. The grain size of the powdered glass sample was 75–150 μm, and the dimension of the coupon glass sample was 10 mm × 10 mm × 1 mm. The samples were cleaned ultrasonically with ethanol.

Magnesium chloride (MgCl<sub>2</sub>) solution and DIW were used as leachant for the leach test. The concentration of Mg in the MgCl<sub>2</sub> solution was adjusted to 1000 μg/cm<sup>3</sup>, which was in the same range as that in Japan's synthetic sea water. Powdered glass sample (1.0 g) and leachant (10 cm<sup>3</sup>) were placed in a Savillex Teflon leaching container, which was rinsed according to a method established by Materials Characterization Center (MCC) [10]. The leaching containers were then placed in an oven maintained at 60°C throughout the experiment for up to 92 days. At the test in MgCl<sub>2</sub> solution, a coupon glass sample was placed together with the powdered one in each container. A leach test was also conducted for powdered glass sample in MgCl<sub>2</sub> solution at 90°C. The leach tests were carried out three times.

After the leaching, the container was cooled to room temperature, and the leachate pH was measured, then the leachate was filtered through a Millipore filter with the nominal pore size of approximately 0.45 μm diameter. The concentrations of boron (B), sodium (Na), Si, and Mg in filtrates were measured by using an inductively coupled plasma atomic emission spectrometry (ICP-AES). The leached powdered glass sample and a coupon glass sample were subjected to surface analyses by use of a scanning electron microscope (SEM) and a secondary ion mass spectrometry (SIMS), respectively.

## 3. Results and Discussions

Figure 1 shows the pH of the leachates in MgCl<sub>2</sub> solution at 60°C and 90°C and in DIW at 60°C. The pHs for MgCl<sub>2</sub> solution at 60°C and 90°C reached 8 and 7 in the first 4 days, respectively, and were stable at around 8 during the rest of the leaching periods, which were lower by about two pH units than those in DIW.

Figures 2(a) and 2(b) show the normalized elemental mass loss (NL) for B, Na, and Si in DIW and in MgCl<sub>2</sub> solution at 60°C, respectively. The NLs were calculated by the following:

$$NL_i (\text{g/m}^2) = \frac{C_i}{f_i} \times \frac{V}{SA}, \quad (1)$$

where  $C_i$  is the concentration (g/m<sup>3</sup>) of element  $i$  in the leachate,  $f_i$  is the mass fraction of element  $i$  in the glass,  $V$  is the volume of the leachate (m<sup>3</sup>), and  $SA$  is the surface area (m<sup>2</sup>) of the glass exposed to the leachate.

The NLs for Na (NL<sub>Na</sub>) and B (NL<sub>B</sub>) were nearly identical during the test period for both test conditions as shown in Figures 2(a) and 2(b), indicating that B and Na congruently dissolved from the glass both in DIW and in MgCl<sub>2</sub> solution. Since B was assumed to be soluble under most experimental conditions and to accumulate in the leachates, the NL<sub>B</sub> has been used most frequently as a reliable quantitative indicator for the corrosion of borosilicate glass [11].

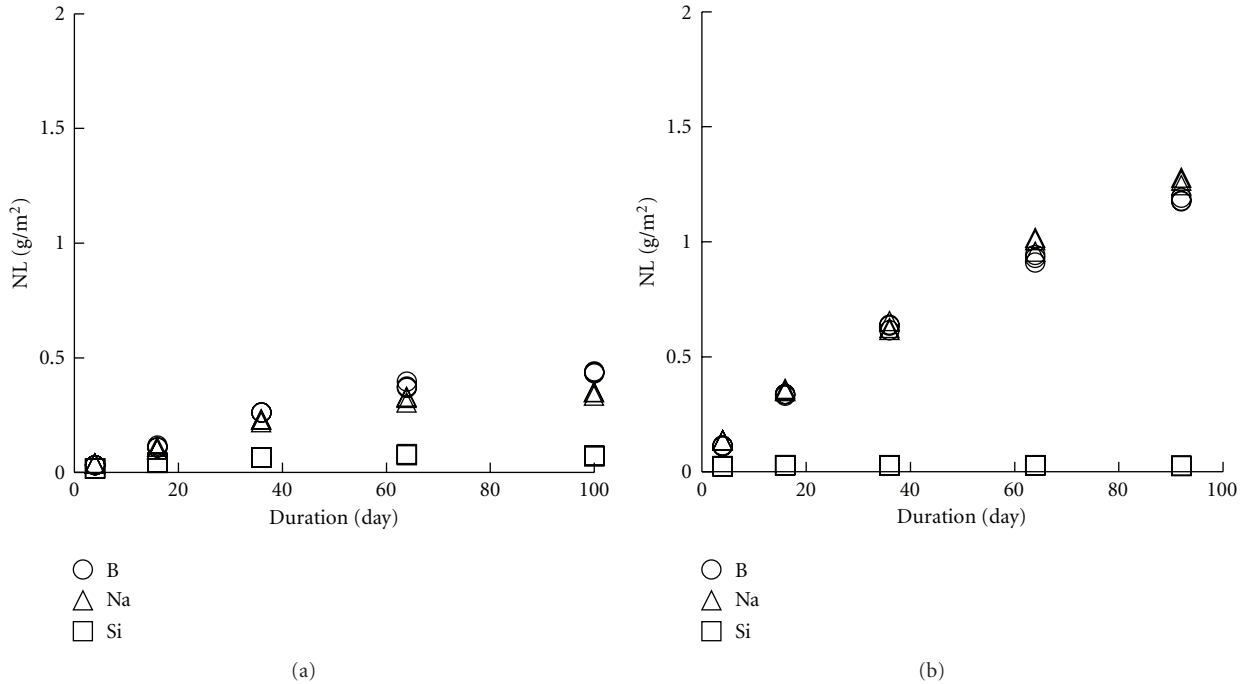


FIGURE 2: The NL for B, Na, and Si versus time for the tests in (a) DIW and in (b)  $\text{MgCl}_2$  solution at  $60^\circ\text{C}$ .

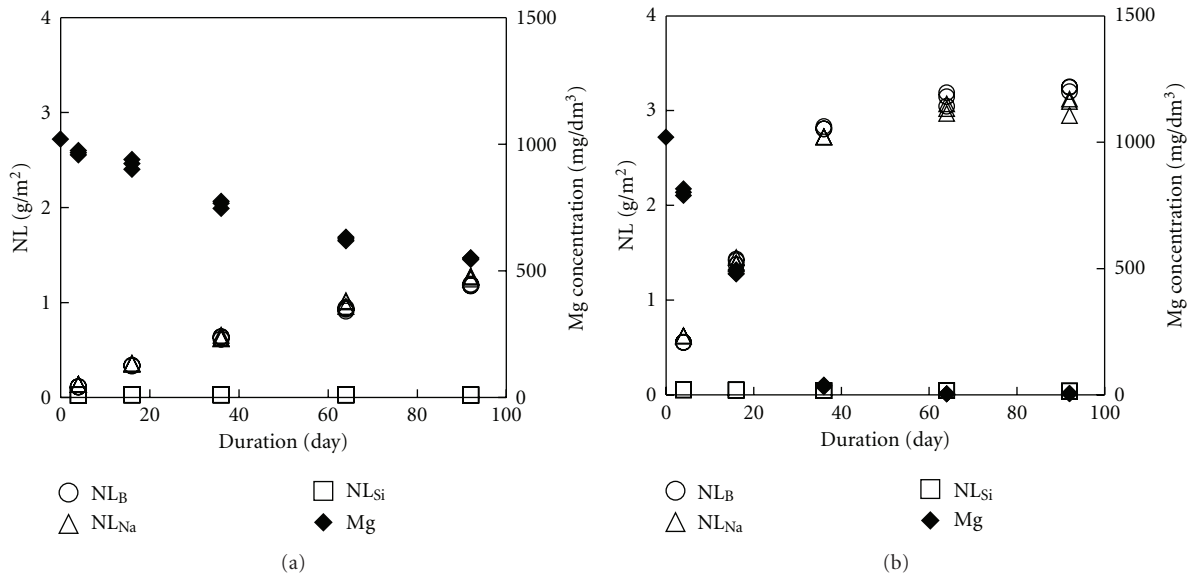


FIGURE 3: The NL for B, Na, Si, and the concentration of Mg in the leachates versus time for the tests in  $\text{MgCl}_2$  solution at (a)  $60^\circ\text{C}$  and (b)  $90^\circ\text{C}$ .

The  $\text{NL}_B$  in Figure 2(a) shows that the dissolution rate of the glass in DIW was nearly constant at initial test period of up to 64 days, then the rate decreased, whilst the NL for Si ( $\text{NL}_{\text{Si}}$ ) was constant throughout the testing period of 92 days. These types of dissolution behavior have been widely observed for HLW glass as the forward rate of dissolution (the so-called “stage I dissolution”) and following steady state rate of dissolution (the so-called “stage II dissolution”). On the other hand, the  $\text{NL}_B$  in  $\text{MgCl}_2$  solution showed

that the glass dissolved more than in DIW, and stage II dissolution was not observed during the test period at  $60^\circ\text{C}$  as seen in Figure 2(b). The  $\text{NL}_{\text{Si}}$  in  $\text{MgCl}_2$  solution was constant and lower than that in DIW for the test period.

Figures 3(a) and 3(b) show the  $\text{NL}_B$ ,  $\text{NL}_{\text{Na}}$ , and  $\text{NL}_{\text{Si}}$  for the tests in  $\text{MgCl}_2$  solution at  $60^\circ\text{C}$  and  $90^\circ\text{C}$ , respectively. Also plotted by solid diamonds are the concentrations of Mg in the leachate. The concentrations of Mg decreased with the

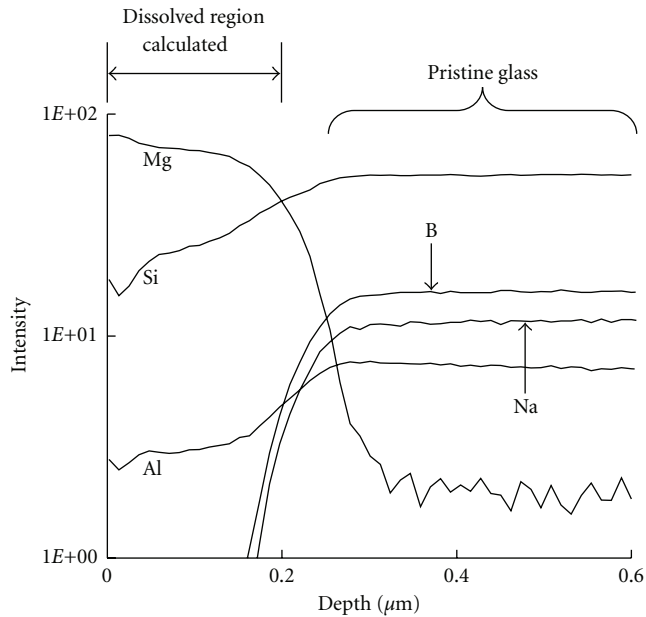


FIGURE 4: SIMS elemental depth profiles at the surface of the glass leached in  $\text{MgCl}_2$  solution at  $60^\circ\text{C}$  for 36 days.

progression of glass dissolution represented by  $NL_B$  both at  $60^\circ\text{C}$  and  $90^\circ\text{C}$ . In addition, Figure 3(b) shows the stage II dissolution after 36 days in which the Mg depleted in the leachate. Comparing Figures 3(a) and 3(b), it is supposed that the corrosion mechanisms were identical for  $60^\circ\text{C}$  and  $90^\circ\text{C}$  and that the reaction was enhanced at  $90^\circ\text{C}$  compared to that at  $60^\circ\text{C}$ .

Figure 4 shows the SIMS depth profiles of B, Na, aluminum (Al), Si, and Mg at the surface of the glass coupon leached in  $\text{MgCl}_2$  solution at  $60^\circ\text{C}$  for 36 days. It can be seen that magnesium-rich altered layer with a thickness of  $0.2\text{--}0.3\ \mu\text{m}$  was formed at the surface of the glass. Soluble elements, B and Na, are depleted in the altered layer. Thickness of the altered layer, calculated based on the  $NL_B$ , was  $0.2\ \mu\text{m}$  for 36 days at  $60^\circ\text{C}$ . The calculated value roughly agrees with that observed in Figure 4, which implies that the altered layer did not dissolve nor flake during leaching in  $\text{MgCl}_2$  solution at  $60^\circ\text{C}$ .

Figure 5 shows SEM images of the surface of the powdered glass leached in  $\text{MgCl}_2$  solution at  $90^\circ\text{C}$  for 64 days. It is observed that net-like altered layer was formed at the surface of the glass and partially flaked from the glass surface.

The thickness of the flaked altered layer measures around  $1.0\text{--}1.5\ \mu\text{m}$ . In contrast, thickness of the altered layer calculated based on the  $NL_B$  is  $1.1\text{--}1.2\ \mu\text{m}$  for 64 days at  $90^\circ\text{C}$ . The calculated value roughly agrees with the measured thickness of flaked layer shown in Figure 5, indicating that the position of the glass surface has not changed during leaching in  $\text{MgCl}_2$  solution at  $90^\circ\text{C}$ .

By the energy dispersive X-ray spectrometry (EDX) analysis for this leached glass, it was found that the altered layer mainly contains Si and Mg, while the pristine glass surface in contact with the altered layer contains Si, Al, iron (Fe), and small amount of Mg. The formation of Si

and Mg-rich layer and the significant decrease of Mg in leachate shown in Figure 3(b) imply that Mg in solution was consumed to form magnesium silicates as a secondary phase at the surface of the leached glass.

Figure 6 shows the molar ratio of Si to Mg in the altered layer as a function of time. The Si/Mg ratios were calculated based on the amount of Si remaining in the layer ( $NL_B - NL_{Si}$ ) and the concentration of Mg consumed from the leachates for the tests in  $\text{MgCl}_2$  solution at  $60^\circ\text{C}$  and at  $90^\circ\text{C}$ . Figure 6 suggests that Si/Mg molar ratio of the altered layer was around 3, which was higher than those for the typical magnesium silicate minerals ( $1.3\text{--}1.5$ ) indicated as dashed lines in Figure 6. The reason comes from that the altered layer includes not only magnesium silicates but also residual Si with Al from the glass network former as shown in the SIMS profile at Figure 4.

As presented above, the stage I dissolution of the glass continued in  $\text{MgCl}_2$  solution until Mg depleted in the leachates, and the stage II dissolution was observed thereafter. Generally, the stage II dissolution is thought to progress under near saturation conditions. Figure 7 shows a thermodynamic diagram of monomeric aqueous species in equilibrium with  $\text{SiO}_2(\text{am})$  as a function of pH at  $90^\circ\text{C}$  [12]. The bold curve is the total concentrations of Si over different Si species and called solubility. The solid triangles in Figure 7 indicate the concentrations of dissolved Si in the leachates obtained in the present study at  $90^\circ\text{C}$ . The degrees of saturation to the solubility of  $\text{SiO}_2(\text{am})$ , difference in concentration between the solid triangles and the bold curve, were maintained at  $40\text{--}50\%$  during the whole of test periods. However, the stage I dissolution ended at initial 36 days, and after that the stage II dissolution progressed with much lower dissolution rate as shown in Figure 3(b).

These results imply that the dissolution stage of the glass cannot be explained by a degree of saturation determined from the concentration of dissolved Si in "bulk" solution. This phenomenon may be dependent on the local chemistry of the leachates.

## 4. Conclusions

Static leach tests were conducted for simulated HLW glass in  $\text{MgCl}_2$  solution for up to 92 days to investigate the dissolution mechanism of HLW glass under coastal repository condition. Under the condition that Mg exists in leachate, the so-called stage I dissolution was observed for the glass with an initial high dissolution rate and the dissolution rate decreased when the Mg depleted in the leachate. It is supposed that Mg was used for forming magnesium silicate as a secondary phase at the surface of the leached glass, and the formation of the secondary phase maintained the stage I dissolution by consuming Si.

In coastal repository condition where highly concentrated Mg can be supplied, HLW glass has a potential to dissolve with high rate for long term even if under virtually closed systems such as geological repository where the groundwater flow rate is quite low.

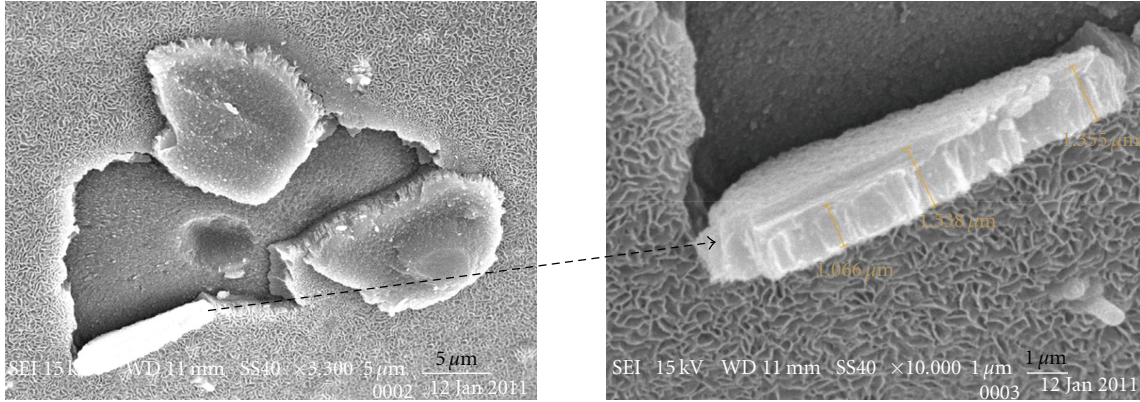


FIGURE 5: The SEM image of the surface of the powdered glass leached in  $MgCl_2$  solution at  $90^\circ C$  for 64 days.

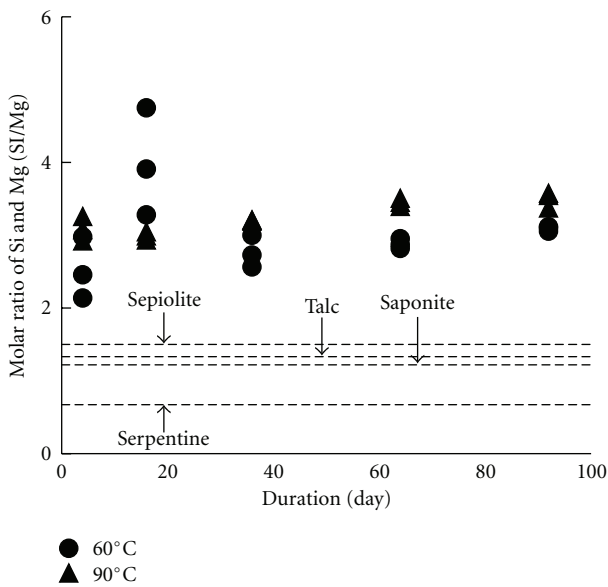


FIGURE 6: Calculated molar ratio of Si to Mg in the altered layers versus time for the tests in  $MgCl_2$  solution at  $60^\circ C$  and at  $90^\circ C$ . The dashed lines indicate the Si/Mg molar ratios of typical magnesium silicate.

**Acknowledgments**

The authors would like to thank Dr. H. Mitamura of Japan Atomic Energy Agency for his contribution to the SEM/EDX analyses. They would also like to thank Mr. K. Hotta of the Radiation Application Development Association and Ms. Imen Bahrini of the University of Pierre et Marie Curie for her contribution to the preliminary leach test.

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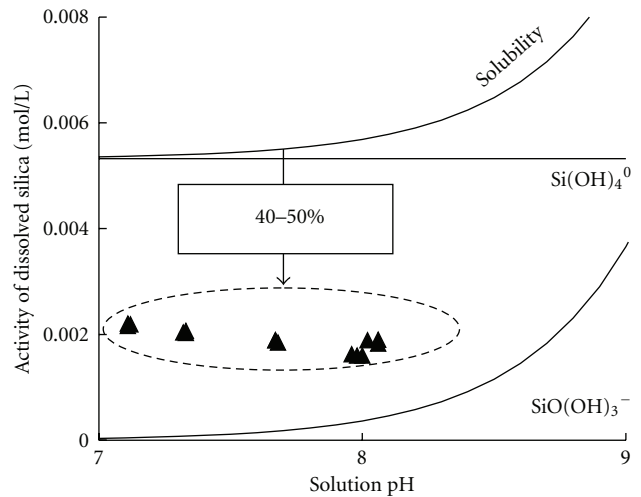


FIGURE 7: A thermodynamic diagram for monomeric aqueous species in equilibrium with  $SiO_2(am)$  as a function of pH at  $90^\circ C$ . The solid triangles represent the concentrations of dissolved Si in the leachates for  $MgCl_2$  solution at  $90^\circ C$ .

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