Accelerated Leach Tests of SRL-165 High-Level Waste Glass in Deionized Water
Solution Analyses and Supplemental SIMS Analyses

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Accelerated short-term leach tests in a laboratory are necessary in order to estimate, with reasonable accuracy, the long-term leaching behavior of high-level waste glass. In the present study, static leach tests of an SRL-165 high-level waste glass were carried out in deionized water at two different glass-surface-area to solution-volume ratios (SA/V-ratio), namely 0.85 and 0.079 cm⁻¹ at 90°C, and 0.85 cm⁻¹ at 40°C.

First, an equation was examined which related Si-concentrations with time, temperature and SA/V-ratio under the present static conditions. The parameter determined at 90°C, 0.85 cm⁻¹ can be used to calculate the Si-concentration at 40°C, 0.85 cm⁻¹. Second, at the low SA/V-ratio of 0.079 cm⁻¹, the concentrations of Ca and Mg in the leachates peaked and then decreased a little. The equation used above does not explain the variation of the concentrations of Ca and Mg at a low SA/V-ratio. The precipitation of Ca and Mg onto the glass surface is probably caused by the adsorption efficiency of the surface layer or the formation of crystalline materials at the low SA/V-ratio of 0.079 cm⁻¹. Third, the in-depth profiles of some elements obtained by secondary ion mass spectroscopy (SIMS) were qualitatively in agreement with the results of solution analyses. This indicates the particular usefulness of SIMS for analyzing leaching behavior of the glass in in-situ burial studies where solution analyses are often impractical.

KEYWORDS: borosilicate glass, high-level radioactive waste glass, solidification, leach tests, leaching, deionized water, radioactive waste disposal, geologic disposal

I. INTRODUCTION
Disposal of high-level nuclear waste (HLW) glass in a geologic stratum is a possible way to isolate HLW from the biosphere⁽¹⁾. Some of the radionuclides can survive for more than a thousand years, and they pose a potential hazard when leached from the glass and carried into the biosphere by groundwater.

Since conducting HLW glass leach tests for thousands of years in a laboratory is impossible, short-term tests in the laboratory are necessary in order to estimate, with reasonable accuracy, the long-term leaching behavior of the glass. One method is to use a high temperature to accelerate the leach-kinetics of the glass⁽²⁾⁻⁽⁴⁾; in addition, a high
temperature generally heightens saturation concentrations of some elements. Another method is to use a high specimen-surface-area to solution-volume ratio (SA/V-ratio) in order to achieve saturation quickly\(^{(5)-(8)}\). In the previous studies\(^{(2)-(8)}\), these two methods were examined separately. However, they may complement each other and a better understanding of the leaching behavior may be obtained by a combination of these methods.

It should be mentioned that both methods have limitations. The leaching mechanism changes easily at a temperature greater than 150\(\degree\)C\(^{(2)}\) or 220\(\degree\)C\(^{(4)}\) and the extrapolation of a leach rate at more than 150 or 220\(\degree\)C to that at a lower temperature may involve some difficulties. On the other hand, with a high SA/V-ratio the particle grains need to be finer\(^{(5)-(8)}\). This can complicate the interpretation of the data due to uneven leaching caused by direct contact between the particles. In the present study, we carry out experiments at 90 and 40\(\degree\)C, both of which are below the aforementioned temperatures of 150 or 220\(\degree\)C. The SA/V-ratios of 0.85 and 0.079 cm\(^{-1}\) are used at 90\(\degree\)C, and 0.85 cm\(^{-1}\) at 40\(\degree\)C; the higher SA/V-ratio is easily obtained, without using powdered glass, by arranging ten plate-specimens in one leach container.

One purpose of this paper is to examine whether or not a general equation based on solution data relates Si-concentrations with time, temperature and SA/V-ratio under the present static conditions. A second objective is to relate in-depth elemental profiles obtained with secondary ion mass spectroscopy to respective values of normalized elemental mass loss.

II. EXPERIMENTAL PROCEDURE

1. Glass Preparation

Simulated HLW glass (SRL-165\(^{(8)}\)) used for the present study was prepared by melting the frit (the composition of which is given in Table 1) obtained from the Savannah River Laboratory. The frit was placed in a platinum crucible, melted at 1,350\(\degree\)C for 2 h, poured into graphite molds, annealed at 500\(\degree\)C for 2 h, and then cooled to room temperature at a cooling rate of less than 2\(\degree\)/min. The resultant glass bars were cut with a diamond saw and polished with dry SiC-papers (#240, then #600) into plates of 12x12x1.2 mm in size. The plate specimens were cleaned in ethyl ether with ultrasonic vibration to remove fine particles from their surfaces\(^{(3)}\).

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.% (^{\dagger})</th>
<th>Mole % of cations (^{\dagger\dagger})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_{2})</td>
<td>54.1</td>
<td>43.2</td>
</tr>
<tr>
<td>Fe(_{2})O(_3)</td>
<td>12.3</td>
<td>7.4</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>10.3</td>
<td>15.9</td>
</tr>
<tr>
<td>B(_2)O(_3)</td>
<td>6.8</td>
<td>9.4</td>
</tr>
<tr>
<td>Li(_2)O</td>
<td>4.7</td>
<td>15.1</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>4.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Mn(_2)O(_3)</td>
<td>2.9</td>
<td>1.6</td>
</tr>
<tr>
<td>CaO</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>NiO</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>F</td>
<td>0.06</td>
<td>—</td>
</tr>
<tr>
<td>Cl</td>
<td>0.05</td>
<td>—</td>
</tr>
<tr>
<td>Pb</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) The values of \(\%\) are used for calculation of \(f_1\) in Eq. (1).

\(^{\dagger\dagger}\) The values of \(\%\) of cations are references for SIMS analyses.

2. Leach Tests

Static leach tests for up to 84 days were carried out by using the MCC-1 standard method\(^{(10)}\) in deionized water with a specific resistance of 1.3x10\(^8\) \(\Omega\) cm. The SA/V-ratios in the present study were modified to be 0.85 and 0.079 cm\(^{-1}\) at 90\(\degree\)C, and 0.85 cm\(^{-1}\) at 40\(\degree\)C. Leach tests at 0.079 cm\(^{-1}\), 40\(\degree\)C were not carried out, since in this case concentrations of elements in the leachates were expected to be very low within the experimental time schedule. The high SA/V-ratio of 0.85 cm\(^{-1}\) was obtained by arranging ten plate-specimens at a fixed interval of more than 1 mm in one 60 ml PFA-Teflon container (Fig. 1). An interval of more than 1 mm is needed for equalizing leach rates of each surface of the specimens\(^{(11)}\). The low SA/V-ratio of 0.079 cm\(^{-1}\) was obtained using one plate-specimen in one container.
The normalized elemental mass loss for element $i$ ($NL_i$) is defined as (10),

$$NL_i = \frac{C_i \times V}{f_i \times SA},$$

where $C_i$ (g/cm$^3$) is the concentration of element $i$ in the leachate, $V$ (cm$^3$) the volume of the leachate, $f_i$ (unitless) the mass fraction of element $i$ in the unleached solid, and $SA$ (cm$^2$) the geometric surface area of the specimen. The value of $NL_i$ is normalized to the weight fraction of element $i$ in the bulk glass, and is therefore suitable for a comparison with those of other elements.

### 3. Analyses

The pH value of the leachates was measured with a pH electrode immediately upon cooling to room temperature (Orion Research, 801A). The concentration of nine elements, i.e., B, Li, Si, Al, Ca, Mg, Fe, Mn and Ni, in the leachates was measured with an inductively-coupled plasma spectrometer (Perkin-Elmer, Plasma II).

In-depth elemental profiles on the surface of the HLW glass after leaching were measured with a secondary ion mass spectroscope (Cameca S.A., 3-F).

### III. RESULTS

#### 1. Leachate Analyses

Figure 2 shows the pH excursion during leaching at 90 and 40°C. The pH value reaches maximum after a short leach time, decreases slightly and then levels off to a constant value (7). The order of pH values at different temperatures and $SA/V$-ratios is:

-(90°C, 0.85 cm$^{-1}$)>(90°C, 0.079 cm$^{-1}$)

>(40°C, 0.85 cm$^{-1}$).

Figure 3(a)~(c) shows the log-log plots of $NL_i$ with time in days. At 90°C, 0.85 cm$^{-1}$, the values of $NL_i$ of nine elements can be ordered as:

(B, Li>Si, Al)>>(Ca, Mg, Fe, Mn, Ni)

At 90°C, 0.079 cm$^{-1}$:

(B, Li>Si>Al)>>(Ca, Mg)>(Ni, Mn, Fe)

At 40°C, 0.85 cm$^{-1}$:

(B, Li, Ca, Si, Mg, Mn)>Al>Ni>Fe.

The values of $NL_B$ and $NL_{Li}$ are higher than those of the others, and the values of $NL_{Fe}$ and $NL_{Ni}$ are lower than those of the others within the present experimental conditions. The values of $NL_{Mn}$ are close to those of $NL_{Fe}$ and $NL_{Ni}$ at 90°C, and Mn is chosen as a normalizing element in the secondary ion mass spectroscopy analysis described below. Chandler et al. also carried out leach tests for 1 cm$^{-1}$ and 0.1 cm$^{-1}$ at 90°C, and their results in the order of $NL$ values are in good agreement with the present ones at 90°C. This indicates that this ranking of $NL$ values can be easily reproduced under similar conditions.
2. Secondary Ion Mass Spectroscopy (SIMS)

Since the degree of leaching at 40°C was low (Fig. 3(c)) and only very slight alteration of the specimen surface was expected, attention was focused on the specimens leached at 90°C at two different $SA/V$-ratios of 0.85 and 0.079 cm$^{-1}$. Figure 4(a)~(c) shows the results of SIMS analyses on the specimens leached at 90°C. The correction for all profiles was made on the assumption that practically no manganese has been leached out$^{12}$. Generally, B and Li are depleted in the surface layers, and this corresponds to the high values of $N_{Li}$ and $N_{B}$ (Fig. 3(a),(b)) obtained from solution analyses. The in-depth profiles for Fe, Mn and Ni are nearly constant in the surface layers, which corresponds to low $NL$ values of these elements. The in-depth profiles for Ca and Mg show that they are nearly constant in the surface layer on the specimen leached at 0.85 cm$^{-1}$ for 28 d (Fig. 4(a)). In contrast, Ca and Mg are depleted in the surface layer on the specimen leached at 0.079 cm$^{-1}$ for 3 d (Fig. 4(b)), and then concentrated on the surface of the specimen leached at 0.079 cm$^{-1}$ for 28 d (Fig. 4(c)).
IV. DISCUSSION

1. Mathematical Modeling of Leach Data

Silicon is a major component of the network structure of the glass, and also a standard element which represents the leaching behavior of the glass. The rate of increase in the Si-concentration in the leachant can be basically written as

\[ \frac{dC_{Si}}{dt} = k \left( \frac{SA}{V} \right) (C_{sat} - C_{Si})^n. \]

The \( C_{Si} \) (g/cm\(^3\)) is the concentration of Si at time \( t \), \( k \) (cm\(^4\)/(g·d) (when \( n=2 \)) is a constant which includes the temperature dependency in the form of \( k = k_0 \exp\left( -\frac{Q}{RT} \right) \), where \( k_0 \) (cm\(^2\)/(g·d)) is the constant, \( Q \) (J/mol) the activation energy, \( R \) (8.31 J/(mol·K)) the gas constant and \( T \) (K) the absolute temperature. The \( C_{sat} \) (g/cm\(^3\)) is the saturation concentration of Si which is a function of the absolute temperature, and \( n \) is an empirical fitting exponent. Equation (2) is integrated to yield,

\[ \frac{C_{Si}}{C_{sat}} = \frac{k(SA/V)t}{1 + C_{sat}k(SA/V)t}, \]

Fig. 4 (a)~(c) SIMS in-depth profiles of specimen leached at 90°C, 0.85 cm\(^{-1}\) for 28 d, 0.079 cm\(^{-1}\) for 3 d and 0.079 cm\(^{-1}\) for 28 d

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(b) 0.079 cm\(^{-1}\) for 3 d

(c) 0.079 cm\(^{-1}\) for 28 d
when \( n \) is assumed to be 2. Experimentally, the arbitrary value of \( n=2 \) resulted in a good fit of the data to the equation (Fig. 5) with the following assumptions.

The value of \( C_{\text{sat}} \) was assumed to be 80 ppm at 90°C and 35 ppm at 40°C. These values were obtained by extrapolation of the Si-concentration in leachates to a time of more than 100 d. The value of \( k \) was assumed to be \( 3.13 \times 10^3 \, \text{cm}^4/(\text{g} \cdot \text{d}) \) at 90°C, and then calculated to be \( 4.52 \times 10 \, \text{cm}^4/(\text{g} \cdot \text{d}) \) at 40°C when the activation energy was 80 kJ/mol\(^{(16)}\).

The calculated curve for the variation of the Si-concentration at 40°C was in good agreement with the data points (Fig. 5). This means that accelerated leach tests can be traced by Eq. (2) under the present static conditions. For example, the degree of acceleration was described in such a way that the value of \( C_{\text{Si}}/C_{\text{sat}}=0.92 \) at 90°C, 0.85 cm\(^{-1} \) and 56 days will be achieved at 40°C, 0.85 cm\(^{-1} \) at the leach time of \( 2.5 \times 10^8 \) yr.

The degree of acceleration in terms of \( SA/V \)-ratio is also expressed by Eq. (2). When \( C_{\text{sat}} \cdot k \) remains constant at a given temperature, then \( (SA/V) t \) determines the value of \( C_{\text{Si}}/C_{\text{sat}} \). For example, when the \( SA/V \)-ratio increases by ten times, the same value of \( C_{\text{Si}}/C_{\text{sat}} \) will be obtained at \( t \) which becomes 1/10 its previous value.

For elements other than Si, theoretical prediction of accelerated leach tests seems to be more complicated than is expressed by Eq. (2). Such examples are observed with Ca and Mg in the next section.

2. Change of \( NL_{\text{Ca}} \) and \( NL_{\text{Mg}} \)

Only \( NL_{\text{Ca}} \) and \( NL_{\text{Mg}} \) show maximum values during leaching at 90°C, 0.079 cm\(^{-1} \), and this is a new finding among the present results. Figure 6 shows the log-log plots of \( NL_{\text{Ca}} \) and \( NL_{\text{Mg}} \) in the case of 90°C, 0.85 and 0.079 cm\(^{-1} \), based on results shown in Fig. 3(a) and (b). At 0.079 cm\(^{-1} \), \( NL_{\text{Ca}} \) and \( NL_{\text{Mg}} \) tend to decline after 7 d, which is in line with the SIMS results in that Ca and Mg concentrate on the surface of the specimen leached at 0.079 cm\(^{-1} \) (Fig. 4(c)). At 0.85 cm\(^{-1} \), \( NL_{\text{Ca}} \) and \( NL_{\text{Mg}} \) do not decline during the leach period of 56 d. Note that the concentrations of Ca and Mg in leachates are 0.135 and 0.39 ppm, respectively, at 0.079 cm\(^{-1} \) at a leach time of 7 d, both of which are lower than the corresponding values at 0.85 cm\(^{-1} \). These results suggest that the occurrence of this kind of excursion in ppm concentrations does not depend only on the absolute ppm concentration of the elements in leachates.

On the other hand, the precipitation of Ca and Mg depends on the pH value of the solution; the elements tend to precipitate more easily in a solution with a higher pH value\(^{(16)}\). However, pH conditions (Fig. 2) do not provide an adequate explanation of the precipitation of Ca and Mg in the present study, since these elements here are seen to precipitate more easily at a lower pH value (Fig. 6).
A possible explanation would be as follows: At a low SA/V-ratio, Si and B on the surface tend to be depleted in the early stage of leaching. As a result, many small capillaries are produced in the surface layer, significantly increasing the adsorption efficiency of the glass surface in contact with solution. There is also the possibility that some crystalline materials which contain Ca and Mg as components may form after a leach time of 7 d. In either case, the tendency for $NL_{Ca}$ and $NL_{Mg}$ to decline at 0.079 cm$^{-1}$ after 7 d is not adequately expressed by equations similar to Eq. (2).

3. In-depth SIMS Profiles

The in-depth profiles of some elements, such as Li and B as soluble elements and Fe, Mn and Ni as insoluble elements, have already been compared with their respective NL values in the results section, and qualitative agreement between the profiles and the NL values was generally observed; when some elements are depleted in the surface layer, the high NL values for those elements are obtained from solution analyses. This bears out an earlier study(17), suggesting that in cases where solution analysis is impossible, the normalized elemental mass loss of these elements may often be estimated from SIMS analysis alone. This is particularly useful for in-situ burial studies(18), where solution analysis is usually impractical.

V. CONCLUSION

Static leach tests of a nuclear waste glass (SRL-165) were carried out in deionized water at two different SA/V-ratios of 0.85 and 0.079 cm$^{-1}$ at 90°C, and 0.85 cm$^{-1}$ at 40°C.

(1) A general equation was examined which related Si-concentration with time, temperature and SA/V-ratio under static conditions. Parameters determined in the equation at 90°C, 0.85 cm$^{-1}$ can be used to calculate the Si-concentration at 40°C, 0.85 cm$^{-1}$.

(2) The precipitation of Ca and Mg onto the glass surface is probably caused by the high adsorption efficiency of the surface layer or the formation of crystalline materials at a low SA/V-ratio of 0.079 cm$^{-1}$.

(3) The in-depth SIMS profiles of some elements were qualitatively in agreement with the results of solution analyses. This suggests that the SIMS data may be especially useful for in-situ burial studies where solution analyses are often impractical.

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