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90-19/U HLW-glass leaching mechanism in underground water

Jiawei Sheng *, Shanggeng Luo

Department of Radiochemistry, China Institute of Atomic Energy, P.O. Box 275(93), Beijing 102413, People's Republic of China

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Abstract

The leaching behavior of the high-level waste (HLW)-glass in underground water was investigated under static leaching tests by solution analysis. Large amounts of ions of Na^+ and Ca^{2+} participated in the ion-exchange reaction with glass. The reactions of glass with H^+ (or H_3O^+) were compressed. The ion-exchange reaction of Na^+ (or Ca^{2+}) with glass components dominated the glass leaching mechanism at a temperature range 50–150°C. The network hydrolysis reaction is weak in underground water (UGW). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Studies of the immobilization of high-level waste (HLW) have been carried out for the past four decades. In most countries including China, the borosilicate glass is selected as the final waste form for HLW introduced by the reprocessing of nuclear fuels. The waste glass is buried deeply underground. The chemical durability of the waste glass with respect to corrosion is of great importance, since the waste solidification is carried out to prevent the dissipation of radioactive elements towards the biosphere. Waste glasses undergo a variety of complex changes in aqueous condition, which is also referred to as glass corrosion or glass dissolution. The experimental evidence suggests that glass corrosion can be interpreted in terms of a limited number of processes, such as ion exchange of network modifiers, hydrolysis of the glass network, and precipitation of secondary phases. Ion exchange, network hydrolysis and precipitation are the major mechanisms for the HLW-glass leaching [1–4]. Recently, research has shown that the precipitation reactions usually play an important role in the leaching under saturation conditions, while ion exchange and network hydrolysis dominate the processes under dynamic and weak corrosion conditions.

Since the 1970s, China Institute of Atomic Energy has investigated the HLW vitrification with several types of matrices including borosilicate glasses, phosphate glasses and Synroc. In the early 1990s, borosilicate glass form 90-19/U HLW glass was developed to solidify the high-sodium-containing HLW [5]. Deep underground burial under an engineered vault in several repository sites in the desert area of west China is being investigated as a possible option for the permanent disposal of HLW. The chemical and physical behaviors of underground water (UGW) are also under investigation. In our previous work, we have studied the corrosion mechanisms of 90-19/U glass in deionized water (DIW) [5,6]. It is quite important to understand the leaching mechanisms of 90-19/U glass in UGW in order to predict its long-term chemical durability. The main purpose of this work is to evaluate the leaching behavior of 90-19/U HLW glass in UGW at repository site.

2. Experimental procedures

The composition of 90-19/U HLW glass is listed in Table 1 on an oxide basis [5]; and the composition of the UGW is shown in Table 2. The glass was melted in a platinum crucible in a furnace at 1150°C for 2 h using surrogate waste material. After pouring, the glass was

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[*] Corresponding author. Present address: Special Division for the Green Life Technology, AIST Kansai National Institute of Advanced Industrial Science & Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan. Tel.: +81-727 51 9642; fax: +81-727 51 9627.

E-mail address: jw-sheng@aist.go.jp (J. Sheng).

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Table 1
Composition of 90-19/U simulated HLW glass

Oxides	wt%	Oxides	wt%
SiO_2	51.66	TiO_2	1.222
B_2O_3	14.87	Fe_2O_3	3.005
Na_2O	10.96	U_3O_8	2.763
Li_2O	2.520	SO_3	0.616
Al_2O_3	3.445	Cs_2O	0.111
CaO	5.376	SrO_2	0.034
MgO	1.848	Others	1.570

Table 2
Composition of the underground water

Composition	Concentration (mg/l)	Composition	Concentration (mg/l)
Na^+	630.99	HCO_3^-	201.64
Mg^{2+}	42.45	SO_4^{2-}	750.98
Ca^{2+}	154.88	Cl^-	645.39
		pH	8.2

annealed at 500°C for 2 h. Glass near the crucible interface was not used for testing, in case the glass melt had reacted with the crucible. Glass was cored and sliced into monoliths for use in leaching test and microstructure examinations. The specimens were polished prior to the leaching test.

The leaching test was carried out using the ASTM standard MCC-1 leaching method [7]. The ratio of glass surface area to leachant volume (SA/V) was 10 ± 0.1 m^{-1}, and the leaching temperature was at 50–150°C. Test duration ranged from 1 to 91 days. The specimens in all tests were monolithic ($16 \times 13 \times 1$ mm^3). The surface area of the sample was calculated by measuring its length, width and thickness with a caliper. The leachate was analyzed using inductively coupled plasma (ICP) spectrometry for the major components of the glass, such as Si, B and Li. The pH values of leachate were determined with a pH-meter. The mass of glass specimen was measured before and after leaching; then the total mass loss ML was calculated as follows:

$$\mathrm{ML} = (m_0 - m_1)/(\mathrm{SA}), \tag{1}$$

where ML = total mass loss (g/m^2); m_0 = original unleached specimen mass (g); m_1 = specimen mass after leaching (g); SA = the sample surface area (m^2).

With regard to the elemental concentration in leachate, the normalized element mass loss NL_i was calculated as follows:

$$\mathrm{NL}_i = C_i \times V/(\mathrm{SA} \times f_i), \tag{2}$$

where NL_i = normalized mass loss of element i (g/m^2); C_i = concentration of element i in leachate (g/m^3); V = volume of leachant (m^3); f_i = mass fraction of element i in the unleached glass.

All the measurements were made in duplicate and the average ML (or NL_i) was reported herein with the estimated error at ±10%. The scanning electron microscopy with energy dispersive spectroscopy (SEM–EDS) technology was utilized to determine the surface layer alteration. The crystallization of surface layer was determined using the X-ray diffraction (XRD).

3. Experimental results

The extent of waste glass reaction is often monitored by boron concentration in the leachate, since boron is very soluble and with few losses in the form of colloids or precipitates. Because of a very high concentration of Na presented in UGW, it was difficult to measure the change of the Na concentration in the solution before and after leaching. Then, ML and the normalized element release rates of B, Si and Li were all used to monitor the 90-19/U HLW-glass leaching behavior in this study.

Fig. 1 presents the values of ML in UGW and in DIW. The values of ML in UGW were much smaller than in DIW at short leaching times (<91 days). However, a reversed result appeared after a 91-day test. Clearly, there was a solubility limit effect in DIW while the ML values were continuously increasing in UGW. A linear relationship was observed between the ML values and the square root of leaching time in UGW. Borosilicate glass leaching could increase the pH values of leachate due to the release of alkali or alkaline-earth elements. As shown in Fig. 2, pH values in UGW are almost stable and much lower than in DIW.

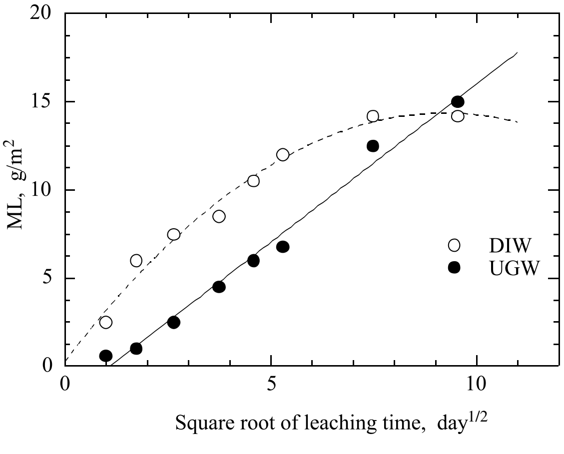

Fig. 1. ML values of 90-19/U HLW glass in the DIW and in the UGW at 90°C.

The normalized element mass losses of Li, B and Si in UGW are given in Fig. 3. At a short leaching time such as a few days, NL values of Li, B and Si were less in UGW than in DIW. After that the NL values of Li and B were greater in UGW than in DIW. The NL_{Si} was less in UGW than in DIW during the entire experimental period and had less change with the increasing leaching time. Temperature readily had an effect on the leaching behavior in UGW. Fig. 4 shows the temperature effect on the NL_B (7 and 28 days, respectively) and NL_{Li} (28 days) in UGW. The linear curves imply that the glass dissolution in UGW was a single-step process [5]. The apparent activation energies in B and Li release in UGW at 50–150°C can be obtained from Fig. 4 as 52.71 kJ/mol (NL_B, 7 days), 56.21 kJ/mol (NL_B, 28 days) and 57.17 kJ/mol (NL_{Li}, 28 days), respectively. The similar values in the activation energies indicate the same effect of the temperature on B and Li release.

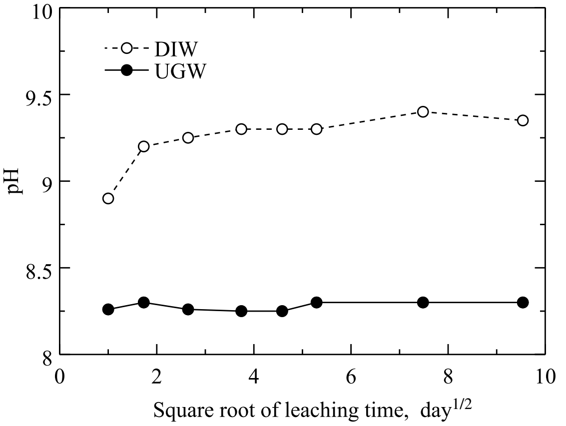

Fig. 2. pH values of leachate during the leaching test at 90°C.

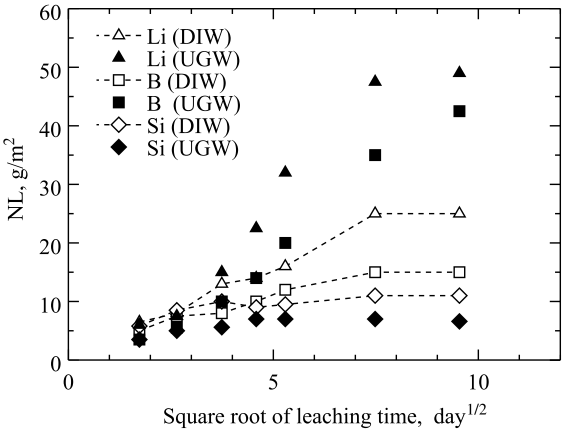

Fig. 3. NL_i variation at different leaching times at 90°C.

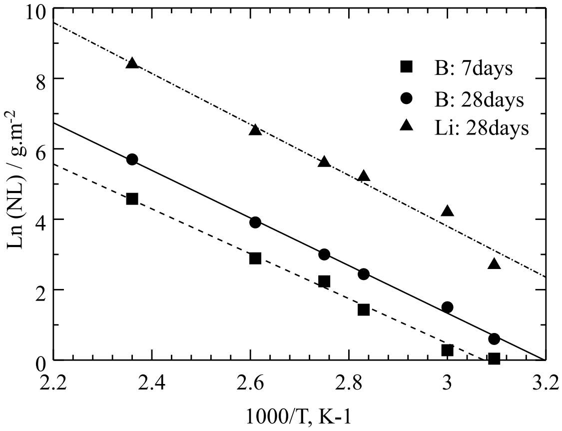

Fig. 4. Temperature effect on the NL_i in the UGW.

The SEM–EDS and XRD were used to determine the glass surface layer alteration. The glass surface formed in UGW is less destroyed than that formed in DIW under the same test condition. Crystals of $CaCO_3$ were observed in the surface layers of all leached samples in UGW. Moreover, the longer the leaching time the larger the size of the crystals. Other precipitates were not obviously observed even after a 91-day test. The Ca in the leachant usually has less effect on the glass leaching behavior. There are two possible ways to form the precipitates of $CaCO_3$ on the glass surface during the leaching experiment. One could be the precipitation of $CaCO_3$ from the solution and the other could be the release of $CaCO_3$ from the glass matrix. Due to the large amount of Ca^{2+} and CO_3^{2-} in UGW, it was most likely that $CaCO_3$ crystal was precipitated from UGW.

4. Discussion

4.1. Introduction of HLW-glass corrosion

Over the past 20 years, the understanding of glass dissolution processes has advanced significantly with a variety of dissolution tests. However, it is still difficult to predict the long-term disposal behavior of HLW glasses due to the very complex compositions. The research on the leaching mechanism of HLW glass has been underway for about 40 years. Modeling the glass leaching mechanism has advanced from fitting the data obtained from the laboratory tests by empirical functions to models based on fundamental principles of physics, chemistry, and thermodynamics [8]. Hench et al. [2] and Ebert [9] have summarized that the reaction of borosilicate waste glass is dominated by two primary reactions: ion exchange to release alkali metals and boron and network hydrolysis to release silicon. These processes are not independent, and one or the other may dominate the reaction at different stages. Generally speaking, the mechanisms of glass corrosion include: (1) water diffuses into the glass matrix, and then the glass undergoes ion-exchange processes between the hydrogen and the most mobile network modifier ions, (2) network hydrolysis reactions break down the glass network and lead to glass dissolution, (3) precipitation/absorption of some hydrolyzed species to form a largely amorphous surface layer.

Ion-exchange reaction involves a hydronium ion from water exchanging with the alkali metal, M^+ in the glass matrix, as shown in the following reaction:

$$\equiv \mathrm{Si{-}O{-}M} + \mathrm{H}^+ \leftrightarrow \equiv \mathrm{Si{-}O{-}H} + \mathrm{M}^+, \tag{3a}$$

$$\equiv \mathrm{Si{-}O{-}M} + \mathrm{H_3O}^+ \leftrightarrow \equiv \mathrm{Si{-}O{-}H} + \mathrm{M}^+ + \mathrm{H_2O}. \tag{3b}$$

The ion-exchange reaction increases the leachate pH value. Diffusion usually plays an important role in the ion-exchange reaction. Lithium has the greatest leaching rate among all glass components as long as the ion exchange reaction dominates glass corrosion [10,11].

Network hydrolysis breaks down the glass network and leads to glass dissolution. The major hydrolysis reactions for nuclear waste glasses can be expressed as follows:

$$\equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{OH}^- \leftrightarrow \equiv \mathrm{Si{-}O}^- + \equiv \mathrm{Si{-}O{-}H}, \tag{4a}$$

$$\equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H_2O} \leftrightarrow 2 \equiv \mathrm{Si{-}O{-}H}. \tag{4b}$$

Not only is silica involved in the above reactions, but also other network-forming elements such as Al, B and Zr participated in the reactions. When the network hydrolysis reaction dominates the glass corrosion, there is no linear relationship between the glass corrosion rate and square root of leaching time. And the glass components have a stoichiometric release [11,12]. The pH value of leachate has a great effect on the glass leaching behavior. Ebert [9] has concluded that the ion-exchange reactions usually dominated the HLW-glass corrosion process in a pH value of leachate less than 9.0 while the hydrolysis reactions controlled the glass corrosion process in a pH value of leachate greater than 9.0.

The model developed by Grambow [13,14] is the most fully developed and widely used model. Grambow concluded that the chemistry of the solution is controlled by the solubility of various minerals/solids that precipitate during the course of reaction. Grambow also assumed that the short-term glass dissolution rate depends explicitly on the concentration of H_4SiO_4, where the rate-limiting step in the mechanism is the removal of a $Si(OH)_4$ group. Utilizing the work on the kinetics of SiO_2 dissolution and the work on the kinetics of mineral dissolution, Grambow proposed a first-order rate law that established a connection between the amounts of glass dissolved in water and time. This model includes a term of dissolution affinity $(1 - [H_4SiO_4]/[H_4SiO_4]_{sat})$, where $[H_4SiO_4]$ is the activity of H_4SiO_4 in solution, and $[H_4SiO_4]_{sat}$ is the saturation value of H_4SiO_4. The increasing H_4 SiO_4 concentration in solution will decrease the dissolution rate of glass. In general, the models based on the assumption that glass corrosion rate is controlled by dissolution affinity have been successfully consistent with a wide variety of experimental observations [15,16].

4.2. Description of 90-19/U HLW-glass leaching behavior in UGW

The model developed by Grambow could not clearly explain the leaching behavior of 90-19/U HLW glass in UGW. For example, the amount of the release of Si was small, while the amounts of the releases of B and Li were much large in UGW. It could be found from Fig. 3 that NL_{Si} was less changed along with the increasing leaching time, while the ML, NL_{Li} and NL_B were linearly increased with square root of the leaching time. Generally, the glass reaction in solution can be expressed as

$$\frac{\mathrm{d}[M_i]}{\mathrm{d}t} = k_i\left(1 - \frac{Q}{K}\right), \tag{5}$$

where $[M_i]$ is the concentration of element i in solution, k_i is the reaction constant related with pH values, Q is the ion activity product of the solution, and K is the apparent solubility product of the glass [8,9]. The term $(1 - Q/K)$ in the Eq. (5) is called chemical reaction affinity. From Eq. (5), it could be found that the large amount of ions in UGW decreased the chemical reaction affinity, which led to the small release of Si at the beginning of the leaching period. However, the glass structure alteration was not considered in Eq. (5) and the leaching behavior of B and Li could not be satisfactorily explained by Eq. (5).

From the viewpoint of waste glass structure, the release of Si is mainly contributed to the network hydrolysis. The network hydrolysis destroys the glass network structure. The Si release in UGW was smaller than that in DIW and was less changed with increasing leaching time; and the glass surface structure was less destroyed. These results implied that the network hydrolysis reaction is weak in UGW. The glass dissolution is determined in part by the leachate pH, particularly if the pH is lower than 9. At low pH solutions, the ion-exchange reaction is stronger than network hydrolysis. According to the above discussion and pH values in the Fig. 2, it could be assumed that ion-exchange reactions dominate the glass dissolution, while network hydrolysis is very weak in UGW. The small chemical reaction affinity can explain the smaller values of NL_{Li} and NL_B in UGW than in DIW at the short leaching times.

There are a large amount of ions of Na^+ and $Ca^{2+}(Mg^{2+})$ in UGW, and such ions will also participate in the ion-exchange reactions with glass components, as shown in reactions (6a) and (6b):

$$\equiv Si{-}O{-}M + Na^+ \leftrightarrow \equiv Si{-}O{-}Na + M^+, \tag{6a}$$

$$\equiv Si{-}O{-}M + Ca^{2+} \leftrightarrow \equiv Si{-}O{-}Ca^+ + M^+. \tag{6b}$$

Feng and Pegg [10] have named such a process the kinetic ion-exchange process. The reactions (3a) and (3b) could be competed by reactions (6a) and (6b). Because the activities or concentrations of Na^+ and $Ca^{2+}(Mg^{2+})$ are much greater than those of H^+ (or H_3O^+), reactions (6a) and (6b) could be much stronger than reactions (3a) and (3b). The reactions (6a) and (6b) would result in the less destruction of glass network, and would lead to less change of the leachate pH values as well. In addition, the less change of the leachate pH values can be partly attributed to the buffer capacity of UGW. The same amount of hydroxide generated in the tests in DIW and UGW, for example, would result in the different pH values due to the different buffer actions of DIW and UGW. The evaluation of quantitative buffer capacity of the UGW was not done here because the pH is used only as a qualitative indication of the extent of glass reaction. Our experimental results supported the kinetic ion-exchange process. We, therefore, adopted this concept of kinetic ion-exchange process and concluded that the ion-exchange reactions dominated the glass leaching behavior in UGW. The linearity over the experimental temperature range in UGW shown in the Arrhenius diagram (Fig. 4) also confirmed the single-step-control leaching mechanism. Fig. 4 also implies the same release mechanism of B and Li in UGW.

5. Conclusion

The reaction of borosilicate waste glass is dominated by two primary reactions: ion-exchange and network hydrolysis. The large amounts of ions in UGW decreased the chemical reaction affinity, which resulted in the less release of glass at short leaching times. The leachate pH values played an important role in the glass leaching behavior. Ions of Na^+ and Ca^{2+} (also Mg^{2+}) in the UGW will participate in the ion-exchange reactions with glass components, and then other ion-exchange reactions of glass with H^+ (or H_3O^+) are compressed. The pH values of leachate have less change and the glass structure has been less destroyed in UGW than in DIW. The ion-exchange reaction of Na^+ (and Ca^{2+}, Mg^2) in UGW with glass components dominated glass leaching mechanism, while the network hydrolysis is weak.

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