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The leaching behavior of simulated HLW glass under repository condition

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Abstract As the multibarrier system has been adopted to dispose HLW glass in geological formation in many countries, it was important to study the leaching behavior of vitrification under geological formation. This article describes the leaching behavior of simulated high level waste glass (90Nd/10), which can incorporate 16 wt.% simulated HLW in five kinds of geological media, such as granite, cement, bentonite, Fe_3O_4, etc. The durable experimental results show that the glass had less mass loss in granite and more mass loss in bentonite after a two-year leaching test. The SEM/XEDS analysis shows some element distributions on the leached specimen's surface, i.e., Na, Si and Mg elements were reduced on the specimen's surface, whereas Ba, Al, and Fe were enriched on the specimen's surface.

Key words Leaching test, Granite, Bentonite, Multi-barrier system, HLW-glass

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1 Introduction

It is very important to safely dispose high level wastes (HLW) in geological formation and isolate them from the biosphere. The multibarrier system is recognized as the best method to dispose high level radioactive waste glass. Some experiments have been carried out to investigate the behavior of HLW vitrification in repositories materials, such as salt, clay, granite, etc. [1-5].

In this article, the interaction between five kinds of geological formation including granite (as host rock), bentonite (as backfill material), cement (as engineering barrier), Fe_3O_4 (as corrosive product), and simulated high-level radioactive waste glass (90Nd/10) are studied. Each of these geological formations represents a single barrier in a multibarrier system. The XRD was used to analyze the new phase formed on the specimen's surface, and the SEM/XEDS was used to analyze the distribution of the element's concentration on the glass specimen's surface. These experiments were continued for two years at 90°C.

2 Experimental

2.1 Equipment and specimens fabrication

According to the selected glass formulation (Tables 1 and 2), the chemicals were put into the mortar, then triturated and mixed equably before they were set into the crucible. The crucibles were placed in an electric furnace, in which the temperature was slowly increased to 1150°C and held on for 3h. The crucibles were then taken out, and the melted glass inside was poured into the graphite matrix. Then, the molding glass was set into the annealing furnace at 500°C for 1 h. After the glass samples were cooled to room temperature, they were taken out for testing. The density of the sample was about $2.59\,g\cdot cm^{-3}$, which was almost the middle-density values of various kinds of HLW glass.

The fabricated samples were cut into 10 mm × 10 mm × 2 mm slices using a cutting machine, and then

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polished using a polishing machine. The cleaned specimens were then placed in the oven at 110 °C and dried mass was obtained.

The leaching containers were cleaned up according to a standard cleaning procedure [6].

Table 1 Composition of the simulated high-level radioactive waste (16 wt.% in all)

Oxides	wt.%	Oxides	wt.%
Na_2O	7.01	Y_2O_3	0.016
BaO	0.021	SrO	0.037
Fe_2O_3	3.24	TiO_2	0.15
K_2O	0.094	NiO	0.59
Cr_2O_3	0.30	P_2O_5	0.071
Nd_2O_3	2.03	Al_2O_3	1.45
MoO_3	0.19	MnO_2	0.014
Cs_2O	0.12	SO_3	0.66

Table 2 Composition of the basic glass (84wt.% in all)

Oxides	SiO_2	B_2O_3	Na_2O	Al_2O_3	Li_2O	CaO	MgO	TiO_2
wt.%	50.23	18.48	4.20	2.94	1.93	4.54	0.84	0.84

The surfaces of the glass specimens after the leaching tests were analyzed by a Rigaku K/max-RB X-Ray diffraction meter (XRD) using Cu K_α ($\lambda = 1.54$ nm) radiation. The microstructure and the elemental compositions of the leached surfaces were determined using a Britain Cambridge S-250 MK3 scanning electron microscope coupled with an X-ray energy dispersive spectroscope (SEM/XEDS).

2.2 Simulated disposal media

Five repository systems were applied to simulate the disposal conditions. The compositions of the five systems were as follows: P1, granite (100%); P2, granite (80%) + cement (20%); P3, granite (80%) + Fe_3O_4 (20%); P4, bentonite (100%); and P5, bentonite (80%) + Fe_3O_4 (20%).

The granite was collected from the Beishan site (a candidate disposal site in Gansu Province, China) and its composition is shown in Table 3. The cement was 525# common cement produced by the Beijing Hancuihe Cement Factory; the bentonite was gathered from Weifang, of Shangdong Province, and its composition is listed in Table 4. Fe_3O_4 is a chemical reagent produced by the Beijing Chemical Factory. All these materials were crushed and passed through the $\varphi = 150$ μm sieve before being used in the experiment.

Table 3 Composition of the granite sample

Oxides	wt.%	Oxides	wt.%
SiO_2	67.20	CaO	3.51
TiO_2	0.61	Na_2O	3.76
Al_2O_3	15.98	K_2O	3.36
Fe_2O_3	0.71	P_2O_5	0.13
FeO	2.48	MgO	0.04
MnO	0.04		

Table 4 Composition of the bentonite sample

Oxides	wt.%	Oxides	wt.%
SiO_2	71.12	MnO	0.03
TiO_2	0.13	MgO	2.63
Al_2O_3	14.16	CaO	1.51
Fe_2O_3	1.77	Na_2O	2.21
FeO	0.39	K_2O	1.37

2.3 Experimental

Three specimens were placed into a container as one group. Deionized water was used as the leachant, media/leachant = 1:1, $SA/V = 20\ \mathrm{m}^{-1}$, where SA is the total surface areas of the three specimens and V is the leachate volume. The media were divided into four parts. Above all, the first part media was put on the bottom of the container, and then one specimen was put on that part media. The same procedure was followed for the other three part media and two specimens. The leaching container set is shown in Fig.1.

The experimental sets were placed in an oven and heated at 90°C. In the first, second, fifth, 15th, and 30th day, the mass of the container was weighed, and then it was also reweighed every month to check the tightness of the containers. If the total mass loss was more than 10 wt.%, the leaching test set was considered to have failed. The experiment lasted for 182, 364, and 728 days, respectively.

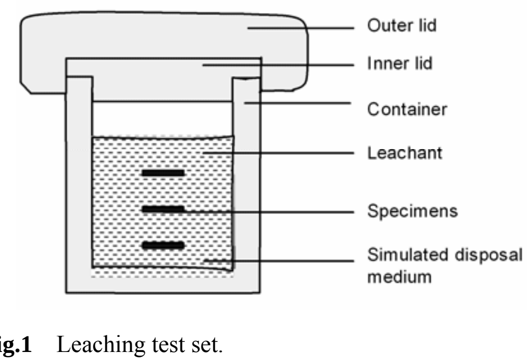

Fig.1 Leaching test set.

3 Results and discussion

3.1 Chemical durability

After the predetermined time, the containers were taken out from the oven and the specimens were cleaned with deionized water, and then dried at 110 °C until the weight was constant. The mass loss of the leached glass specimens was calculated according to the following expression:

$$NL = \frac{W_0 - W_e}{SA} \tag{1}$$

where NL is the mass loss (g·m^{-2}); W_o is the glass specimen weight before the leaching test (g); W_e is the glass specimen weight after the leaching test (g); and SA is the surface area of the glass specimen (m^2).

Table 5 shows the results of the mass loss of the glass specimens after six months, one year, and two years of leaching.

Table 5 Results of the mass loss after the leaching test

Leaching time / a	Glass specimens' mass loss in different simulated disposal media / g·m^{-2}				
	Granite	Granite + Cement	Granite + Fe_3O_4	Bentonite	Bentonite + Fe_3O_4
0.5	2.88	19.2	9.72	12.5	13.1
1	5.86	24.4	15.9	22.8	23.0
2	6.15	31.6	30.2	37.8	37.4

From Table 5, it was found that (1) the mass loss of granite was stable after one year, and that of the others were still rising. It was suggested that granite might be the best geological medium for HLW to resist corrosion. The mass losses of bentonite and "bentonite + Fe_3O_4" after one year were larger than that of the others, suggesting that bentonite and "bentonite + Fe_3O_4" might cause more corrosion to the HLW glass than granite, "granite + cement" and "granite + Fe_3O_4"; (2) after the two-year test, there was more corrosion on the simulated HLW glass in the simulated disposal media with Fe_3O_4. It indicated that Fe_3O_4 could increase the corrosion of the glass specimens.

Hence, granite, "granite + cement" and "granite + Fe_3O_4" are better geological media for disposing HLW glass when compared with bentonite and "bentonite + Fe_3O_4", and granite is considered the best.

3.2 XRD analyses of leached specimens' surfaces

The XRD results of the leached glass specimens in the granite and the "granite + cement" media are given in Fig. 2. The XRD patterns of the glass specimens leached in other media were similar to that in the "granite + cement" medium.

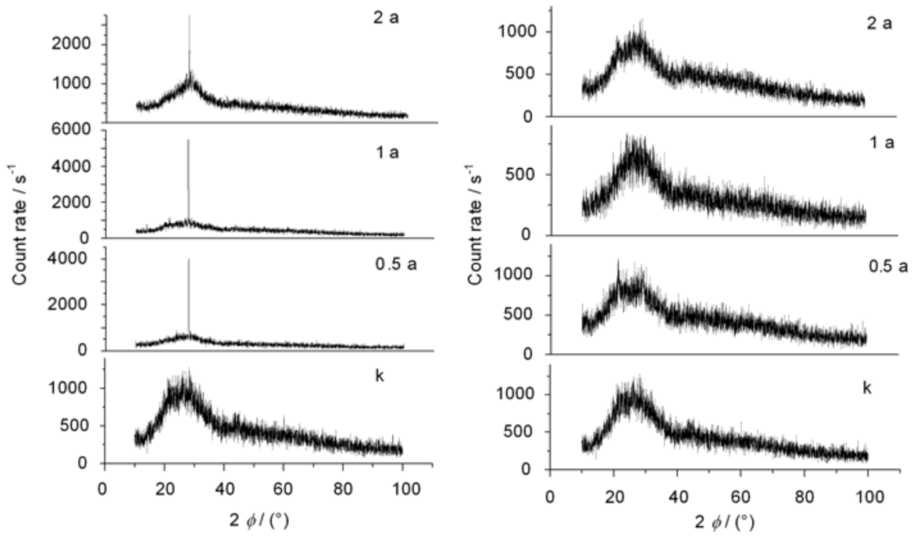

Fig. 2 XRD pattern of the leached glass specimens after two years.

(Left: in granite; Right: in "granite + cement")

It was found from the above figure that (1) except for the glass specimens leached in granite, no obvious diffraction peaks appear in the XRD pattern of the specimens in the other four test media. This indicates that there was no crystal phase formed on the specimens' surfaces in the bentonite, "bentonite + Fe_3O_4", "granite + Fe_3O_4" and "granite + cement" media, respectively; (2) there were few diffraction peaks appearing on the glass specimens' surfaces in the granite media leached for 0.5 to 2 years. Since these crystal phases did not increase the specimens' corrosion as shown in the mass loss calculation, the peaks may have been caused by some crystal phases, which were stuck on the specimens' surfaces.

3.3 SEM analyses of leached specimen's surface

The analysis of the leached specimen's surface was carried out by SEM and XEDS, respectively.

3.3.1 SEM analysis

Fig.3 shows the specimen's surface images. The following facts can be verified:

(1) There was more corrosion present on the leached specimen's surface in the bentonite and "bentonite + Fe_3O_4" media, and there were some nets formed, which could not come into contact with each other to break off from the specimen's surface, thereby causing a lot of corrosion pit formed on the specimen's surface. No sediment was formed on the specimen's surface, which was consistent with the XRD results.

(2) The glass specimens that were leached in three simulated media, i.e. granite, "granite + cement", and "granite + Fe_3O_4", had many corrosion pits on the specimen's surface after six months. At the end of the two-year leaching test, some gel was formed on the surface that may protect the glass specimen

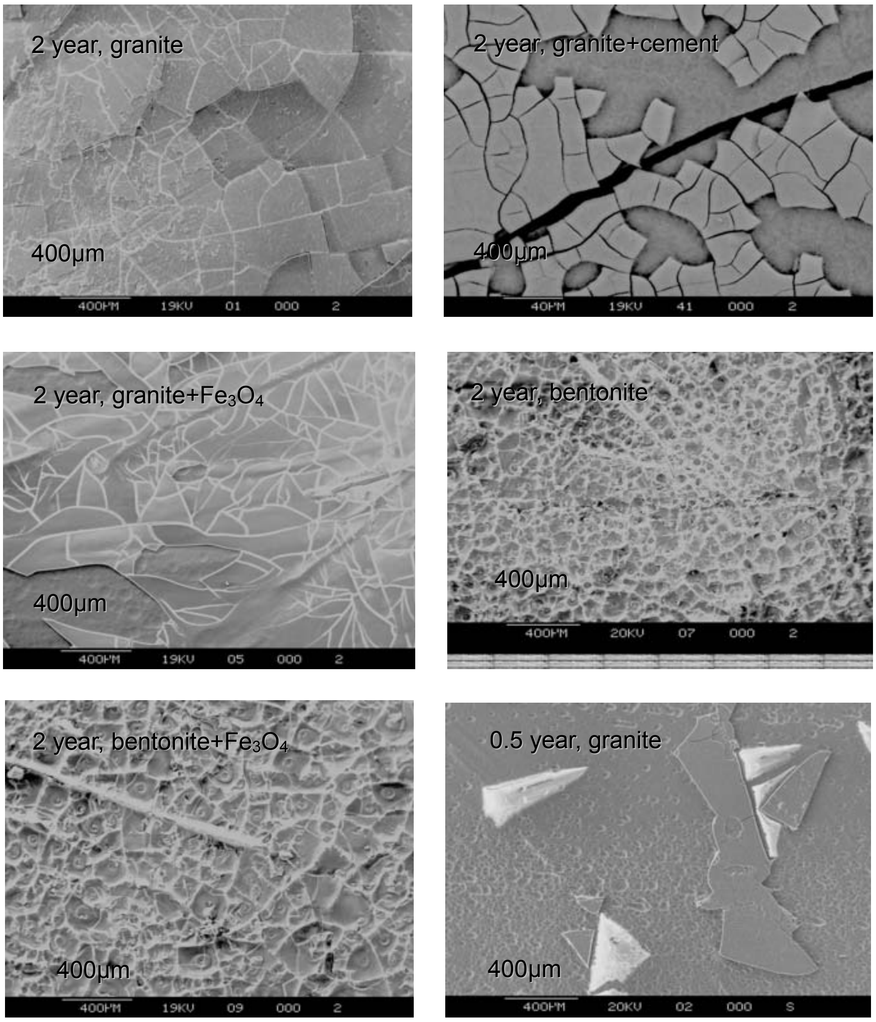

Fig. 3 SEM patterns of leached glass specimen's surface in five simulated disposal media.

from corrosion. It was found from the SEM pattern of "granite+ Fe_3O_4" that the gel formed on the specimen surface was the thinnest when compared with other media. Fe_3O_4 decreases the gel forming on the surface and increases the corrosion, which is consistent with the results of the mass loss calculation.

3.3.2 XEDS analysis

Some white needle-like materials were found on the SEM pattern, which result in the small diffraction peaks. Their composition was analyzed by XEDS and the result is shown in Fig. 4.

It is found from Fig. 4 that the main component is Si, mixed with small quantities of Al, Mg, Na, and Ca. This Si-rich material forms a protective gel to decrease the glass corrosion, which explains the lower mass loss in the granite system.

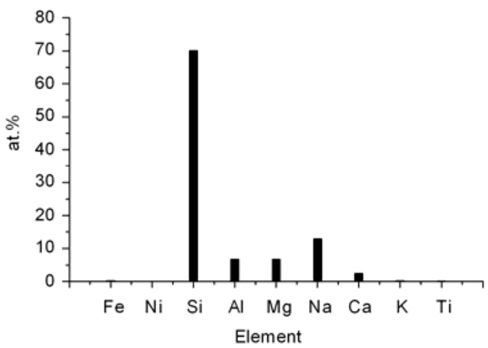

Fig.4 Composition of the sediment formed on the specimen's surface in granite.

The atomic contents of the six main elements in specimen's surface were analyzed by XEDS and the results are shown in Fig.5.

The following conclusions can be drawn:

(1) Except "granite+cement", the Si element was slightly depleted on the specimen's surface leached in other media. After the two-year leaching test, the Si content on the specimen's surface had the following order: "granite+ cement" > "granite+ Fe_3O_4"> granite > "bentonite+ Fe_3O_4" ≈ bentonite.

(2) The content of the Fe element had no change in "granite+cement" and "granite+ Fe_3O_4"; and the content of Fe was enriched in the other three media with an order: bentonite > bentonite+ Fe_3O_4 > granite.

(3) The Al element was enriched in five media and had an order: "bentonite+ Fe_3O_4" ≈ "granite+ Fe_3O_4" > granite > bentonite > "granite+ cement".

(4) The content of the Mg element was slightly depleted in the five media and had no significant change. The Ca element in the five media was slightly enriched. Except in "granite+ cement", the Na element on the specimen's surface was almost depleted completely. The Na element was slightly depleted in "granite+ cement", indicating that cement could prevent the specimen from corrosion.

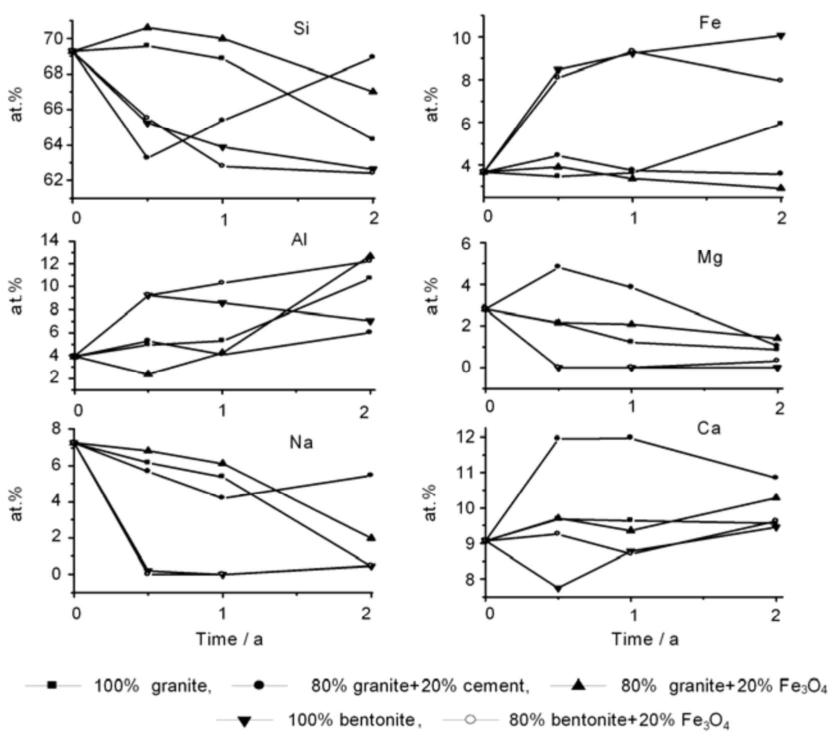

Fig. 5 The atomic contents of the six main elements in the specimens' surface.

The corrosion process of glass includes four main reactions, i.e. ion exchange, hydrolysis, network hydrolysis, and network dissolution. Al, Mg, Fe, and Ca participate in the ion-exchange reactions. Because their valences were more than 1, these were always enriched on the specimens' surfaces. While taking part in the hydrolysis reaction, Na is always depleted completely, because Na^+ can exchange with H^+. Finally, Si participates in the hydrolysis reaction, which causes the glass network dissolution.

From the results mentioned above, it has been found that the glass corrosion processes were almost similar in the five simulated geological media. However, bentonite and "bentonite + Fe_3O_4" seemed to be more corrosive on the simulated HLW glass when compared to the others. "granite + cement" maintains the same reaction phase with the others in the beginning, but it prevents Si and Na from decrease at last. This may be the result of its alkaline environment.

4 Summary

(1) The mass losses of the glass specimens leached in the bentonite and "bentonite + Fe_3O_4" media were larger than that in the other testing media, and the glass specimens leached in the granite media had the least mass loss.

(2) There was some Si-rich crystal formed on the specimen's surface in the granite media, which may protect the glass specimen from corrosion.

(3) The elements of Al, Fe and Ca were slightly enriched on the glass specimen's surface. The contents of Si and Mg were slightly reduced on the specimen surface, while Na was almost depleted completely during the leaching tests.

(4) The atom content results suggested that bentonite and "bentonite + Fe_3O_4" seemed to be more corrosive than the others, and "granite + cement" eased up the corrosion on the simulated HLW glass because of its alkaline environment, after one year.

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