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The Effects of pH and Buffer Materials on the Leaching of Simulated Waste Glass

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Abstract

Effects of pH, bentonite and Portland cement on the leaching of the simulated waste glass were investigated. The simulated waste glass showed the low leach rate in the neutral pH region, while the leach rate in both acidic and alkaline regions increased. Addition of bentonite to the leachant enhanced the leaching of the waste glass. When the waste glass was leached at 72℃ for 36 days in the ground water with gel state Na-bentonite, approximately 2.2 μm of the surface was corroded out and the large amount of Ti, Nd, and Zr was observed on the surface. The amount of B leached from the simulated waste glass in the presence of domestic bentonite was about three times higher than that in the presence of Aldrich bentonite as well as Portland cement.

1. Introduction

Borosilicate glass has been assessed as one of the best matrix materials for the immobilization of high-level nuclear wastes. In order to isolate the radioactive waste safely from the biosphere for more than several thousands years, many environmental factors such as ground water, metal barrier, buffer material, backfill material and rock should be considered in the leaching process of a borosilicate waste glass.

The pH of leachant, which is considered as one of the most important parameters affecting glass corrosion, was found to be varied with the temperature, the ionic strength, the ratio of glass surface area to solution volumn(SA/V), the leach rate of Na^+ ion, the flow rate of ground water, etc.[1]. In general, dissolution of waste glass is very low in the pH range of 5 to 9. Activation energy of leaching is very high in neutral solution and the values in pH 3 and 11 solutions are similar each other[2.3]

It is well known that the backfill or buffer materials such as clay (smectite, illite, bentonite) and sand can increase glass corrosion remarkably due to the persistent removal of silicate ions from the leachant[4-6]. Sorption or dissolution with reprecipitation of a silica-rich clay have been proposed as possible mechanisms for the silica consumption. However, activated bentonite did not increase glass corrosion[7]. The dissolution of the Pamela\DWK SM513 glass was not affected by bentonite when Boom clay was a host rock[8]. Godon reported that the corrosion of radioactive R7T7 glass doped with Np-237 and Pu-239 can be limited by supplying silicon from the bentonite to the solution[9].

For the Portland cement, the actinides sorb mainly onto the cement, whereas Cs and Sr sorb preferentially onto the clay. Cement-glass interaction appears to accelerate the alteration of the glass[10].

This paper presents the variation of the leachability of simulated waste glass in different pH' s of leachant. The effects of Na-bentonite on the leaching of waste glass are discussed, and those of domestic Ca-bentonite and Portland cement are also compared.

2. Experimental

2.1. The Preparation of Simulated Waste Glass

Disc-shaped samples of a simulated borosilicate waste glass (it will be called "SW-glass" from now) were prepared by a molding method. The stoichiometric amounts of SiO_2, B_2O_3, Na_2CO_3, CaO, Al_2O_3, TiO_2, Nd_2O_3, etc. were thoroughly mixed for 30 minutes using a tungsten carbide mill (Table 1). Approximately 100 g of the powdered mixture in an alumina crucible was heated to 1200 ℃ by 10℃/min. and maintained at 1200℃ for 2 hours in muffle furnace. A sample rod was made by pouring the molten glass into a bright-red preheated cylinderical molder with a diameter of 12 mm. It was then annealed at 500℃ for 20 minutes and slowly cooled to room temperature by 3℃/min. The cooled glass rod was cut by 2 mm thickness with diamond blade. The surface of glass plate was polished with a 1000 grit SiC sandpaper.

Powdered sample of SW-glass was prepared by crushing the SW-glass with a tungsten carbide milling machine and sifting with screens of 100/200 mesh. Some of the powdered sample was dissolved in mixed acids of HF, HNO_3 and HCl by microwave digestion method for the composition analysis of SW-glass prepared. Both powdered and disc-shaped samples were cleaned ultrasonically in petroleum ether, isopropanol and acetone for 15 minutes[11], and finally reannealed at 500℃ for 1 hour.

Perfluoralkoxy(PFA) teflon bottles were used for

Table 1. Composition of Simulated Waste Glass (wt. %)

Oxide	Reactant	Product[a]
SiO_2	45.8	48.6
B_2O_3	15.3	12.6
Na_2O	10.2	10.0
CaO	3.1	2.7
Al_2O_3	2.9	5.5
BaO*[b]	0.5	
TiO_2	3.1	2.8
Fe_2O_3	2.0	2.0
Li_2O	1.0	
RuO_2*	1.0	
MoO_3*	2.0	
Cr_2O_3	0.5	
Nd_2O_3*	5.1	4.9
ZnO	2.6	
ZrO_2*	1.8	
La_2O_3*	1.0	
SmO	0.3	
Ce_2O_3*	0.8	
NiO*	1.0	

[a] product of SW-glass was analyzed only the major elements.

[b] The asterisk marks (*) are for fission product elements.

leaching experiment after cleaning with diluted NaOH and HNO_3 solutions based on the Ebert's method[12]. Composition of leachate solutions was analyzed by Inductively Coupled Plasma Atomic Emission Spectrography(ICP-AES), after filtering on 0.45 ㎛ Durapore® Membrane to remove the solid materials and precipitates. All experiments were carried out on 2~4 duplicated samples simultaneously.

2.2. Leaching of the SW-Glass in Different pH Solutions

0.1 g of SW-glass powder was added to the solutions whose pH had been adjusted at 3.2~9.6 using KOH or HNO_3 at room temperature. The solutions were stored at 72℃ for 7 days. However, the pH of all leachants changed to 6~8 after leaching, which makes it difficult to examine the effect of pH on the glass corrosion. Thus, preleaching method was employed. pH's of the 8 solutions were adjusted at 2~11.6 after leaching the powdered SW-glass in demineralized water(DW) at 72℃ for 5 days. Then, the solutions were kept at 72℃ for 9 days.

Table 2. Ion Concentration Released in N_2-Purged Solutions with Various Additives at 72℃

Element	Unit : ㎍/m l			Final
Condition	B	Si	Al	pH
DW[a] + SW[b]	4.65	19.3	0.55	7.8
DW + Ben1[c]	0.15	58.3	0.29	
DW + SW + Ben1	45.3	91.5	0.72	
DW+SW+Ben1+Fe_2O_3	31.6	69.1	0.53	
Boric acid sol.[d] +Ben1	19.1	58.3	0.70	
GW[e]	0.04	6.5	0.06	
GW + SW	2.22	15.5	0.44	8.3
GW + Ben1	0.16	63.3	0.32	
GW + SW + Ben1	34.0	84.4	0.37	
GW + SW-ds[f] + Ben1	2.71	58.0	0.09	
GW+SW-ds+Ben1+Fe_2O_3	2.44	61.3	0.42	

[a] DW : Demineralized water [b] SW : SW-glass powder
[c] Ben1 : Bentonite from Aldrich Co.
[d] Boric acid sol. : Initially, B concentration was 20 ppm and pH of the solution was adjusted to 7.0 with KOH solution.
[e] GW : Ground water [f] SW-ds : SW-glass disc

2.3. Leaching of the SW-Glass in Leachants with Bentonite

Commercial Na-bentonite (Aldrich Co.), domestic Ca-bentonite and Portland cement were used in the leaching experiment to study the effect of a

Table 3. Compositions of Bentonites and Portland Cement(wt. %)

	Bentonite		
	Ben1[a]	Ben2[b]	Portland Cement
Si	39.8	32.3	12.7
O	35.0	32.3	24.5
Al	14.1	15.5	3.98
Fe	7.25	16.1	4.49
Mg	1.28	0.96	1.35
Ca	0.85	0.97	50.1
S	0.35	0.17	2.45
K	0.14	0.34	
Na	0.99	0.27	
Ti	0.07	0.73	0.11
P	0.02	0.08	0.09
Re	0.04	0.05	0.06
Ba	0.03	0.09	
Sr	0.04	0.04	0.04
Zr	0.02	0.04	0.01
Ga	0.01	0.01	
Th	0.01		
Mn		0.01	0.02
Cu		0.01	0.02
Pt		0.02	
Y		0.01	
Cl			0.04
Cr			0.02
Zn			0.01
Pb			0.01
Total	100.00	100.00	100.00

[a] Ben1 : Bentonite from Aldrich Co.
[b] Ben2 : Domestic bentonite

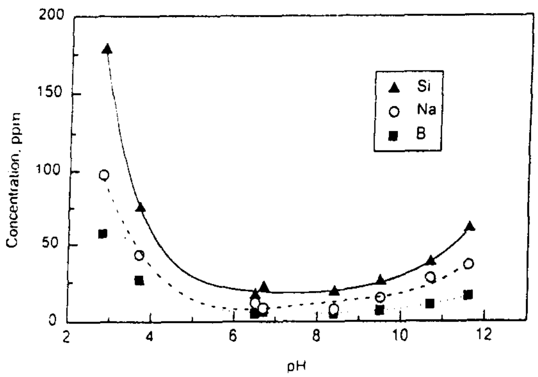

Fig. 1. The Concentration of Some Leached Ions from SW-Glass as a Function of pH

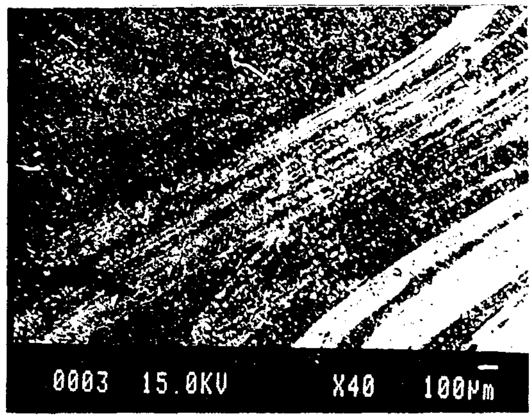

Fig. 2. SEM Photograph of SW-Glass Surface After Leaching for 36 days in the Ground Water with Bentonite Additive

buffer or backfill materials on the leaching of waste glass. Only 1.0 g of Aldrich bentonite was added to 15 ml DW in order to observe the pH change of solution and to determine the dissolved ion concentrations from bentonite for the background test. The solution was filtered with 0.45μm filter.

0.1 g of SW-glass powder, 0.15 g of Fe_2O_3 and 0.5 g of bentonite or cement were added to 15 ml DW or ground water(GW) following the experimental conditions shown in Table 2. The compositions of bentonite, Portland cement and ground water are listed in Table 3 and 4. The solutions were kept at 72℃ for 36 days in the closed bottles filled with nitrogen gas or air. The leached solutions were centrifuged at 4000 rpm/min. for 30 minutes and were filtered by 0.45 μm. The element of the clear solution was analyzed by ICP-AES. The disc samples were also leached in GW by the same procedure and then the surface of the discs was cleaned ultrasonically in methanol.

3. Results and Discussion

3.1. The Preparation of SW-Glass

Result of elemental analysis of SW-glass indicated that the contents of major starting elements were not changed during the firing process at 1200℃ for 2hr, except for boron and aluminium (Table 1). The boron content decreased by 18 % due to the evaporation of B_2O_3 having low melting point. On the other hand, the aluminium content almost doubled due to the contamination from the alumina crucible. The density of SW-glass was measured by the picnometer and known to be 2.72 g/cm^3. X-ray diffraction pattern of the prepared SW-glass showed only the peaks of RuO_2. This is the consistent with the report that platinum group is not vitrified with glass frits[13].

3.2. The Effect of pH

The initial pH's, 3.2~9.6, of unbuffered leachants changed to 6~8 after leaching experiment in the earlier stage, which might be due to the low ionic strengths of the solutions. Thereafter, preleaching method was used in the leaching experiments, because the leached solution of borosilicate glass is buffered with the release of constituent ions such as Si and B[1].

Experimental results showed that the amount of Si, Na, and B leached from the SW-glass was minimized in neutral pH range(Fig. 1). On the other hand, acidic solution was particularly corrosive to waste glass because of the exchange of cations of the glass by hydrogen ions[14], although the solubility of silica is small. In basic solution, glass dissolution increased with increasing pH due to the increase of silica solubility.

3.3. The Effect of Bentonite

In the background test with the addition of 1.0 g Aldrich bentonite to 15 ml DW, the pH of the solution increased to 9.3 in 3 days and was finally stabilized at 9.4~9.5 in 10 days. The solution was filtered with 0.45μm filter and analyzed by ICP. The concentrations of B, Si, Al and Na of the filtered solution were 0.126, 38.9, 8.05 and 129 ppm, respectively. Boron has been used as an indicator of the leaching of waste glass, because the amount of B dissolved from bentonite was very small. Moreover, we confirmed that boron is not adsobed on the bentonite(Table 2).

Results of leaching experiment of the SW-glass in various conditions with Aldrich bentonite are summarized in Table 2. Addition of bentonite in the leachant increased SW-glass corrosion greatly.

When disc samples in the GW solution or powdered samples in the DW solution were leached in the presence of bentonite, addition of Fe_2O_3 decreased the B concentration of the leachates. This is coincident with the Fe_2O_3 effect on the leaching of SON68 waste glass in the solution with the ratio of water : clay : Fe_2O_3 = 12 : 3 :1[15]. The decreasing effect of Fe_2O_3 on the glass corrosion in the presence of bentonite has been explained either by the formation of passivating surface layer on the glass samples or by the increase of silicate concentration in solution through an exchange of Si and Fe between solution and bentonite[15]. However, we observed neither the increase of iron on the surface of disc sample nor the increase of Si concentration in solution with SW-glass powder.

Demineralized water leached SW-glass powder more than ground water did in the absence of bentonite additive, although the pH of the DW solution was slightly lower than that of the GW solution. This may be due to the high ionic content in the ground water.

The microstructural change on the glass surface of glass disc after leaching experiment was examined in the presence of Aldrich bentonite. The smooth surface of SW-glass was changed to the fractured surface just like the surface of ground

Table 4. Compositions of Ground Water

Element concentration : μg/m l

pH	Cl	SO_4	F	NO_3	Ca	K	Mg
7.5	0.5	6.2	2.8	<0.1	3.8	0.6	0.3
Mn	Na	Fe	Si	HCO_3	Mn	B	
< 0.1	25	< 0.1	5.1	14	< 0.1	<0.1	

Table 5. Comparison of Ion Concentrations Released in Aerated Leachants with Bentonites and Portland Cement at 72℃

Element / Condition	B	Si	Na	Al	Mo	Nd
	unit : ppm					
DW[a]+Ben1[b]	0.22	63.8	171	0.57	0.21	-
DW+Ben2[c]	0.55	44.0	32.9	0.22	0.02	0.03
DW+Port[d]	1.39	0.27	34.7	0.38	0.07	0.32
DW+SW[e]+Ben1	39.6	81.4	259	1.00	16.1	-
DW+SW+Ben2	131	101	95.0	6.03	41.4	0.06
DW+SW+Port	38.9	0.38	209	0.75	5.69	0.30
GW[f]+SW+Ben1	42.2	91.4	287	1.43	16.8	0.05
GW+ SW+Ben2	126	107	104	9.13	39.8	0.08
GW+SW+Port	33.3	0.33	216	0.76	5.12	0.25

[a] DW : Demineralized water
[b] Ben1 : Bentonite from Aldrich Co.
[c] Ben2 : Domestic bentonite
[d] Port : Portland Cement
[e] SW : SW-glass powder
[f] GW : Ground water

after a long period of drought. White stripes in Scanning Electron Microscopy(SEM) were also observed after leaching (Fig. 2). Electron Probe Microanalysis(EPMA) results indicated that the area of white stripes contained more insoluble elements such as Ca, Ti, Zr, Ru and Nd than dark area. The large amount of insoluble elements observed on the surface of SW-glass after leaching were confirmed by X-ray Photoelectron Spectroscopy(XPS). The microfocus measurement showed that the white area was corroded more by about 2.2 μm than dark area.

Leaching effect of domestic bentonite, Aldrich bentonite and Portland cement on the SW-glass was compared in Table 5. Domestic bentonite increased B concentration approximately three times more than the other additives, while the increase of Na concentration remained low. This result suggests that the Ca ion from domestic bentonite (Ca-bentonite) forms the precipitates in leachant more easily than the Na ion from Aldrich bentonite (Na-bentonite) does, which decreases the concentration of silicate ion in leachant. It has been known that the leaching of glass decreases as the silicate concentration in leachant increases[14]. The effect of Portland cement was similar to that of Aldrich bentonite.

4. Conclusions

The leaching of SW-glass was minimized in the neutral pH range and increased in acidic and alkaline pH regions. Bentonite enhanced the leaching of SW-glass, whose effect was greater than that of Fe_2O_3 additive. The glass surface was corroded unevenly by 2.2 μm in the presence of bentonite at 72°C for 36 days. Na-bentonite and Portland cement is the better candidate of a buffer material than Ca-bentonite in the leaching of waste glass.

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