ELSEVIER

Journal of Nuclear Materials 298 (2001) 163–167

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Release and retention of uranium during glass corrosion

T. Maeda [a,*], T. Banba [a], K. Sonoda [b], Y. Inagaki [c], H. Furuya [c]

[a] *Japan Atomic Energy Research Institute, Tokai Research Establishment, Department of Fuel Cycle Safety Research, Disposal Safety Laboratory, Ibaraki 319-1195, Japan*
[b] *NGK Insulators, LtD, Japan*
[c] *Kyushu University, Japan*

Abstract

In order to investigate the release and retention of uranium during glass corrosion, static leach tests were performed on a simulated waste glass doped with uranium in deionized water for up to 423 days. Observation and analysis of the alteration layer formed on glass surface were carried out by means of optical microscopy, scanning electron microscopy (SEM) and analytical electron microscopy. Elemental concentrations of leachate were determined by ICP atomic emission spectroscopy, atomic absorption spectrometry and kinetic phosphorescence analyzer (KPA) (for uranium). An analytical electron microscopy provided that fibrous phase were developed on the outer surface of the alteration layer, as secondary phase, which should be clay minerals such as nickel–nontronite, or nickel-rich chlorite. Absence of uranium and rare earth elements (REEs) in the fibrous minerals suggests that the release of uranium and REEs can be controlled by precipitation of hydroxides rather than uptake in clay minerals. Experimental results and thermodynamic calculations suggest that the uranium concentration in the leachate is controlled by solubility of uranyl hydroxides such as $UO_2(OH)_2$ (s). © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In the field of radioactive waste disposal in geological repositories, many corrosion tests on actinide-doped waste glasses were performed and the release of actinides from the glass has been investigated for the prediction of the long-term leaching behavior of actinides [1–4]. Further, vitrified waste forms such as molten forms are thought to have excellent properties for stabilization of radionuclides [5]. It is well known that heavy elements are retained at the alteration layers formed on experimentally leached borosilicate glass [6,7]. However, geochemical mechanism of the retention of actinides in the alteration layers has not been investigated sufficiently.

The purpose of this study is to investigate the mechanism of the retention of uranium in the alteration layer, such as precipitation of simple hydroxides or incorporation into minerals formed in the alteration layer of the glass. Static corrosion tests were performed on a borosilicate glass doped with ^{238}U in deionized water at 90°C up to 423 days. After the tests, observation and analysis of the alteration layer formed on glass surface were carried out by means of optical microscopy, scanning electron microscopy (SEM) and analytical electron microscopy.

2. Experimental

A simulated waste glass doped with uranium ($^{238}U_3O_8$; 0.9 wt%) was used as glass specimen. Table 1 shows the composition of the simulated waste glass. The glass specimen ($5.0 \times 5.0 \times 2.0$ mm^3) and deionized water (40 ml) were placed in a Teflon container with a S/V ratio of 10 m^{-1} and static corrosion tests were performed at 90°C in aerated condition for periods of up to 423 days.

At the end of the corrosion tests, the Teflon container was cooled to room temperature. The leachate was passed through filters with pore size of 450 nm to remove the suspended fractions after measurement of pH.

---

[*] Corresponding author. Tel.: +81-29 282 5085; fax: +81-29 282 5934.

E-mail address: toshi@koala.tokai.jaeri.go.jp (T. Maeda).

0022-3115/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(01)00587-6

Table 1
Composition of uranium-doped simulated waste glass

Component	Content (%)	Component	Content (%)
SiO_2	45.15	BaO	0.62
B_2O_3	13.90	La_2O_3	0.31
Al_2O_3	4.89	CeO_2	1.01
Li_2O	2.00	Pr_6O_{11}	0.49
Na_2O	9.79	Nd_2O_3	1.65
CaO	4.00	Sm_3O_3	0.33
ZnO	2.47	Eu_2O_3	0.06
Rb_2O	0.12	Gd_2O_3	0.04
SrO	0.34	SeO_2	0.02
Y_2O_3	0.19	RuO_2	0.80
ZrO_2	2.64	Fe_2O_3	2.90
MoO_3	1.73	NiO	0.40
MnO_2	0.26	Cr_2O_3	0.50
Ag_2O	0.03	P_2O_5	0.30
CdO	0.03	Ru	0.12
SnO_2	0.02	Rh	0.15
Sb_2O_3	0.004	Pd	0.43
TeO_2	0.23		
Cs_2O	0.97	UO_2	0.90

Then the concentrations of uranium and major glass constituents in the filtrates were measured by kinetic phosphorescence analyzer (KPA) and ICP atomic emission spectroscopy.

The leached glass specimen was immersed in ethanol immediately to replace water in the alteration layers. The epoxy resin was poured onto the ethanol-immersed specimen to hold the alteration layer. The specimens impregnated with epoxy resin were sliced perpendicularly to the original glass surface. The sliced sections were observed and analyzed by an optical microscope, SEM with EDX. Further, ultra thin (<100 nm) sections of the alteration layers were prepared by use of the ultramicrotomic technique [8,9] and analyzed by an analytical electron microscope technique.

3. Results and discussions

3.1. Analysis of alteration layers

Fig. 1 shows the back-scattered electron image of cross-section of the alteration layer formed on the specimen after 423 days of corrosion time with the EDX line profiles for some elements. The profiles show the elemental depletion and enhancement in the layer. Similarly to the previous works [9,10], silicon was enriched at glass/layer interface and depleted gradually from the interface to the surface. Sodium was depleted in the layer. Uranium and cerium (rare earth element (REE)) were enriched in the layer. Fig. 2 shows the thickness of the layer as a function of corrosion time. The layer grew up for about 60 μm during the first 56 leaching days, and kept constant in the longer test periods up to 423 days.

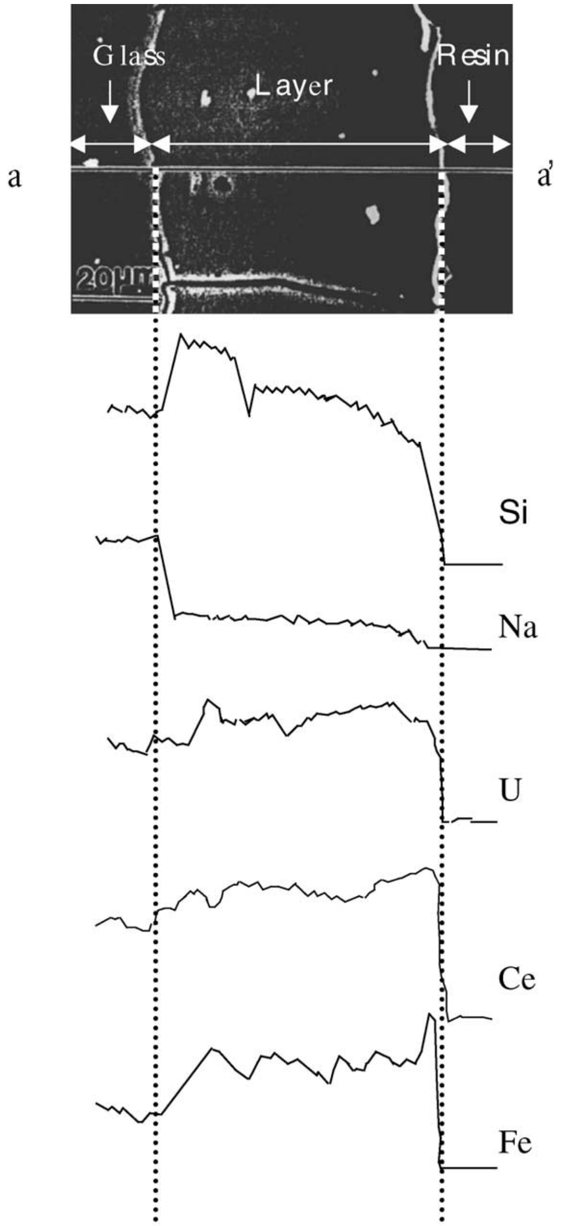

Fig. 1. Back-scattered electron micrograph of cross-section of the alteration layer and EDX line profiles for five elements along the line a–a′ (423-day leached sample).

Fig. 3 shows the schematic feature of the alteration layer. The alteration layer was dominated by an amorphous phase with a mottled texture. This phase is called as 'mottled phase' [11,12]. About 400 nm thick of fibrous phase was developed on the outermost of the alteration layer. The fibrous minerals were observed partly in the

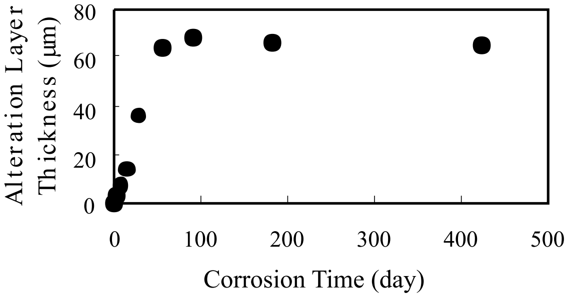

Fig. 2. Alteration layer thickness of the U-doped glass as a function of corrosion time at 90°C (error bars represent the variabilities of the layer thickness).

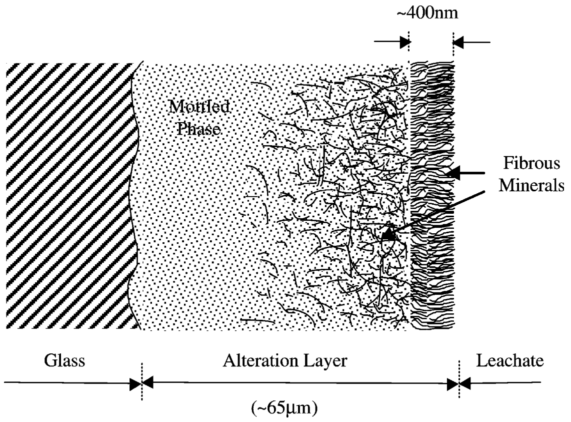

Fig. 3. Schematic feature of alteration layer of the U-doped glass leached for 423 days at 90°C.

mottled phase. The mottled phase is more fibrous toward the layer/solution interface. No fibrous minerals were included at near the glass/layer interface. Since formation of the fibrous minerals needs content of water, it is suggested that penetration of water in the alteration layer can lead to the growth of the fibrous minerals.

Fig. 4 shows the transmission electron micrograph of the fibrous minerals. From both the measurement of lattice fringes and the result of selected-area electron diffraction (SAED) pattern, the basal (0 0 1) spacing of the fibrous minerals was observed to be about 1.4 nm. Fig. 5 shows the EDX profiles of the mottled phase and the fibrous minerals in alteration layer. Mottled phase was enriched in silicon and iron, while fibrous minerals were enriched in silicon and nickel. It is obvious that the fibrous minerals are clay minerals on the basis of the fact as follows; (1) low crystallinity, (2) high content of water, (3) large amount of silicon and iron, and (4) slight amount of aluminium, calcium and manganese. The fibrous clay minerals are thought to be smectite clays because the basal spacing of the fibrous minerals was about 1.4 nm, which is same as those of smectite clays [13]. Previous work noticed that the fibrous clay minerals such as nickel–nontronite and chlorite were observed in the surface layer of the glass leached at 90°C for 14 days [12]. Nickel–nontronite is a kind of a 2:1 layer type smectite clay [11]. Chlorite has a octahedral brucite layer ($Mg(OH)_2$) in the interlayer position of 2:1 smectite [14]. From these results, the fibrous clay minerals could be nickel–nontronite (smectite clay) or nickel-rich chlorite. Nickel-rich smectite is not often observed naturally [15], but it is possible that nickel replaces magnesium due to its similar ionic radius [16].

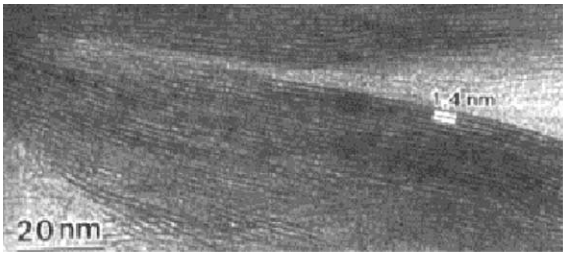

Fig. 4. Transmission electron micrograph of the fibrous minerals that grew in the alteration layer. The basal spacing of the fibrous minerals are mostly 1.4 nm.

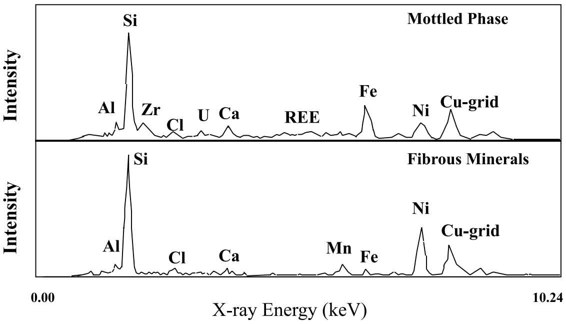

Fig. 5. EDX profiles of mottled phase and fibrous minerals in alteration layer of the U-doped glass leached for 423 days at 90°C.

In Fig. 5, uranium and REEs can be observed in mottled phase but they were not included in the fibrous minerals. Absence of uranium in the fibrous minerals suggests that uranium is not incorporated to the clay minerals.

3.2. Analysis of solution

Fig. 6 shows the pH of the leachate. The pH increased at a few days and became stable at around 9. Fig. 7 shows normalized concentrations of uranium and major glass constituents in the leachates. The normalized concentration (NC_i) was calculated from the

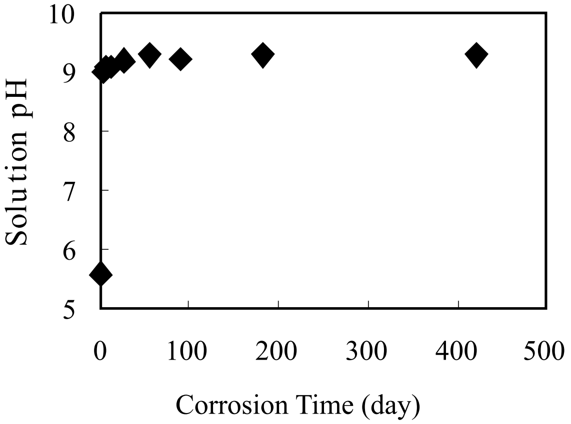

Fig. 6. pH of the leachate as a function of corrosion time at 90°C.

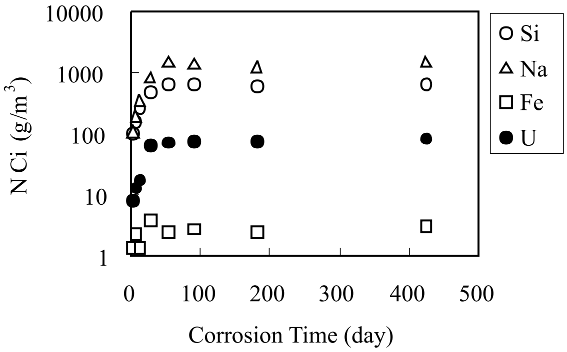

Fig. 7. Normalized elemental concentration of leachate as a function of corrosion time at 90°C.

concentrations in the 450 nm filtrates by the following equation [2,4,17],

$$\mathrm{NC_i} = C_\mathrm{i}/f_\mathrm{i}, \tag{1}$$

where, C_i is the solution concentration of element i, and f_i is the original fraction of element i in the glass. The NC of uranium increased up to 28 days and kept constant in the longer test periods. The NC of uranium is one order of magnitude lower than the NC of major glass constituents such as silicon and sodium.

In order to predict the chemical speciation of uranium in the leachate, the equilibrium calculations were carried out on the basis of thermodynamic data related to uranium chemistry, which are listed in Table 2 [18,19]. Elemental concentrations and the pH value of the leachate were also used for the calculation.

The results calculated for the leachate of 423 days are shown in Table 3. The feasible reaction controlling the solubility of uranium under the present condition is

$$\mathrm{UO_2(OH)_2\ (s) + 2H^+ = UO_2^{2+} + 3H_2O.} \tag{2}$$

The four complexes of uranium are thought to exist in the leachate. The total solubility of these four complexes is calculated to be 2.5×10^{-6} mol/l. The concentration of uranium was measured to be 2.4×10^{-6} mol/l in the leachate. A relatively good agreement is found between the total of calculated uranium solubilities and the measured uranium concentration. According to the results of calculation, it is suppose that $UO_2(OH)_2$ (s) is precipitated as the solubility limiting solid phase in the leachate at 90°C and that dominant species dissolved in this condition is $UO_2(OH)_2^0$.

Table 2
Thermodynamic data used for the estimation of uranium specification in leaching solution

	log *K*	Δ*H* (kcal/mol)
Precipitates		
$\gamma\text{-}UO_3 + 2H^+ = UO_2^{2+} + H_2O$	7.73	−19.40
$UO_3(am) + 2H^+ = UO_2^{2+} + H_2O$	10.40	−7.30
$UO_2(OH)_2 + 2H^+ = UO_2^{2+} + 2H_2O$	4.94	13.60
$UO_2(OH)_2 \cdot H_2O + 2H^+ = UO_2^{2+} + 3H_2O$	4.82	0.00
$UO_2CO_3 + 2H^+ = UO_2^{2+} + CO_3^{2-}$	−14.40	−1.58
Complexes		
$UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$	−5.20	10.32
$UO_2^{2+} + 2H_2O = UO_2(OH)_2^0 + 2H^+$	−11.50	13.60
$UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	−19.20	4.60
$2UO_2^{2+} + H_2O = (UO_2)_2(OH)^{3+} + H^+$	−2.70	−40.80
$UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$	−5.62	9.00
$3UO_2^{2+} + 4H_2O = (UO_2)_3(OH)_4^{2+} + 4H^+$	−11.90	−50.20
$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$	−15.55	23.22
$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$	−31.00	−24.20
$4UO_2^{2+} + 7H_2O = (UO_2)_4(OH)_7^+ + 7H^+$	−21.90	−58.60
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3^0$	9.63	−1.92
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	17.00	3.58
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.63	−9.16

Table 3
Comparison between calculated uranium solubility and measured uranium concentration of the 423-day leachate

Calculated solubility of uranium	Measured uranium concentration in leachate
Precipitate $UO_2(OH)_2$ (s) $+ 2H^+ = UO_2^{2+} + 3H_2O$	
Complexes $UO_2(OH)_2^0 = 1.7 \times 10^{-6}$ mol/l $UO_2(OH)_3^- = 7.4 \times 10^{-7}$ mol/l $UO_2(OH)_4^{2-} = 4.9 \times 10^{-8}$ mol/l $UO_2(CO_3)_2^{2-} = 2.8 \times 10^{-8}$ mol/l	
Uranium total $= 2.5 \times 10^{-6}$ mol/l	Uranium total $= 2.4 \times 10^{-6}$ mol/l

3.3. Leaching behavior of uranium

Uranium is suppose to exist in the glass as a modifier in the form of uranyl ion (UO_2^{2+}) [20]. As the results of the hydration and dissolution of the silica network, the alteration layer is formed at the glass surface. Since the alteration layer contains water, the uranyl ions are partly hydrated at glass/layer interface as the glass corrosion proceeds. The hydrated ions migrate in the porous alteration layer towards layer/solution interface, but the solubility limit of the uranyl hydroxide ceases the migration, and precipitation occurs as $UO_2(OH)_2$ (s) both in the layer and near the layer/solution interface. Therefore, uranium is accumulated in the layer, and present in the mottled phase as precipitated $UO_2(OH)_2$ (s) and not incorporated in the fibrous clay minerals.

In the solution, the concentration of uranium is probably controlled by the solubility of $UO_2(OH)_2$ (s) which is precipitated on the surface of the glass.

4. Conclusion

During the static corrosion tests of a simulated waste glass doped with uranium, an alteration layer with a thickness of 60 μm was formed on the surface of the glass. The alteration layer was dominated by mottled phase, and fibrous mineral phase with a thickness of 400 nm was developed on the outermost of the alteration layer. The fibrous minerals were observed partly in the mottled phase, the mottled phase being more fibrous toward the layer/solution interface. No fibrous minerals were included at near the glass/layer interface. The fibrous minerals can be suggested to be clay minerals such as nickel–nontronite (smectite clay) or nickel-rich chlorite. Uranium was accumulated in the alteration layer. Uranium was rich in the mottled phase but absent in the fibrous minerals, which suggests that uranium cannot be incorporated into the fibrous clay minerals but will be precipitated as uranyl hydroxide such as $UO_2(OH)_2$ (s). Thermodynamic calculations suggest that the concentration of uranium released from glass can be controlled by the solubility of $UO_2(OH)_2$ (s).

References

[1] L. Wang, P. Van Iseghem, Mater. Res. Soc. Symp. Proc. 294 (1993) 155.
[2] B. Grambow, A. Loida, L. Kahl, W. Lutze, Mater. Res. Soc. Symp. Proc. 353 (1995) 39.
[3] J.A. Fortner, J.K. Bates, Mater. Res. Soc. Symp. Proc. 412 (1996) 205.
[4] Y. Inagaki, A. Sakai, et al., Mater. Res. Soc. Symp. Proc. 465 (1997) 213.
[5] T. Amakawa, K. Adachi, S. Yasui, CRIEPI Report No. W95005, 1995.
[6] D.M. Strachan, Nucl. Chem. Waste Manage. 4 (1990) 177.
[7] J.E. Mendel, et al., PNL-5157, Pacific Northwest Laboratory, Richland, Washington, 1984, p. 2.9.
[8] G. Ehert, J. Crovisier, J.P. Eberhart, J. Non-Cryst. Solids 86 (1986) 72.
[9] C.R. Brandler, N.L. Dietz, J.K. Bates, Mat. Res. Soc. Symp. Proc. 254 (1992) 279.
[10] Materials Characterization Center, Nuclear Waste Materials Handbook, DOE/TIC-11400, Pacific Northwest Laboratory, Richland, WA, 1985.
[11] T. Banba, T. Murakami, H. Isobe, Mater. Res. Soc. Symp. Proc. 176 (1990) 363.
[12] T. Murakami, T. Banba, M.J. Jercinovic, R.C. Ewing, Mater. Res. Soc. Symp. Proc. 127 (1989) 65.
[13] W.A. Deer, R.A. Howie, J. Zussman, in: An Introduction to the Rock-forming Minerals, Longman Scientific and Technical, England, 1992, p. 355.
[14] H. Sirozu, in: Introduction to Clay Mineralogy, Asakura-shoten, Japan, 1988, p. 38.
[15] Mineralogical Society, in: A.C.D. Newman (Ed.), Chemistry of Clays and Clay Minerals, Longman Scientific and Technical, England, 1987.
[16] G.W. Brindley, Z. Maksimovic, Clay Miner. 10 (1974) 271.
[17] Y. Inagaki, H. Sakata, et al., Mater. Res. Soc. Symp. Proc. 506 (1998) 177.
[18] I. Grenthe, et al., Chemical Thermodynamic of Uranium Draft, OECD, Nuclear Energy Agency, Data Bank, Gif-sur-Yvette, France, 1990.
[19] R.J. Silva, Mater. Res. Soc. Symp. Proc. 257 (1992) 323.
[20] D.G. Karraker, J. Am. Ceram. Soc. 65 (7) (1982) 53.