FORMATION OF HYDROTALCITE-LIKE COMPOUNDS DURING R7T7 NUCLEAR WASTE GLASS AND BASALTIC GLASS ALTERATION

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Abstract—Alteration experiments have been performed using R7T7 and synthetic basaltic glasses in $MgCl_2$-$CaCl_2$ salt solution at 190°C. The duration of experiments ranged from 0.25 to 463 days. The alteration products were studied by Scanning Electron Microscope (SEM), Scanning Transmission Electron Microscope (STEM), X-ray diffraction (XRD) and Electron Spectrometry for Chemical Analysis (ESCA). For both glasses, the early alteration product is a hydrotalcite-like compound $[Mg_6Al_2CO_3(OH)_{16}\cdot4H_2O]$ in which HPO_4^{2-}, SO_4^{2-} and Cl^- substitutes for CO_3^{2-}. The measured basal spacing is 7.68 Å for the hydrotalcite formed from R7T7 glass and 7.62 Å for the hydrotalcite formed from basaltic glass which reflect the high Al/Al + Mg ratios x ($0.34 \leq x \leq 0.46$). The chemical microanalyses show that the hydrotalcite is subsequently covered by a silica-rich gel which evolves into saponite after a few months. These results support the use of basaltic glasses alteration patterns in Mg-rich solution, to understand the long-term behavior of R7T7 nuclear waste glass.

Key Words—Basaltic glass, Experimental alteration, Hydrotalcite-like compounds, $MgCl_2$-$CaCl_2$ salt solution, R7T7 nuclear waste glass, Saponite.

INTRODUCTION

Industrial nuclear energy production produces necessarily radioactive wastes such as Sr, Zr, Pu and Am. These wastes are incorporated into a borosilicate glass matrix (Sombret 1987) containing about 13% of radioactive elements including long half-life alpha emitters. The disposal of nuclear waste glass is a unique environmental problem in that it requires a solution that remains technically valid on geological time scales (10^3–10^5 years). One proposed method is to embed the nuclear waste glass in an underground repository. In Germany, the Gorleben salt dome has been selected for the construction and operation for a repository for nuclear waste. The nuclear glass will be surrounded by stainless steel canisters embedded into the dome. After disposal several tens of megawatts of heat are produced in the sealed repository. This may result in maximum temperature at the bore-hole surface of 200°C (Lutze and Grambow 1992). Remobilization of the waste by corrosion and transport of radionuclides by groundwater loaded with dissolved salts ($MgCl_2$, $MgSO_4$, $CaCl_2$, NaCl . . .) are the only events for radioactivity to find its way back to the environment. The performance of the glass has to be evaluated by studying the corrosion process in salt solution at this elevated temperature. The identification of stable secondary phases

formed on the surface of glass is essential because these phases may control the concentrations of dissolved elements in the leaching solution (Crovisier *et al* 1987; Lutze *et al* 1989) and as a consequence, influence directly the glass leaching rate (Grambow 1985). Natural basaltic glasses provide analogue materials for the study of the alteration of nuclear glasses (Ewing 1979; Malow and Lutze 1984; Lutze *et al* 1987; Crovisier *et al* 1988; Petit 1992).

MATERIAL AND METHODS

Preparation of samples

The glasses used in this study are the French Cogema R7T7 waste glass and a synthetic basaltic glass. R7T7 glass was obtained by melting oxides and carbonates at 1200°C (Pacaud *et al* 1989). The basaltic glass was similarly prepared following the method of Crovisier *et al* (1983). The compositions of the glasses are given, respectively, in Tables 1 and 2. For the corrosion tests with the glass surface area to solution volume (SA/V) ratios of 10 and 50 m^{-1}, glass specimens were cut in rectangular blocks ($10 \times 10 \times 1$ mm) and set vertically in 100 cm^3 Teflon-lined autoclaves filled with salt solution. Glass powders with an average grain size of 75 μm in diameter (maximum 100 μm, minimum 50 μm) were added to the brine to attain SA/V ratios about 20,000 m^{-1} and placed on the bottom of the Teflon containers. The autoclaves were sealed and placed in

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Table 1. Chemical composition of the R7T7 nuclear waste glass (wt. %) (Nogues *et al* 1985).

SiO_2	45.48	MnO_2	0.72
Al_2O_3	4.91	CoO	0.12
B_2O_3	14.02	Ag_2O	0.03
Na_2O	9.86	CdO	0.03
CaO	4.04	SnO_2	0.02
Fe_2O_3	2.91	Sb_2O_3	0.01
NiO	0.74	TeO_2	0.23
Cr_2O_3	0.51	Cs_2O	1.42
P_2O_5	0.28	BaO	0.60
ZrO_2	2.65	La_2O_3	0.90
Li_2O	1.98	Ce_2O_3	0.93
ZnO	2.50	Pr_2O_3	0.44
SrO	0.33	Nd_2O_3	1.59
Y_2O_3	0.20	UO_2	0.52
MoO_3	1.70	ThO_2	0.33
Total			100

Table 3. Chemical composition of the salt solution in molality (Grambow and Müller 1990).

Cations		Anions	
Na	0.083	Cl^-	11.538
K	0.022	SO_4^{2-}	0.001
Mg	5.401		
Ca	0.316		
Σ^+	11.539	Σ^-	11.540
pH	4.25		

a drying oven heated at $190 \pm 2°C$. The composition of the initial salt solution is given in Table 3 and corresponds to a type of brine which occurs in the domed salt formation in Germany. Before analysis of the alteration products, monolithic and granular samples were washed in bi-distilled water heated at 80°C. The run times are summarized in Table 4.

Electron microscopy

The morphology and chemical composition of the alteration products were determined by scanning electron microscope (SEM; Jeol JSM 840 equipped with a Tracor TN 5400 energy-dispersive X-ray spectrometer), transmission electron microscope (TEM; Philips EM300) and scanning transmission electron microscope (STEM; Philips CM12 equipped with an EDAX PV9900 spectrometer). For electron microdiffraction and chemical composition, thin sections, a few hundred of angstroms (Å) in thickness, were obtained by pouring an epoxy resin onto the altered surface under vacuum and pulling off the resin after polymerization. The sample is embedded once more and sliced by the ultramicrotome (Ehret *et al* 1986).

Photoelectron spectrometry

The surface compositions of the glass samples altered for short time periods were determined by ESCA analysis in a CAMECA Nanoscan 50 apparatus equipped with an Al Kα source and Mac II electron analyser which was set at 1 eV resolution. This method permits detection of all elements present at the surface except hydrogen with a sensitivity of about one atomic percent. The analysed depth is about 50 Å. The charging effects observed on the spectra were corrected by sweeping carbon peak energy at 284.6 eV.

X-ray powder diffraction

The identity and crystallinity of secondary phases were determined by X-ray diffraction using a Philips 1120/90 X-ray diffractometer with Ni-filtered Cu Kα radiation at 40 kV and 20 mA.

RESULTS

Scanning electron microscopy

The appearance of crystals on the surface of the monolithic R7T7 glass after 24 hours of interaction is shown in the SEM picture (Figure 1a). It consists of agglomerates of thin, hexagonal, plate-like crystals of hydrotalcite about 1 μm in size. The crystallite size increased with increasing time of alteration (Table 5). After 1 to 92 days of alteration, the morphology of the crystals evolves by the formation of a deposit similar in composition to saponite (Figure 1b). Saponite, powellite: $(Na, Ca, Nd, Pr, La)MoO_4$, cerianite: CeO_2, barite: $(Ba, Sr)SO_4$ were observed on the sample reacted

Table 2. Chemical composition of the basaltic glass (wt. %) (Crovisier *et al* 1983).

SiO_2	50.76
Al_2O_3	13.62
Na_2O	2.48
MgO	7.35
CaO	10.72
Fe_2O_3	4.08
FeO	8.18
K_2O	0.18
TiO_2	1.66
P_2O_5	0.10
MnO	0.16
Total	99.29

Table 4. Run times and SA/V of the studied samples.

R7T7 glass		Basaltic glass	
Time	SA/V (m^{-1})	Time	SA/V (m^{-1})
6 hours	10	2 hours	50
1 day	50	7 hours	10
2 days	50	1 day	50
3 days	10	*24 days	20,000
36 days	10	*120 days	20,000
92 days	10		
*463 days	21,700		

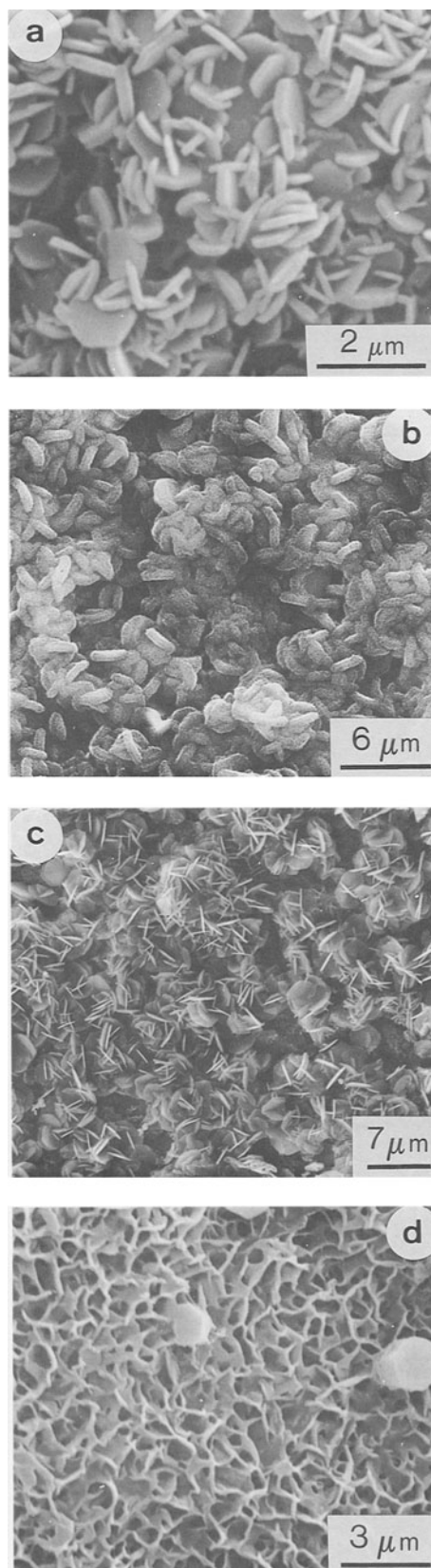* Mixture of monolithic and granular glass.

Table 5. Evolution of the crystallite size determined from SEM micrographs with alteration duration (R7T7 glass).

Temperature (°C)	190	190	190
SA/V (m⁻¹)	10	10	10
Time (days)	0.25	3	36
Size (μm)	1–2	3	5–6

for 463 days in salt brine (Abdelouas 1992; Rother *et al* 1992).

After seven hours of alteration, the basaltic glass sample was covered by hydrotalcite (Figure 1c). These crystals have a more distinct hexagonal outline than those of hydrotalcite formed on the nuclear glass. With increasing time (24 days), hydrotalcite is associated with a Mg-Al-rich smectite (Figure 1d).

Photoelectron spectrometry

Figure 2 shows ESCA spectra of the R7T7 glass before and after alteration in salt solution. The unleached glass reference sample (Figure 2a) has strong Si 2s and Si 2p peaks. It also shows strong O 1s and Na 1s peaks. The high C 1s peak ($E_L = 284.6$ eV) corresponds to the carbon contamination. After one day of alteration, sodium and zinc disappeared from the spectra. The surface of the altered glass is strongly enriched in magnesium, chlorine, aluminium and zirconium (Figure 2b) due to the precipitation of hydrotalcite. The carbonate ion (CO_3^{2-}) peak ($E_L = 288.5$ eV) and phosphorus peak are absent. Thomassin (1984) identified the CO_3-hydrotalcite as an alteration product of synthetic basaltic glass in seawater and showed that this mineral gives an ESCA spectrum in which the carbonate ion peak appears at 288.5 eV. Silicon can also be detected on the surface of the alteration layer.

The basaltic glass sample, having been leached in salt solution for seven hours, also shows marked changes in the outermost surface layer. The unleached sample presents high O 1s and C 1s peaks (Figure 3a). The leached sample also shows an enrichment of magnesium, chlorine and aluminium (Figure 3b). The silicon and calcium content decrease drastically in this sample. The carbonate ion has not been detected in the alteration layer.

X-ray powder diffraction

XRD analysis reveals the presence of hydrotalcite on the surface of the R7T7 glass sample altered for one

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Figure 1. (a) Hydrotalcite formed on the R7T7 glass surface (one day); (b) hydrotalcite covered by a silica-rich deposit after two days of alteration; (c) hydrotalcite crystals formed on basaltic glass surface after seven hours of alteration. (d) After 24 days, the basaltic glass surface is covered by saponite.
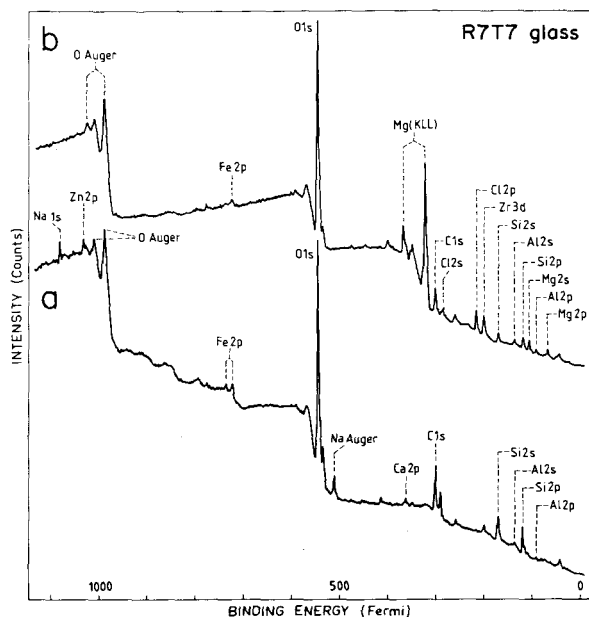
Figure 2. ESCA spectra of R7T7 glass before (a) and after (b) corrosion for 24 hours at 190°C in salt solution.

Figure 4. X-ray diffractograms of hydrotalcite formed on the surface of the R7T7 nuclear waste glass and basaltic glass. The values given on both diffractograms are in Å.

day (Figure 4). The d spacings measured for the hydrotalcite are similar to those obtained by Gastuche *et al* (1967) for a synthetic Al-rich hydrotalcite (Table 6, columns 1 and 3). After 463 days of alteration, saponite (14.91; 4.52; 3.22 and 1.53 Å) and powellite (3.13; 1.99; 1.43; 1.20 and 1.18 Å) were identified.
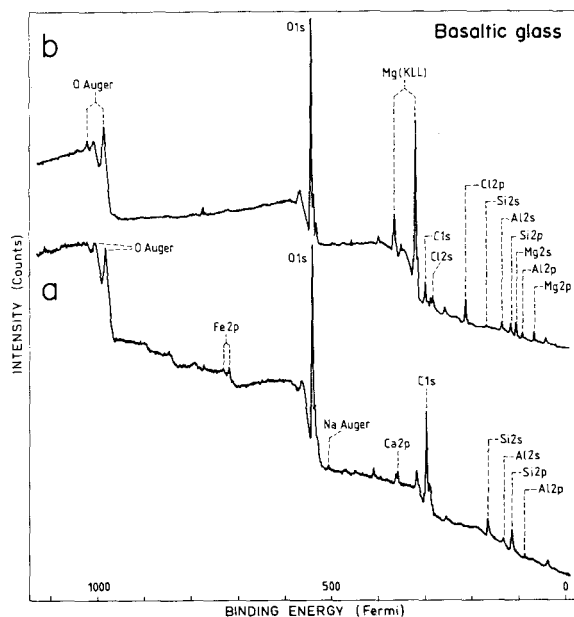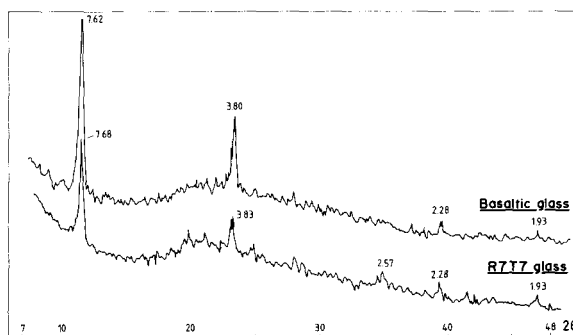
The observed d spacings for the hydrotalcite formed on the surface of the basaltic glass after seven hours of alteration are similar to those measured from the hydrotalcite formed on the R7T7 glass surface (Table 6, column 2). The hydrotalcite formed from R7T7 glass gave a more diffuse X-ray pattern than those formed from basaltic glass alteration (Figure 4). Saponite (14.75; 4.43; 3.02 and 1.52 Å) was identified after 24 days of alteration.

Scanning transmission electron microscopy

Observations by STEM showed the presence of crystallized platelets (Figure 5a) for the R7T7 glass samples altered from 1 to 36 days. The d spacings measured on electron diffraction patterns obtained from the alteration layer are also compatible with hydrotalcite (Figure 5b). Electron diffraction patterns obtained from different crystals of hydrotalcite show a basal d spacing of about 7.7 Å. The EDX microanalyses obtained from different particles in the internal part of the alteration layer confirm the composition of hydrotalcite (Mg, Al) and permit us to establish that HPO_4^{2-}, SO_4^{2-} and Cl^- occupied the inter-layer positions (Table 7, column 1).

Figure 3. ESCA spectra of basaltic glass before (a) and after (b) corrosion for seven hours at 190°C in salt solution.

Table 6. Comparison between X-ray data obtained from the hydrotalcite formed on the surface of the R7T7 nuclear waste glass (1), basaltic glass (2) and hydrotalcite synthesized by Gastuche *et al* (1967) (3).

$d_{obs.}$ (Å)		
1	2	3
7.68	7.62	7.63
		4.57
3.83	3.80	3.81
2.57		2.60
		2.532
2.28	2.28	2.36–2.20
		2.01–1.91
1.93	1.93	1.897
		1.523
		1.493
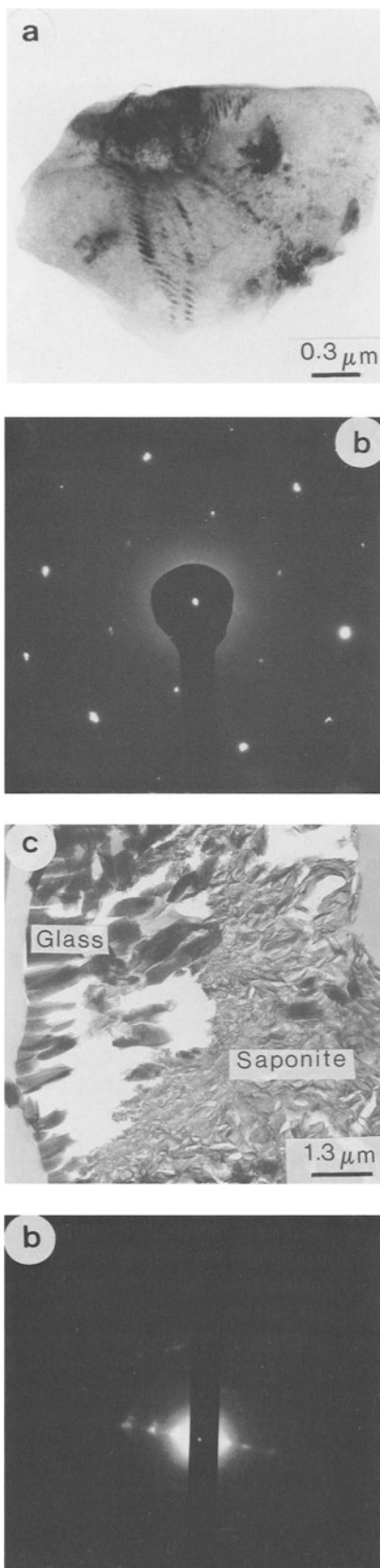
Some crystals contain Cr, Zr, Fe and Nd (Table 7, column 2). The Al/Al + Mg ratio x of about 0.46 reflects the low value of the basal d spacing. After 92 days of alteration, the hydrotalcite was identified in association with antigorite (Table 7, column 3) and saponite (Table 7, column 4). After 463 days of alteration, the predominant alteration product is a saponite (Figures 5c and 5d). The chemical composition of the saponite did not change significantly between 92 and 463 days.

Alteration of basaltic glass in salt solution leads to the formation of Cl-rich hydrotalcite (Table 7, column 5). There is a remarkable homogeneity in the composition of individual hydrotalcite platelets. Electron diffraction patterns obtained in the individual platelets are characteristic of hydrotalcite with a basal d spacing of about 7.6 Å which reflects a high Al/Al + Mg ratio x = 0.34. As with the R7T7 glass, the hydrotalcite persisted only for a short time period and subsequently was covered by a silica-rich gel. The most evolved alteration product is a saponite, the composition of which is given in Table 7, column 6.

DISCUSSION

Borosilicate and basaltic glasses exhibit similarities in corrosion behavior in salt solution. For short periods of alteration (few hours to one day), both glasses were covered by a hydrotalcite-like compound in which the CO_3^{2-} is essentially replaced by HPO_4^{2-} (from glass), SO_4^{2-} and Cl^- (from solution) for the R7T7 glass and by Cl^- for basaltic glass. Andriambololona *et al* (1992) performed *in situ* testing in a saline environment at an underground laboratory in New Mexico with R7T7 glass for periods of 0.5, 1 and 2 years. They observed an Mg, Fe and Cl-enrichment of the glass surface altered in contact with salt and concluded that the main alteration product was a magnesium silicate in association with a Zr-rich product.

Synthesis of Cl-rich hydrotalcite in a complex system has been achieved by Miyata (1975). This author has shown that the hydrotalcite-like compounds can be

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Figure 5. Characterization by scanning transmission electron microscopy of the alteration products formed on the R7T7 nuclear waste glass surface: (a) bright-field image showing the plate-like morphology of hydrotalcite; (b) electron microdiffraction pattern obtained in the previous particle (2.63 and 1.52 Å); (c) ultramicrotomic thin section performed in the external part of the altered glass (463 days). From the right to the left of the micrograph we can distinguish an alteration layer, about 7 μm thick, and the fresh glass (black fragments); (d) electron diffraction pattern obtained in the alteration layer (463 days). The measured interval is 10.87 Å (001 reflections) which corresponds to a dehydrated saponite under the electron beam.

Table 7. Chemical microanalyses (STEM, wt. %) of alteration products of monolithic R7T7 glass (1–4) and basaltic glass (5, 6) in salt solution at 190°C.

	1 HT (R7T7)	2 HT (R7T7)	3 Antigorite (R7T7)	4 SAP (R7T7)	5 HT (basalt)	6 SAP (basalt)
MgO	34.9 ± 5.2	25.4	42.5 ± 4.2	22.5 ± 0.9	41.6 ± 1.5	25.9 ± 1.9
Al_2O_3	42.8 ± 4.8	32.4	3.7 ± 1.7	5.4 ± 0.9	31.8 ± 1.3	14.0 ± 1.2
SiO_2		3.4	46.7 ± 6.6	61.7 ± 3.1	4.5 ± 1.5	53.3 ± 1.9
P_2O_5	8.4 ± 4.0	14.1			0.1 ± 0.1	
SO_3	2.8 ± 2.6	2.3	2.4 ± 2.6		0.6 ± 0.7	
Cl	6.8 ± 2.0	2.3	4.7 ± 2.6		17.4 ± 2.7	
CaO	1.3 ± 0.6	3.8		0.8 ± 0.4	0.6 ± 0.2	1.0 ± 0.6
K_2O	1.1 ± 1.5					
Nd_2O_3		2.4		0.5 ± 0.5		
CrO		7.6				
Fe_2O_3	1.9 ± 1.7	3.2		4.3 ± 0.4	1.6 ± 0.5	5.1 ± 1.0
ZnO				0.6 ± 0.3		
UO_2				1.5 ± 1.5		
MoO_3				1.5 ± 0.8		
ZrO_2		3.1		1.2 ± 1.2		
TiO_2					1.8 ± 0.4	0.7 ± 0.4
N.A.	11	1	10	20	7	6

HT: hydrotalcite; SAP: saponite; N.A.: number of analyses.

expressed by the formula $[M_x^{2+} M_y^{3+} (OH)_{2(x+y)}]^{y+}$ $\cdot [A_{z1}^- A_{z2}^{2-} \cdot mH_2O]^{-(z1+z2)}$ where M^{2+} and M^{3+} denote di- and trivalent cations, A^- and A^{2-} denote mono- and divalent anions, respectively, and $y = z_1 + 2z_2$. He has also shown that Cl-hydrotalcite has a similar structure to CO_3-hydrotalcite but the basal d spacing is larger (d = 7.86 Å) and Cl^- is easily substituted by CO_3^{2-}. Miyata (1983) studied the anion-exchange properties of hydrotalcite-like compounds in complex systems: NO_3^-, Cl^-, SO_4^{2-}, F^-, Cl^-, Br^-, I^-, OH^-, SO_4^{2-} and CO_3^{2-}. He suggests that the hydrotalcite may readily remove HPO_4^{2-} from waste waters. Pausch et al (1986) synthesized hydrotalcite-like compounds in different conditions and showed that the result of the synthesis depended on temperature, pressure, the Al/Al + Mg ratio x, and the CO_2 content of the starting material. They also showed that the x value of the synthesized product may reach 0.44 when an x value of the starting material ranged between 0.25 to 0.44, the water pressure was about 100 MPa and the temperature between 100 and 350°C. For our experiments, particularly for the R7T7 glass, the high Al amount in the hydrotalcite is probably due to the water pressure generated in the autoclaves during heating (Pausch et al 1986). The low basal d spacing of the hydrotalcite-like compound synthesized in our study may be explained by the high substitution of Mg^{2+} by Al^{3+} which increases the electrostatic attraction between the layers. In addition, Miyata (1980) indicated that interlayer water content decreased with increasing Al content in the crystals and, consequently, the basal d spacing decreased.

Some hydrotalcite formed from R7T7 glass contain Cr, Zr, Ca, Fe and Nd. The ability of the hydrotalcite to retain Zr and Nd is indicative of the ability of the alteration products to trap toxic elements under conditions of waste package failure. The saponite which seems the more persistent secondary phase for a long time of alteration (>1 year) also contains a small amount of Zr, U, Nd and Mo.

For both glasses, the enrichment of solution in silica with increasing time of alteration favours the transformation of hydrotalcite to an Mg-Al-rich silicate and the precipitation of saponite. After one day to a few months of alteration, the crystals were covered by an amorphous silica-rich deposit whose chemical composition and structure changed into saponite. Similar results have been obtained by Thomassin and Touray (1982) and Crovisier et al (1982, 1983, 1985) for basaltic glass altered in seawater. Crovisier et al (1982) have observed the crystallization of hydrotalcite after 20 days of alteration of the basaltic glass in seawater at 50°C. They also showed that the crystals were covered by a silico-alumino-magnesian gel whose composition evolves to a saponite (480 days). The association of hydrotalcite with saponite has also been observed by Schmitz et al (1982) in marine sediments from the Galapagos rifts, and by Larsen et al (1991) for basaltic glass altered experimentally in deionized water. Thomassin (1984) studied the transformation of hydrotalcite to smectite during the alteration of basaltic and andesitic glasses in seawater. The author distinguished two stages of transformation of hydrotalcite to a silicate-rich phase. During the first stage, the hydrotalcite transformed to aluminium-rich serpentine. The second stage is accompanied by a decrease of crystallinity of the particles and the transformation of Al-rich serpentine to smectite.

Thermodynamic modelling made by Crovisier et al (1985) using the computer code DISSOL (Fritz 1975,

1981) showed that hydrotalcite is not stable for long-term in seawater. The replacement of this mineral by saponite during basaltic glass alteration was predicted by the geochemical code DISSOL as the result of magnesium decrease and silica increase in solution.

SUMMARY AND CONCLUSION

Results of these experimental studies of R7T7 nuclear waste glass and basaltic glass in $MgCl_2$-$CaCl_2$ salt solution lead to the following conclusions:

The same successive steps of the formation of secondary phases have been identified during the corrosion of the synthetic basaltic and R7T7 nuclear waste glasses: the early alteration product is a hydrotalcite-like compound containing HPO_4^{2-}, SO_4^{2-} and/or Cl^- and the most evolved product is saponite which persists for more than one year. In this type of brine, the abundance of Mg in solution permits the formation of similar Mg-rich secondary phases on the glass samples independently of the nature of the initial glasses.

The mineralogical sequences precipitated on the surfaces of the synthetic basaltic and R7T7 glasses altered in $MgCl_2$-$CaCl_2$ saturated solution are similar to those of the natural and synthetic basaltic glasses altered, respectively, under natural and experimental conditions in seawater.

These results support the use of basaltic glass alteration patterns in Mg-rich solution (seawater, brine), to understand the long-term (10,000 to 100,000 years) behavior of R7T7 nuclear waste glass and to evaluate the stability of secondary minerals.

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