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Role of neoformed phases on the mechanisms controlling the resumption of SON68 glass alteration in alkaline media

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Abstract

The alteration of SON68 glass (inactive R7T7 type glass) in alkaline (NaOH and KOH) solution was studied at pH 11.4 at 90 °C and at an S/V ratio of 65 cm^{-1}. Under these conditions the glass alteration rate initially diminished due to the formation of a protective gel layer, as observed during alteration of the same glass at lower pH (7–10). After a time varying from 14 to 28 days, depending on the nature of the base, alteration subsequently resumed. This study confirms the latest results showing that the phenomenon is due to the crystallization of zeolite phases such as analcime or merlinoite at the gel surface. These phases initially consume the aluminum in solution, then all the aluminum and a fraction of the silicon in the gel. When the solution pH is artificially decreased to 9.5 during the renewed alteration stage, the zeolites gradually dissolve and glass dissolution ceases. The instability of these secondary phases at low alkaline pH shows that nucleation of the phases is not the phenomenon limiting the glass alteration kinetics, and that a resumption of alteration due to the precipitation of these phases is unlikely in nuclear glass disposal conditions (pH 7–10).

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1. Introduction

The radioactive waste remaining after reprocessing of spent uranium fuel from nuclear power plants is vitrified in a silicate glass. In France, the glass is produced at industrial scale by COGEMA in the R7 and T7 facilities at La Hague. The glass canisters are intended for long-term disposal in a deep geological formation. In these conditions groundwater will be the main factor of alteration of the glass matrix and the main vector liable to disperse the radionuclides.

The processes of alteration of a silicate glass in contact with an aqueous solution have given rise to numerous studies [1–6].

For nuclear glass, and especially for SON 68 glass, an experiment in pure water in static mode or with little solution renewal, leads to a very brief step dominated by interdiffusion followed by an initial dissolution step at the maximum rate corresponding to hydrolysis of the silicate network without any effect of dissolved species. This step is followed by an intermediate step during which the concentrations in solution increase more slowly. The alteration rate then diminishes by several orders of magnitude compared with the initial rate (4 orders of magnitude at 90 °C).

The initial dissolution is congruent for all the major glass components (Si, B, Na, Al, etc.). The second step is characterized by incongruent dissolution related to the development of a gel-like alteration layer formed by recondensation of the partially hydrolyzed Si–OH bonds, and which retains some heavy or sparingly soluble elements. This gel is the main constituent of the alteration layer, which may also include crystallized phases precipitated from solution (mainly phyllosilicates or rare earth element phosphates).

There is currently no consensus on the mechanisms leading to the decreasing rate. Two types of mechanisms

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are presented in the literature to account for the decreasing alteration rate of nuclear glasses with the reaction progress:

(1) chemical affinity, based on the notion of an equilibrium between the solution and the glass: the rate of hydrolysis of the Si–O–Si bonds decreases as the dissolved silicate species accumulate in solution and their concentration approaches saturation [7];
(2) diffusion through the gel which, if sufficiently dense, can limit the mass transfer between the glass and the external solution [8–10].

The first approach has been challenged in theory by Jégou [11] and experimentally by Leturcq et al. [6], Linard [12] and Gin et al. [13]. The hypothesis according to which the alteration rate is limited by the chemical affinity, and especially by the activity of orthosilicic acid in solution, had been proposed in order to account for the effects of the S/V ratio [14] or the flow rate, but is contradicted by experimental evidence – in particular the behavior of a pristine glass sample in a saturated solution, or the behavior of a glass specimen previously altered in a confined medium with a high S/V ratio and then placed in pure water. These experiments, and others, show the predominant role of the alteration layer [10,15]. In particular, recent works using Monte-Carlo simulation show that the silicon recondensation in the gel can greatly limit the water accessibility at the interface by closing the porosity and thus decrease the glass hydrolysis rate [16,17].

Models describing the long-term behavior of nuclear waste glasses developed in France are based on knowledge of the mechanisms controlling glass alteration in a closed system and in particular on the limiting role of the gel formed during the alteration process [18]. However, the persistence of the protective effect of the gel on the alteration kinetics must first be demonstrated. A major research program in this area has been conducted by the CEA in France to identify the phenomena capable of destroying the protective properties of the gel, and to evaluate the probabilities of occurrence in a geological repository, i.e. to determine whether a stable long-term protective gel could be formed under realistic conditions.

An example of such a phenomenon is given by some experiments, generally at high reaction progress, showing a potential third alteration step, following the decreasing reaction rate step and characterized by a sudden, spontaneous acceleration of glass alteration.

The first reports of this resumption of alteration were attributed to cracking or desquamation of the protective gel layer [19,20]. It is now clear, however, that the renewed alteration occurs together with the precipitation of secondary crystalline phases, usually zeolitic aluminosilicates [21–23]. Depending on the alteration parameters, the solution composition could evolve into a domain in which these phases are oversaturated and precipitate at the interface between the gel layer and solution. Renewed alteration has generally been observed under conditions with high surface-to-volume (S/V) ratios for glasses with high alkali content (e.g. Hanford glasses), but also for some aluminum-rich glasses [22,24–28], and at high reaction temperatures ranging from 100 to 250 °C [29,30].

However, the mechanism by which these secondary phases affect the alteration rate has not been completely elucidated.

One hypothesis assumes that the precipitation of these new phases modifies the saturation state of the solution, hence the term 'chemical affinity', leading to increased glass dissolution. Depending on their composition, the precipitating phases consume silica, and could control the residual affinity, maintaining the silicon concentration in solution below its saturation value [9]. The affinity induced by the precipitation of silicate phases depends on their stability, their stoichiometry and their precipitation rate [24,31–33]. Another hypothesis assumes that secondary phases precipitating on the surface of the alteration gel layer alter its properties, causing the gel layer to lose its protectiveness with respect to the glass [34].

During experiments on SON68 glass at an imposed pH condition and at a surface-to-volume ratio of 50 cm^{-1}, Gin and Mestre [34] observed a resumption of alteration after nearly 50 days at pH 11.5 or 220 days at pH 11.0. No such phenomenon has been observed in tests lasting 600 days at pH 10.5. The renewal of alteration is attributed to the precipitation at the gel/solution interface of a zeolitic aluminosilicate with higher aluminum content than the gel, and with precipitation kinetic high enough to induce partial dissolution of the gel. The possibility of a resumption of alteration over the very long-term in a more realistic pH range ($7 < pH < 10$) cannot be excluded – particularly if it is assumed that the only prerequisite for zeolite precipitation is to reach a given solution composition. Gin showed that the fact that renewed alteration has not been observed below pH 10.5 can not be explained by thermodynamic constraints, as the solutions are supersaturated with respect to the zeolites observed above pH 7.

The work discussed in this article is a continuation of the preceding study. Based on the observation that leaching solutions are always supersaturated with respect to zeolites, and that these mineral phases are only observed at very high pH, kinetic constraints must be taken into account to interpret the observations.

To better understand the mechanisms involved, the effect of the base (NaOH or KOH) used to reach a highly alkaline pH (11.5) on the nature and reactivity of the newly-formed phases was investigated first. A more specific experiment was then performed in which SON68 glass was first altered under these alkaline conditions leading to renewed alteration; after what the solution was acidified to the equilibrium pH of this glass (pH 9.5 in water at 90 °C). The alteration kinetics are then interpreted in terms of the driving force behind the process associated with the renewal of alteration, the possibility of occurrence of such a phenomenon under repository conditions is discussed.

2. Experimental

The test glass was the French SON68 inactive reference glass used to simulate the nuclear glasses produced by COGEMA at La Hague. The composition of SON68 glass is given in Table 1.

2.1. Glass specimen preparation

The 125–160 μm size fraction was obtained by milling and sieving crushed glass rods. The powder was cleaned ultrasonically in acetone, then in alcohol and finally in ultrapure water. The specific surface area as determined by Kr adsorption, using the BET method, was 510 ± 30 cm^2 g^{-1}.

2.2. Leaching solutions

The tests were conducted with sodium hydroxide (NaOH, Merck) or potassium hydroxide (KOH, Prolabo) solutions prepared with a concentration of about 0.25 M to obtain a pH of 11.40 ± 0.15 at 90 °C.

2.3. Test procedure

The tests were carried out in a static system using PTFE reactors (Savillex® 120 ml), with low-speed magnetic stirring at a temperature of 90 ± 2 °C.

Initially about 7.71 g of glass was placed in contact with 60 ml of a 90 °C alkaline solution, leading to a glass-surface-area-to-solution–volume (S/V) ratio at the beginning of the test of 65 cm^{-1}. The pH was measured at several time intervals, and solution and sometimes solid samples were taken.

Each solution sample (0.3 ml) was diluted with ultrapure water (3 ml) then ultrafiltered to 10 000 Dalton (cutoff threshold about 2 nm), and finally acidified with 1 N HNO_3 (1 ml).

The solutions were analyzed for Si, B, Na, K, Al, Ca and Cs by ICP-AES and ICP-MS at the *Service Central d'Analyse* (CNRS, Solaize, France). The uncertainty range was 3–5% depending on the elements.

Solid samples (a few mg of powder) were rinsed with ultrapure water, and then dried at room temperature before characterization by scanning electron microscopy (JEOL JSM6330F, 15 kV) and X-ray diffraction (Phillips X'Pert, $\lambda_{Cu} = 1.54018$ Å, 40 kV, 40 mA).

2.4. Expression of results

Boron is a good alteration tracer for this type of glass, as it is primarily a network-former and is not retained in the alteration products [35].

At each sampling interval the percentage of altered glass was determined from the following relation:

$$\%\mathrm{AG} = \frac{m_i}{m_0} \times 100 = \frac{100}{m_0} \times \left(\frac{[\mathrm{B}]_i \times V_i}{X_\mathrm{B}} \right),$$

where m_0 is the initial powder mass (g), X_B the boron mass fraction in the glass, V_i the volume of solution at the interval i (l), and $[\mathrm{B}]_i$ the boron concentration in solution (g l^{-1}) at the same time.

These tests resulted in considerable alteration; the glass surface area was therefore recalculated at each interval using a shrinking-core model to allow for the reduction in the grain size. In this model, grains were assumed to be spheres 142.5 μm in diameter. The reactive surface area at interval i was thus:

$$S_i^{\mathrm{BET}} = m_0 \times S_0^{\mathrm{BET}} \times \left(1 - \frac{[\mathrm{B}]_{i-1} \times V_{i-1}}{m_0 \times X_\mathrm{B}} \right)^{2/3}.$$

The normalized mass losses (in g m^{-2}) were calculated from the following relation:

Table 1
Composition in weight oxide of the glass SON68

Oxide	wt%	Oxide	wt%	Oxide	wt%	Oxide	wt%
SiO_2	45.85	Nd_2O_3	2.04	Pr_2O_3	0.46	Ag_2O	0.03
B_2O_3	14.14	Li_2O	1.99	NiO	0.43	CdO	0.03
Na_2O	10.22	MoO_3	1.78	MnO_2	0.39	SnO_2	0.02
Al_2O_3	5.00	Cs_2O	1.12	SrO	0.35		
CaO	4.07	Ce_2O_3	0.97	P_2O_5	0.29		
Fe_2O_3	3.03	La_2O_3	0.93	TeO_2	0.23		
ZrO_2	2.75	BaO	0.62	Y_2O_3	0.20		
ZnO	2.53	Cr_2O_3	0.53				

$$\mathrm{NL}(i) = \frac{[i] \times V_i}{X_i \times S_i^{\mathrm{BET}}}.$$

The normalized mass losses calculated from the mobile elements (B, Na) indicate the quantity of glass altered per unit area. Those calculated from the less mobile or sparingly soluble elements, notably silicon and aluminum, allowed to determine the retention factor of the element in the alteration products.

The retention factor of element i in the glass alteration products was defined by comparison with boron using the following relation:

$$f_i = 1 - \frac{\mathrm{NL}(i)}{\mathrm{NL(B)}}.$$

For each alkaline solution (NaOH and KOH) one test (N1 or K1, respectively) was not disturbed: the pH was allowed to vary freely from the initially imposed value of 11.40. For the NaOH series, one test (N2) was disturbed after 14 days. For the KOH series, three tests were disturbed after 63 days (K2), 77 days (K3) or 91 days (K4). The disturbance consisted in adding about 0.01 mole of HCl to lower the solution pH to around 9.5 (this pH was chosen because it corresponds to the equilibrium pH value of SON68 glass leached in pure water).

3. Results

3.1. Alteration at pH 11.40 in NaOH and KOH solutions

The elemental analyses of the leaching solutions for tests N1 and K1 are given in the Tables 2 and 3, respectively, with the altered glass percentages, the normalized mass losses, and the silicon retention factor in the alteration layer.

Fig. 1 shows the evolution of the normalized boron mass losses in function of time. A drop in the glass alteration rate is observed after 14 days in NaOH solution or 28 days in KOH solution. The normalized boron mass losses subsequently increased very quickly, and the boron concentration in solution rose from 300 $\mathrm{mg\,l^{-1}}$ to about 2500 $\mathrm{mg\,l^{-1}}$. This evolution corresponds to a resumption of alteration. After about 100 days the alteration diminished again in both NaOH and KOH solutions. The percentage of altered glass stabilized at around 42–44%.

The behavior of the silicon in solution was quite different. In both alkaline media the concentrations in solution increased significantly from 800 $\mathrm{mg\,l^{-1}}$ to nearly 1800 $\mathrm{mg\,l^{-1}}$ at the moment of the resumption of alteration (Fig. 2). The silicon concentration then began to decrease progressively to 1200 $\mathrm{mg\,l^{-1}}$ after 28 days in NaOH or 63 days in KOH. The maximum Si concentration was thus observed while the boron concentration kept rising and renewed alteration continued.

In both tests the silicon retention in the alteration products increased regularly over time despite the renewed alteration, and reached a value of 93% after one year of alteration (Tables 2 and 3). It had been established [34] that between pH 9 and 11 and in the absence of renewed alteration the quantity of dissolved silicon was proportional to the quantity of altered glass. Fig. 3, in which the normalized silicon mass loss is plotted versus the normalized boron mass loss, confirms this behavior up to 1 $\mathrm{g\,m^{-2}}$, i.e. just before the resumption of

Table 2
Elemental analyses of solutions, % of altered glass (%AG), normalized mass losses, retention factor in silicon (f_{Si}) in the alteration layer for the test N1 (solution NaOH pH 11.4, free)

Time (days)	pH (90 °C)	Concentrations in solution ($\mathrm{mg\,l^{-1}}$)						%AG	Normalized mass losses ($\mathrm{g\,m^{-2}}$)						
		Si	B	Al	Na	Ca	Cs		Si	B	Al	Na	Ca	Cs	f_{Si} (%)
0.3		316	77	41.3	5137	26.9	17.7	1.4	0.22	0.27	0.24		0.14	0.26	16
1	11.11	486	138	55.1	5211	6.64	28.2	2.4	0.35	0.48	0.32		0.03	0. 41	28
4	11.22	648	208	55.9	5239	6.85	41.9	3.6	0.46	0.72	0.32		0.04	0. 61	36
7		717	240	51.0	5244	4.95	46.6	4.2	0.52	0.85	0.30		0.03	0.69	39
14	11.26	820	306	34.6	5233	17.3	53.3	5.3	0.59	1.08	0.20		0.09	0. 78	45
21	11.27	1475	756	8.71	5746	11.2	82.5	13	1.07	2.67	0.05		0.06	1. 21	60
28	10.94	1795	1203	5.78	5770	11.9	77.1	21	1.36	4.45	0.04		0.07	1. 19	69
56	10.51	1551	2355	5.22	6375	8.18	33.8	40	1.23	9.09	0.03		0.05	0. 54	87
91	10.52	1419	2690	10.3	6852	5.09	12.0	44	1.32	12.21	0.08		0.03	0. 23	89
119	10.56	1350	2831	10.3	6986	3.35	10.7	46	1.30	13.28	0.08		0.02	0. 21	90
151	10.44	1137	2559	9.7	6105	1.17	10.2	40	1.09	11.95	0.08		0.01	0. 20	91
196	10.23	1204	2886	11.7	6805	2.68	12.4	44	1.05	12.32	0.08		0.02	0. 22	91
245	10.39	1173	2908	10.8	6964	1.47	12.5	43	1.04	12.59	0.08		0.01	0. 23	92
365	10.32	1197	3505	32.5	7756		15.7	49	0.98	13.98	0.22			0.26	93

Table 3
Elemental analyses of solutions, % of altered glass (%AG), normalized mass losses, retention factor in silicon (f_{Si}) in the alteration layer for the test K1 (solution KOH pH 11.4, free)

Time (days)	pH (90 °C)	Concentrations in solution (mg l^{-1})							%AG	Normalized mass losses (g m^{-2})						
		Si	B	Al	Na	Ca	Cs	K		Si	B	Al	Na	Ca	Cs	f_{Si} (%)
7	11.56	536	184	36.8	420	12.87	42.9	9256	3.2	0.38	0.64	0.21	0.84	0.07	0.62	40
14	11.50	609	222	29.1	466	7.80	50.5	9253	3.9	0.44	0.78	0.17	0.95	0.04	0.74	44
28	11.37	731	292	20.3	578	5.81	65.4	9197	5.1	0.52	1.02	0.12	1.17	0.03	0.95	49
56	11.22	1650	1332	2.38	2111	5.73	141	7564	22	1.16	4.57	0.01	4.19	0.03	2.01	75
63	11.07	1681	1601	3.36	2461	4.30	143	7142	27	1.34	6.20	0.02	5.53	0.03	2.30	78
70	10.96	1683	1783	2.73	2732	6.76	141	6903	29	1.37	7.09	0.02	6.29	0.04	2.33	81
77	10.95	1670	1932	2.62	2953	6.49	134	6872	31	1.38	7.77	0.02	6.88	0.04	2.24	82
84	10.97	1623	1912	6.33	3012	<0.14	124	6546	32	1.41	8.12	0.04	7.41	0.00	2.19	83
91	11.08	1612	2008	6.56	3156	<0.14	112	6394	33	1.40	8.49	0.05	7.73	0.00	1.97	84
112	10.88	1530	2295	7.24	3539	<0.14	111	6094	37	1.31	9.61	0.05	8.58	0.00	1.93	86
119	10.90	1545	2389	6.87	3677	<0.14	110	6066	38	1.36	10.30	0.05	9.18	0.00	1.97	87
151	10.67	1359	2453	8.30	3686	0.75	47.8	5498	38	1.18	10.40	0.06	9.05	0.00	0.84	89
196	10.54	1307	2684	9.18	4006	0.83		5508	40	1.09	10.94	0.06	9.46	0.01		90
245	10.65	1190	2691	9.47	4008	0.81	67.0	5152	41	1.04	11.46	0.07	9.88	0.01	1.19	91
365	10.56	1167	3525	9.21	5011		65.1	5527	49	0.94	13.83	0.06	11.39		1.06	93

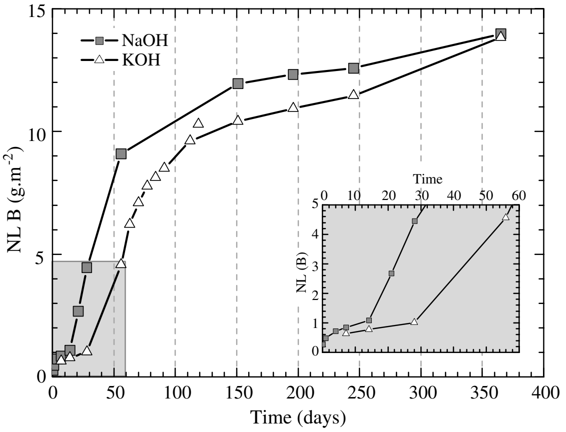

Fig. 1. Evolution of the normalized boron mass loss for tests N1 (NaOH) and K1 (KOH). A resumption of alteration was observed after 14 days in NaOH solution or 28 days in KOH solution.

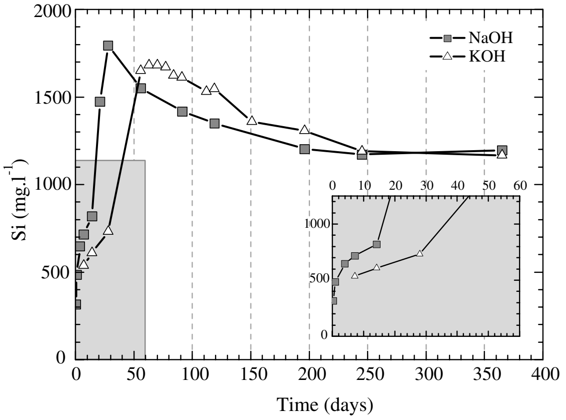

Fig. 2. Dissolved silicon concentration (mg l^{-1}) versus time for tests N1 (NaOH) or K1 (KOH) at pH 11.4. [Si] reached a maximum of 1800 mg l^{-1} during renewed alteration.

alteration. Above 1 g m^{-2} the mechanisms involved lead to significant silica precipitation that results in major divergence from the proportionality line.

Fig. 4 shows the evolution of the pH and the potassium and sodium concentrations in solution against time. At the beginning of alteration, the pH rose slightly due to the preferential release of alkalis weakly bonded to the glass network. When alteration resumed the pH quickly decreased to about 10.5. At the same time, the concentration of potassium (an element not found in the glass) decreased in solution; the potassium was highly integrated into the alteration products. Conversely, the quantity of sodium in solution greatly increased during both tests, particularly on resumption of alteration, due to the sudden release of sodium from the glass. In test K1, the increase in the Na concentration compensated for and even exceeded the consumption of K by the secondary phases. The observed drop in the pH thus occurred while the total quantity of alkali in solution increased. So, alteration products consume a large part of the hydroxide ions, and the potassium cations, but a less part of the sodium leached from the glass.

The pH drop during these tests could be related to the solubilization of a large quantity of boron at the time

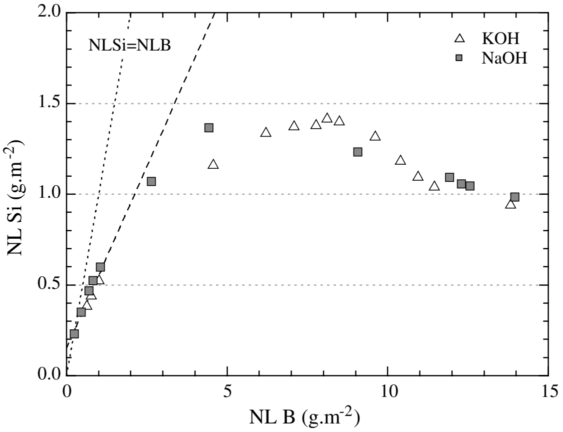

Fig. 3. Normalized silicon mass loss versus the quantity of altered glass for tests N1 and K1. NL(Si) is proportional to the quantity of altered glass before the renewal of alteration as shown by previous work. Above 1 g m^{-2} silicon becomes largely integrated in the alteration products.

of renewed alteration. Boron acts as a buffer, and tends to stabilize the solution pH at the pK value of the reaction of dissociation of boric acid H_3BO_3 into $H_2BO_3^{2-}$ (pK 9.2) [36]. Note that the pH values follow the variation of the sum of the molar concentrations [Na + K − B] (Fig. 5).

The evolution of the aluminum concentration in solution (Fig. 6) is another important point of this study. [Al] increased to about 60 mg l^{-1} after 4 days of alteration in NaOH solution or 40 mg l^{-1} after 7 days in KOH solution, then quickly dropped to about 3 mg l^{-1}. Finally, as the alteration continued, the aluminum concentration stabilized at about 10 mg l^{-1}. The aluminum concentration thus peaked during the initial alteration, and then decreased well before the resumption of alter-

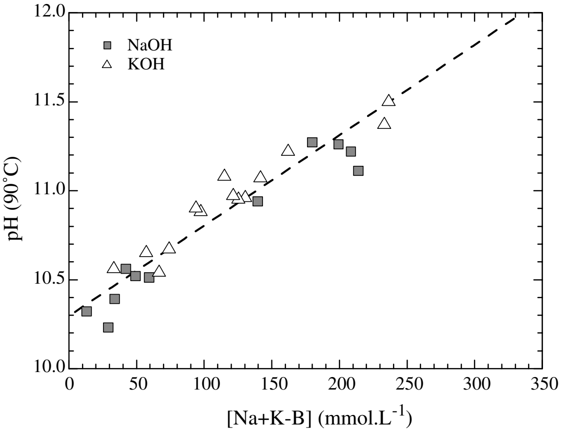

Fig. 5. Variation of pH versus the (Na + K − B) concentration in solution. The decreasing pH is attributed to the solubilization of boron.

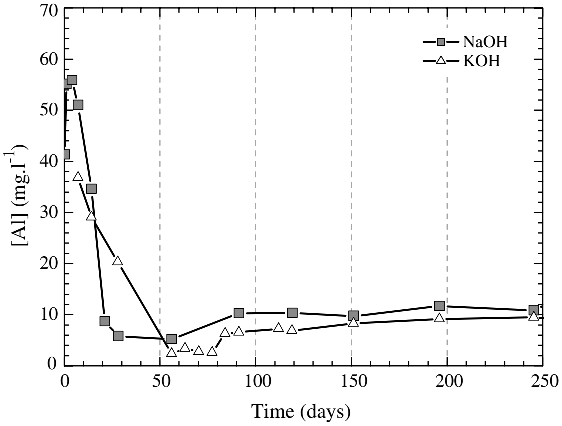

Fig. 6. Aluminum concentration (mg l^{-1}) in solution versus time for tests N1 (NaOH) and K1 (KOH) at pH 11.4. [Al] decreased before a resumption of alteration was observed.

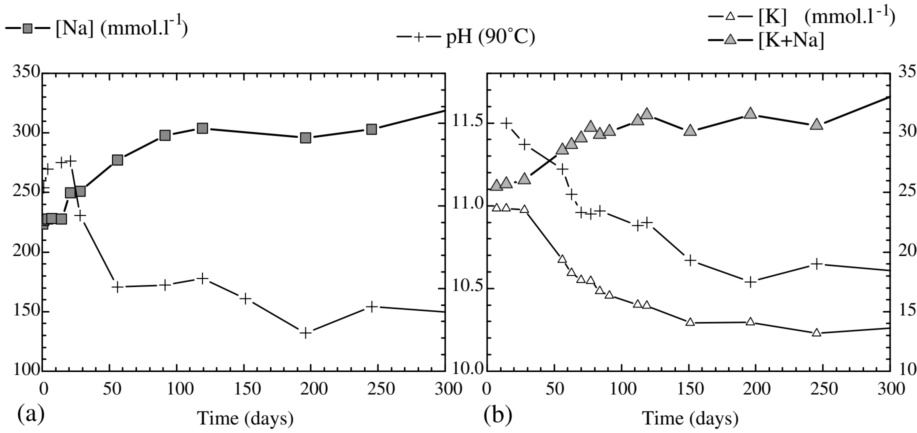

Fig. 4. (a) Evolution of pH and sodium concentration in solution for test N1; (b) evolution of pH and potassium and sodium concentrations for test K1.

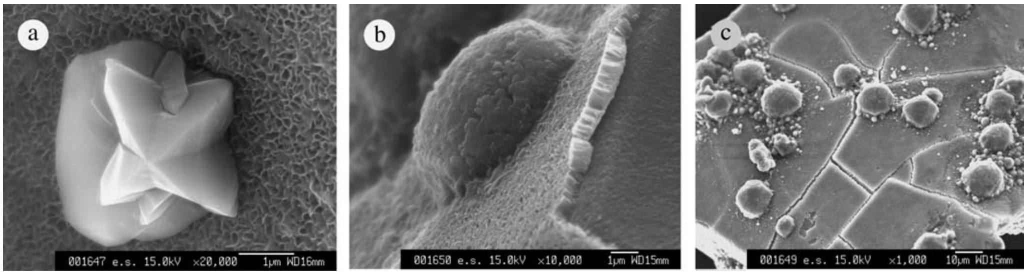

Fig. 7. SEM images of the SON68 glass surface altered in NaOH solution after (a) 14 days (×20 000) and (b, c) 91 days of alteration (×10 000). Analcime crystals are visible on the glass surface after the resumption of alteration.

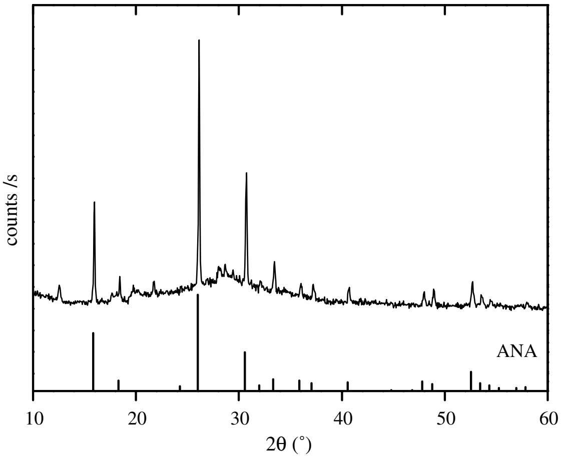

Fig. 8. XRD of a SON68 glass sample leached in 0.3 M NaOH solution. The marked peaks correspond to the analcime phase (JCPDS-41-1478).

ation was detected by a large quantity of boron in solution. At the moment of renewed alteration, the aluminum concentration was less than 10 mg l^{-1}.

3.2. Characterization of the altered solids

Samples of altered glass powder were taken at different time intervals during the alteration experiments. Scanning electron micrographs and X-ray diffraction pattern of the solid are shown, respectively, in Figs. 7 and 8 for alteration in NaOH and in Figs. 9 and 10 for KOH solution.

3.2.1. 0.25 M NaOH solution

After 14 days of alteration the glass surface was completely covered by a layer with a honeycomb structure characteristic of a phyllosilicate phase. Over this layer, a few crystals about 3 μm in diameter are visible.

After 91 days of alteration, the surface of the grains was covered by a similar layer of phyllosilicates less than 1 μm thick. This layer was severely cracked during drying. In some places, the visible surface below the phyllosilicates corresponds to a hydrated glass surface. Numerous crystals can be seen above the phyllosilicates. These spherules about 12–15 μm in diameter are often associated with smaller ones (1–2 μm).

The evolution of the alteration products between 14 and 91 days clearly shows the growth of this crystalline phase during the reaction.

The spectrum of X-ray diffraction of a glass altered for 218 days under similar conditions is shown in Fig. 8. The diffraction peaks match well with those corresponding to analcime, a zeolite with the theoretical chemical formula $Na(AlSi_2O_6) \cdot H_2O$. This finding is consistent with the SEM results.

The characteristic phyllosilicate peaks were not detected, either because of its limited crystallinity or its limited abundance.

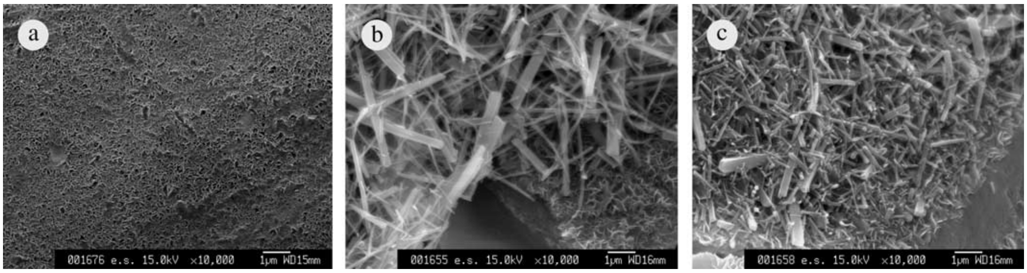

Fig. 9. SEM image (×10 000) of the surface of SON68 glass leached in KOH solution after (a) 28 days (b) 56 days and (c) 84 days of alteration.

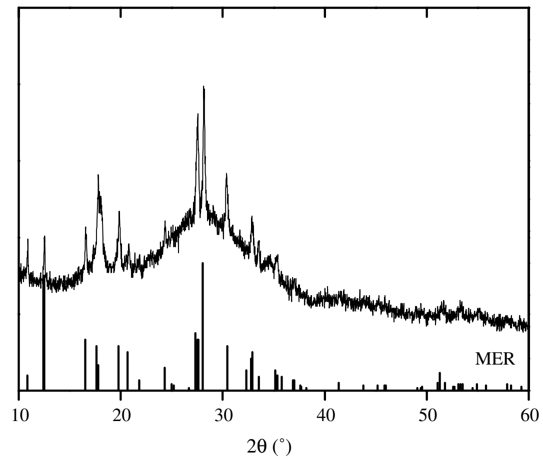

Fig. 10. XRD of SON68 glass sample leached in KOH solution at pH 11.4 [34]. The marked peaks correspond to the merlinoite phase (JCPDS 29-0989).

This phase has been already observed on this type of glass: Caurel [33] reported the presence of analcime during alteration of SON68 glass in pure water but at a higher temperature (over 150 °C).

3.2.2. 0.25 M KOH solution

After 28 days of alteration, the grains were covered only by a layer of phyllosilicates (Fig. 9(a)). After 56 days (Fig. 9(b)) and 84 days of alteration (Fig. 9(c)), the phyllosilicate layer was covered by acicular crystals. Although their size seemed not to change very much between successive time intervals, the number of crystals and their density increase as the alteration progressed.

The X-ray diffraction spectrum of a glass sample altered under the same conditions [34] is shown in Fig. 10. The crystalline phase can be identified as a zeolite with the following chemical formula $K_5Ca_2(Al_9Si_{23}O_{64})\cdot 24H_2O$, and named merlinoite.

3.3. Experiments with disturbance of the leaching solution pH

Four more specific experiments, N2, K2, K3 and K4, have been conducted involving a disturbance of the leaching solution.

SON68 glass was initially altered in NaOH (N2) or KOH (K2, K3, K4) solution at pH 11.4 under the same conditions as for tests N1 or K1, then disturbed by adding few milliliters of HCl solution (12 N and 1.2 N) to lower the leaching solution pH during the renewed alteration step after 14 days (N2), 63 days (K2), 77 days (K3) or 91 days (K4). The solution analysis results are discussed only for the KOH medium, but the same considerations also apply to the NaOH solution tests.

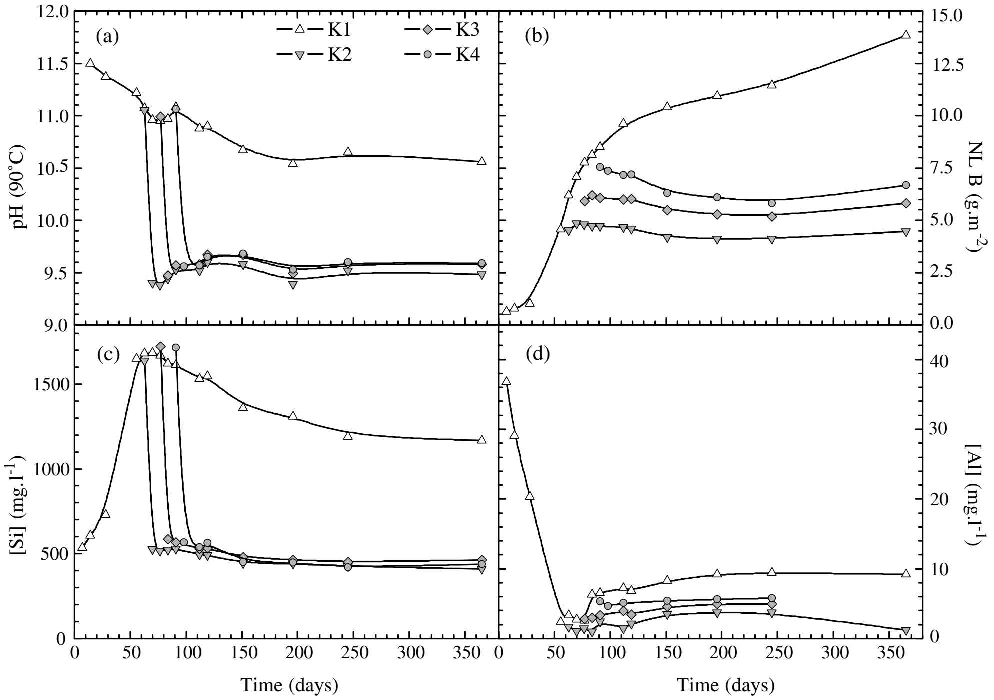

Fig. 11. (a) pH of solution at 90 °C, (b) normalized boron mass loss, (c) silicon concentration, (d) aluminum concentration in solution for the tests in KOH solution disturbed after 63 days (K2), 77 days (K3), 91 days (K4). Test K1, undisturbed, is shown for comparison.

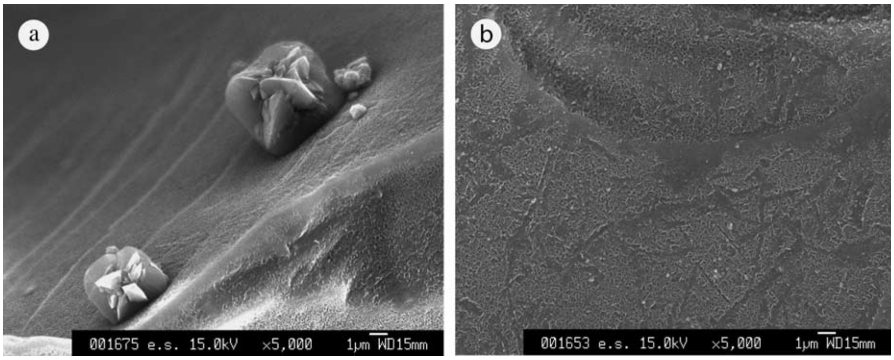

Fig. 12. SEM examination of the surface of the glass N2 (glass SON68 leached in NaOH solution) after (a) 14 days (b) 91 days of alteration.

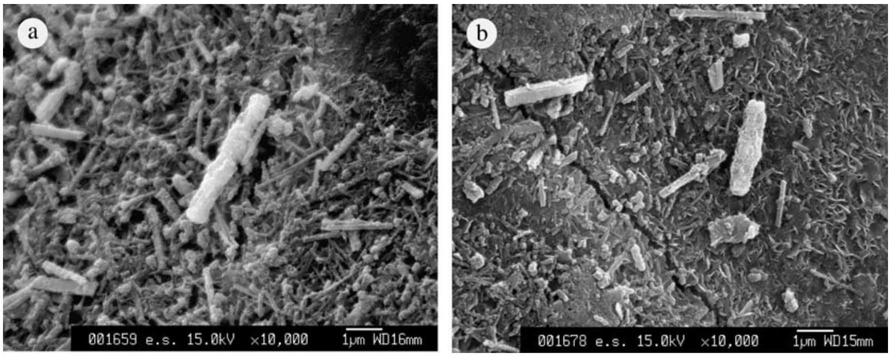

Fig. 13. SEM examinations of the surface of glass for the test K2 (SON68 leached in KOH solution at pH 11.4) after (a) 84 days (b) 119 days of alteration. Compared with Fig. 10(c), a gradual dissolution of the zeolites is observed after the drop of pH.

Fig. 11(a) shows the evolutions of the pH of solutions K1, K2, K3 and K4. The pH remained stable after the disturbance.

Fig. 11(b) shows the evolutions of the normalized boron mass loss. Modifying the pH immediately resulted in a significant drop in the alteration rate: just after the pH was lowered, the normalized boron mass losses returned to the level observed prior to the disturbance for all three tests K2, K3 and K4.

A slight but real decrease was observed after the solution acidification. However, no boron-contained alteration phases are known to precipitate. More likely, a surface sorption process of boron species may be involved due to the pH decrease and the modification of the surface state.

Lowering the pH also significantly reduced the silicon concentration from 1600 to 1700 $\mathrm{mg\,l^{-1}}$ before the operation to about 550 $\mathrm{mg\,l^{-1}}$ (Fig. 11(c)). As the alteration progressed, the silicon concentration for all three tests stabilized at around 420 $\mathrm{mg\,l^{-1}}$.

Fig. 11(d) shows the variations of the aluminum concentration in solution for tests K1, K2, K3 and K4. The pH disturbance occurred at a low aluminum concentration, and thus did not cause aluminum precipitation: the concentration was nearly the same before and after the disturbance. [Al] tended to increase as the alteration progressed, but did not exceed the value of 10 $\mathrm{mg\,l^{-1}}$ measured during the undisturbed test (K1).

SEM images of altered glass grains after the pH decrease are shown in Fig. 12 (NaOH solution) and Fig. 13 (KOH solution). In both media the crystals progressively dissolved after the disturbance. They disappeared from the surface of the N2 grains after 91 days (Fig. 12(b)) and only a phyllosilicate type layer remained. For test K2, crystals were still visible 56 days after the pH drop (Fig. 13(b)) because of the larger quantity of crystals present before the disturbance but their shape is clearly altered.

4. Discussion

In both experimental media, NaOH and KOH, the imposed high pH (11.4 at 90 °C) resulted in significant dissolution of the glass, and renewed alteration was observed. The following discussion focuses on this phenomenon in particular to evaluate its occurrence in conditions corresponding to a geological repository.

The general process could be summarized as follows:

During the initial decreasing alteration rate step the aluminum concentration in solution reached a maximum value then decreased over time. At this time, observations of the glass showed only one type of crystalline phase, apparently a phyllosilicate. When the dissolved aluminum concentration reached a minimum of a few milligrams per liter, the glass dissolution rate suddenly increased, highlighted by the large increase of boron and sodium concentration in solution. At the same time, a new zeolitic crystallized phase appeared. The zeolites increased in size and coexisted with the phyllosilicates. The solution pH tended to decrease, with the glass alteration rate.

The experimental conditions, and particularly the nature of the alkali cation, affect both the duration of the transition period (before the alteration resumption) and the nature of the zeolites formed. In KOH solution, alteration resumed after about 30 days, and the precipitated phase was orthorhombic. XRD analysis of a sample altered under the same conditions [34] suggests it could be merlinoite $(K,Ca)_7Si_{23}Al_9O_{64} \cdot 24H_2O$ [37]. This phase has been observed in geological media as an alteration product of rhyolitic glass or directly from a thermal treated aluminosilicate gel [38]. To the authors' knowledge it has never been observed during alteration of nuclear glasses. In NaOH solution, alteration resumed sooner, after about 14 days, and the precipitated crystals exhibited the features of analcime ($NaAlSi_2O_6 \cdot H_2O$) [39]. Analcime has often been observed on the surface of nuclear glasses altered under various conditions [40,41].

In a previous study, Gin suggested a five-step mechanism to account for the resumption of SON68 glass alteration in highly alkaline media [34]. This present study emphasized these different steps:

(1) The glass is significantly dissolved at pH 11.4 due to high solubility of silica at this pH. The concentration of aluminum – also highly soluble at this pH – may exceed 50 mg l^{-1}.
(2) The dissolved aluminum is consumed by the nucleation of zeolites at the gel/solution interface. These conditions are compatible with the formation of a protective gel layer.
(3) When there is no longer enough aluminum in solution, the gel layer partly dissolves to allow the growth of zeolites.
(4) At this time, the gel layer loses its protective properties and alteration resumes (some previous EDS examinations had revealed the total disappearance of the aluminum in the gel layer).
(5) The precipitation of zeolites continues as long as the pH remains around 11.

In the case of the R7T7 glass, the pH after the renewed alteration decreased due to a large solubilization of boron and the alteration rate decreased on its own.

As reminded in the introduction, the efficiency of the gel formed during the alteration of nuclear glasses towards the transport of the aqueous species depends on the conditions of alteration. It had been established qualitatively that the more the gel density, the less the aqueous species diffusion rate [42]. This is due to the fact that when the gel density increases either the pore size decreases or the closed porosity becomes more important. Some works are carried out at the CEA to go further into this area. The studies presented in this article help us to check if this tendency can be confirmed: the gel density is calculated from a mass balance between the analyzed solutions and the theoretical chemical composition of the zeolites. This calculation, based only on the silicon which is the major component of the glass, the gel and the zeolites, assumed that all the aluminum is incorporated into the zeolites; this hypothesis was substantiated by SEM-EDS examination of the alteration layers. Besides, for this calculation phyllosilicates were classified as zeolites: the Si/Al stoichiometry was assumed to be the same for both crystalline phases. Taking into account the dissolved silica fraction, the silicon quantity in the gel would reach 0.32 $g_{Si}\,cm^{-3}$ after 119 days of alteration in the potassic medium or 0.34 $g_{Si}\,cm^{-3}$ in the sodic solution. These values should be compared with the density of silicon in the glass (0.57 $g_{Si}\,cm^{-3}$) or with the density calculated from free pH experiments at high S/V ratio (values between 0.45 and 0.55$g_{Si}\,cm^{-3}$) leading to a rate drop by 4 orders of magnitude from the initial rate. Therefore, the gels formed under the conditions of renewed alteration are not very dense. In comparison, gels formed at lower pH (between 8 and 9) but presenting equal density (low S/V or high flow rates conditions) cause the alteration rate to drop only by 1–2 orders of magnitude from the initial rate. This calculation could explain the fact that the gel formed in high pH conditions leading to a renewed alteration, is relatively non-protective and not very dense. Some future analyzes of the porous texture of the gel should confirm the results quantitatively. We can keep in mind that these results at high pH experiments are consistent with the results in deionized water, and that this particular behavior of the glass at very alkaline pH (resumption of alteration) is due to an impoverishment of the gel in its main formers (Si, Al).

The available literature concerning the phases that precipitated during these experiments allowed us to improve the interpretation of the experimental data. Many natural alteration processes of volcanic rocks (rhyolitic, basalts, etc.) in brine or seawater lead to the formation of a large range of natural zeolites [43–49].

The formation of zeolite phase at the surface of the nuclear glasses could involve the same well-known mechanism of dissolution/reprecipitation involved in their formation from alteration of natural glasses [50]. When a sufficient amount of elements such as Si, Al, alkalis and alkaline earths enters solution by alteration of the glass and the zeolite solubility limit is reached, zeolites precipitate by nucleation in solution [51,52]. Growth occurs at the surface of the altered glass, which supplies network-forming elements.

At 90 °C and pH 11.5, the glass dissolution rate is very high and the solution quickly becomes supersaturated with respect to many mineral species. A high degree of super-saturation contributes to the precipitation of thermodynamically metastable phases (gel, phyllosilicates, poorly crystallized zeolites, etc.) because of their fast formation kinetics [53]. The evolution of the system toward more stable phases is favorable from an energy standpoint, but could take a long time. The issue is thus to consider some kinetic constraints.

Phyllosilicates are the only phases observed during alteration of SON68 glass leached in pure water at 90 °C, when the equilibrium pH is about 9.2. The zeolitic crystalline phases appear only at temperatures exceeding 150 °C [33] or with an alkaline solution at pH greater than 11. According to Hay [44], phyllosilicates are formed preferentially in solutions with neutral pH, high H^+ to Na^+, K^+, and Ca^{2+} ratios, and with a high Mg^{2+} activity. Conversely, the growth of zeolites is favored at more alkaline pH.

The mineral saturation state of some of solutions encountered during the alteration of SON68 glass in high-alkaline media had been studied using the EQ3/6 geochemical code [54]. The results for kaolinite, gyrolite, nontronite (phyllosilicates), albite, K-feldspar (tectosilicates), analcime, natrolite (zeolites) and gibbsite are given in Table 4. According to these calculations, the solutions are supersaturated with respect of numerous phyllosilicate or feldspar-type phases during the all process of alteration. The solutions become supersaturated with respect with some zeolitic-phases only when the alteration resumes. So, the coexistence of both phyllosilicates and zeolites is observed. It may be assumed that the growth of the two types of minerals is not limited by the same chemical element, i.e. that the phyllosilicates and zeolites are not in competition under the experimental conditions. Elements such as iron or zinc could limit the growth of the phyllosilicates. Recent SIMS analyses have indeed shown that these elements are largely incorporated in the phyllosilicate structure [42]. Also, a simplified glass with 7 oxides (SiO_2, B_2O_3, Na_2O, CaO, Al_2O_3, ZrO_2, Ce_2O_3) and the same stoichiometry as SON68 glass develops an alteration gel layer with the same protective properties as nuclear glass, but no phyllosilicate phase due to the absence of zinc and iron [11,55]. The solutions are not saturated with respect to $Al(OH)_3$ phase. So the Al network-former must be supplied by dissolving the aluminum contained in the gel layer at the surface of the glass. In the system studied, it is the aluminum which limits the growth of zeolites.

In the new experiment in which the pH was lowered after the resumption of alteration cessation of alteration and dissolution of the zeolites are clearly observed. There is no doubt that the two processes are related, considering the preceding discussion. In slightly alkaline media, zeolites appear to be less stable than phyllosilicates. The observations can be explained by assuming that the dissolution of zeolites after lowering the solution pH is due to the high sensitivity of these phases to the external medium. Work by Dibble and Tiller [53] corroborates this hypothesis. According to these authors, zeolites must be considered as metastable mineral structures that evolve with temperature and/or time

Table 4
Log Q/K values of some minerals return by EQ3/6 geochemical code for solutions in test K1 (solution KOH, free), N1 (solution NaOH, pH free), K2 (solution KOH, disturbance 63 days), N2 (solution NaOH, disturbance 14 days) for different times of alteration

$\log Q/K$	Kaolinite	Gyrolite	Nontronite	Albite	K-feldspar	Analcime	Natrolite	Gibbsite
K1_7d	−5.06	5.16	12.27	−1.38	1.96	−0.52	−0.70	−1.89
K1_28d	−5.26	4.76	12.72	−1.11	2.11	−0.37	−0.57	−2.13
K1_91d	−3.82	0.76	14.85	1.12	3.48	1.20	1.86	−2.08
K1_245d	−1.89	1.08		2.33	4.46	2.10	3.36	−1.42
N1_4d	−5.06	3.63	11.73	−0.81		0.24	1.18	−1.65
N1_14d	−5.13	4.69	12.27	−0.60		0.32	1.17	−1.82
N1_91d	−0.45	2.12	18.64	3.52		2.99	4.82	−1.01
N1_245d	0.04	0.62		3.75		3.15	5.08	−0.83
K2_70d	−7.75	3.35	13.08	−2.19	0.33	−1.31	−2.36	−3.24
N2_21d	−6.31	4.27	10.34	−1.95		−0.65	−0.35	−2.02

toward denser phases with higher Si concentrations according to a dissolution/reprecipitation mechanism. In our study, however, the dissolution of the analcime or merlinoite phases did not lead to the precipitation of new, more siliceous phases. This suggests either that the growth rate of zeolites with a high Si/Al ratio is much slower, or that our system evolved toward greater phyllosilicate stability, and that the phyllosilicates persisted even after the zeolites had disappeared. Another possibility is that the nucleation of another type of zeolites could be stopped due to the lack of aluminum in solution after the drop of the pH.

5. Conclusion

The study shows that the resumption of SON68 glass alteration at pH 11.5 is a direct consequence of the precipitation of zeolitic aluminosilicate crystals. The nucleation processes probably from dissolved species. These phases appear to be related to a critical aluminum concentration in solution of about 40–60 $\mathrm{mg\,l^{-1}}$ at the test pH. Afterwards, the growth of the zeolites proceeds to the detriment of the gel, which retains too little silicon to cause a great drop in the glass alteration rate. The originality of the study is to show that these aluminosilicates formed at pH 11.5 are metastable because they are progressively dissolved when a pH around 9.5 is imposed after their formation.

It can therefore be assumed that the zeolites observed at high pH will not precipitate in a solution at pH 9.5. Resumption of alteration is thus unlikely under the conditions prevailing in a nuclear glass disposal repository.

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