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Protective properties and dissolution ability of the gel formed during nuclear glass alteration

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Abstract

The protective properties and the dissolution ability of different gels formed during alteration from the SON68 glass (nuclear glass R7T7-type) and from two simplified glasses are assessed. The method consists in a first glass alteration in order to form gels at different alteration progresses and, in a second alteration after a renewal of the solution in the same experimental conditions. The kinetics of the second alteration is analyzed in two steps. Firstly, the gel properties are related to its morphological evolution. For the SON68 glass, the increase of the protective properties corresponds to an increase of the thickness of the density gradient within the gel. At high reaction progress, when the gel presents a dense and thin zone located at the gel–glass interface, the protective properties remain constant. Secondly, the ability of the gel to get back its protective properties after the solution renewal is observed. The amount of dissolved gel is calculated and discussed for SON68 glass.

1. Introduction

More than 20 years ago, France adopted borosilicate glasses and particularly the French R7T7 glass [1] as containment matrix for long-life nuclear waste. In a geological repository approach, natural barriers limiting radioactive species diffusion in biosphere will be in contact with glass package. In order to demonstrate the safety of a high-level radioactive waste repository, it is necessary to assess the long-term behavior of nuclear glass packages in geological conditions, particularly the alteration by aqueous solution.

In contact with water, the SON68 glass (R7T7-type) presents three dissolution steps and develops a so-called alteration film [2]. Simultaneous alteration kinetics and morphological studies [3,4] at 50 °C and 90 °C have related these three steps to the morphology of the alteration layer. During the first step of the alteration, when the glass is altered at a rate close to the maximum rate (r_0 so-called), the alteration layer is constituted of a desalkalinized glass layer with a gel having an open porosity. The gel is an amorphous and hydrated material formed by recondensing cross-linking species (Si, Al, ...). Subsequently the gel becomes denser as the alteration rate decreases. In the third step, the pore size

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increases and simultaneously a dense and thin zone within the gel is formed when the alteration rate is close to the residual rate [5]. This zone could constitute an important diffusive barrier for the reactive species (water molecules, dissolved silica...). The gel has also the ability to retain radioactive species contained in the glass [5,6]. Predictive and scientific models integrate the protective properties of the gel [7]. In order to improve these models, it is necessary to better demonstrate the role of the gel as a diffusive barrier and to relate its properties to its morphology.

The first requirement in the study of the protective properties of the gel is to be able to give a clear definition of the term 'protective'. Jegou [8] defined a protective gel as a diffusive barrier for the reactive species contributing to the glass alteration. Gin [9] showed that an altered glass formed in non-renewed medium is less altered than pristine glass after renewal of the solution at the pH of equilibrium (pH = 9) and in the same alteration conditions. Gin attributes this decrease of the alteration to a protective gel. Indeed, the protective properties of the gel depend on the glass composition as well as on the alteration conditions. Indeed, Chick et al. [10] observed that a gel formed in a diluted medium, with respect to silica, had no protective properties after renewal of the solution.

Our investigation is based on the same type of experiment as previously performed by Gin [9]. This experiment is considered as a way to assess the protective properties of the gels and their dissolution ability. We have used the SON68 glass and two simplified glasses containing the same primary components at the same molar ratio as glass SON68 and which present different alteration kinetics and gel morphologies as shown in Fig. 1. At high reaction progress, the gel of glass 1 (SiO_2, B_2O_3, Na_2O, Al_2O_3, CaO), as the gel of glass SON68, present a thin and dense zone within the gel located at the gel–glass interface [4]. In glass 2 Al is replaced by Zr, which results in quite different gel composition and structure. TEM observations and X-ray reflectometry analysis have shown a glass 2 alteration layer containing two parts: a moderately dense and thin zone over a less dense gel located at the glass surface [4]. These glasses are altered for different periods of time in order to form different gels. Firstly, the protective properties and the dissolution ability of the resulting gels are assessed and related to their morphology. Secondly, these experiments being also perturbations for the altered glass, the evolution of the alteration kinetics is analyzed and the gel dissolution is calculated in the case of glass SON68.

2. Materials and methods

The main glass used is the SON68 glass [1], a R7T7-type nuclear glass, whose composition is detailed in Table 1. Two simplified glasses (glass 1 and 2), containing the same primary components at the same molar ratio as glass SON68 [8,11] are also studied (Table 1). Glass 1 has an initial dissolution rate in pure water

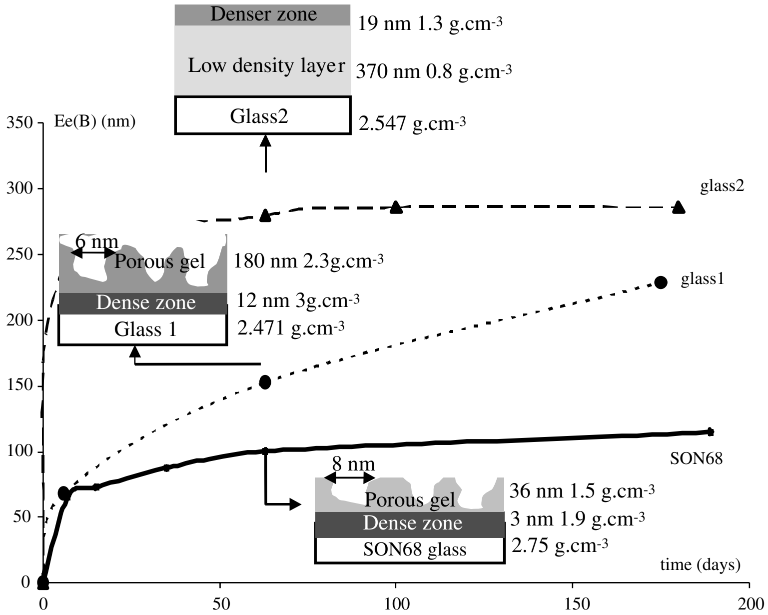

Fig. 1. Altered glass thickness Ee(B) as a function of time and morphologies of the glass alteration layers for the SON68 glass, glass 1 and glass 2 altered at $S/V = 8000\ \mathrm{m}^{-1}$, 90 °C and pH = 9 [4].

Table 1
Composition (wt.%) of SON68 and of simplified glasses 1 and 2 [8]

Oxide	SON68 glass	Glass 1	Glass 2
SiO_2	45.48	58.07	59.80
Al_2O_3	4.91	6.27	
B_2O_3	14.02	17.92	18.45
Na_2O	9.86	12.59	12.95
CaO	4.04	5.15	5.31
Li_2O	1.98		
ZnO	2.50		
ZrO_2	2.65		3.49
Fe_2O_3	2.91		
NiO	0.74		
Cr_2O_3	0.51		
P_2O_5	0.28		
Ce_2O_3	0.93		
Others	9.19		

($r_{0(90\,°C,pH = 9)} = 2.4\ g\,m^{-2}\,day^{-1}$) close to that of SON68 ($r_{0(90\,°C,pH = 9)} = 2.2\ g\,m^{-2}\,day^{-1}$). In static mode, this glass is approximately two or three times more altered than glass SON68 and presents a continuous decrease of the alteration rate at a glass-surface-area-to-solution–volume ratio (S/V) of $8000\ m^{-1}$, $T = 90\ °C$ and pH = 9 [11]. The initial dissolution rate of glass 2 is higher ($r_{0(90\,°C,pH = 9)} = 8.5\ g\,m^{-2}\,day^{-1}$) [8,11] but in static mode an abrupt stop of alteration can be observed as shown in Fig. 1. The alteration kinetics and the alteration films of these three glasses have been already studied [4].

Glass powders were prepared by grinding and sieving monolith glass blocks. Size fractions obtained were 40–63 μm for SON68 glass, 5–40 μm for glass 1 and 40–63 μm for glass 2. These fractions were cleaned first in acetone, then in ethanol and finally in deionized water. Specific surface areas measured by krypton adsorption are for the SON68 glass, the glass 1 and 2, $0.134 \pm 0.001\ m^2\,g^{-1}$, $0.319 \pm 0.001\ m^2\,g^{-1}$ and $0.192 \pm 0.001\ m^2\,g^{-1}$, respectively. Furthermore, the glass-surface-area-to-solution–volume ratio (S/V) influences the alteration kinetics whereas the specific surface area differences do not for these size fractions.

All experiments were based on the same procedure as that used by Gin [9] with the SON68 glass. In these experiments, after a first alteration at 90 °C and pH = 9 and $S/V = 5000\ m^{-1}$ for the SON68 glass, and $8000\ m^{-1}$ for the simplified glasses, the leachate is replaced by a solution at the pH of equilibrium (pH = 9), in the same alteration conditions. The pH is adjusted at pH = 9 during the experiment.

These experiments were carried out in static mode in a PTFE reactor. The alteration solutions were prepared with ultrapure water and KOH (Prolabo 'Normapur') in order to adjust the pH to 9 ± 0.1. The solutions were heated before the experiments during 2 h in an oven regulated at the alteration temperature of 90 ± 2 °C. Solutions were stirred using a magnetic rod bar during the experiment.

Table 2
Duration of the alteration for the different tests at 90 °C, 5000 m^{-1} for SON68 glass and 8000 m^{-1} for the simplified glasses at pH = 9; $Ee(B)_1$: altered glass thickness after the first alteration; ρ_{SA}: density of the altered film; m_{AS}: mass of the altered film; AG: altered glass; PG: pristine glass

Tests	Time (days)	$Ee(B)_1$ (nm)	ρ_{SA} ($g\,cm^{-3}$)	m_{SA} ($mg\,m^{-2}$)
SON68 PG	0	–	–	–
SON68 AG1	22	75	1.56	117
SON68 AG2	63	100	1.64	164
SON68 AG3	189	115	1.72	198
SON68 AG 6 [9]	604	150	1.72	258
Glass 1 PG	0	–	–	–
Glass 1 AG1	175	229	1.57	360
Glass 1 AG2	224	328	1.56	512
Glass 2 PG	0	–	–	–
Glass 2 AG1	7	248	1.52	377
Glass 2 AG2	100	286	1.54	440

The accuracy is around 15%.

In a first step, SON68 glass and simplified glasses were altered during different periods of time in order to have different gels. The first alteration durations are presented in Table 2. After, the leachate is removed from the reactor, and the altered glass powders were rinsed three times with the solution at pH = 9 and at 90 °C. Then, in a second step, the solution at pH = 9 and 90 °C was added with the same S/V ratio.

Solution samples were taken before the renewal of the solution and during the second alteration. Solution samples were ultrafiltered to 10,000 Da and diluted in an equivalent volume of 1 N HNO_3. Acidified solutions were analyzed to determine atomic concentrations.

3. Solution analysis

Concentrations in solution were determined by plasma atomic emission spectroscopy for Si, B, Na, Li, Al, and Ca. The accuracy is roughly 5% when the concentrations are above the detection limit ($0.05\ mg\,L^{-1}$). After correcting the concentration values by the dilution factor that is due to dilution in the acid solution, the normalized mass losses NL_i ($g\,m^{-2}$) were calculated with the following relation (1):

$$NL_i = \frac{C_i}{x_i \cdot \frac{S}{V}}, \tag{1}$$

where C_i ($mg\,L^{-1}$) is the concentration of element i and x_i is the mass fraction of element i in the glass. NL_i ($g\,m^{-2}$) is used to estimate the altered glass thickness Ee(B) (μm) calculated with a mobile element (B, Na) (2):

$$\mathrm{Ee(B)} = \frac{\mathrm{NL}_i}{\rho_\mathrm{G}} \tag{2}$$

ρ_G (g cm^{-3}) is the glass density.

The retention factor is calculated using the normalized mass loss in boron and in element *i* (3):

$$F_i = 1 - \frac{\mathrm{NL}_i}{\mathrm{NL(B)}}. \tag{3}$$

The density of the altered glass ρ_SA (g cm^{-3}) (4) corresponds to a glass in which the oxides are dissolved in a volume corresponding to the thickness of the altered glass Ee(B):

$$\rho_\mathrm{SA} = \frac{m_\mathrm{G} - m_\mathrm{oxy}}{m_\mathrm{G}} \rho_\mathrm{G}, \tag{4}$$

where m_G (g) is the glass mass and m_oxy (g) is the dissolved oxide mass in solution.

The mass of altered film per surface area unit m_SA (10^{-3} g m^{-2}) is defined by the following expression (4):

$$m_\mathrm{SA} = \rho_\mathrm{SA} \times \mathrm{Ee(B)} \times S_\mathrm{spe}, \tag{5}$$

where S_spe (m^2 g^{-1}) is the specific surface area of the glass.

All the characteristics of the altered glasses (thickness Ee(B)$_1$, density ρ_SA and mass of the altered film m_SA) are presented in Table 2. To simplify, for the SON68 glass, the totality of the altered glass will be considered as a gel and the secondary phases existing on the gel surface will be neglected.

4. Results and discussion

After the first alteration and the solution renewal, the alteration kinetics were investigated at different times:

- just after perturbation, in order to assess the protective properties and dissolution ability of the gel,
- at high reaction progress, to observe the evolution of the alteration kinetics and particularly the effect of the perturbation.

4.1. Protective properties and dissolution ability of gels at different alteration progresses

A gel can be protective in specific alteration conditions (high *S*/*V* ratio for example) and lose its protective properties after renewal of the solution at a low *S*/*V* ratio. This is particularly the case if the gel dissolution is too important after perturbation. Thus, we will assess the protective properties of the gel, exclusively, when the conditions of the gel formation are the same as the alteration conditions after renewal of the solution.

In this study, a gel is considered as being protective, if the altered glass amount after renewal of the solution is less important than that coming from pristine glass for the same alteration conditions. Furthermore, the gel is considered all the more stable that its dissolution is low after perturbation.

In order to assess the protective properties and the stability of the gel, it is required to observe boron and silicon amounts (silicon is the major component of the gel so it gives an evidence of the gel dissolution) for the short alteration durations after renewal of the solution at the pH of equilibrium. Indeed, the concentrations of the elements in solution just after renewal of the solution are low; it is possible to dissociate the effects of concentration in solution from the protective properties of the gel and its stability.

The normalized mass losses in boron and silicon 5 h after renewal of the solution for the different tests are presented in Fig. 2. Elements as lithium and sodium present the same kinetics as boron. Aluminum and calcium were also analyzed and their concentrations were not detectable.

Firstly, Fig. 2 shows that the normalized mass losses in boron 5 h after perturbation for the altered glass (tests SON68 AG1 to AG4) are less important than that of pristine glass (test SON68 PG). This proves that the gel contributes to decrease the glass alteration. Moreover, the increase of the gel amount and/or the duration of the first alteration lead to a small decrease of the altered glass thickness after renewal of the solution. The gel amount and/or the duration of the first alteration do not seem to have any influence for the tests SON68 AG3 and AG4. The various intensities of the protective properties of gel can be explained by its morphological evolution. The morphological analysis of the gel from SON68 glass show that a density gradient is formed within the gel when the alteration rate decreases [3,4]. At higher alteration progress a dense zone within the gel at the glass surface is formed. This dense zone could

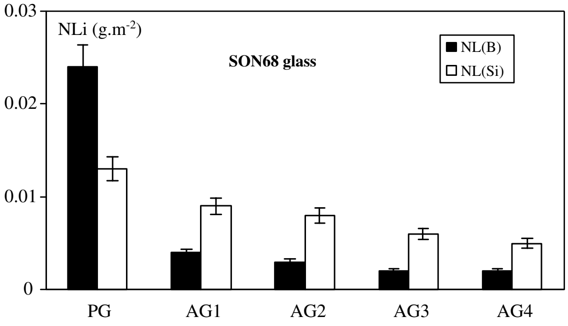

Fig. 2. Normalized mass losses NL$_i$ (g m^{-2}) 5 h after renewal of the solution at *S*/*V* = 5000 m^{-1}, 90 °C and pH 9, for the tests SON68 PG and SON68 AG1 to AG4.

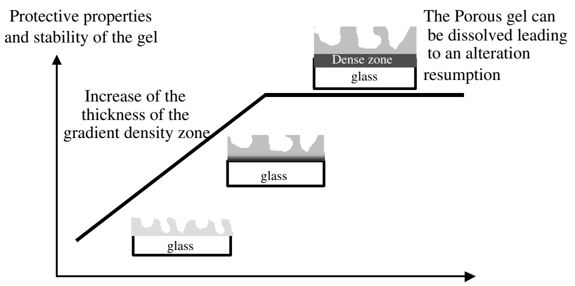

Fig. 3. Schematic evolution of the protective properties, stability and morphology of the alteration layer for SON68 glass as a function of the duration of the first alteration.

constitute a constant diffusive barrier leading to constant protective properties. Fig. 3 schematically illustrates the evolution of the protective properties of the gel as a function of the first alteration duration and of its related morphology.

Secondly, Fig. 2 shows that the normalized mass losses in silicon, 5 h after perturbation, are more important than that in boron, meaning that most of the silicon in the solution comes from the gel. The silicon concentrations in solution decrease with the increase of the gel amount and/or the duration of the first alteration. An effect of composition and/or of local structure could cause this phenomenon. Indeed, during the glass alteration the gel is also altered. An increase of the specific surface area and of the porosity is observed [4]. This altered gel part, in contact with water, is essentially composed of cross-linking species (Si, Al, Zr, ...). The gel is more and more altered with the alteration progress and consequently contains less and less silicon. This phenomenon could explain the decrease of silicon amount with the increase of the duration of the first alteration. Moreover, the gel dissolution does not cause a resumption of the glass alteration. The dissolved part of the gel after perturbation could probably not contribute to the protective properties of the gel. Fig. 3 illustrates this phenomenon.

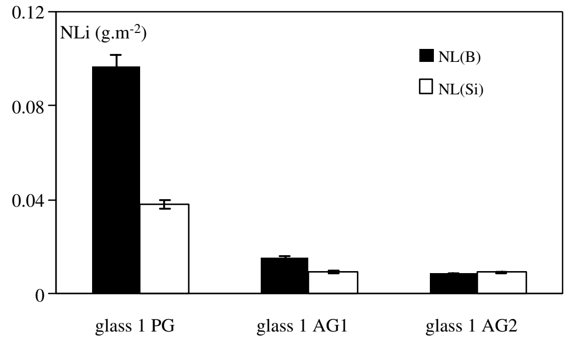

Fig. 4. Normalized mass losses NL_i ($g\,m^{-2}$) 8 h after the renewal of the solution at $S/V = 8000\ m^{-1}$, 90 °C and pH 9, for the tests glass 1 PG and glass 1 AG1 and AG2.

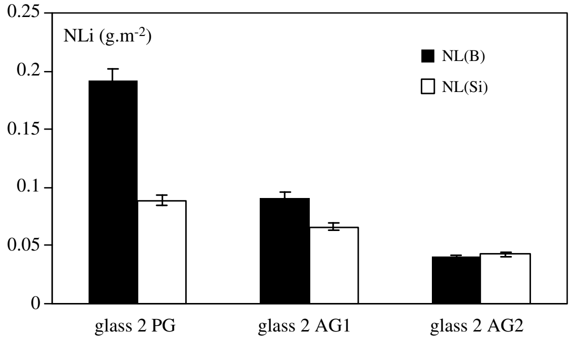

Fig. 5. Normalized mass losses NL_i (g m) 8 h after the renewal of the solution at $S/V = 8000\ m^{-1}$, 90 °C and pH 9, for the tests glass 2 PG and glass 2 AG1 and AG2.

For the tests on glasses 1 and 2, the normalized mass losses in boron and silicon, 8 h after the renewal of the solution, are presented in Figs. 4 and 5, respectively. For all the tests on the simplified glasses, after the solution renewal, the altered glass is less altered than the pristine glass and the boron and silicon amounts decrease with the gel amount and/or the duration of the first alteration. These results give an evidence of the gel as a time-depending diffusive barrier. The alteration film of glass 1 at high alteration progress presents a dense zone within the gel on the glass surface. In the same way as for SON68 glass, the increase of the thickness of this dense zone could contribute to the decrease of the normalized mass loss in boron with the first alteration progress (tests glass 1 AG1 and AG2). The alteration film of glass 2 presents a moderately dense zone on a less dense gel at high reaction progress. This dense zone can be a denser gel playing the role of a diffusive barrier [4] or can be a metastable phase containing silica (Fig. 11 presents a decrease of silicon concentration during the alteration). This phase, in equilibrium with the solution, could lead to an abrupt stop of the alteration observed in Fig. 1. In the case of glass 2 AG1, the duration of the first alteration is too short (7 days) to present an abrupt stop so we can assume that the moderately dense zone is not yet formed. Fig. 5 shows that even without this dense zone the gel is protective. The difference between the protective properties of the gel from the test glass 2 AG1 and AG2 could coming from the thickness difference of 13% (Ee(B) = 248 nm for glass 2 AG1 and Ee(B) = 286 nm for glass 2 AG2) or the dense zone.

As for the stability of the gel, it is difficult to assess it for simple glasses. Indeed, it is impossible to dissociate the silicon fractions coming from the glass and from the gel.

The common points between the gels from the three glasses are their time-depending protective properties and stability. The behavior of the gel from glass 1 and SON68 glass are close, which could be explain by their similar morphologies and glass alteration kinetics. However the level of their protective properties differs. SON68 glass is two to three times less altered after the renewal of the solution than the glass 1 and fifty times less than the glass 2.

4.2. Evolution of the glass dissolution kinetics after renewal of the solution

In these experiments, the renewal of the solution is also a perturbation. This perturbation gives an evidence if the gel is able to get back its protective properties. It also brings some important information about the glass–gel-solution interactions.

The evolutions after renewal of the solution of the altered glass thicknesses and of silicon concentrations as a function of time are presented in Figs. 6 and 7 for SON68 glass, in Figs. 8 and 9 for glass 1 and in Figs. 10 and 11 for glass 2. Because the ionic strength is low and these tests are controlled (pH = 9), the activities of

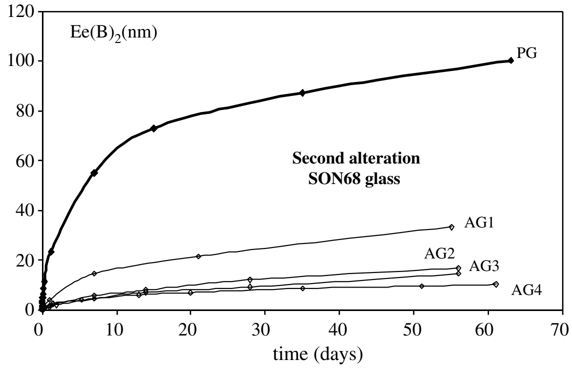

Fig. 6. Evolution of the altered glass thickness during the second alteration at 5000 m^{-1}, 90 °C and pH = 9 for the tests SON68 PG, SON68 AG1 to AG4.

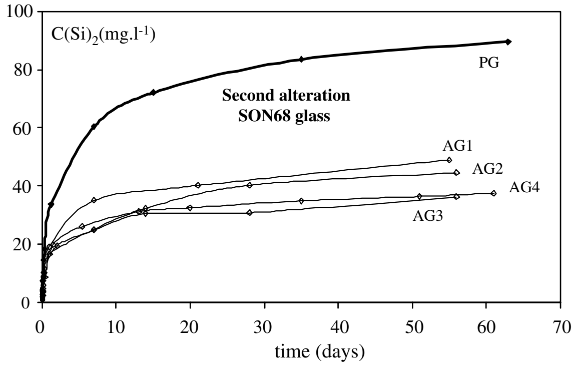

Fig. 7. Evolution of the silicon concentration $C(Si)_2$ during the second alteration at 5000 m^{-1}, 90 °C and pH = 9 for the tests SON68 PG, SON68 AG1 to AG4.

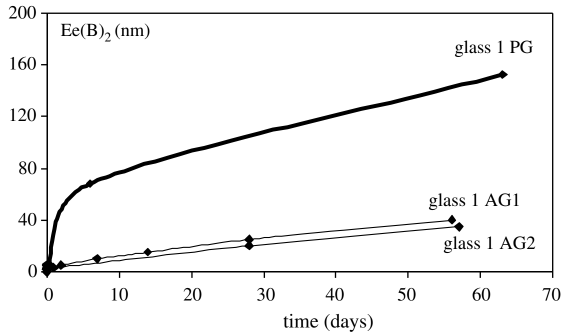

Fig. 8. Evolution of the altered glass thickness during the second alteration at 8000 m^{-1}, 90 °C and pH = 9 for the tests glass 1 PG, glass 1 AG1 and AG2.

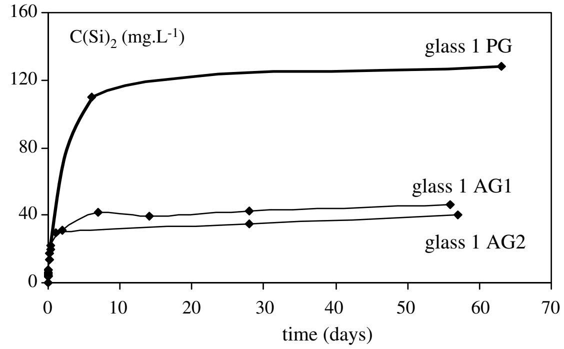

Fig. 9. Evolution of the silicon concentration $C(Si)_2$ during the second alteration at 8000 m^{-1}, 90 °C and pH = 9 for the tests glass 1 PG, glass 1 AG1 and AG2.

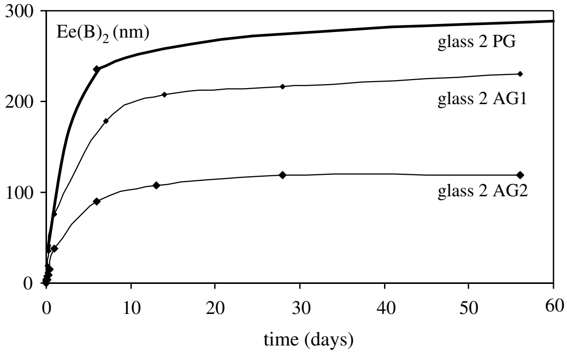

Fig. 10. Evolution of the altered glass thickness during the second alteration at 8000 m^{-1}, 90 °C and pH = 9 for the tests glass 2 PG, glass 2 AG1 and AG2.

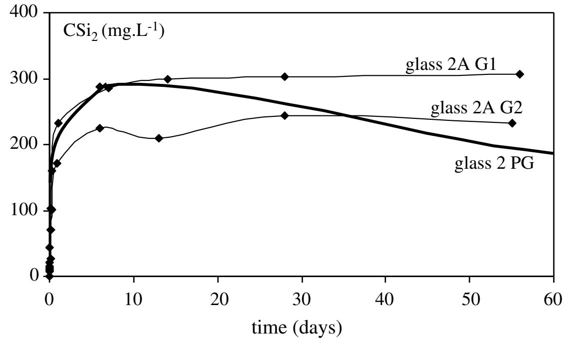

Fig. 11. Evolution of the silicon concentration $C(\mathrm{Si})_2$ during the second alteration at 8000 m^{-1}, 90 °C and pH = 9 for the tests glass 2 PG, glass 2 AG1 and AG2.

the dissolved species can be assumed to be equal to their concentrations.

The general trends observed for short alteration duration after renewal of the solution at the pH of equilibrium are the same 56 days after the perturbation. The altered glass thickness and the silicon concentrations decrease with the increase of the duration of the first alteration and/or the amount of gel.

4.2.1. Ability of the gel to get back its protective properties

The renewal of the solution is a perturbation for the altered glass. It is a good method to assess the ability of the gel to get back its protective properties. Fifty six days after the renewal of the solution, the alteration rates for tests SON68 AG1 to AG4 are close to the residual rate [9] ($2 \times 10^{-4} < r_R < 9 \times 10^{-4}\ \mathrm{g\,m^{-2}\,day^{-1}}$) (Table 3 and Fig. 6). Thus this perturbation does not drastically modify the protective properties of the gel. For the tests glass 1 AG1 and AG2, the glass alteration rate is about the same order of magnitude as it is for the pristine glass (test glass 1 PG) (Table 3 and Fig. 8). The test glass 2 AG1 does not present an abrupt stop of the alteration as for the test glasses 2 PG and AG2 (Table 3 and Fig. 10).

Table 3
Results of solution analysis, 56 days after the renewal of the solution, at 5000 m^{-1} for the SON68 glass and 8000 m^{-1} for the simplified glasses, pH = 9 and 90 °C (except for the PG tests)

Tests	$\mathrm{Ee(B)_2}$ (nm)	$C(\mathrm{Si})_2$ ($\mathrm{mg\,L^{-1}}$)	$r(\mathrm{B})$ ($\mathrm{g\,m^{-2}\,day^{-1}}$)
SON68 PG	95	90	13×10^{-4}
SON68 AG1	33	49	9×10^{-4}
SON68 AG2	17	45	5×10^{-4}
SON68 AG3	15	36	5×10^{-4}
SON68 AG4 [9]	10	37	2×10^{-4}
Glass 1 PG	153	128	19×10^{-4}
Glass 1 AG1	40	47	13×10^{-4}
Glass 1 AG2	35	40	13×10^{-4}
Glass 2 PG	290	182	$\leqslant 10^{-6}$
Glass 2 AG1	230	307	12×10^{-4}
Glass 2 AG2	119	233	$\leqslant 10^{-6}$

$\mathrm{Ee(B)_2}$: altered glass thickness after perturbation, $C(\mathrm{Si})_2$: silicon concentration after perturbation and $r(\mathrm{B})$: alteration rate after perturbation calculated between 28 and 58 days perturbation. The accuracy is around 5% for the thickness and concentrations and about 100% for the alteration rate.

Even after a perturbation, the gel gets back its protective properties when it evolves in this medium ($S/V = 5000\ \mathrm{m}^{-1}$, 90 °C, pH = 9).

4.2.2. Evaluation of the gel dissolution kinetics for the SON68 glass

As Fig. 2 shows, in the case of SON68 glass, an important part of the silicon in solution comes from the gel. In order to estimate the dissolution kinetics of the gel during the glass alteration, we made some calculations using two hypotheses. Firstly, we assumed that the gel dissolution occurs at constant volume. The real case could be an alteration from the pores surface, leading to an increase of the porosity. Secondly, we considered for the silicon that its retention factor within the gel was equivalent to that existing in the gel formed during the first alteration. This approach, considering the gel as a homogeneous and uniform material, is a severe simplification of the real system but it is a simple method to evaluate its dissolution.

The normalized mass losses in boron and silicon, 56 days after perturbation, are presented in Table 4. Fig. 12 shows a schematic representation of the altered glass after perturbation.

The total gel thickness after renewal of the solution $\mathrm{th_{gel}}$, can be defined by the following Eq. (6):

$$\mathrm{th_{gel}} = \mathrm{Ee(B)_1} + \mathrm{Ee(B)_2} - \mathrm{Ee(Si)_{gel}}, \tag{6}$$

where $\mathrm{Ee(B)_1}$ is the altered glass thickness before perturbation, $E(\mathrm{B})_2$ is the altered glass thickness after perturbation and $\mathrm{Ee(Si)_{gel}}$ is the dissolved gel thickness.

Assuming that the retention factor of silicon after perturbation, $F(\mathrm{Si})_2$, equivalent to the one existing

Table 4
Normalized mass losses calculated for boron $\mathrm{NL(B)_2}$ and silicon $\mathrm{NL(Si)_2}$, 56 days after renewal of the solution at 5000 m^{-1}, pH = 9 and 90 °C for the tests SON68 PG and SON68 AG 1 to AG4

Tests	$\mathrm{NL(B)_2}$ ($\mathrm{g\,m^{-2}}$)	$\mathrm{NL(Si)_2}$ ($\mathrm{g\,m^{-2}}$)
SON68 PG	0.260	0.075
SON68 AG1	0.092	0.044
SON68 AG2	0.046	0.037
SON68 AG3	0.040	0.032
SON68 AG4 [9]	0.028	0.030

The accuracy is around 10%.

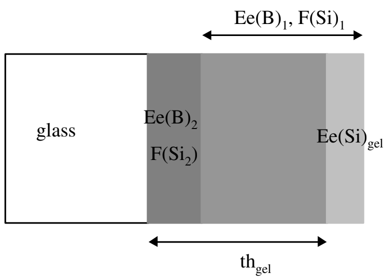

Fig. 12. Schematic representation of the alteration of the altered glass after the renewal of the solution. Ee(B)$_1$: altered glass thickness before perturbation; F(Si)$_1$: retention factor of the altered glass thickness before perturbation; Ee(B)$_2$: altered glass thickness after perturbation; F(Si)$_2$: retention factor of the altered glass thickness after perturbation; Ee(Si)$_{gel}$: dissolved gel thickness after perturbation, th$_{gel}$: total gel thickness after perturbation.

before the renewal of the solution, F(Si)$_1$, it is possible to write (7):

$$F(\mathrm{Si})_1 = F(\mathrm{Si})_2 = 1 - \frac{\mathrm{NLSi}_2 - \mathrm{NL(Si)}_{2\mathrm{gel}}}{\mathrm{NL(B)}_2} \qquad (7)$$

with $\mathrm{NL(Si)}_2 = \mathrm{NL(Si)}_{2\mathrm{gel}} + \mathrm{NL(Si)}_{2\mathrm{glass}}$.

$\mathrm{NL(Si)}_2$ and $\mathrm{NL(Si)}_{2\mathrm{gel}}$ are, respectively, the total normalized mass loss in silicon and the normalized mass loss coming from the gel after renewal of the solution.

The normalized mass loss coming from the gel after the renewal of the solution can be written using the following equation:

$$\mathrm{NL(Si)}_{2\mathrm{gel}} = \mathrm{NL(Si)}_{\mathrm{TOT2}} + \mathrm{NL(B)}_2 \cdot (F(\mathrm{Si})_1 - 1). \qquad (8)$$

For each test, the evolution of the normalized mass losses for the total silicon, the silicon coming from the gel and from the glass, are presented in Fig. 13. This figure shows that for the test SON68 AG1, the silicon comes from the glass and from the gel. This is not the case for the other tests; most of the silicon comes from the gel.

The dissolved gel thickness E(Si)$_{gel}$ can be written as follow:

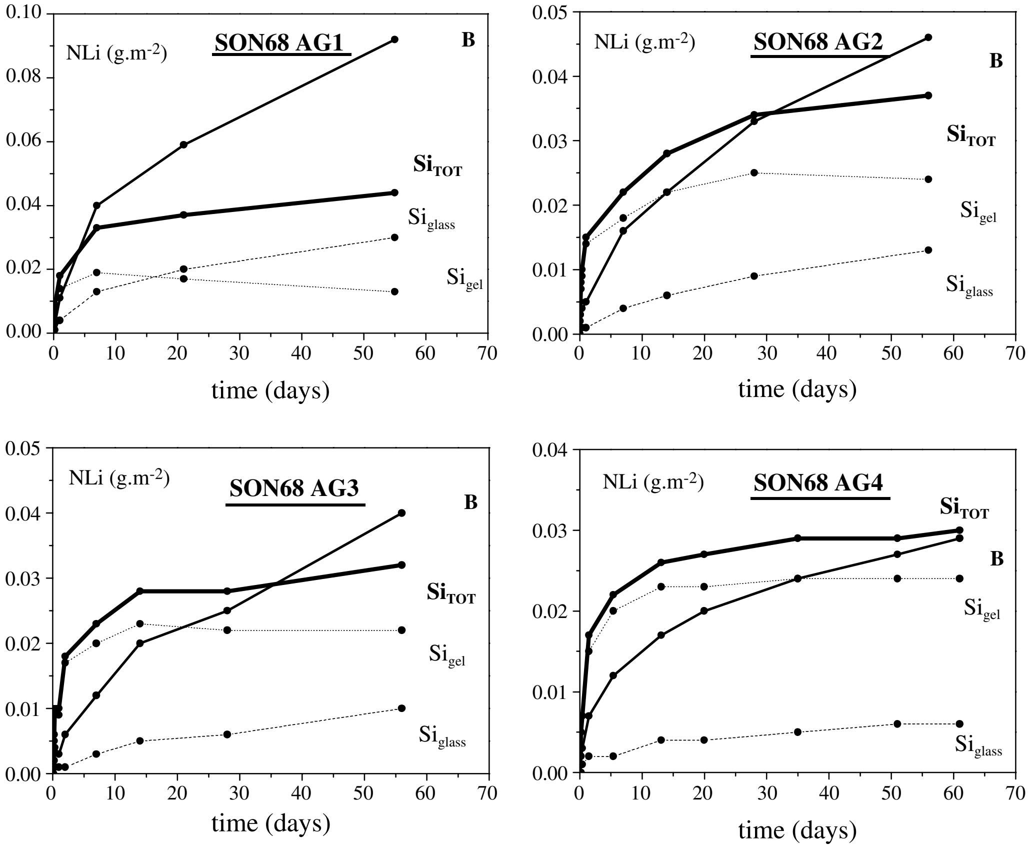

Fig. 13. Normalized mass losses in boron, total silicon (Si$_{TOT}$), silicon coming from the glass (Si$_{glass}$) and the gel (Si$_{gel}$) after the renewal of the solution at $S/V = 5000\ \mathrm{m}^{-1}$, 90 °C and pH = 9 for the tests SON68 AG1 to AG4.

Table 5
Evaluation of the alterated gel thickness $Ee(Si)_{gel}$ and of the gel thickness th_{gel} for tests SON68 PG and SON68 AG1 to AG4, 56 days after the renewal of the solution at 5000 m^{-1}, pH = 9 and 90 °C

Tests	$Ee(B)_2$ (nm)	$Ee(Si)_{gel}$ (nm)	th_{gel} (nm)
SON68 PG	90	0	90
SON68 AG1	37	5	107
SON68 AG2	25	9	116
SON68 AG3	15	8	122
SON68 AG4 [9]	14	9	155

The accuracy is around 5%.

$$E(\mathrm{Si})_{\mathrm{gel}} = \frac{\mathrm{NL(Si)}_{2\mathrm{gel}}}{\rho_{\mathrm{G}}} = \frac{\mathrm{NL(Si)}_{\mathrm{TOT2}} + (F(\mathrm{Si})_1 - 1)\cdot \mathrm{NL(B)}_2}{\rho_{\mathrm{G}}}. \quad (9)$$

The values of the dissolved gel thickness and of the gel thickness after the renewal of the solution are reported in Table 5. In the case of tests SON68 AG2 to AG4, the dissolved gel thicknesses $Ee(Si)_{gel}$ are comparable. This confirms the constant stability of gel described in Fig. 3.

The amount of gel and/or the duration of the first alteration conditions the altered glass thickness and the silicon amount in solution after perturbation.

The silicon concentrations in solution after perturbation are different for all the tests. This phenomenon highlights several things. Firstly, if secondary phases exist on the gel surface, they do not control the silicon concentrations in solution. Secondly, 56 days after the renewal of the solution, most of the silicon in solution comes from the gel dissolution. However, it is not possible to define a gel-solution equilibrium because the silicon activity in solution, 56 days after perturbation, is different. Two interpretations are possible: the equilibrium gel-solution does not exist, or, if this equilibrium exists, different silicon concentrations in solution correspond to different gels.

Moreover, these results show there is a certain amount of gel and/or a minimum of duration of the first alteration, which leads to the same altered glass thickness and to the same dissolved gel thickness after perturbation. The protective properties and the stability of these types of gels are constant. Two phenomena can explain this result: a minimum of silicon must diffuse in the solution to bring the system to the equilibrium and/or the gel is constituted of two parts, a dense part less accessible to water and which could be a diffusive barrier, and a porous part in contact with water which could be easily altered. This kind of morphology has been previously described for gel at high reaction progress [4].

5. Conclusion

The gels from two simplified glasses and SON68 glass do not present the same protective properties and the same stability. These properties depend on the gel morphology and on the glass composition. They increase with the alteration progress. The renewal of the solution which is a perturbation does not decrease the protective properties of the gel. This phenomenon can be explained by the two different parts in the gel for glass SON68 and glass 1: a porous layer in contact with water and a dense layer at the gel–glass interface which constitutes a diffusive barrier. The dense zone could, in part, explains the residual rate which is the most important phase in geological repository.

Others studies must be investigated to better understand the stability of the gel and the origin of the residual rate: the modification of the gel (porosity, structure), the thermodynamic evolution (recrystallisation) and the water diffusion. Experiments are in progress to find out the water penetration profile in the gel at high reaction progress in order to determine the water diffusion coefficient in the different parts of the gel.

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