



Present understanding of R7T7 glass alteration kinetics and their impact on long-term behavior modeling

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Abstract

Glass alteration is a complex phenomenon, the kinetics of which result from the convolution of numerous mechanisms, most of which depend not only on the intrinsic glass properties (composition, structure, surface condition, etc.) but also on the environment (leaching solution volume, flow rate and composition, temperature, pH, surrounding materials, etc.). Considerable progress has been made during the last two decades toward understanding these mechanisms and their interrelations, largely through studies undertaken to predict the long-term behavior of nuclear waste containment glasses. By the mid-1990s, most of these basic mechanisms were thought to be well known, and their interdependence relatively well described by models based essentially on the concepts of chemical affinity. For nuclear waste glasses, if allowance is made for the diffusion and sorption of silica in the gel layer, this kind of model seems satisfactory to account for a single set of data. However, for different data sets, the solubility parameter (C^* or K , depending on the model) must be fitted to the leaching conditions and environment. This point clearly demonstrates that this parameter, the value of which depends on the way in which it was reached, is not a thermodynamic property of the material: C^* is clearly not an intrinsic glass solubility limit. A major research effort was therefore undertaken in France to identify the true causes of the significant drop in the alteration rate observed under 'saturation conditions', and to assess the extent to which the available long-term behavior models had to be revised. The main results of this work on SON68 ('R7T7') glass are reviewed, and their impact on glass modeling is discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Basic mechanisms of glass alteration

1.1. Interdiffusion and hydrolysis

When water comes into contact with the glass, it first diffuses into the pristine glass (hydration), then exchanges with the most highly mobile modifier ions (interdiffusion). A reaction zone is created within which a hydration and H^+ /alkali (or H_3O^+ /alkali) interdiffusion profile forms [16,17]. Interdiffusion occurring during the initial moments can be represented schematically by the following reaction:



This causes the pH to rise in a closed system, and the higher the ratio of glass surface area to solution volume (S/V), the greater the increase.

The hydrated silicate network then dissolves, as indicated by the following reaction:



This initially results in hydrolysis of all the glass constituents (i.e., congruent dissolution) [1,2].

The competition between interdiffusion and dissolution has been investigated for many years [18]. These studies have shown that if the hydrolysis rate r is constant, after a characteristic time τ the concentration profiles in the hydrated glass tend toward steady-state conditions. An 'alteration front' (or 'reaction zone') with a constant thickness λ is formed and advances at a rate r into the pristine glass.

Interdiffusion predominates during the initial instants of leaching ($t \ll \tau$): the alteration front is forming. Over the longer term ($t \gg \tau$), surface dissolution becomes the

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dominant phenomenon, and the thickness of the alteration front becomes

$$\lambda = \frac{\tilde{D}}{r} \quad (3)$$

determined by the interdiffusion coefficient \tilde{D} and the rate r of glass dissolution by the surface reaction. The characteristic time after which the alteration front is established is

$$\tau = \frac{\tilde{D}}{r^2}. \quad (4)$$

In basic media, where interdiffusion is a slow process and the silicate network dissolves at a high rate, τ and λ are low (τ typically ranges from a few hours to a few days, and λ from a few nanometers to a few hundred nanometers at 90°C) and interdiffusion quickly becomes negligible at laboratory scale, except for the establishment of the pH at the beginning of the leaching process. Even in basic media, however, if for any reason the dissolution rate tends toward zero, λ tends towards infinity and interdiffusion could again predominate in the transfer of material into solution. Considering the value of the interdiffusion coefficients (typically a value below $10^{-18} \text{ m}^2 \text{ s}^{-1}$ can be estimated for R7T7 glass at 100°C from nuclear reaction profiles [19]), however, this would still result in negligible long-term release for most HLW glasses.

In acidic media, where the interdiffusion kinetics are higher and the silicate network dissolves at a lower rate, τ reaches higher values. Under these conditions, steady-state dissolution often cannot be obtained at laboratory scale and persistent selective dissolution may be observed [20]. This is also the case at lower temperatures.

1.2. Initial rate of HLW glass dissolution and rate under 'saturation conditions'

Following the initial interdiffusion phase, the aqueous dissolution of glass generally becomes congruent for the major elements (Si, B, Al, Na, etc.); during this phase the glass dissolves at its 'initial rate' r_0 . This intrinsic glass matrix stability parameter corresponds to the maximum rate of hydrolysis in pure water. The value of the initial rate depends mainly on the glass composition [21], the temperature (the activation energy is about 75 kJ mol^{-1} for borosilicate glass) and the pH (with the lowest rate at neutral pH).

Under static leaching conditions or with very low solution renewal, as is typical of a geological repository environment, this linear phase is quickly followed by an intermediate phase during which the concentrations in solution increase more slowly (Fig. 1). For R7T7 and most HLW glasses, 'saturation conditions' with a quasi-steady-state Si concentration are then reached after a period that varies with the S/V ratio; under these conditions the glass alteration rate drops by several orders of magnitude below r_0 [12].

This behavior can be attributed to two principal causes:

1. The decreasing chemical affinity of the glass dissolution chemical reaction as the solution gradually becomes increasingly concentrated with dissolved species [4,22].
2. The development of a protective alteration film that limits exchanges between the glass and solution [23–26].

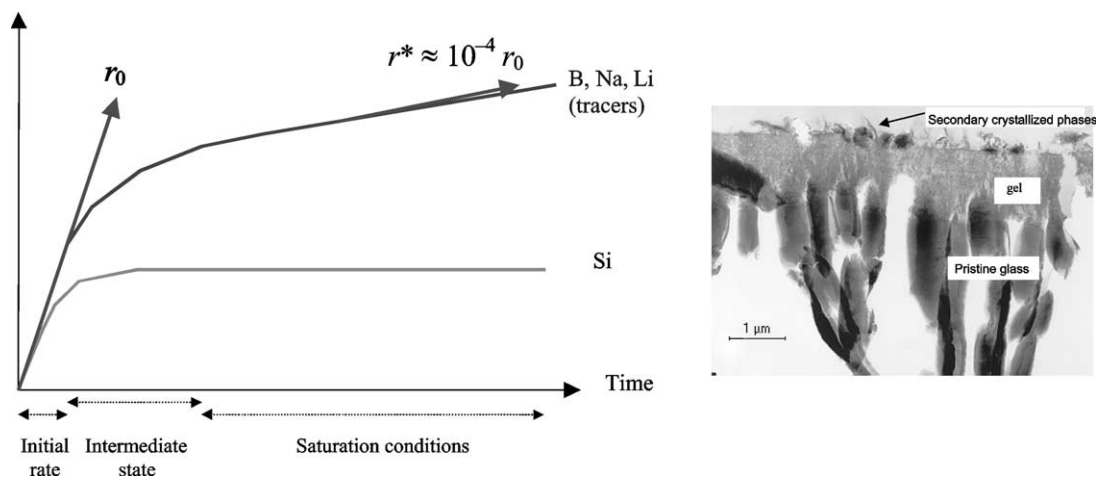


Fig. 1. R7T7-type glass alteration phenomenology in a static system, and transmission electron micrograph of the alteration film formed under these conditions.

1.3. Classical kinetic law of glass alteration

A long-running debate has opposed the proponents of these two hypotheses. In the mid-1980s, the chemical affinity explanation appeared to be generally accepted [6,7,9–14]; when glass specimens that had developed thick alteration layers were placed in pure water, they exhibited the same leaching behavior as the pristine glass [27]; the gel layers formed under conditions far from saturation were nonprotective. Most of the long-term behavior models developed during this period were thus based on a chemical affinity function derived from the general law proposed by Aagaard and Helgeson [28]

$$r = k^+ \exp\left(-\frac{E_a}{RT}\right) \prod_i a_i^{n_i} \left[1 - \left(\frac{Q}{K}\right)^\sigma\right], \quad (5)$$

where r is the dissolution rate, k^+ the forward rate constant ($\text{g m}^{-2} \text{s}^{-1}$), E_a the activation energy (J mol^{-1}), a_i the activity of i th aqueous species and n_i the corresponding stoichiometric coefficient, Q is the ion-activity product of the rate controlling reaction, K the equilibrium constant of this reaction and σ the net reaction order. A simplified expression of this law is

$$r = r_0 \left[1 - \left(\frac{Q}{K}\right)^\sigma\right], \quad (6)$$

where r_0 is the initial dissolution rate (depending mainly on the glass composition, on the temperature and on the pH) and $1 - (Q/K)^\sigma$ is an affinity term characterizing the decreasing solution aggressiveness with respect to the glass as it becomes increasingly concentrated in dissolved elements and as the ion activity product Q of the reactive species approaches the material solubility product K .

This kinetic law was adapted by Grambow [4], who postulated that hydrolysis of the silica in the glass is the rate limiting step

$$r = r_0 \left(1 - \frac{C_{\text{Si(solution)}}}{C_{\text{Si(saturation)}}^*}\right). \quad (7)$$

The simple expression is Grambow's well-known 'first-order law', in which only the silica from the glass is assumed to limit the dissolution reaction. This type of law assumes that an intrinsic saturation constant C^* exists for the SiO_2 that is supposed to represent the glass, and that it depends only on the glass composition, temperature and pH.

Various models derived from the Aagaard–Helgeson equation are indicated in Table 1.

2. Shortcomings of affinity laws in accounting for the alteration kinetics of glass in confined media

Dedicated experiments were carried out to discriminate between chemical affinity effects and effects related to the degree of protection provided by the gel. All the results showed that the significant drop in the alteration rate of nuclear HLW glass under apparent saturation conditions with respect to dissolved silicon does not correspond to a thermodynamic equilibrium between the glass (or the SiO_2 that is supposed to represent the glass) and the solution containing glass alteration products. These experiments established the following points for the French 'R7T7' nuclear glass:

- There is no one-to-one relation between the H_4SiO_4 activity and the dissolution kinetics.
- A pristine glass coupon placed in a 'saturated' leachate is altered at a high rate until a protective gel layer has formed.
- The value of C^* is not intrinsic to a given glass composition, but depends on how the equilibrium conditions were obtained;
- C^* is highly dependent on the S/V ratio.

Table 1
Kinetic laws of glass alteration

Model	Gel layer	$r \propto$
Grambow's simple model [4]	Not taken into account	$1 - \frac{a_{\text{H}_4\text{SiO}_4}}{a_{\text{H}_4\text{SiO}_4}^*} = 1 - \frac{C_{\text{Si}}}{C^*}$
Grambow's model [15] with Si diffusion in the gel	Protective effect that modifies the Si activity at the glass/gel interface	$1 - \frac{a_{\text{H}_4\text{SiO}_4}^{\text{int}}}{a_{\text{H}_4\text{SiO}_4}^*} = \frac{1 - \frac{C_{\text{Si}}}{C^*}}{1 + \frac{r_0 C_{\text{Si}}^{\text{alt}}}{DC^*}}$
Variants of Grambow's model [29,30]	Not mass transport taken into account	$1 - \left(\frac{C_{\text{Si}}^\alpha C_{\text{Al}}^\beta C_{\text{Fe}}^\gamma}{K}\right)^\sigma$
Global solubility [3]	Not taken into account	$1 - \frac{Q}{K_{\text{glass}}}$
Bourcier's model [10]	Controls solution chemistry. Its dissolution kinetics control those of the glass	$1 - \frac{Q}{K_{\text{gel}}}$

- The chemical affinity term can at best account for a rate decrease by a factor of 5, and not by the observed factor of 10^4 .
- A chemical affinity function taking all the glass elements into account does not provide a more satisfactory fit.

2.1. Relation between the H_4SiO_4 activity and the dissolution kinetics

Table 2 clearly shows that for a given glass composition (French SON 68 glass in this case), there is absolutely no one-to-one relationship between the H_4SiO_4 activity and the dissolution kinetics for experiments conducted under very different conditions. (Although only the total silica concentrations are indicated, they are directly proportional to the H_4SiO_4 activity considering the pH (<9) and the low ion concentration.) The evolution of the alteration rate by up to several orders of magnitude thus cannot be attributed to a decrease in the chemical affinity.

2.2. Behavior of a pristine glass in a saturated leachate

When a pristine glass specimen is placed in a saturated leachate, it is altered rapidly at first; the alteration rate then very quickly diminishes. In every case, the evolution of the Si, B, Na or Li concentrations follows the pattern shown in Fig. 2, regardless of the initial solution ‘saturation’ concentration. As the rate decreases by several orders of magnitude without any significant change in the ion activity product, this decrease is attributed to the formation of a protective gel layer.

This phenomenon is not always easy to demonstrate, as the increasing concentrations of dissolved species following alteration of the pristine glass are often lost in the uncertainty on the concentrations measured in the saturated leachate. An R7T7-type glass specimen containing no lithium (the small Li content of SON68 glass

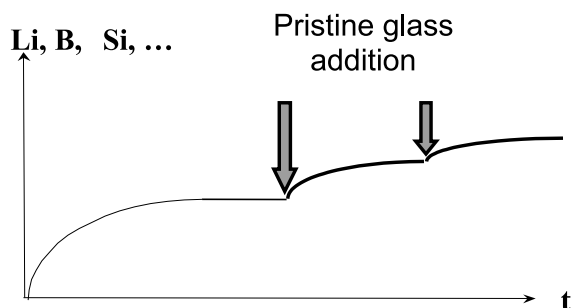


Fig. 2. Schematic evolution of elemental concentrations when a pristine glass specimen is placed in an apparently saturated leachate.

was replaced by Na, with a minimal effect on the glass composition) was therefore altered at 90°C and $S/V = 50 \text{ cm}^{-1}$ for three months to obtain the following apparent steady-state conditions [33]: $C_{\text{Si}} = 77 \text{ mg l}^{-1}$ ($H_4SiO_4 = 10^{-2.94} \text{ mol l}^{-1}$), $\text{pH} = 9.09$. Under these conditions, the final alteration rate measured by the variation of the boron concentration was $r_f = 4 \times 10^{-4} \text{ g m}^2 \text{ d}^{-1}$ (i.e., $r_0/5000$).

The lithium-free glass specimen was then removed and replaced by a pristine glass specimen containing lithium. The lithium concentration subsequently measured in solution was thus indicative of the alteration of the second pristine specimen. Fig. 3 clearly shows that despite the apparent saturation of the leachate, the fresh specimen was initially altered at practically the same rate as in pure water; the alteration rate then diminished sharply with the formation of a protective gel. Secondary ion mass spectrometry (Fig. 4) showed that, after 91 days in the saturated leachate ($S/V = 10 \text{ m}^{-1}$), a gel $0.5 \mu\text{m}$ thick with significant boron depletion formed within a few days on the pristine glass surface, confirming that the lithium signal was indeed a good glass alteration tracer and did not correspond to interdiffusion at the surface of the pristine glass.

Table 2

Comparative review of effects observed in leaching experiments (90°C)

Parameter	pH	C_{Si} (mg l^{-1}) (ultrafiltered)	r ($\text{g m}^{-2} \text{ d}^{-1}$)	Remarks
Flow rate effect [31]	8.7	34	0.04	1 ml min^{-1}
	8.7	34	0.61	10 ml min^{-1}
Environmental material effect [32]	8.5	20	<0.0007	Pure water
	8.0	23	0.06	Pure water + clay
	8.3	46	0.02	Granitic mockup
	8.2	49	0.17	Clay mockup
Time and clay effect [32]	7.0	61	0.06 (500 d)	Clay mockup (extended duration experiment)
	7.1	61	0.02 (1000 d)	
	7.1	61	<0.0001 (2500 d)	

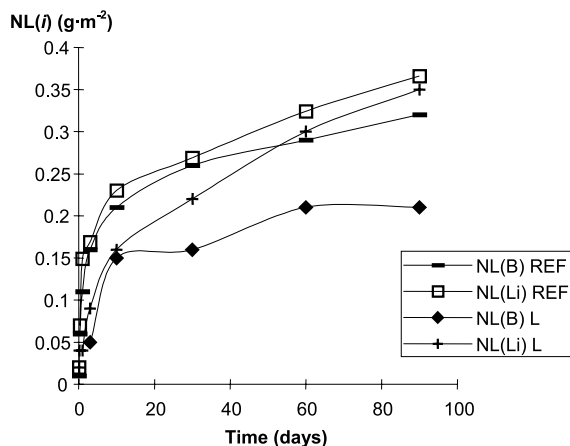


Fig. 3. Normalized Li and B mass losses versus time for reference tests (REF) in pure water and for tests (L) in saturated leachate ($S/V = 1000 \text{ m}^{-1}$).

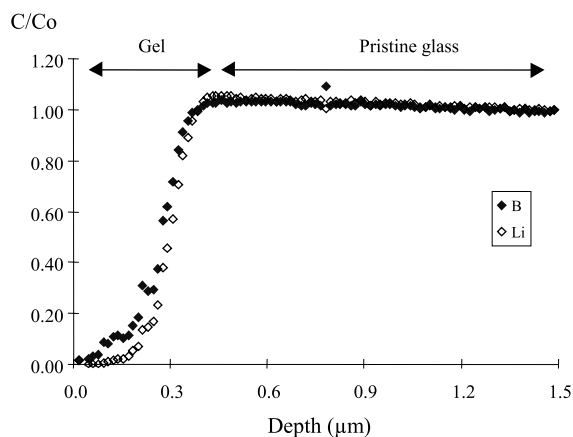


Fig. 4. SIMS profiles for B and Li at the surface of a pristine glass specimen immersed in a saturated leachate ($S/V = 10 \text{ m}^{-1}$).

This experiment may be considered in the light of the work described by Vernaz and Gin [34] in which glass powder was added periodically to the leaching vessel: in each case, a new apparent silicon equilibrium was reached. These experiments showed that a pristine glass coupon placed in a ‘saturated’ leachate is altered at a high rate until an alteration film forms.

2.3. The value of C^* depends on how equilibrium conditions were reached

Fig. 5 shows the steady-state dissolved silica concentrations obtained for two specimens of the same glass composition under identical conditions, except that one of the specimens had previously been leached for one

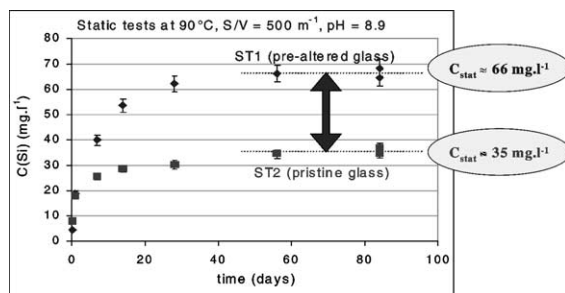


Fig. 5. Steady-state silica concentration obtained for two glass specimens leached under identical conditions, except that one specimen was previously altered.

week in a dilute medium (90°C , $S/V = 50 \text{ m}^{-1}$ and a renewal rate of 1.87 d^{-1}). The apparent solubility C^* of pre-leached specimen was twice that of the pristine specimen. The explanation for this behavior is given by Gin et al. [23] (in this issue). This result confirms that the value of C^* is not intrinsic to a given glass composition, but depends on how the equilibrium conditions were obtained.

2.4. Effect of S/V ratio on apparent solubility C^*

C^* is highly dependent on the glass-surface-area-to-solution-volume (S/V) ratio in particular. This dependence was long attributed to a pH effect: the higher the S/V ratio, the greater the role of interdiffusion and the higher the leachate pH [12]. However, careful experimentation at constant pH with variable S/V ratios (Fig. 6), and with constant S/V ratios but variable pH [34], showed that C^* depends to a great extent on the S/V ratio irrespective of any pH effect. For R7T7 glass, the dissolved silicon concentration under steady-state conditions typically varies from 50 to 150 mg l^{-1} at pH 8.5 [34].

Fig. 7 shows that even in the absence of environmental materials, simply modifying the S/V ratio at the same pH completely obscures any direct correlation

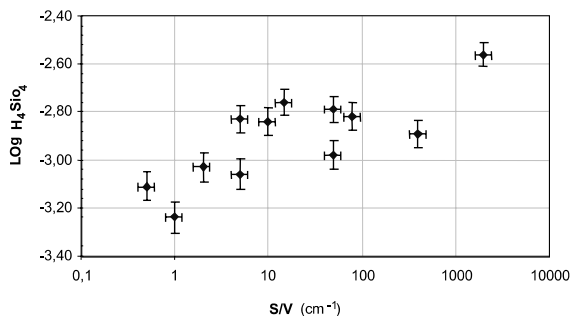


Fig. 6. R7T7 glass leached for 1 year at 90°C : effect of S/V ratio on steady-state H_4SiO_4 concentration ($r < 10^{-3} r_0$ in every case).

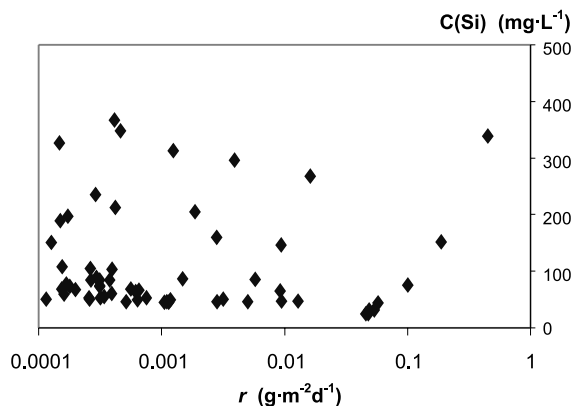


Fig. 7. Glass alteration rate versus dissolved silica concentration during experiments at imposed pH and variable S/V ratios (Fig. 6).

between the alteration rate and the silica concentration in solution.

2.5. Estimating the solution inhibition factor related to chemical affinity

Fig. 8 [33] shows the ‘solution inhibition factor’, defined as the ratio between the normalized glass mass loss as measured in initially pure water, and as measured in a saturated leachate. It allows a global measurement of the effect of solution chemical activity, at ‘saturation’, on the rate. Experiments were performed at 90°C and different S/V ratio and duration. It can be seen that this ‘solution inhibition factor’ never exceeds 5 and could in no case account for the factor of 10^4 observed for R7T7 glass.

2.6. Overall solubility

Various authors have proposed to improve the affinity law by taking a larger number of glass constituent

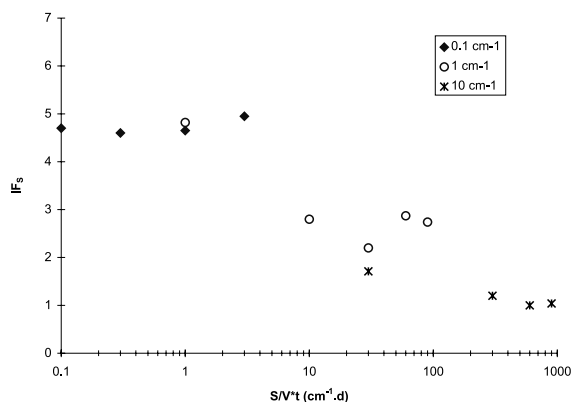


Fig. 8. Solution inhibition factor versus reaction progress.

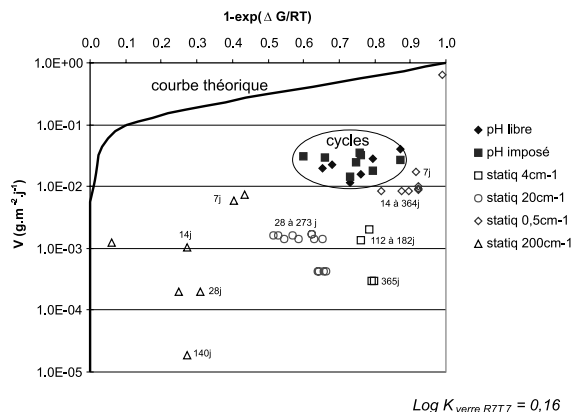


Fig. 9. R7T7 glass alteration rates measured and calculated using an affinity model taking into account all the glass constituent elements [29].

elements into account [29,30]. Fig. 9 compares the R7T7 glass alteration rate measured at different S/V ratios with the theoretical alteration calculated using an overall solubility model, i.e., a model in which the glass constituents are taken into account to calculate the reaction affinity. The glass solubility product was calculated from the free energy of formation of all the oxides or oxide groups in the glass [33]. Here again, there is no direct correlation between the alteration rate and the affinity when experiments carried out under different conditions are compared.

3. Impact on long-term behavior

3.1. Current understanding of glass alteration kinetics

The current state of our knowledge of these phenomena can be summarized as follows:

- The glass hydrolysis reaction is always followed by an inverse condensation reaction that is at the origin of the gel formation.
- For subsequent glass dissolution, water and hydrolyzed silica must diffuse within the gel.
- The recondensed silica fraction increases with the dissolved silica concentration in solution; for R7T7 glass this fraction can be described by an exponential law (Fig. 10).
- As the recondensed silica concentration increases in the gel, its density increases and its porosity diminishes [35]. The hydrolyzed silica diffusion coefficient also diminishes [36].
- For most glasses, the dissolution rate is not controlled primarily by the chemical affinity of the hydrolysis reaction, but rather by the transport properties of the reacting species through the gel

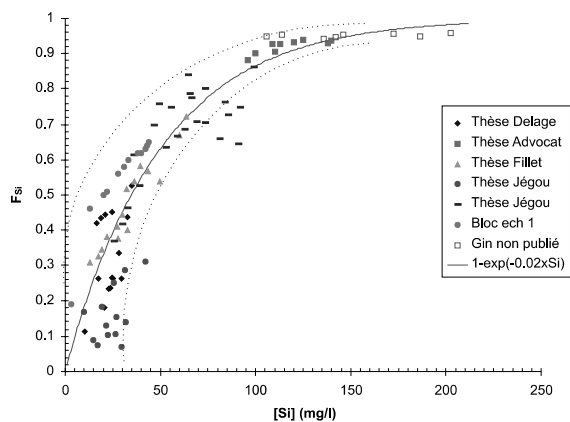


Fig. 10. Recondensed silica fraction in the gel versus dissolved silicon concentration (R7T7-type glass at 90°C).

layer, which evolve significantly during glass leaching.

It is difficult at the present time to affirm that the highly protective properties observed under ‘saturation’ conditions (i.e., when the dissolved silicon concentration reached a quasi-steady-state value) is attributable to the entire gel layer or only to a very small fraction near the ‘alteration front’. Fig. 11 shows that the greater the confinement of the medium (represented in this case by high S/V ratios), the greater the recondensed silica fraction and the lower the silica diffusion coefficient in the gel. It is clear that a gel layer a few tens of nanometers thick with a silica diffusion coefficient of $10^{-19} \text{ m}^2 \text{ s}^{-1}$ is sufficient to account for a drop of four orders of magnitude in the alteration rate [34].

From this new perspective, the role of dissolved silica remains incontestable. For an isolated experiment, it might appear that a sort of solubility limit C^* was reached when the gel became so dense that it virtually became a barrier against alteration. And yet this ap-

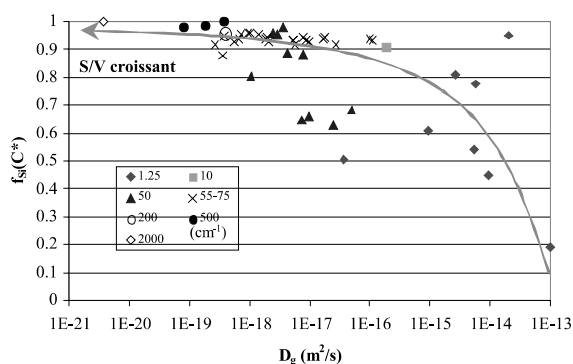


Fig. 11. Silica diffusion coefficient in the gel versus retained silica fraction.

parent solubility limit does not correspond to an actual glass solubility limit, nor to an intrinsic solubility of the gel. It is an empirical parameter reflecting the dynamic – and not thermodynamic – equilibrium that is reached between the quantity of silica hydrolyzed from the glass and gel, and the amount of silica recondensed into the gel.

3.2. Effect of environmental materials

The effect of the environmental materials on the glass alteration kinetics is directly related to the capacity of the medium to consume silica released by glass alteration. In the presence of most clays and some metallic corrosion products with a high silica sorption capacity, the glass is altered virtually at its initial dissolution rate r_0 until most of the sorption sites have become saturated [5,8,37]. At first view, this behavior could be explained by an affinity model (sorption maintains a low silica concentration in solution) or by a gel effect (sorption prevents the formation of a protective gel by limiting recondensation). A closer analysis, however, shows that the second hypothesis is the more plausible. Consider, for example, the long-term integral experiment in Boom clay for which the results are indicated in Table 2: over a 2500-day period the glass alteration rate dropped by 2 orders of magnitude, while the dissolved silica concentration – and thus the affinity – remained constant. SEM analysis of the alteration film also revealed that the layer formed during the first three years was highly porous, with major silica depletion; this corresponds to the period during which the clay rapidly consumed silicon. After 1000 days, most of the sorption sites were saturated, and the rate dropped sharply; the SEM observations showed the formation of a dense and highly siliceous gel. It is interesting to note that after more than 2000 days, silica continued to be consumed at a low rate by the clay due to the precipitation of siliceous polymorphs in the clay [38]. This slow precipitation did not prevent the formation of protective gels, however, and the dissolution rate dropped by 4 orders of magnitude as would be the case in pure water.

The decisive factor governing silica recondensation within the gel is therefore not the absolute silica concentration in solution, but rather the transfer flux into the environment. Here again, the formation of the gel does not imply that a solubility limit is reached in the thermodynamic sense of the term, but rather a dynamic equilibrium between the hydrolyzed and recondensed silica fractions. Numerous other experimental findings corroborate this observation and will be discussed in future publications.

Our current understanding of the effect of environmental materials can thus be summarized as follows: rapid transfer phenomena such as sorption prevent silica

from recondensing in significant quantities in the gel, and maintain high alteration rates. Slow precipitation phenomena occurring within the clay engineered barrier do not prevent recondensation of the silica within the gel, and have no significant effect on the protective role of the resulting gel. It may also be noted that a few percent of glass frit or siliceous additives in the clay completely eliminate the sorption phase that is so penalizing for the glass [39,40].

3.3. Effect of new secondary phases

The role of the precipitation of new secondary phases in possible renewed alteration remains unchanged from the affinity concept [41]. High silica consumption at the gel/solution interface or within the gel would result in silica depletion, and would eventually lead to a significant loss of its protective properties. However, the control of silica at the interface by secondary phases such as zeolite (analcime, herschelite, etc.) depends directly on the glass stoichiometry with respect to the newly-formed phases, and particularly on the Si/Al ratio [42,43]. This ratio is much higher for the French ‘R7T7’ nuclear glass than for the analcime phases; the formation of such phases over the very long term would have only a minor impact in terms of silicon consumption. Moreover, such secondary phases have never been observed at below pH 10 in this glass [44].

3.4. Impact on modeling

It is clear today that the effects of solution chemistry and of the protective gel properties are not contradictory, and must be considered together to account for experimental reality. Even if the glass alteration kinetics are not directly controlled by ‘chemical affinity’, the silicon concentration in solution is still a key parameter because of its impact on the gel properties. The apparent solubility C^* remains to this day the only parameter capable of accounting for the virtual cessation of alteration under ‘apparent saturation’ conditions, and is indispensable in establishing operational models. The LIXIVER and PREDIVER models developed in France [45,46] have already combined these three phenomena:

- a first-order law describing the dissolved silicon concentration;
 - a silicon retention factor in the gel, which increases with the silicon concentration in solution;
 - a diffusion function characterized by the apparent silicon diffusion coefficient D_{gel} in the gel layer.
- The following equations are conserved in the model:
- Glass alteration rate law:

$$\frac{\partial x}{\partial t} = r = r_0 \frac{1 - \frac{C_{\text{Si}}(t)}{C^*}}{1 + r_0 \frac{C_{\text{slb}} \cdot x}{D_{\text{gel}} \cdot C^*}}$$

- Silicon partitioning between the gel and solution:

$$C_{\text{slb}} = C_{\text{glass}}[1 - f_{\text{Si}}(C_{\text{Si}}(t))],$$

$$f_{\text{Si}} = 1 - \exp(-\alpha C_{\text{Si}}).$$

- Silicon mass balance:

$$\frac{\partial C_{\text{Si}}(t)}{\partial t} = r C_{\text{slb}} \frac{S}{V} F (C_0 - C_{\text{Si}}(t)).$$

- Relation to experimental results:

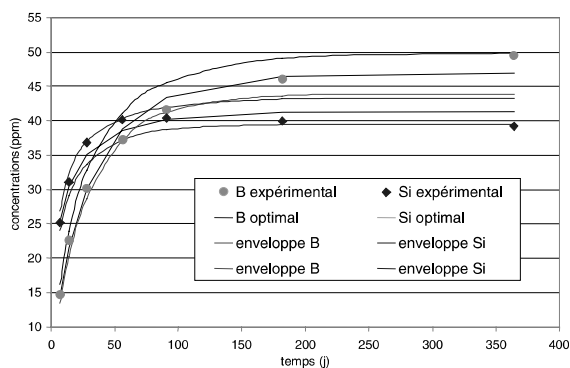
$$x = f(C_{\text{B}}(t)).$$

Here C_{Si} is the silicon concentration; C_{B} is the boron concentration; x is the altered glass thickness; C_{slb} is the solubilizable Si concentration at glass/gel interface; f_{Si} is the Si retention function in the gel; α is the coefficient, typically 0.03 ppm⁻¹ for R7T7 at 90°C (continuous line in Fig. 10); D_{gel} is the Si diffusion coefficient in the gel; C^* is the Si concentration when glass–gel transformation ceases; F is the flow rate; C_0 is the silicon concentration in the leachant.

However, the underlying hypotheses have been modified. The apparent solubility C^* is no longer considered to be a true glass solubility limit, as was the case in the models mentioned in Table 1. It is assumed to correspond to the Si concentration at the glass/gel interface for which the gel inhibits any further glass alteration. It is indeed an empirical parameter reflecting the fact that above a given silica concentration, the gel becomes highly protective and corrosion virtually ceases. This parameter must be fitted according to the leaching conditions (temperature, pH, S/V ratio, etc.), and is applicable only after the end of the rapid sorption phase that may be observed in the presence of some materials.

Moreover, the determination of the model parameters and the field of application have been revised. The predictive performance of the model thus depends largely on the ability to assess the variation range of the model parameters (C^* , D_{gel} , α) according to the package environmental conditions. Work has been completed using inversion calculations to bracket these parameters with respect to the glass composition, the temperature, the pH, the kinetics of removal of leached species, etc. An example of this inversion is given in Fig. 12 for an R7T7-type glass altered for one year at 90°C and $S/V = 6000 \text{ m}^{-1}$.

Similar calculations to determine the optimum values were performed on over 50 separate experiments at temperature between 50°C and 90°C, pH values between 7 and 9, solution renewal rates between 0 and 1.24 d⁻¹, and S/V ratios between 125 and 20000 m⁻¹. The results cannot be discussed here, but will soon be published [47]. The three model parameters Table 3 varied by 1 or 2 orders of magnitude under the environmental conditions of these studies. These variations have little impact, however, on the lifetime of a nuclear glass package, which remains extremely long (over a million years) as a



Parameter	Min.	Optimum	Max.
D_{gel} ($m^2 \cdot s^{-1}$)	4.0×10^{-18}	5.3×10^{-18}	1.0×10^{-17}
C^* (ppm)	39.5	41.3	43.3
α (ppm^{-1})	0.062	0.065	0.068

Fig. 12. Typical fit for an experimental data set with three model parameters: C^* , D_g and α .

Table 3
Optimization parameter ranges

S/V (m^{-1})	100	10 000
D_{gel} ($m^2 s^{-1}$)	10^{-15}	10^{-17}
C^* (ppm)	10	100
α (ppm^{-1})	0.3	0.03

result of the formation of protective gels in media with low renewal and in the absence of high silica sorption capacities.

Note. The hypothesis of an iso-volumic glass alteration and a constant D_{gel} over all the gel thickness, allows a good description of the lab work (gels from 10 nm to 10 μ m) but will be difficult to verify on the very long term. To be conservative, the thickness of a protective layer should be limited in operational model.

4. Conclusions

A general consensus exists that for most (borosilicate, aluminosilicate) nuclear waste glasses, the dissolution rate decreases over time and reaches a very low value under the ‘saturation conditions’ expected in most repository environments. These ‘saturation conditions’ may be reached after a delay due to the sorption capacity of the environment, however, or for some compositions may be perturbed by the precipitation of secondary phases. This point must be taken into account in specifying the glass composition.

Considerable evidence now exists indicating that the major rate decrease under ‘saturation conditions’ is not directly related to a drop in the chemical affinity of the dissolution reaction, but rather to transport processes in a portion of the gel that becomes highly protective under ‘saturation conditions’. This complicates the situation to some extent, in that it introduces a kinetic rather than a thermodynamic limitation. This point appears to be inherent in the repository itself, which will return to thermodynamic equilibrium only when all the engineered barrier materials will have disappeared. The crux of the matter is thus the kinetics of this transformation. Observations of natural glasses confirm that the kinetics may be extremely slow, or even virtually impeded at low temperatures.

The range of factors affecting the kinetics have been largely documented for nuclear waste glasses. Although all the phenomena cannot be described at an atomistic level because of the complexity of the reactions involved, and additional serious fundamental research is necessary on glass alteration, our understanding is sufficient today to develop operational models and specify their uncertainty limits.

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