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SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model

P. Frugier [a,*], S. Gin [a], Y. Minet [a], T. Chave [a], B. Bonin [b], N. Godon [a], J.-E. Lartigue [a], P. Jollivet [a], A. Ayral [c], L. De Windt [d], G. Santarini [e]

[a] *CEA Marcoule, DTCD/SECM/LCLT, BP 17171, 30207 Bagnols-sur-Cèze cedex, France*
[b] *CEA Saclay, DEN/DIR/DS, 91191 Gif-sur-Yvette cedex, France*
[c] *IEM/CNRS-ENSCM Université Montpellier 2, CC 047, Place Eugène Bataillon, 34095 Montpellier cedex 5, France*
[d] *ENSMP, CG, 35 rue St Honoré, 77305 Fontainebleau cedex, France*
[e] *CEA Saclay HC/CAB, 91191 Gif-sur-Yvette cedex, France*

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ABSTRACT

This article summarizes the present state of knowledge concerning aqueous alteration of R7T7-type nuclear containment glasses, represented mainly by the inactive reference glass designated SON68. Based on this review, we propose to describe the glass alteration kinetics up to and including the final residual rate regime by means of a new mechanistic model known as GRAAL (*glass reactivity with allowance for the alteration layer*). Phenomenological analysis findings are reviewed for the various glass alteration regimes: interdiffusion, initial rate, rate drop, residual rate and, under very particular circumstances, resumption of alteration. These alteration regimes are associated with predominant mechanisms. Published work interpreting and modeling these mechanisms was examined in detail. There is a broad consensus on the general mechanisms of the initial rate and even the interdiffusion regime, whereas the mechanisms controlling the rate drop remain a subject of dispute not only with regard to nuclear glasses but also for the dissolution of silicate minerals. The reaction affinity responsible for the rate drop is expressed differently by different authors and depending on the underlying theories. The disagreement concerns the nature of the phase (glass or gel) or the activated complex controlling the rate drop, which in turn determines the elements that must be taken into account in the overall affinity term. Progress in recent years, especially in identifying the mechanisms responsible for the residual rate, has shed new light on these issues, allowing us to propose new theoretical foundations for modeling the different kinetic regimes of SON68 nuclear glass dissolution. The GRAAL model considers that water diffusion in the passivating reaction zone (the gel formed under saturation conditions) is a rate-limiting step in the overall glass dissolution kinetics. Moreover, this passivation zone is a soluble phase whose stability is directly dependent on the nature of the secondary phases likely to precipitate and on the solution renewal conditions.

1. Introduction

The reference option in France for the management of vitrified high-level waste packages is deep geological disposal (Act 2006-739 dated 28 June 2006). Although the final site has not yet been selected, research has focused on a Callovian–Oxfordian clay layer in the northeastern Paris basin [1]. ANDRA has been operating an underground laboratory in this layer since the early 2000s. The current disposal concept for vitrified wasteforms is based on three containment barriers: the glass package, inside a stainless steel container (primary canister), a carbon steel overpack 55 mm thick, and a layer of argillite. Demonstrating the safety of the concept implies assessing the long-term behavior of the glass in contact with groundwater during the thousands of years necessary for decay of the radionuclides incorporated in the glass structure. Over time scales inaccessible to laboratory experimentation, and faced with the chemical complexity of the glass and its environment, modeling is the principal mean of assessing the source term, i.e. the flow of radionuclides released from the glass over time. Although the source term depends on thermal, hydraulic, mechanical, chemical, radiological or even microbiological phenomena, coupling between chemical and hydraulic phenomena is the key issue for source term prediction.

The chemical compositions of the nuclear containment glasses produced at La Hague lie within a range specified by AREVA. The range takes into account the variability of the waste composition in the feed stream, and was determined to meet the technological requirements of glass fabrication (viscosity of the glass melt) and to guarantee the fundamental material properties (homogeneity,

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* Corresponding author. Tel.: +33 466797724; fax: +33 466796620.
E-mail address: pierre.frugier@cea.fr (P. Frugier).

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Table 1
SON68 glass composition (reference TC42c) in oxide wt%

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

thermal stability and crystallization limits, chemical durability). Within this specification range the inactive reference material is SON68 glass. Its chemical composition is indicated in Table 1. This glass contains neither radioactive elements, which are instead simulated by other elements, nor platinum-group metals, which cannot be incorporated in the glass structure.

This article begins with a bibliographical summary of the aqueous alteration mechanisms of SON68 glass followed by a discussion of the fundamental basis for a kinetic model describing the different alteration regimes. This model incorporates the predominant glass alteration mechanisms and allows the glass source term to be coupled with a nearfield geochemical model. In the French disposal concept the nearfield materials at the moment water is expected to come into contact with the glass should mainly consist of the corrosion products of the metal containers (the primary canister and the overpack) together with argillite. The glass alteration model is therefore necessarily based on a detailed description of the system chemistry and the diffusive and convective transport properties of aqueous species through the nearfield materials, as well as their chemical reactivity [1]. Only the model describing the glass alteration kinetics is discussed in this article, however. The source term model intended for use with a coupled chemistry-transport calculation code is based on two fundamental and inseparable parts: a glass dissolution rate law taking into account the key mechanisms, and a description of the assemblage of amorphous and crystallized phases arising from glass alteration in its environment.

2. From phenomena to mechanisms and modeling

Published studies of nuclear glass alteration generally approach the process by a phenomenological description involving five rate regimes (Fig. 1) [2]:

I. Initial diffusion or interdiffusion.
II. The initial or forward rate.
III. The rate drop.
IV. The residual rate.
V. A possible resumption of alteration in particular conditions.

This approach based on observation of the alteration kinetics, which in turn are determined from concentration variations of the mobile elements (boron, alkali metals) in solution, can be related to the nature of the underlying mechanisms. The correlations between the kinetic regimes and these mechanisms are not trivial and are sometimes subject to different interpretations. In this overview of SON68 glass alteration mechanisms it is therefore useful to review the interpretation criteria reported in the literature for glass and crystallized minerals.

2.1. Initial diffusion (regime I)

The term *interdiffusion*, as reported in the literature, refers to the exchange between glass network-modifying cations and protons in solution. This mechanism has been identified experimentally during leaching of many minerals and natural glasses, especially in acidic media [3]. The interpretation is based on observation of anti-correlated sigmoidal concentration profiles in the hydrated glass between alkali ions and protons. Its diffusive nature makes this the overriding phenomenon during the initial moments of leaching of a glass or mineral. In a diffusive process the concentration variations of aqueous species can often be expected to follow a $\sqrt{t}$ relation, with a rate derived from the concentrations exhibiting inverse square root time-dependence: $1/\sqrt{t}$). For a very brief period of time these kinetics exceed the hydrolysis rate of the silicate network. The analytical solution for a diffusion mechanism concomitant with a constant-rate hydrolysis mechanisms has been the subject of many studies [4]. In the more general case where the hydrolysis rate is not constant only a numerical solution is possible. Finally, in the simple case where the hydrolysis rate is zero, the diffusion coefficient is constant and the glass is considered as a semi-infinite medium, the one-dimensional solution to Fick's second law results in concentration variations in the solid described by the following equation [5]:

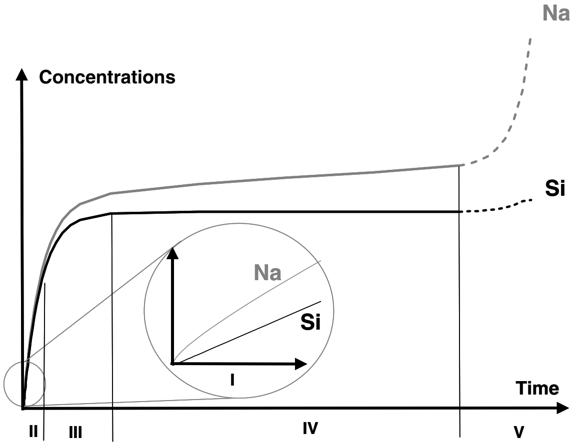


Fig. 1. Time sequence of different rate regimes and sodium and silicon concentrations in solution: I – initial diffusion, II – initial rate, III – rate drop, IV – residual rate, V – resumption of alteration in particular conditions.

$$\frac{C - C_1}{C_0 - C_1} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad \text{where} \quad \mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-y^2)\mathrm{d}y, \qquad (1)$$

C_0: initial concentration in the pristine glass (g m^{-3}); C_1: concentration at the glass-solution interface (g m^{-3}); in this case, $C_1 \ll C_0$; D: diffusion coefficient of the species considered (m^2 s^{-1}); t: time (s); and x: position in the solid with respect to the initial interface (m).

On contact with a homogeneous aqueous solution, the concentration of glass species i in solution varies with the integral over time of the flow extracted at x = 0:

$$C_i = 2\sqrt{\frac{Dt}{\pi}}\rho x_i \frac{S}{V} \qquad (2)$$

C_i: concentration of glass element i in the aqueous solution (g m^{-3}); ρ: glass density (g m^{-3}); x_i: mass fraction of element i in the glass (g g^{-1}); S: glass surface area (m^2); and V: solution volume (m^3).

More recent work with borosilicate glass has shown that the initial diffusion mechanisms are not limited only to interdiffusion of protons and alkali ions. Silicate glasses containing boron are characterized by the immediate release in solution of this element following an inverse square root function of time when leaching is carried out in a silica-saturated solution to prevent hydrolysis of the glass network [6–8]. In neutral or basic media, the release kinetics of boron in solution and its concentration profile in the alteration film is practically equivalent to those of alkali ions. Boron, however, is a glass network former; there is no reason for it to be involved in ion exchange with protons or hydronium ions in solution. The diffusion process, especially in slightly basic media, is therefore more complex than simple ion exchange. Bouyer et al. [9] showed that the release of alkali ions from a sodium borosilicate significantly modifies the structure of the glass network, and especially the boron coordination number: substituting a hydronium ion for a Na^+ ion bound to a tetrahedral boron atom breaks a covalent bond and leaves the boron at coordination number III: the proton does not appear to be capable of compensating the formal charge of four-coordinate boron. The authors concluded by noting that simple alkali-proton exchange cannot occur in the glass structure without causing a local reorganization. In the remainder of this article, the term 'reactive diffusion' refers to the process of water diffusion in the glass, ion exchange, and the resulting reorganization of the glass network. Under these conditions, the species transfer coefficient is an apparent coefficient.

2.2. Initial rate (regime II)

Hydrolysis of the glass network is the mechanism responsible for the initial dissolution rate also called forward rate. Hydrolysis profoundly modifies the silicate network by attacking bridging bonds (Si–O–Si, Si–O–Al, Si–O–Zr, etc.) in the interphase created by the release of mobile elements. Water molecules thus act on the glass by directly affecting network connectivity, leading to matrix dissolution according to the reaction: $\equiv\text{Si—O—Si}\equiv + H_2O \rightarrow 2\equiv\text{Si—OH}$. The rupture of the four bridging bonds likely to surround a silicon atom in the glass ultimately leads to the release of orthosilicic acid, H_4SiO_4. This reaction depends on the nucleophilic character of water, and is thus facilitated in basic media.

The term 'initial dissolution rate' noted 'r_0' is used when the leaching solution is sufficiently dilute to prevent any feedback effect of aqueous species from the glass on the glass hydrolysis kinetics. Dissolution is then congruent (all the elements are leached at the same rate) and no alteration products are formed. This situation is, in fact, never observed in nuclear glasses. In practice, few experimental conditions can prevent precipitation of the least soluble phases or hydrolysis of the most rigid bonds (such as Si–O–Zr): even during SON68 glass alteration in Soxhlet mode [10], which implies a very high solution renewal rate on the surface of the glass, a zirconium-enriched gel highly silicon-depleted compared with the pristine glass is observed together with a few precipitated phyllosilicates on the surface. At a macroscopic level, glass dissolution under these conditions appears to be virtually congruent, especially for the major elements (Si, B, Na, Al, Ca) [11].

The hydrated and dealkalinized layer formed during the initial instants (regime I) very quickly reaches a very small constant thickness under r_0 conditions (see Fig. 1, phase I) and further contributes to the virtually congruent dissolution of SON68 glass in Soxhlet mode. The analytical solution for a diffusion mechanism concomitant with a constant-rate hydrolysis mechanisms is given by Boksay's model [4]. A graphical overview of the model's solutions is given in Fig. 2: with a hydrolysis rate of 10^{-2} µm d^{-1} (order of magnitude for r_0 near 50 °C) and a reactive diffusion coefficient of 10^{-21} m^2 s^{-1} (value justified in Section 2.4.1), the nomogram in Fig. 2 gives an interphase thickness of 10 nanometers.

The initial dissolution rate depends essentially on the temperature, the pH and the glass composition [12,13]. For Oelkers [14] and de Combarieu [15] it depends on the aluminum and iron concentrations in solution. Other ions can catalyze or inhibit these kinetics [16]. For SON68 glass r_0 was determined as a function of the pH and temperature for temperatures ranging from 25 to 100 °C and pH values between 6 and 10 [13]. This leads to the following equation [17]:

$$r_{0(T,\mathrm{pH})} = k_+[\mathrm{H}^+]^n e^{\frac{-Ea}{RT}} \tag{3}$$

$k_+ = 1.2 \times 10^8$ g m^{-2} d^{-1} ($\sigma = 0.4 \times 10^8$ g m^{-2} d^{-1}); $n = -0.4$ ($\sigma = 0.1$) pH dependence coefficient of initial rate; $Ea = 76$ kJ mol^{-1} ($\sigma =$ 5 kJ mol^{-1}) apparent activation energy of initial rate; $R = 8.31 \times 10^{-3}$ kJ mol^{-1} K^{-1} ideal gas constant.

At 90 °C and pH 9, the initial dissolution rate of SON68 glass with a relative density of 2.8 is 5.5 g m^{-2} d^{-1}, id est 2 µm d^{-1}.

Many attempts have been made to relate the initial dissolution rate value to various structural properties of the glass: the number of nonbridging oxygens [18], a thermodynamic model based on the standard enthalpy of formation of the oxide depending on its

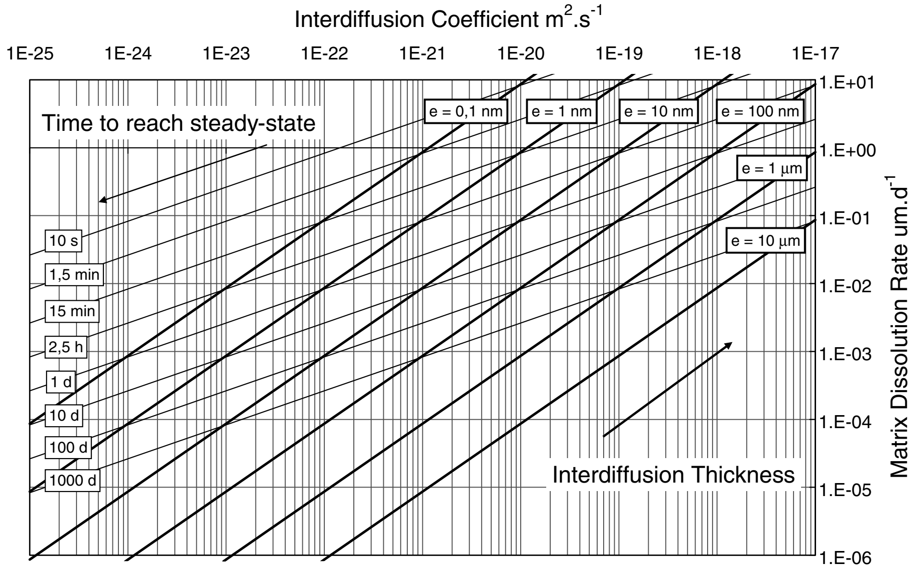


Fig. 2. Orders of magnitude of the time necessary to reach steady-state conditions and of the altered glass thickness versus the reactive diffusion coefficient and matrix dissolution rate (Boksay's model). Example: a glass, with a dissolution rate of 10^{-2} µm d^{-1} and a reactive dissolution coefficient of 10^{-21} m^2 s^{-1}, will reach steady-state conditions in less than 10 days and the interdiffusion thickness will be 10 nm.

structural role [19], a thermodynamic model based on the free enthalpy of glass hydration [20,21]. While all these models qualitatively account for the trends observed, none of them is quantitatively satisfactory or applicable outside a narrow composition range [22]. At the present time, these models cannot be used without experimental measurements. Moreover, none of these models allows for the existence of a hydrated and dealkalinized surface layer, and yet it is conceptually obvious that the initial diffusion is more rapid than hydrolysis during the initial instants, so the latter is not applicable directly to the pristine glass. Allowance for the existence of the hydrated layer could therefore facilitate the development of models predicting the hydrolysis kinetics according to glass composition.

2.3. Rate drop (regime III)

The rate drop is without any doubt the most complex kinetic regime, and its potential effect in predictive models is very significant, as it ranges over several orders of magnitude.

The rate drop is first observed only when the dissolved silicon in solution reaches a sufficient concentration, about 1 mg L^{-1} at 90 °C. Under these conditions, a fraction of the dissolved silicon recondenses to form an amorphous, porous, hydrated phase commonly referred to as the 'gel' [23]. Until recently, two opposing approaches dominated in the literature to account for the rate drop, one based on the chemical affinity expressed with respect to the initial glass, and the other on the passivating effect of the alteration gel [24,25]. The efforts undertaken notably in the framework of the European GLAMOR Program [2] have since contributed to the convergence of these two approaches. A brief historical review is necessary to understand the progress achieved in research with the objective of proposing a glass alteration law to account for the rate drop.

2.3.1. Mechanistic models based on the Aagaard–Helgeson law and transition state theory

Most of the work on the alteration kinetics of silicate minerals and glasses is based on the kinetic law proposed by Aagaard and Helgeson in the early 1980s [26]; they extended the kinetic formalism of an elementary reaction in a homogeneous medium to overall processes in heterogeneous media, assuming they are constituted by a series of elementary steps. The Aagaard–Helgeson law is founded on two main hypotheses:

- The general material leaching mechanism can be broken down into a unique series of elementary steps:

$$\text{Mineral} \xleftrightarrow{1} \xleftrightarrow{2} \ldots\ldots \xrightarrow{j} \ldots\ldots \xleftrightarrow{i-1} \xleftrightarrow{i} \ldots\ldots \xleftrightarrow{s} \text{Species in solution} \tag{4}$$

- the kinetics of the overall mechanism are identified with those of a single rate-limiting step j (while the others elementary reactions are at thermodynamic equilibrium).

The law comprises a kinetic term that incorporates the activity products for the rate-limiting step j and a general chemical affinity term:

$$v_{\text{net}}^{\text{tot}} = k_{\min} \prod_i a_i^{-n_{i,j}} f(A). \tag{5}$$

For Aagaard and Helgeson the affinity function $f(A)$ for the reaction process (Eq. (4)) is of the same form as that associated with an elementary reaction, except for the σ_j coefficient,

$$f(A) = \left(1 - \exp\left(-\frac{A}{\sigma_j RT}\right)\right), \tag{6}$$

$v_{\text{net}}^{\text{tot}}$: dissolution/precipitation rate of a phase mineral; $k_{\min}$: kinetic constant of hydrolysis of the mineral; a_i: chemical activity of surface species i; $n_{i,j}$: stoichiometric coefficient of reactant i in the limiting reaction j; R: ideal gas constant; T: temperature; and A: chemical affinity of the overall dissolution/precipitation reaction.

$$A = -RT \ln\left(\frac{Q}{K}\right), \tag{7}$$

Q: activity product of the reaction products weighted by their stoichiometric coefficients; K: activity product of the reaction products weighted by their stoichiometric coefficients at thermodynamic equilibrium; and σ_j: stoichiometric coefficient of rate-limiting elementary reaction j in the overall reaction.

Applied to glass dissolution, this law was the starting point for many kinetic approaches based on a thermodynamic equilibrium between the glass and solution [27,28]. However the reasoning adopted by Aagaard and Helgeson, identifying the chemical affinity of the rate-limiting elementary reaction and the overall chemical affinity, gave rise to ample confusion in the literature [29]. In the case of minerals, the focus was on the form of the affinity function $f(A)$ rather than on its content; conversely, the main approaches adopted with glass often take into account only some of the glass matrix constituents (network-forming or intermediate elements) in formulating the chemical affinity term A. The justification for including an element in the affinity function lies in the composition of the activated complex, the formation of which could be the limiting step in the dissolution reaction. Initially applied to the dissolution of minerals, Oelkers proposed to apply transition state theory to glass as well [14,30]. Thermodynamic equilibrium would then no longer be expressed with regard to the overall equation, but only to the elementary reaction limiting the overall mechanism. The form of the affinity function $f(A)$ of the general mechanism as well as its content (A) is thus often identified with that of an elementary step (see Eq. (4)). Grambow [31] and later Advocat et al. [13] proposed a general law of nuclear glass alteration dependent only on the activity of the aqueous species H_4SiO_4 at the reaction interface. The activated complex limiting dissolution would thus be intermediate between the atomic configuration corresponding to the adsorption of a water molecule on the matrix-O–Si$(OH)_3$ bond and orthosilicic acid in solution. The affinity function is then expressed as follows (Fig. 3):

$$v = k\left[1 - \frac{a_{H_4SiO_4}^{\text{int}}}{a_{H_4SiO_4}^{*}}\right], \tag{8}$$

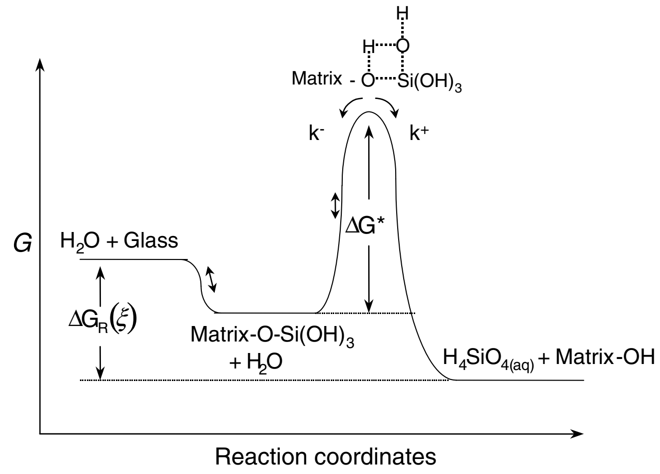


Fig. 3. Nuclear glass dissolution reaction mechanism according to Grambow [31]. The dissolution of the activated complex (rupture of the X–O–Si$(OH)_3$ bond) is the rate-limiting step of the overall glass dissolution reaction.

a^{int}: dissolved silicon activity at the reaction interface; a^{*}: dissolved silicon activity at the reaction interface at saturation with the glass; and k: kinetic constant related to reaction progress [12,31].

McGrail et al. [32] described the alteration of a borosilicate glass designed to immobilize low-level radioactive waste by considering an aluminosilicate activated complex, and thus an affinity function $f(A) = (1 - (C_{Si}^{\alpha}C_{Al}^{\beta}/K)\sigma)$ in which α and β are assumed equal to 1 to correspond to an $AlSiO_4^-$ activated complex.

For Lasaga, however, there is no relation between the rate-limiting elementary step and the contents of the affinity function [33]. He maintains that transition state theory can be used to determine the rate term associated with an elementary step but cannot address the evolution of the affinity term, which derives from classical thermodynamics. In other words, the hypothesis that hydrolysis of the Si–O bond controls the alteration of a silicate is not sufficient to justify taking only silicon into account in the affinity function (it would be necessary for this purpose to demonstrate that the general alteration mechanism is identified with a pure siliceous phase). Lasaga et al. [33] propose a generalized rate law in which the affinity term contains all the constituents of the material, but with no hypothesis concerning its mathematical form,

$$r_{\text{net}}^{\text{tot}} = k_0 S e^{-Ea/RT} a_{H+}^{n_{H+}} g(I) \prod_i a_i^{n_i} f(A), \tag{9}$$

$\prod a^{n_i}$ includes all the species liable to catalyze or inhibit the overall reaction. These kinetic effects must be distinguished from those related to the affinity function; n_i: stoichiometric coefficient of reactant i reflecting its inhibiting or catalyzing effect. a_{H+}: activity of the proton in solution; $g(I)$: term including the effects of the ionic strength of the solution on the rate; k_0: intensive kinetic constant; S: reactive surface area of the mineral; and $f(A)$: affinity function associated with the overall mineral dissolution reaction.

This law uses global parameters, and avoids any notion of elementary steps and any description of an alteration mechanism.

The applicability of the overall affinity concept to a description of the diminishing alteration rate of nuclear borosilicate glasses was investigated by Linard et al. [28] for simplified three-oxide compositions. They determined the free energy of formation of a simple borosilicate glass by calorimetry [34], then calculated $\log K$ for the glass and compared this value with the ion activity product measured after more than a year of leaching in initially pure water at a high glass-surface-area-to-solution-volume ratio. They noted that the ionic product reached in solution was well below the value determined from the free energy measured by calorimetry, and that the observed rate drop therefore cannot be attributed to the onset of saturation with respect to the glass, which was still far from the case.

There are thus two opposing schools of thought with regard to a description of the leaching kinetics of glass and silicate minerals under near ‘saturation’ conditions: for Lasaga or Hellmann [35] an overall affinity term containing all the elements initially in the mineral must be taken into account; for Oelkers the activated complex corresponding to the rate-limiting step defines the nature of the elements that must be taken into account in the affinity term. These theoretical disagreements in the literature with regard to minerals are naturally echoed in the literature concerning glass alteration. For glass, the dispute focuses essentially on the nature of the elements to be taken into account in the affinity function. Only transition state theory is capable of taking into account a limited number of elements from the initial mineral in the affinity term.

2.3.2. Allowance for alteration films in an affinity law

By definition, thermodynamic equilibrium implies equality between the kinetics of dissolution and the kinetics of formation for an elementary reaction. The reverse reaction of formation of the phase must therefore exist under the chemical conditions in which equilibrium is observed in order to apply Eq. (5). However, the true notion of thermodynamic equilibrium between a glass and a solution can be called into question by a simple observation: it is impossible to form a complex silicate glass from an aqueous solution. Sverdrup and Warfvinge [36] emphasize the need to discriminate between minerals that dissolve irreversibly (glass, feldspar, pyroxene, etc.) and those which can be formed from solution (salts, amorphous aluminosilicates, carbonates, etc.).

Some authors, observing that the main product of nuclear glass alteration is an amorphous aluminosilicate gel, have proposed a model according to which the glass dissolution rate follows the chemical affinity function of gel dissolution. The gel is assumed to be at thermodynamic equilibrium with the solution, and to contain elements capable of participating in the reverse ‘condensation’ reactions. Bourcier et al. [37,38] and Cunnane et al. [39] proposed that the solution composition be used to recalculate the gel composition at each sampling interval and then – considering the gel as an ideal solid solution of amorphous phases and hydroxides – to compute its thermodynamic properties in order to determine the constant K.

Daux et al. [40] studied basaltic glass in an attempt to reconcile the relatively contradictory theoretical work of Bourcier and Oelkers. They noted that if the objective is to describe a thermodynamic equilibrium in solution, it is more reasonable to establish it with respect to a hydrated basaltic glass (HBG) than with respect to the pristine glass. They also proposed a rate law in terms of transition state theory in a continuation of Oelkers’ work. Finally, they established a link between the two approaches by proposing that the stoichiometry of the activated complex should follow that of the HBG. This implicitly acknowledges the passivating role of the hydrated glass with respect to the pristine glass. This approach shows how two different theories, transition state theory and the theory of a passivating layer, could converge toward an identical mathematical formalism for the rate law, using the same affinity term. However, one postulates the existence of an intermediate reaction product, whereas the other describes the formation of a massive solid involved in the reaction mass balance and limiting the transfer of reactive species between the pristine glass and the bulk solution.

By the 1990s the need for an explicit description of the presence of the gel and/or the hydrated glass (depending on the authors) raised the issue of its potential role in passivating the pristine glass. The models based on Bourcier’s work assume the existence of a perfectly passivating gel, since the glass alteration rate is assumed to fall to zero when the gel is at equilibrium with solution. Experimental findings have shown, however, that the rates of release of the mobile elements – alkalis and boron – into solution never reach zero. This finding has led many authors to take into account transport phenomena coupled with affinity phenomena. However the nature of the elements transported and the zone in which the transport occurs were another subject of controversy.

Dynamic leaching experiments [41] showed that the alteration film played a protective role that depended to a large extent on the leaching conditions (S/V, silicon concentration in the leachate, etc.). As a result of these tests, Grambow’s law (Eq. (8)) was supplemented with a function for silicon diffusion in the alteration film; the concentration at the reaction interface was then determined from the concentration in solution and an apparent silicon diffusion coefficient in the gel (Eq. (10)),

$$r = \frac{r_0\left(1 - \frac{C_{\text{Si}}}{C_{\text{Si}}^{*}}\right)}{1 + r_0 \frac{f(C_{\text{Si}}) \cdot x_{\text{Si}}^{v} \cdot e}{D_{\text{Si}} C_{\text{Si}}^{*}}}, \tag{10}$$

C^*_{Si}: silicon concentration at saturation; C_{Si}: silicon concentration in the homogeneous solution; x^v_{Si}: silicon mass fraction in the glass; e: altered glass thickness; D_{Si}: apparent silicon diffusion coefficient in the interstitial solution of the alteration film; and $f(C_{Si})$: function accounting for silicon retention in the gel proportional to the silicon concentration in solution: $f(C_{Si}) = a + bC_{Si}$ [41].

This equation was the basis for the $r(t)$, LIXIVER and PREDIVER models used from 1993 to 2000 to predict the long-term behavior R7T7-type nuclear glass [42]. To account for glass dissolution kinetics it was necessary to diminish the value of the apparent silicon diffusion coefficient in the alteration film (an adjustable parameter in the model) as the reaction progressed. This is consistent with the formation of an alteration film that becomes increasingly dense and protective as the concentrations increase in solution, but raises a major problem: the dependence of the silicon diffusion coefficient on an extensive parameter, the glass-surface-area-to-solution-volume ratio (S/V) [2].

The transport phenomena occur within a very limited spatial range (from about ten to a hundred nanometers); Devreux and Barboux [43] therefore proposed to use a stochastic atomistic technique, kinetic Monte Carlo modeling, to account for the gel formation. By assigning each glass constituent element a dissolution and condensation probability, two fundamental mechanisms are placed in competition: the leaching of mobile elements, and the construction of a gel by condensation of hydrolyzed silicon until alteration becomes totally inhibited by closure of the gel porosity. This approach pursued by Ledieu et al. [44,45], then Arab et al. [46] and Cailleteau et al. [47] led to considerable progress in our knowledge of the relationships between the glass composition, the gel structure (density, porosity, etc.) and the extent to which the gel can limit glass alteration.

Although it has now been established that the rate drop can be attributed to the combined effects of affinity and passivation related to the gel, i.e. exclusively to hydrolysis and condensation mechanisms, several issues remain:

- Can it be assumed that the gel formed by recondensation is at thermodynamic equilibrium with the homogeneous solution?
- Which elements constitute this amorphous phase and which elements precipitate in crystallized secondary phases or are found in solution? This question evokes the choice of elements included by some authors in the affinity term historically attributed to glass.
- How can its passivating character be described?

2.4. Residual alteration rate in a closed system (regime IV)

The residual rate in a closed system refers to the glass alteration kinetics in a closed system over an extended time period following the exponential rate drop. This definition corresponds to the intrinsic glass behavior, since only glass dissolution determines the solution chemistry. It differs from the residual rate in a reactive environment, which also depends on the nearfield materials, on the diffusion of elements in the near field, and on the solution renewal conditions. The term ‘residual rate’ (without any additional qualifier) traditionally refers to the residual rate regime in a geological disposal environment and also includes the hydrolysis and condensation mechanisms described in the preceding section concerning the rate drop. The following paragraphs discuss the additional mechanisms to be taken into account specifically in conjunction with the residual rate in a closed system.

In this kinetic regime the rate is generally slowly decreasing (Fig. 4) or remains constant (Fig. 5). Two concomitant mechanisms account for this phenomenology in SON68 glass [6]: reactive diffusion of the hydrated elements in the gel and precipitation of secondary phases.

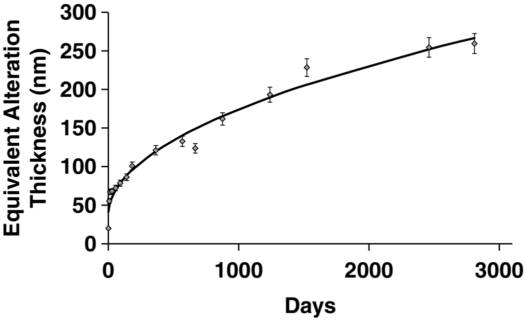


Fig. 4. Equivalent boron alteration thickness versus time during SON68 glass leaching in initially pure water at 90 °C and 80 cm^{-1}: comparison with a $y = ax^{1/2} + b$ regression.

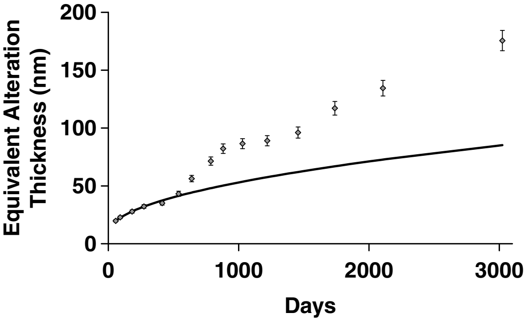


Fig. 5. Equivalent boron alteration thickness versus time during SON68 glass leaching in initially pure water at 90 °C and 2000 cm^{-1}: comparison with a $y = ax^{1/2} + b$ regression applied to the first 600 days.

2.4.1. Reactive diffusion

The first mechanism involves reactive diffusion of water and glass elements through the gel. When activities of the gel-forming elements (Si, Al, Ca, etc.) tend toward steady-state conditions in solution the glass network hydrolysis rate diminishes exponentially. Under these conditions the mechanisms of diffusion in the solid, which had become negligible after a few instants, again become predominant.

For many years only interdiffusion between alkali ions and protons in solution was taken into account. The results was that the boron release in solution from nuclear glasses could only be explained by the dissolution law of Eq. (9). This situation was a source of problems in developing models, especially for simulating the concentrations obtained in solution at high glass-surface-area-to-solution-volume ratios. These difficulties contributed to the divergence between advocates of affinity concepts and those of a passivating gel, until these conflicting viewpoints subsequently converged – especially under the European contract GLAMOR – on the need to supplement the rate law by allowing for the transport of reactive species to account for experimental data [2].

The first studies taking into account a kinetic inhibition related to diffusive transport of reactive species in the gel were carried out in the 1990s [41]. The species considered at that time was silicon, and transport occurred in the alteration gel characterized by a constant-volume process (the gel occupies the altered glass volume). As noted above, the parameters of the models allowing for this phenomenon vary according to extensive quantities, such as the S/V parameter.

This observation led Grambow and Muller [48] to propose the GM2001 model in which silicon diffusion in the gel was supplemented with a water diffusion term in the pristine glass reflecting the glass hydration mechanism. This term accounts for ion exchange resulting in diffusive extraction of alkalis from the glass – and even boron, which they observed experimentally released together with alkali ions; the result was a partially dealkalinized and deborated zone of hydrated glass. However, the authors chose to conserve the terms ‘ion exchange’ and ‘hydrated glass’: even though one of the glass network formers is no longer present, the hydrated glass probably remains structurally related to a large extent with the underlying pristine glass. The water diffusion coefficients determined from the experimental data, ranging from 10^{-18} to 10^{-24} $m^2\ s^{-1}$, are used to quantify the importance of this mechanism in establishing the concentrations of the alkalis and boron in a closed system.

The phenomenological justification of this mechanism of diffusive extraction of the mobile elements (alkalis, boron, molybdenum) is based on two additional experimental findings [6]:

- The rate variation over time varies with inverse square root time-dependence ($1/t$) (Fig. 4). This is consistent with diffusion in a semi-infinite solid as mentioned above [7].
- Concentration variations after reaching saturation are proportional to the S/V ratio. This is explained schematically in Fig. 6: when the dissolution rate of a phase is controlled only by the onset of saturation in solution (solubility model), it drops to zero in a saturated solution. The concentrations in solution after a sufficiently long time are therefore constant regardless of the S/V ratio. However, if the rate is controlled by a diffusion mechanism in the solid, the latter continues after the solution becomes saturated. Under these conditions the concentrations are proportional to the S/V ratio. The results obtained with SON68 glass at 90 °C after one year of leaching show the boron concentration was never constant, but varied with the S/V ratio (Fig. 7).

Fig. 6 postulates the notion of equivalent thickness: i.e. the glass thickness that must be leached to reach the observed concentration in solution of a given element. In a closed system it is calculated using Eq. (11), based on the mass balance between the quantity released by glass dissolution and the quantity accumulated in solution,

$$\frac{\mathrm{d}e_i}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{C_i}{\rho x_i \frac{S}{V}}\right), \qquad (11)$$

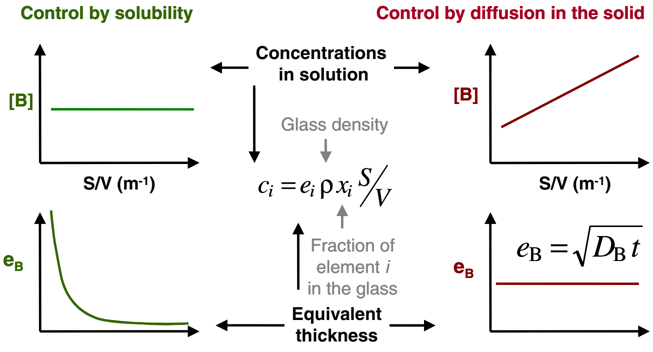


Fig. 6. Simplified overview of the effect of S/V ratio after one year of alteration in a closed system. It is assumed that the leaching time was long enough to consider that saturation was achieved with respect to H_4SiO_4. Two hypotheses are shown for boron (as for alkalis).

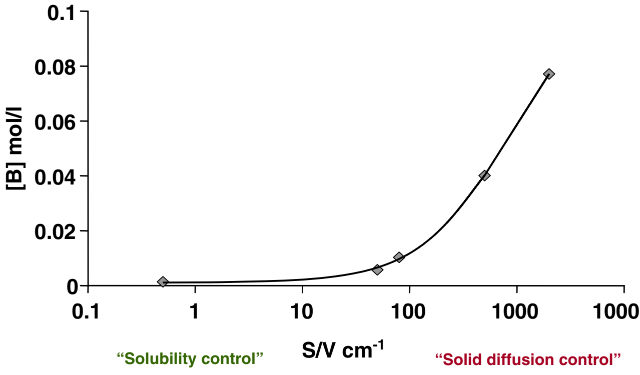


Fig. 7. Total boron concentration in solution after one year of SON68 glass leaching at 90 °C in initially pure water: effect of S/V ratio.

e_i: equivalent alteration thickness for element i (m of altered glass); C_i: concentration of element i in solution ($g\ m^{-3}$); ρ: glass density (g/m^{-3}); x_i: mass fraction of element i in the glass ($g\ g^{-1}$); S: glass surface area (m^2); and V: solution volume (m^3).

In the case of a purely diffusive mechanism as in Eq. (2): $e_i = 2\sqrt{\frac{Dt}{\pi}}$.

Ferrand et al. [49], Ojovan et al. [8] and Mitsui and Aoki [50] confirmed the importance of diffusion of the mobile elements and showed it to be temperature- and pH-dependent. Chave et al. [7] quantified this mechanism with SON68 glass, not only from analysis of the elements released into solution but also, for first time, from analysis of the chemical profiles in the solid through the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) on the altered glass. The results demonstrate that S/V and ionic strength are not key parameters. The diffusion coefficient decreases significantly when the pH rises from 8 to 10 at 90 °C. Variations with temperature can be modeled using an Arrhenius law.

2.4.2. Precipitation of secondary phases

In a closed system, reactive diffusion results in a continuous rise in the concentrations of mobile glass constituents in solution. This raises the issue of long-term pH variations, and more generally of the geochemical evolution of the entire system comprising the solution, the gel, and crystallized secondary phases. The precipitation of crystallized secondary phases can sustain glass alteration: this is the second mechanism proposed to account for the residual alteration rate [6]. In a closed system over the long-term, the leach rate of many glasses no longer decreases with the square root of time but instead remains at a relatively low but virtually constant rate. This is the case for SON68 glass (Fig. 5) as well as for AVM glass [51] and Magnox glass [52]. To measure the virtually constant residual rate observed with SON68 glass, we must not only wait for the drop in the residual diffusion rate, but also ensure that the S/V ratio and reaction time are sufficient to detect concentration variations in solution. For SON68 glass a virtually constant residual rate of $1.7 \times 10^{-4}\ g\ m^{-2}\ d^{-1} \pm 0.2 \times 10^{-4}\ g\ m^{-2}\ d^{-1}$ is established after one year of leaching at 90 °C at 2000 cm^{-1} (Fig. 5). Curti [52] measured a rate of $1.3 \times 10^{-4}\ g\ m^{-2}\ d^{-1} \pm 0.3 \times 10^{-4}\ g\ m^{-2}\ d^{-1}$ after a comparable time period, but at an S/V ratio of 12 cm^{-1}. The mechanism by which precipitation of crystallized secondary phases could sustain the residual rate by consuming key elements in the gel will be discussed below after determining the balance of the mineral phases observed (to refer to the following paragraphs).

2.5. Resumption of alteration (regime V)

A resumption of alteration refers to a significant increase in the alteration rate following the rate drop in a closed system.

Irrespective of the type of borosilicate, the resumption of alteration appears to be related to massive precipitation of crystallized zeolite secondary phases [53,54]. What distinguishes this regime from the second mechanism mentioned above for the residual rate is that precipitation occurs suddenly and after an extended time: it must therefore be kinetically limited or highly activated when an activity or pH threshold in solution is exceeded. The precipitation of this phase must also be self-sustaining. This destabilizes the gel, glass alteration resumes and, given the alkali concentration of the glass, the solution pH increases, maintaining the precipitation of zeolites. Following this resumption of alteration, new steady-state conditions of zeolite precipitation and glass dissolution can be expected to occur, resulting in the establishment of a residual rate that may be constant if the pH stabilizes. The rate during the resumption of alteration does not exceed the initial rate at the same pH. Although the mechanism has now been clearly identified, no kinetic model has ever been published in view of the major difficulty of modeling amorphous phases, i.e. the passivating gel prior to the resumption of alteration or the depleted gel following precipitation of zeolites.

2.6. Summary of kinetic models of glass dissolution

Most articles concerning the dissolution of minerals focus on the dissolution kinetics and the affinity function. They therefore describe experimental data obtained in systems with leachate renewal, often far from 'equilibrium' conditions rather than in a closed system. Under these conditions, modeling transient diffusive phenomena and the precipitation of secondary minerals formed in more confined environments is of lesser importance. For leaching of radioactive waste containment glass, however, disposal in a deep geological formation implies a high degree of confinement, for which experiments in a closed system at high S/V ratios are more representative. These methodological differences at least partially account for the conceptual differences mentioned above.

Although considerable progress has been made in identifying nuclear glass alteration mechanisms, most of the remaining work to consolidate the robustness and predictive capabilities of the models will involve modeling the chemical complexity – especially when it comes to simulating the repository environment. Frugier et al. [6] insisted on the need for accurately describing the mass balance of the elements distributed between crystallized phases, the amorphous gel, and solution. Indeed, the work described above leads to the emergence of a fundamental concept: supplying gel constituents favors the rate drop, whereas supplying constituents of the crystallized secondary phases can sustain alteration. Each element must therefore be examined to determine its affinity for specific phases, and to describe how it should be taken into account in the model.

3. The amorphous layer and crystallized mineral phases of the alteration film on SON68 glass

3.1. Amorphous phases

Two types of mechanisms are responsible for the formation amorphous interphases on SON68 glass: hydrolysis-condensation mechanisms, and reactive diffusion mechanisms in the general sense. As explained at the beginning of this article, these mechanisms comprise water diffusion in the glass, interdiffusion between protons and alkali ions (exchange reaction), and solvated ion diffusion (in the case of boron). These mechanisms require us to differentiate among several amorphous zones in the glass alteration film.

3.1.1. Zone of water interdiffusion with alkali ions and solvated ions

The mechanism of water and solvated ions interdiffusion leads to the formation of this first zone, in which it is more rapid than the hydrolysis mechanism involving cross-linking elements. This zone could conceivably be subdivided into three parts by discriminating between molecular water diffusion in the glass, exchanges between protons and alkali ions, and solvated ion diffusion.

3.1.1.1. Hydrated glass zone arising from molecular water diffusion in the glass structure. During the initial stage of leaching it is commonly acknowledged that one of the first reactions affecting the glass is the penetration of water into the solid in ionic ($H+/H_3O^+/OH^-$) or molecular form. Glass may incorporates water while still conserving all its other constituents. According to Bunker [55], molecular water diffusion in the structure of a material is relatively rapid (less than 10^{-15} m^2 s^{-1}) when the structure contains voids of sufficient size (>0.7 nm) compared with the kinetic diameter of a water molecule (0.28 nm). Otherwise, the only way for water to penetrate into the structure is by hydrolysis of its bonds. Under the temperature and pH conditions relevant to this study (pH 7–11, $T < 100$ °C), a proton-enriched zone without depletion of any glass constituent elements has never been identified, even after extended leaching [56,49]. Should it exist, it must be very thin.

3.1.1.2. Zone of proton/alkali ion exchange. The hydration reaction is followed by an exchange reaction between protons and alkali or alkaline-earth ions in the glass. This mechanism appears to be significant mainly in acidic media. In neutral or basic media, ToF-SIMS (time-of-flight secondary ion mass spectrometry) analysis reveals a zone in which only the alkali ions (especially lithium) are depleted along a concentration profile anticorrelated with the hydrogen profile [56]. In this zone we can imagine that the glass structure is preserved and that the weakest bonds are not yet broken. The exchange reaction responsible for creating this zone is the first quantifiable step in the reactive diffusion process. However, as this zone is much thinner than the third zone, it may be reasonable as a rough approximation in alkaline media to disregard it in accounting for the alkali concentrations in solution [7]. It appears that the structural changes arising from the exchange of alkali ions quickly lead to leaching of boron in particular, whose structural roles in the glass are very different from that of the alkalis.

3.1.1.3. Passivating reactive interphase. When the solution becomes saturated a third zone forms [7] in which all the gel-forming elements (Si, Ca, Al, Zr, etc.) are preserved. This zone, called Passivating Reactive Interphase (PRI) is characterized by a concentration gradient both for the mobile elements (alkalis, B, Mo) and for the elements that limit the formation of crystallized phases (Zn, Ni, etc.). The concentrations of these elements vary from the glass concentration to zero in general near the outer interface. The thickness of this zone can be calculated by considering a simple diffusion process in a semi-infinite solid [7]. In this zone all the elements follow the same diffusion profile irrespective of their role in the initial glass structure: the apparent diffusion coefficients for the network-modifying alkalis and network-forming boron are nearly identical, suggesting that water diffusion is likely to be the rate-limiting process in this zone rather than the transport of solvated ions. The apparent diffusion coefficients range from 10^{-21} to 10^{-24} m^2 s^{-1}; its activation energy of 85 kJ mol^{-1}, substantially higher than for ion diffusion in solution, illustrates the reactivity of the process [7]: major structural changes may occur in this zone, given the large molar fraction of mobile elements – about 1/3 for SON68 glass. It is particularly difficult to characterize this zone given its minimal thickness and frequent coexistence with the depleted gel (see below). Small Angle X-ray Scattering [57] on grains leached at 2000 cm^{-1} at 90 °C under conditions where most of the amorphous layer consisted of the PRI revealed no porosity exceeding one nanometer in diameter (Frugier and Gin, unpublished data). This result is consistent with a passivating effect of this zone. The chemical environment of the atoms in the glass [58] and in the gels [59] can be determined by structural characterization, especially by nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy, but has never been applied to this layer that is often only a few nanometers thick. Ledieu et al. [44], however, carried out a ^{29}Si NMR examination of a less passivating and therefore thicker amorphous layer of depleted gel, and demonstrated the structural reorganization of the gel layer in which the silica network, no longer containing boron and alkali ions, is more polymerized than in the initial glass. Silicon can thus reorganize itself to form a network with a structure minimizing its free energy. This reorganization is particularly effective for passivating the glass in that its constituent elements (Si, Ca, Al, Zr, etc.) are reorganized *in situ* without a fraction being consumed to saturate the solution. That's why we have chosen to call this dense zone [60], which by its reactivity controls the concentrations of its constituent elements (Si, Al, Ca, Zr, Fe) and passivates the underlying pristine glass, the 'passivating reactive interphase' (PRI). Some authors refer to a hydrated glass [48] or gel [61] depending on the importance they attribute to its being a residual solid (hydrated glass) or a reorganized solid (gel), but admittedly this solid is certainly formed by both mechanisms. Moreover, it is not impossible that an element absent from the glass but supplied by the environment could take part in its formation and modify the diffusion processes. A such mechanism has been illustrated by Chave [56] working on a simplified glass.

3.1.2. Depleted gel

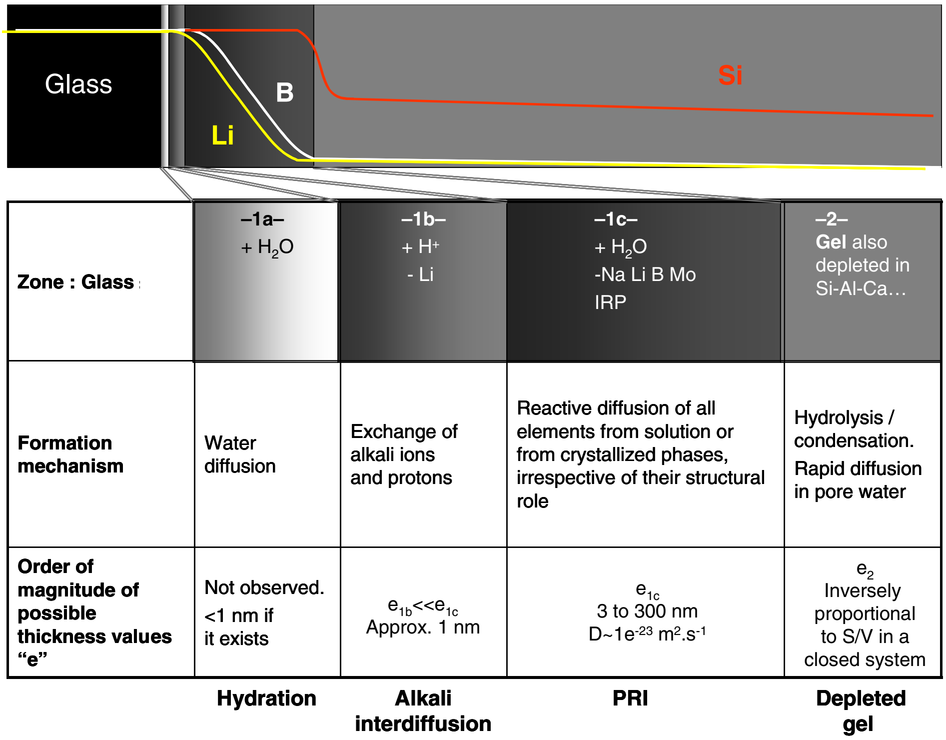
When the glass is significantly altered – for example by renewal of a pure water solution or when the glass thickness that must be dissolved to saturate the solution is no longer negligible compared with characteristic diffusion thickness resulting in the PRI – a low-density gel forms that is highly depleted in Si, Al and Ca compared with initial glass. The passivating role of this amorphous and porous structure is significantly diminished [62]. It is the seat of dissolution-condensation reactions that produce a smooth solid/solution interface corresponding to Porod regimes identified by Small Angle X-ray Scattering [57]. The density, composition, and passivating properties of this gel can vary with the leaching conditions. All these gel compositions can be assigned solubility products, provided a satisfactory thermodynamic description is available. This task is potentially complex, and we can question its interest, as even minor changes in composition and density are liable to modify the transport capabilities of these materials by several orders of magnitude [62]. What is important in the geological disposal context is to determine whether the gel producing the optimum rate decrease (PRI) is likely to form or not.

Fig. 8 is a simplified representation of the four zones defined above and their presumed formation mechanisms.

3.2. Crystallized secondary phases

Three main difficulties are encountered in observing and identifying crystallized secondary phases:

- The quantities of these phases are sometimes small, especially during residual rate conditions with SON68 glass, and the crystals are often very small: suitable separation and characterization techniques must therefore be used [56].
- SON68 glass contains a large number of elements: the effects of the glass composition on the nature of the crystallized minerals formed [63] must be determined, particularly through the study of simplified glass compositions. It is difficult to characterize phases with a large number of elements and to evaluate their free enthalpies of formation considering the numerous substitutions and solid solutions likely to exist in such systems.



Zone : Glass	–1a– + H_2O	–1b– + H^+ - Li	–1c– + H_2O -Na Li B Mo IRP	–2– **Gel** also depleted in Si-Al-Ca…
Formation mechanism	Water diffusion	Exchange of alkali ions and protons	Reactive diffusion of all elements from solution or from crystallized phases, irrespective of their structural role	Hydrolysis / condensation. Rapid diffusion in pore water
Order of magnitude of possible thickness values "e"	Not observed. <1 nm if it exists	e_{1b}<<e_{1c} Approx. 1 nm	e_{1c} 3 to 300 nm D~1e^{-23} m^2.s^{-1}	e_2 Inversely proportional to S/V in a closed system
	Hydration	**Alkali interdiffusion**	**PRI**	**Depleted gel**

Fig. 8. Diagram of the different amorphous phases likely to be observed and their formation mechanisms.

- The formation of crystallized secondary phases can be kinetically limited: the investigation of natural or archaeological analogs can provide precious data [64,65].

The following crystallized secondary mineral phases are observed when borosilicate glass is leached:

- *Phyllosilicates*: these structures organized in sheets can be observed by scanning and transmission electron microscopy [66] (Fig. 9 and Fig. 10). They are difficult to characterize by X-ray diffraction analysis (XRD), although Muller et al. identified nontronite $(Na,K)_{0.8}(Fe,Mg)_{1.3}(Al,Si)_4O_{10}$ in glass formulated to immobilize West Valley nuclear waste [63]. T. Chave [56], using XRD after separating the alteration products from the SON68 glass, demonstrated the formation of nontronite, sauconite, and pimelite with the following generic formulas: $Na_{0.3}\mathbf{Fe}^{3+}_2Si_3AlO_{10}(OH)_2\cdot 4(H_2O)$, $Na_{0.3}\mathbf{Zn}_3Si_3AlO_{10}(OH)_2\cdot 4(H_2O)$ and $Ni_3Si_4O_{10}(OH)_2\cdot 5(H_2O)$. None of these studies proposes a precise analysis of the composition of these phases, although SIMS and ToF-SIMS analyses [67,56] show that they are the seat of recondensation of zinc, nickel, manganese and, to a lesser extent, iron. In a closed system, their Zn/Ni/Mn stoichiometry is near that of the initial glass. These analyses also showed that an appreciable fraction of sodium and especially lithium from the glass is incorporated in these phases.

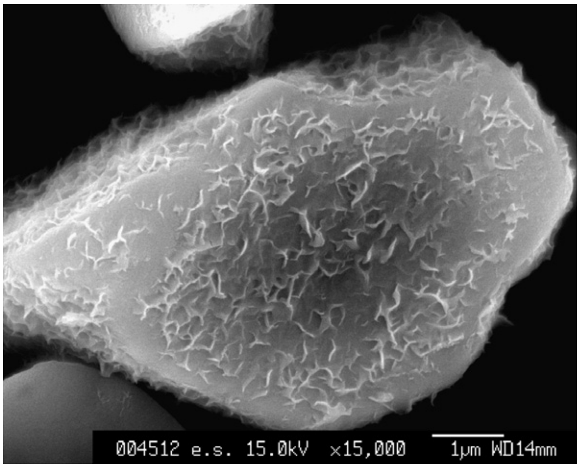


Fig. 9. Phyllosilicate flakes on the surface of SON68 glass grains leached for 1600 days at 90 °C at 2000 cm^{-1}.

- *Calcium and rare-earth phosphates*: the small concentrations of these elements in the glass SON68 often make it necessary to leach large quantities of glass for scanning electron microscope observation [68,16,69]. These minerals generally exhibit very low solubility, and can be observed in Soxhlet mode when leaching glass rich in phosphorus and calcium [70].

At temperatures exceeding 150 °C or at pH values above 10 at 90 °C, the following phases are also likely to precipitate:

- *Zeolites*: the phases identified on SON68 glass include analcime $NaAlSi_2O_6\cdot H_2O$, and pollucite $(Cs,Na)_2Al_2Si_4O_{12}\cdot 2H_2O$ [71,72,54,56]. When the initial composition of glass formulated to immobilize West Valley nuclear waste included potassium, Muller et al. [63] also observed phillipsite $(K,Na,Ca_{0.5})_{1-2}(Si,Al)_8O_{16}\cdot 6H_2O$.
- *Hydrated calcium silicates*: the consumption of aluminum from the gel by precipitation of zeolites destabilizes the gel. This mechanism could account for the precipitation of hydrated calcium silicates generally concomitant with the formation of zeolites (Fig. 12) observed by Ribet and Gin [54], Muller et al. [63] and Chave [56]. Although the reports did not specify their exact compositions, their Si/Ca ratio can be expected to depend on the availability of the two elements and to diminish with the pH given the decreasing solubility of silica and the increasing solubility of calcium hydroxide as the pH diminishes.

The mechanisms limiting the formation of these phases must still be determined to evaluate their role with regard to the residual rate:

- Phyllosilicates precipitate rapidly at equilibrium with solution. Valle [62,72] showed that the ^{29}Si and ^{18}O isotopic ratios observed in phyllosilicates are the same as in the leaching solution (enriched in these isotopes for experimental purposes). Their precipitation kinetics should thus be limited by the availability of a constituent element: Zn, Ni, Mg or even Fe [6]. This hypothesis is supported by experiments conducted by Chave [56] in which the addition of Zn^{2+} and Ni^{2+} in solution led to the formation of sauconite and hemimorphite (for Zn) and pimelite (for Ni), thereby sustaining glass alteration near the initial rate.
- The pH is a key parameter for zeolite precipitation. Gin et al. [53] showed by controlled pH experiments that the pH at 90 °C must exceed 10 to initiate the precipitation of sodium zeolites during SON68 glass leaching. Ribet et al. [73] studied

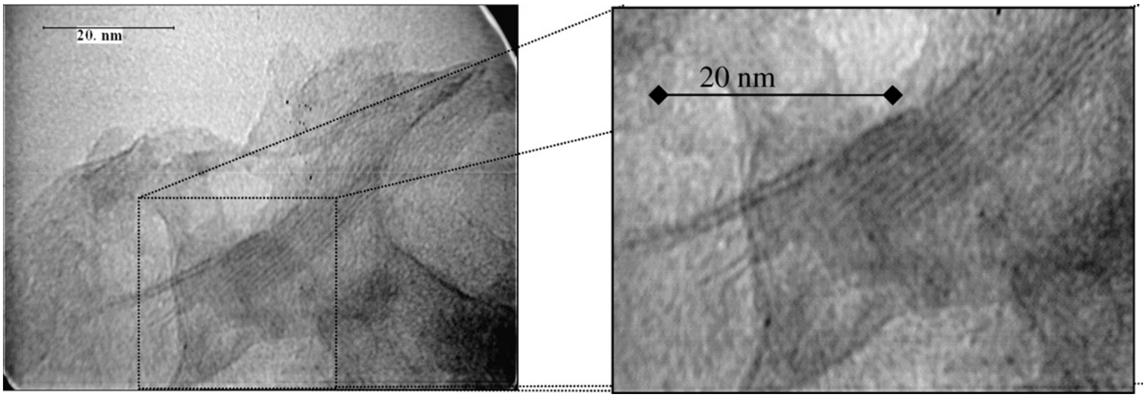


Fig. 10. Transmission electron microscope images of phyllosilicates precipitated on the surface of SON68 glass after 304 days of leaching in initially pure water at 150 °C at 2000 cm^{-1}.

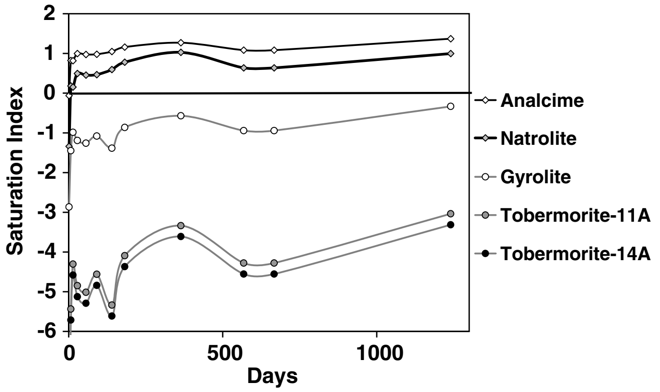


Fig. 11. Saturation indexes calculated for two zeolites and three calcium silicates (SON68 glass leached in initially pure water at 90 °C and 80 cm^{-1}). During this experiment the pH at 90 °C stabilized at 9.3 ± 0.1 after a few weeks and remained practically constant thereafter.

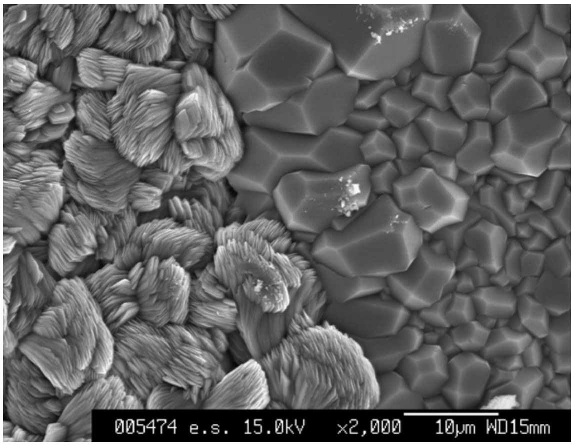


Fig. 12. SEM images of hydrated calcium silicates (left) and zeolites (right) in SON68 glass alteration products after 550 days of leaching in initially pure water at 165 °C and 2000 cm^{-1} [56].

100 glass compositions leached for ten years in initially pure water at 90 °C in a closed system, and observed that only the glasses that reached a pH above 9.6 at 90 °C were subject to precipitation of potassium zeolites. In this case they also observed a resumption of alteration. The only conditions under which zeolites have been observed during SON68 glass leaching are for temperatures exceeding 150 °C or for pH values above 10 at 90 °C. Three hypotheses can account for their absence at 90 °C at pH values of less than 10:

- A thermodynamic limitation. This hypothesis does not appear to be supported by calculations: the saturation indexes of solutions with respect to analcime and natrolite in the chess.tdb database [74] taken from the EQ3/6 database [75] show that these phases quickly approach equilibrium or even become slightly supersaturated when SON68 glass is leached in initially pure water (Fig. 11).
- Kinetic limitations during nucleation or growth. Few zeolite crystals are observed, and they may even be localized on the reactor walls in large dimensions [56] suggesting that the nucleation kinetics can be the limiting factor.
- Techniques poorly suited to the objects being observed. The crystals may well be small and poorly crystallized, making them difficult to identify. Under residual rate conditions SON68 glass is leached to a depth of about twenty nanometers a year. This indicates the very small dimensions of the neoformed zeolites that could be expected if they were uniformly distributed on the surface, or the small number that would be obtained if they were of larger size.

4. GRAAL model

This exhaustive review of SON68 nuclear glass alteration mechanisms in relation with the different kinetic regimes highlights recent progress in understanding the phenomena involved. It is now possible to propose a new model, better suited than the previous ones for simulating the long-term behavior of this glass under geological repository conditions.

Generally the model is based on identifying the predominant mechanisms together with a few simplified hypotheses. By disregarding secondary mechanisms the model can be developed with a limited number of parameters compatible with the quantity of experimental data that can be acquired. These simplified hypotheses have been validated by the ability of the model not only to account for the experimental data with sufficient precision but also to predict results.

The key mechanisms of SON68 glass alteration described in detail in the first part of this article are summarized below and shown graphically in Fig. 13:

- Exchange and hydrolysis reactions involving the mobile glass constituents (alkalis, boron, etc.) rapidly occur during the initial instants.
- Slower hydrolysis, especially of silicon, results in the existence of an initial glass dissolution rate.
- The difference between these two kinetics results in the creation of an amorphous layer at the glass/solution interface regardless of the alteration conditions. This layer is gradually reorganized by hydrolysis and condensation mechanisms.
- The amorphous layer dissolves as long as the solution is not saturated with respect to its constituent elements (Si, Zr, Al, Ca, etc.). Renewal of a pure water solution sustains the dissolution process.
- The amorphous layer constitutes a barrier against the transport of water toward the glass and of solvated glass ions into solution. The existence of this transport-inhibiting effect rapidly causes this layer to control glass alteration.
- Some glass constituent elements precipitate as crystallized secondary phases. The precipitation of these crystallized

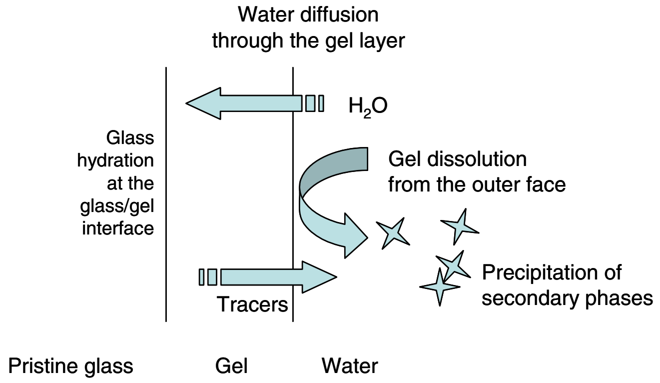


Fig. 13. Simplified diagram of the predominant mechanisms of SON68 glass alteration taken into account in the GRAAL model.

phases on the external surface or in solution can sustain glass alteration.

The principal simplifying hypotheses are the following:

- Only water diffusion in the PRI is considered to be rate-limiting. A single apparent diffusion coefficient is used to simulate water diffusion in the PRI and diffusion of hydrolyzed and solvated glass constituent elements in solution.
- Zones 1a (water diffusion in the glass), 1b (proton/alkali ion exchange) and 2 (depleted gel) are ignored.
- The reactivity of the PRI with the leaching solution is described by a thermodynamic equilibrium.

The model based on these hypotheses is known as GRAAL, for *Glass Reactivity with Allowance for the Alteration Layer (Graal is the French translation for Grail)*. Regardless of whether via the PRI or crystallized secondary phases, the complete alteration film determines the reactivity of the glass in solution. The equations used in this model are described below with the following simplification: only boron and silicon described. As a rough approximation the behavior of the mobile elements is thus considered comparable to boron, and that of the gel-forming elements comparable to silicon. This simplification does not dissimulate the need for applying this formalism to all the chemical elements of the glass.

4.1. Model equations

The simplified system is described by five basic equations:

(1) an equation describing the kinetics of dissolution of the PRI,
(2) an equation describing the kinetics of formation of the PRI,
(3) an equation describing the kinetics of precipitation of neoformed phases,
(4) a silicon mass balance equation,
(5) a boron mass balance equation.

The following nomenclature is used in the equations.

- *Observable quantities*
  - $e(t)$, μm: PRI thickness at time t
  - $E(t)$, μm: total dissolved PRI thickness at time t
  - $C_{\mathrm{Si}}(t)$, kg m^{-3}: silicon concentration in the aqueous solution at time t
  - $C_{\mathrm{B}}(t)$, kg m^{-3}: boron concentration in the aqueous solution at time t
  - $M_{\mathrm{pr}}(t)$, kg: mass of precipitate at time t
- *Leaching conditions*
  - S, m^2: reactive surface area of the glass
  - Ω, m^3: reactor volume
  - Q, m s^{-1}: solution volume flow rate
- *Intrinsic glass parameters*
  - $C_{v\mathrm{Si}}$, kg m^{-3}: silicon mass concentration in SON68 glass
  - $C_{v\mathrm{B}}$, kg m^{-3}: boron mass concentration in SON68 glass
- *Model parameters*
  - C_{sat}, kg m^{-3}: silicon concentration at saturation in equilibrium relation between PRI and aqueous solution. The effect of silicon speciation is not described here
  - r_{hydr}, m s^{-1}: hydrolysis rate of soluble glass constituents (boron, alkali ions) during creation of the PRI
  - r_{disso}, m s^{-1}: PRI dissolution rate in pure water
  - D_{PRI}, m^2 s^{-1}: water diffusion coefficient in PRI
  - k, m s^{-1}: precipitation rate parameter for secondary silica phases
  - S, m^2: surface area on which secondary phases precipitate
  - ρ, kg m^{-3}: density of secondary phases

Note: only a single type of secondary phase is considered here.

4.1.1. Eq. (12): dissolution of the passivating reactive interphase

The PRI is assumed to dissolve as a result of the affinity of silicon – its main constituent – with respect to the aqueous solution. A first-order law is postulated to describe this affinity effect with two parameters: r_{disso} corresponding to pure water, and C_{sat} corresponding to the H_4SiO_4 concentration at which dissolution ceases. This gives the following equation:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = r_{\mathrm{disso}}\left(1 - \frac{C_{\mathrm{Si}}(t)}{C_{\mathrm{sat}}}\right). \tag{12}$$

4.1.2. Eq. (13): formation of the passivating reactive interphase

The PRI is assumed to form by water diffusion at the interface with the pristine glass, which hydrolyzes the most soluble glass elements, especially boron. The water diffusion coefficient in the PRI, D_{PRI}, is characteristic of a reactive interdiffusion coefficient of about 10^{-22} m^2/s. Moreover, hydrolysis of the B–O–Si bonds is theoretically limited by kinetics expressed as a rate, r_{hydr}. This gives the following equation, in which the water diffusion profile in the PRI is assumed linear in the interval $[E(t), E(t) + e(t)]$:

$$\frac{\mathrm{d}e}{\mathrm{d}t} = \frac{r_{\mathrm{hydr}}}{1 + \frac{e r_{\mathrm{hydr}}}{D_{\mathrm{IRP}}}} - \frac{\mathrm{d}E}{\mathrm{d}t}. \tag{13}$$

4.1.3. Eq. (14): secondary phase precipitation kinetics

In the GRAAL model, secondary phase precipitation concerns only silicon by a sink term; it is assumed that only a single phase is formed. The precipitate mass formed over time is assumed in this model to follow a linear relation described by the following equation, in which the rate term k' is applicable to a precipitation surface area S' for a precipitate of density ρ':

$$\frac{\mathrm{d}M_{\mathrm{pr}}}{\mathrm{d}t} = \rho' k' S'\left(\frac{C_{\mathrm{Si}}(t)}{C_{\mathrm{sat}}}\right). \tag{14}$$

4.1.4. Eq. (15): silicon balance

- The silicon concentration variation in the reactor volume Ω is determined by the algebraic sum of the following three terms:the silicon contribution (source term) due to dissolution of the PRI, with a surface area S and a silicon mass concentration equal to $C_{v\mathrm{Si}}$.
- The sink term corresponding to the mass of silicon precipitated in the reactor, given by relation (14).
- The sink term due to silicon removal by the volume flow rate Q.

This gives the following equation:

$$\Omega\frac{\mathrm{d}C_{\mathrm{Si}}}{\mathrm{d}t} = SC_{v\mathrm{Si}}\frac{\mathrm{d}E}{\mathrm{d}t} - QC_{\mathrm{Si}}(t) - \frac{\mathrm{d}M_{\mathrm{pr}}}{\mathrm{d}t}. \tag{15}$$

4.1.5. Eq. (16): boron balance

The boron balance (boron is an overall glass alteration tracer) is obtained in a similar manner to the silicon balance, except that boron does not precipitate and the source term is specified from the total quantity of altered glass, $E(t) + e(t)$:

$$\Omega \frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = SC_{v\mathrm{B}} \frac{\mathrm{d}(E+e)}{\mathrm{d}t} - QC_{\mathrm{B}}(t). \tag{16}$$

4.2. Discussion

Although this overview of the current state of knowledge focuses mainly on SON68 glass, the phenomena described can to a large extent be generalized to other compositions (nuclear glasses, natural or archaeological silicate glasses), although glass composition variations can be expected to modify key parameter values (initial rates, diffusion coefficients, residual rates, solution pH, etc.) and therefore the predominance of certain mechanisms depending on the alteration conditions. Nevertheless, the nature of the precipitated secondary minerals is only indirectly related to the glass composition; only the thermodynamic and kinetic data intrinsic to the chemical nature of the precipitate mineral are pertinent: the data acquired on secondary mineral phases can therefore be used independently of the particular glass being investigated. The question remains open as to whether this is also the case, even as a rough approximation, for the chemical properties of the passivating reactive interphase. Can the PRI legitimately be described as a mineral phase in its own right at equilibrium with solution? If not, what are the repercussions of this error?

Kinetic laws have long focused exclusively on the hydrolysis mechanisms resulting in congruent dissolution and have therefore encountered difficulties in accounting for glass behavior under all experimental conditions, especially when two other key mechanisms are involved: diffusion phenomena in the solid (which are no longer negligible when the rates drop below about $10\,\mathrm{nm\,d^{-1}}$) and phenomena involving reorganization of the gel and precipitation of crystallized secondary phases: the importance of these mechanisms on kinetic predictions – especially in a reactive environment (for example the reaction between silicon and metal corrosion products) – is such that a kinetic model of glass alteration cannot omit a comprehensive formal description.

Experience has shown that the glass alteration rate can be constant, exponentially decreasing, or slightly decreasing especially as a function of $t^{-1/2}$. Existing laws attempt to account for these kinetics and thus tend to converge toward mathematical formalisms that are often similar (the onset of saturation with or without allowance for diffusive transport) and even identical in some cases. Yet they are based on very different theories: an overall affinity function taking all the glass constituent elements into account, transition state theory, and the theory of a passivating interphase. The phenomenology of SON68 glass alteration in initially pure water reviewed here is not sufficient to establish any particular kinetic law. The law must also be applied to a variety of glass compositions in a range of chemical environments to consolidate its robustness and guarantee its predictability.

5. Concluding remarks

Investigating the phenomena involved and the effects of influential parameters contributes to identifying the mechanisms and kinetics of nuclear glass alteration and to developing a model. We have therefore reviewed the phenomenological aspects observed when SON68 glass is leached in initially pure water with two main objectives: define a rate law for glass alteration, and describe the assemblage of amorphous and crystallized phases arising from glass alteration in its environment.

The development of the formal model for SON68 glass and its confrontation with experimental data will be the subjects of two additional articles.

- The first will describe the solution to the system of differential equations derived from the preceding hypotheses. It will propose a simplified chemical description (silicon and the mobile elements will be described). Its primary objective will be to determine the characteristic time values and orders of magnitude according to different hypotheses concerning the disposal concept.
- The second will be based on a code of speciation and thermodynamic solid/solution equilibria. It will propose and justify a simplification of the equations necessary for a detailed description of the evolution of each chemical element during leaching. It will be capable of predicting element distributions between the solution, the gel and crystallized secondary phases, of predicting the pH and, more generally, of coupling geochemical transport processes in the gel at nanometer scale and in the near field at centimeter scale.

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