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Simulated alteration tests on non-radioactive SON 68 nuclear glass in the presence of corrosion products and environmental materials

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Abstract

Alteration tests with non-radioactive French SON 68 (R7T7-type) nuclear glass in the presence of simulated metal canister corrosion products (CP) or environmental materials (EM) were simulated using the LIXIVER 2 computer code. The code incorporates hypotheses concerning glass alteration in aqueous media based on the first-order kinetic law for total silicon with variable silicon retention in the gel and silicon diffusion in the gel interstitial water, coupled with silicon adsorption and diffusion in the materials in contact with the glass. The canister CP are considered as a localized medium with a mass adsorption capacity R_{ad}, while the EM are considered as a porous medium with a diffusion coefficient D_p and a distribution coefficient K_d. LIXIVER 2 simulates these media in one-dimensional Cartesian geometry. The K_d values determined by simulating alteration tests logically increase with the aggressiveness of the materials with respect to the glass. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Calculation codes describing glass alteration in aqueous media, including GLASSOL [1,2], STRAG 4 [3] or LIXIVER [4], were developed from numerous leaching experiments with high-level waste containment glass. These models, however, are unable to account for the results of leach tests performed in the presence of simulated corrosion products (CP) from a metal canister or overpack; similarly, glass alteration in the presence of environmental materials (EMs) such as clay or granite, or of materials constituting a possible nearfield engineered barrier, is not satisfactorily modeled.

In a geological repository environment, the glass would be altered in the presence of these materials. The models must therefore satisfactorily account for their effects in order to estimate the alteration rate of a glass block. A new version of the LIXIVER code, LIXIVER 2, was developed to take into account the effects of CP as well as engineered barrier or site materials. The validity of the hypotheses used to simulate CP and EM effects on the alteration of non-radioactive French SON 68 (R7T7-type) nuclear glass was tested by comparing the results of leach tests with the calculated results provided by LIXIVER 2.

It must be noted that LIXIVER 2 is a scientific code based on several hypotheses taking into account the current knowledge of the glass alteration mechanisms. The aim of this work is to estimate the pertinence of hypotheses used to take into account the CP and EM influences on glass alteration. The results of these calculations will help to develop an operational code destinated to glass performance assessment studies in a geological repository.

2. The LIXIVER 2 code

LIXIVER 2 uses the basic hypotheses of the LIXIVER code to describe the principal glass alteration mechanisms, and is applicable to monolithic glass specimens leached at laboratory scale. The borosilicate glass alteration rate is controlled both by H_4SiO_4 activity in solution [5] and by silicon diffusion in the gel. The gel is

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Notation

a,b	retention function parameters
C_g	silicon concentration in the glass
$C_{Si}(t)$	silicon concentration in the leachate at the gel/solution interface
C_{Si}^{int}	total silicon concentration at the pristine glass/gel interface
C_{Si}^{slb}	solulizable silicon concentration
C_{Si}^{0}	initial silicon concentration in the leachate
C_1	silicon concentration at the material/reactor interface
C_{EM}^{0}	initial silicon concentration in the pores of the environmental material
C^*	total silicon concentration at saturation with respect to the glass
$\bar{C}$	silicon mass concentration fixed on the environmental material (ratio of Si mass to EM mass)
$C(y,t)$	silicon concentration in environmental material pore water
D_g	bulk silicon diffusion coefficient in gel pore interstitial water
D_p	silicon diffusion coefficient in environmental material pores
f	silicon retention factor in the gel
f_{max}	maximum silicon retention factor in the gel
F	leaching solution renewal rate (corresponding to solution flow rate)
K_d	silicon distribution coefficient in EM
L	thickness of environmental material
M_{CP}	corrosion product mass in the reactor
M_{Si}^{CP}	silicon mass adsorbed on CP
r	glass dissolution rate
r_0	initial glass dissolution rate
R	silicon retardation factor in the EM
R_{ad}	corrosion product adsorption capacity
S	glass specimen surface area
t	time
t_0	corrosion product saturation time
V	leaching solution volume surrounding the glass
x	gel thickness (time-dependent)
x_0	gel thickness at time t_0
y	spatial variable in environmental material
ρ	dry material density
ω	material porosity

thus considered as a porous medium constituting a diffusion barrier and partially retaining silicon. Glass alteration is described by the following six hypotheses:

(1) The gel is considered as a porous medium constituting a diffusion barrier and partially retaining silicon.

(2) The alteration rate is based on a first-order law with respect to the deviation of the silicic acid activity from saturation. However, as the pH at the glass/gel reaction interface is assumed equal to the solution pH, the activity ratio is thus equal to the concentration ratio; hence the following kinetic law:

$$r = r_0\left(1 - \frac{C_{Si}^{int}}{C^*}\right), \tag{1}$$

where r is the instantaneous glass dissolution rate, r_0 the initial glass dissolution rate, C_{Si}^{int} the total silicon concentration at the pristine glass/gel interface, and C^* is the total silicon concentration for which glass alteration stops (r_0, C_{Si}^{int} and C^* are pH- and temperature-dependent).

(3) Silicon retention in the gel formed during glass alteration is taken into account by a retention factor f according to an empirical relation [4]. The silicon retention factor f corresponds to the part of silicon resulting from glass dissolution and trapped at the pristine glass surface to form the gel layer. The silicon retention factor in the gel varies as a linear function of the silicon concentration in the leachate

$$f = a + bC_{Si}(t), \tag{2}$$

where $C_{Si}(t)$ is the silicon concentration in the leachate at the gel/solution interface. The a and b parameter values are determined experimentally; f_{max} is the upper limit on the value of f, and is near the maximum value of 0.95 observed during leach testing at a high degree of reaction progress.

(4) Silicon diffusion in the gel is modeled by an apparent silicon diffusion coefficient D_g in the gel pore water. This coefficient takes into account diffusion per se, as well as silicon hydrolysis and condensation phenomena. The apparent diffusion may be very low compared with the diffusion of a chemical species in the water.

(5) The silicon concentration gradient in the gel interstitial water is assumed linear. Allowing for the equal material flows at the pristine glass/gel interface, Eq. (1) becomes

$$r = r_0\left(\frac{1 - (C_{Si}(t)/C^*)}{1 + r_0(C_{Si}^{slb}x/D_g C^*)}\right), \tag{3}$$

where D_g is the apparent silicon diffusion coefficient in gel pore interstitial water, x the time-dependent gel thickness, C_g the silicon concentration in the glass, and C_{Si}^{slb} is the solubilizable silicon concentration:

$$C_{Si}^{slb} = C_g(1 - \min[f_{max}; f]). \tag{4}$$

(6) Glass alteration is assumed to be a constant-volume phenomenon, i.e., the gel thickness is equal to the

altered glass thickness. This hypothesis is experimentally checked for glass alteration in the presence of CP and EM, except for Boom clay.

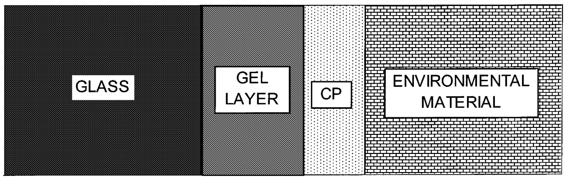
Combining the above relations with the silicon material balance in the leachate yields the following equation system [6] describing glass alteration in an aqueous medium in the absence of CP and EM:

$$\begin{aligned}
&\frac{\partial x}{\partial t} = r,\\
&\frac{\partial C_{\mathrm{Si}}(t)}{\partial t} = rC_{\mathrm{Si}}^{\mathrm{slb}}\frac{S}{V} + F\left(C_{\mathrm{Si}}^{0} - C_{\mathrm{Si}}(t)\right),\\
&C_{\mathrm{Si}}^{\mathrm{slb}} = C_g(1 - \min\,[f_{\max};f]),\\
&r = r_0\left(\frac{1-(C_{\mathrm{Si}}(t)/C^*)}{1+r_0(C_{\mathrm{Si}}^{\mathrm{slb}}x/D_{\mathrm{g}}C^*)}\right),\\
&C_{\mathrm{Si}}(0) = C_{\mathrm{Si}}^{0}, \qquad x_{t=0} = 0,
\end{aligned} \tag{5}$$

where t is the time, S the glass specimen surface area, V the leaching solution volume around the glass, F the leaching solution renewal rate (solution flow rate), and C_{Si}^{0} is the initial silicon concentration in the leachate.

Two categories of solids liable to be in contact with the glass in a geological repository environment were defined: products simulating those produced by corrosion of the metal canister, and materials constituting the nearfield engineered barrier and the surrounding geological formation. Their influence on the glass alteration kinetics, as determined by leach tests performed with such materials, was taken into account differently for each category. Silicon adsorption alone is considered for the simulated CP, while silicon diffusion in the material pores is also taken into account for the EM.

The CP and EM are taken into account as shown schematically in the following diagram, where the gel, the CP and the EM are porous media:



When no canister CP are present, the EM are directly in contact with the gel.

2.1. Modeling the influence of corrosion products

The hypotheses used to model the influence of the CP are based on observations [7] during leach tests with non-radioactive SON 68 glass in the presence of materials simulating metal canister degradation products. The tests resulted in very low silicon concentrations in solution at the beginning of the leaching period, subsequently rising to the levels obtained during tests without CP. The time period during which the silicon concentrations remained low was proportional to the CP mass. Consequently, the influence of CP is modeled by assuming silicon is adsorbed on them until saturation occurs, after which alteration continues as if the CP were inert with respect to the glass.

The influence of the CP on glass alteration was taken into account by the following hypotheses:

- The leachate pH is considered constant during a given time period. Several time periods can be defined. A different pH value can be used for each time period.
- The quantity of CP present in the reactor is taken into account by their mass M_{CP}.
- Silicon adsorption on the CP is taken into account by assuming a dimensionless adsorption capacity R_{ad} expressed in grams of silicon per gram of CP.
- Until silicon saturation occurs in the CP, the Si concentration in the leaching solution is nil: $C_{\mathrm{Si}}(t) = 0$.
- When the CP are saturated (i.e., when they have adsorbed a quantity of silicon equal to the product $M_{\mathrm{CP}} \times R_{\mathrm{ad}}$), glass alteration is calculated by considering $C_{\mathrm{Si}}(t) \neq 0$, with the initial conditions $C_{\mathrm{Si}}(t_0) = 0$ and $x_{t-t_0} = x_0$ (where t_0 is the instant of CP saturation [1] and x_0 is the gel thickness at time t_0).

2.2. Modeling the influence of environmental materials

Leach tests [8] have shown that non-radioactive SON 68 glass alteration is larger when EM – notably clay – are present. This phenomenon can be ascribed to the interaction between silicon (a glass network former) and clay. Silica may be consumed by clay materials according to various mechanisms, directly from the interstitial fluid, or through interactions with clay constituents, or by crystallization of clay phases in the presence of excess silicon in solution. The silica consumption mechanisms are the following:

- Nucleation and growth from the interstitial fluid [9–11]. Silicic acid may precipitate as various forms of silica (opal, chalcedony, etc.) through a homogeneous seeding process.
- Silica growth from pre-existing siliceous phases [10,12,13] (e.g., detrital quartz) and by adsorption on phyllosilicates (e.g., smectite, kaolinite) through a heterogeneous seeding process on a surface.
- Transformation of the initial clay into more siliceous clay: smectitization [14,15].
- Interfoliar silicon retention [16].
- Siliceous phase deposits and plugging, combining chemistry with transport in clay media [9,10].

Faced with the complexity of the potential mechanisms, we modeled silicon adsorption on the EM in LIXIVER 2

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[1] $t_0 = 0$ if no corrosion products are present.

by means of a silicon distribution coefficient K_d between the solution and the EM. All the SON 68 glass alteration experiments with various clays showed that high alteration rates were maintained over the time necessary to saturate the clay adsorption sites; the time period is proportional to the ratio of the clay mass and the glass surface area. No effect of possible secondary silicon precipitation has been identified to date for this type of glass. As the EM are porous media, we also allowed for silicon removal from the EM by diffusion. Silicon diffusion in the EM is handled by Fick's second law in one-dimensional Cartesian geometry. The GLADIS code [17] was also developed from these hypotheses. The main differences between the two codes are that GLADIS does not take into account the protective properties of the gel that forms on the glass surface, and that it is applicable in cylindrical geometry.

The following hypotheses are postulated to allow for the effect of the EM on glass alteration:

- The leachate pH is considered constant during a given time period. Several time periods can be defined. A different pH value can be used for each time period. Most tests conducted with EM show that the leachate pH tends toward constant values, probably as a result of the buffering effect of the EM.
- Silicon is assumed to be the only glass element interacting with the EM.
- When both CP and EM are present, silicon adsorption occurs on the EM after saturation of the CP.
- The silicon distribution between the solution and the solid EM is assumed to be linear and reversible, resulting in a constant silicon distribution coefficient K_d

  $$K_\mathrm{d} = \frac{\overline{C}}{C(y,t)}, \tag{6}$$

  where $\bar{C}$ is the silicon mass concentration fixed on the environmental material (ratio of Si mass to EM mass) and $C(y,t)$ is the silicon concentration in environmental material pore water.
- The preceding hypothesis leads to allowance for silicon adsorption in the environmental material by means of a retardation factor R

  $$R = 1 + \frac{1-\omega}{\omega}\rho K_\mathrm{d}, \tag{7}$$

  where ω is the material porosity and ρ is the dry material density.

3. Model parameters

Glass alteration and the influence of the CP and/or EM are solved by means of the following coupled equation systems.

3.1. Glass alteration prior to corrosion product saturation

$$\begin{gathered}
\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{r_0}{1 + (r_0 C_\mathrm{Si}^\mathrm{slb} x / D_\mathrm{g} C^*)}, \\
C_\mathrm{Si}(t) = 0, \\
\frac{\mathrm{d}M_\mathrm{Si}^\mathrm{CP}}{\mathrm{d}t} = S C_\mathrm{Si}^\mathrm{slb} \frac{\mathrm{d}x}{\mathrm{d}t} + FVC_\mathrm{Si}(0), \\
x_{t=0} = 0, \\
M^\mathrm{CP}_{\mathrm{Si}\ t=0} = 0, \\
M^\mathrm{CP}_{\mathrm{Si}\,t=t_0} = S C_\mathrm{Si}^\mathrm{slb} x_{t=t_0} + (1 - Ft_0) V C_\mathrm{Si}(0) = M_\mathrm{CP} R_\mathrm{ad},
\end{gathered} \tag{8}$$

where $M_\mathrm{Si}^\mathrm{CP}$ is the silicon mass adsorbed on the CP and $C_\mathrm{Si}(0)$ is the initial silicon concentration in the leachate. Equation system (8) is solved for any time t up to and including t_0.

3.2. Glass alteration after corrosion product saturation

$$\begin{gathered}
\frac{\mathrm{d}x}{\mathrm{d}t} = r_0 \left(\frac{1 - (C_\mathrm{Si}(t)/C^*)}{1 + r_0 (C_\mathrm{Si}^\mathrm{slb} x / D_\mathrm{g} C^*)} \right), \\
\frac{\mathrm{d}C_\mathrm{Si}}{\mathrm{d}t} = S C_\mathrm{Si}^\mathrm{slb} \frac{\mathrm{d}x}{\mathrm{d}t} - F(C_\mathrm{Si}(t) - C_\mathrm{Si}(0)), \\
x_{t=t_0} = x_0, \\
C_\mathrm{Si}(t = t_0) = \max \left[0; C_\mathrm{Si}(0) - \frac{M_\mathrm{CP} R_\mathrm{ad}}{V} \right],
\end{gathered} \tag{9}$$

Equation system (9) is solved for any t after t_0.

3.3. Glass alteration in the presence of environmental materials

$$\begin{gathered}
\frac{\partial C(y,t)}{\partial t} = \frac{D_\mathrm{p}}{R} \frac{\partial^2 C(y,t)}{\partial y^2}, \\
C_\mathrm{Si}^\mathrm{slb}(C(0,t)) \frac{\mathrm{d}x}{\mathrm{d}t} = -\omega D_\mathrm{p} \frac{\partial C(0,t)}{\partial y}, \\
\omega D_\mathrm{p} \frac{\partial C(L,t)}{\partial y} = -\frac{FV}{S}(C(L,t) - C_1), \\
\frac{\mathrm{d}x}{\mathrm{d}t} = r_0 \left(\frac{1 - C_\mathrm{Si}(t)/C^*}{1 + r_0 C_\mathrm{Si}^\mathrm{slb} x / D_\mathrm{g} C^*} \right), \\
C(y,0) = C^0_\mathrm{EM};\ x_{t=0} = 0,
\end{gathered} \tag{10}$$

where D_p is the silicon diffusion coefficient in the material pores, y spatial variable in the environmental material ($y = 0$ at the gel/EM interface, $C(0,t)$ thus corresponds to $C_\mathrm{Si}(t)$), L the material thickness, C_1 the silicon concentration at the material/reactor interface, and C^0_EM is the initial silicon concentration in the material pores.

The behavior of boron (a glass alteration tracer) in the environmental material is described by equation system (10) where $R = 1$, since boron is not adsorbed by the EM. The boron concentrations at the pristine glass/gel interface are given by the glass matrix alteration rate.

3.4. *LIXIVER* 2 code input parameters

Lixiver 2 requires input data concerning the glass and the simulated test conditions. Some parameter values are fixed, while others are adjusted to fit the experimental results. All the simulated tests discussed in this article were carried out at 90°C. The input parameters included the following:

- Test temperature: $T = 90°\mathrm{C}$.
- Leachate pH.
- pH-dependent variation of r_0 according to the following relation [18]: $r_0 = K[\mathrm{H}^+]^{-N}$ at 90°C, where $K = 2.0 \times 10^3$ g m^{-2} d^{-1} and $N = 0.39$.
- Apparent glass solubility (mol$_{\mathrm{Si}}$ l^{-1}); the default value of $10^{-3.01}$ mol l^{-1} was measured by Advocat [19], but this value is adjustable.
- Leaching solution renewal rate: $F = 0$ d^{-1}, since all the tests were simulated under static conditions.
- Glass specimen surface area to leaching solution volume ratio: S/V (cm^{-1}).
- Silicon concentration in the leachate: $C^0_{\mathrm{Si}} = 0$ g m^{-3} (all the tests were simulated in ultrapure water).
- Silicon retention factor in the gel: $f = 0.2 + 0.008 \times C_{\mathrm{Si}}(t)$, with $f_{\max} = 0.95$.
- Bulk silicon diffusion coefficient in gel pore interstitial water: D_{g} (m^2 s^{-1}) (adjustable parameter).
- Corrosion product mass in the reactor: M_{CP} (g).
- Corrosion product adsorption capacity: R_{ad} (g Si/g CP) (adjustable parameter).
- Environmental material thickness: L (cm).
- Environmental material porosity: ω (dimensionless).
- Environmental material density: ρ (kg m^{-3}).
- Silicon distribution coefficient in the environmental material: K_{d} (m^3 kg^{-1}) (adjustable parameter).
- Silicon diffusion coefficient in the environmental material pores: D_{p} (m^2 s^{-1}) (adjustable parameter).
- Initial silicon concentration in the environmental material pore water: C^0_{EM} (g m^{-3}).
- Silicon concentration at the EM/reactor interface: $C_{\mathrm{I}} = 0$ g m^{-3}.

lixiver 2 thus includes five adjustable parameters: two to describe glass alteration (C^* and D_{g}), one to allow for the CP (R_{ad}) and two to allow for the EM (D_{p} and K_{d}).

Note: The apparent solubility C^* should normally be dependent only on the glass composition and the test temperature, i.e., C^* should be constant in this case. However, recent work [20] has shown that this parameter does not reflect inherent glass solubility, but rather the result of a dynamic equilibrium between the quantity of hydrolyzed silica and the quantity of silica condensed in the gel. We therefore refer to C^* as the 'apparent solubility' rather than the 'true solubility' corresponding to a thermodynamic equilibrium with the solution. As the nature of the gel depends on the experimental conditions in which it is formed, it is thus reasonable to consider C^* as an adjustable, rather than a fixed parameter.

The fit between the calculated and experimental results is based primarily on comparing the boron and silicon concentrations in solution. Boron is taken into account as the true glass alteration tracer, and silicon is measured because the kinetic alteration law is based on this element. The best fit is based primarily on the boron concentration in solution.

All the pH values were measured at 90°C in the leaching solutions. pH is used for calculating total silicon concentrations in solution ($C_{\mathrm{Si}}(t)$ and C^*) according to the $\mathrm{H_4SiO_4}$ dissociation in $\mathrm{H_3SiO_4^-}$ and $\mathrm{H_2SiO_4^{2-}}$.

4. Simulated tests in the presence of corrosion products

The leach tests were performed in static mode at an S/V ratio of 0.5 cm^{-1} ($S = 14$ cm^2 and $V = 28$ cm^3) in the presence of products simulating corrosion of the metal canister. The experiments involved leaching a nonradioactive SON 68 glass coupon weighing 3 g in 30 cm^3 of demineralized water in a Teflon reactor together with 0.05 or 0.5 g of CP. The CP were obtained by dissolving NS24 steel (63% Fe, 23% Cr, 13.5% Ni) in *aqua regia* ($\mathrm{HNO_3 + HCl}$) and then precipitating iron, chromium and nickel hydroxides with sodium hydroxide. The precipitates were rinsed in demineralized water until the rinsing solution reached neutral pH. The specific surface area of the resulting CP was 339 m^2 g^{-1}.

The test results obtained with 0.05 g of CP are indicated in Table 1. The best fit between the calculated and experimental results was obtained with a C^* value of $10^{-2.87}$ mol l^{-1}, a diffusion coefficient D_{g} of 10^{-13} m^2 s^{-1} and an R_{ad} value of 0.065. The calculated CP saturation time t_0 was 47 days, in good agreement with the experimental values ranging from 28 to 56 days. As shown in Fig. 1, this set of parameters satisfactorily accounts for the experimental evolution of the silicon and boron concentrations.

The test results obtained with 0.5 g of CP are indicated in Table 2. The C^* and R_{ad} values determined for the 0.05 g CP test were maintained for this test. The best fit with the experimental results was obtained with a D_{g} value of 3×10^{-14} m^2 s^{-1}. As shown in Fig. 2, very good agreement was obtained between the calculated and experimental boron concentrations, and an acceptable approximation was obtained for the silicon concentrations. It was not possible to determine a precise R_{ad} value for this test, however, since at values above 0.014 the CP saturation time t_0 exceeded 1 year: all the boron and silicon concentrations calculated between 0 and 1 year were therefore identical. For this test, R_{ad} was most likely between 0.014 and 0.065 (it would have been necessary to continue leaching well beyond one year to determine the actual R_{ad} value).

Table 1
Glass alteration in the presence of 0.05 g of NS24 steel corrosion products

Time (days)	[Si] exp ($g\ m^{-3}$)	[B] exp ($g\ m^{-3}$)	$pH_{(90°C)}$ exp	[Si] calc ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	$pH_{(90°C)}$ LIX (imposed)
1	2.2	3.2	4.27	0	0.9	5.00
3	4.1	5.2	5.17	0	2.5	5.00
7	3.8	6.2	4.70	0	5.6	5.00
16	4.6	8.6	–	0	10.4	5.00
28	7.4	9.9	6.59	0	18.5	8.75
56	35.7	34.4	8.50	25.9	46.3	8.75
84	49.4	51.4	8.76	51.3	57.1	8.75
126	55.1	61.3	8.92	59.4	61.7	8.75
182	64.3	66.1	8.78	61.3	62.9	8.90
273	68.4	70.3	8.86	70.8	70.1	8.90
364	73.3	71.1	8.98	71.4	70.7	8.90

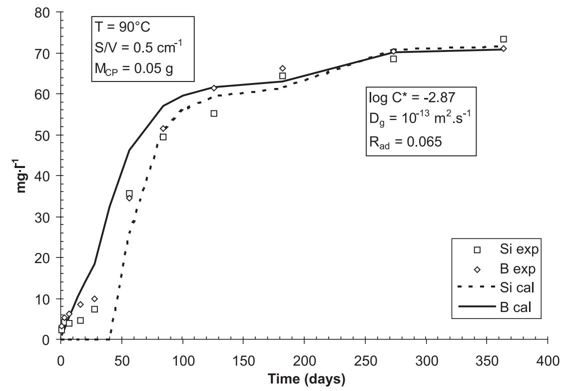

Fig. 1. Experimental and calculated silicon and boron concentrations versus time during glass alteration in the presence of 0.05 g of NS24 steel corrosion products.

The experiment done in the presence of 0.5 g of CP leads to a lower pH value than for the 0.05 g experiment. A gel formed at a low pH has a different composition from a gel formed at pH 8 or 9. This difference should be seen on the C^* value. But, until 1 year of leaching, the CP is not still silicon saturated. It is why C^* value variation could not be determined by simulating the experiments.

It should be noted that a single set of (C^*, D_g, R_{ad}) parameters was able to account for the evolution of the experimental boron and silicon concentrations. Moreover, the gel formed during glass alteration in the presence of CP is much less protective than the gel formed under identical test conditions but without any CP. Glass alteration without CP results in a D_g value [4] on the order of 10^{-15} $m^2\ s^{-1}$ compared with about 10^{-13} $m^2\ s^{-1}$ in the presence of CP.

5. Simulated tests in the presence of granite

Three leach tests with non-radioactive SON 68 glass coupons in 30 cm^3 of deionized water were carried out in static mode at 0.5 cm^{-1} in the presence of 50 g of granite with different grain size fractions: ‘gravel’ (1.6–2.5 mm), ‘sand’ (0.3–0.63 mm) and ‘silt’ (<0.16 mm). Considering the reactor geometry, the granite formed an EM thickness of 1 cm in contact with the glass. The granite porosity was primarily external, due to the intergranular

Table 2
Glass alteration in the presence of 0.5 g of NS24 steel corrosion products

Time (days)	[Si] exp ($g\ m^{-3}$)	[B] exp ($g\ m^{-3}$)	$pH_{(90°C)}$ exp	[Si] calc ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	$pH_{(90°C)}$ LIX (imposed)
1	2.2	2.8	4.51	0	0.8	4.60
3	3.1	3.8	4.57	0	2.2	4.60
7	1.4	4.2	5.09	0	4.5	5.10
16	1.6	8.0	–	0	7.6	5.10
28	3.3	12.3	5.17	0	12.3	5.40
56	5.0	17.4	5.26	0	19.2	5.40
84	5.4	23.5	5.49	0	24.6	5.40
126	5.1	28.0	5.38	0	31.9	5.40
182	5.8	36.2	5.55	0	38.7	5.40
273	9.1	50.6	5.54	0	48.6	5.40
364	9.4	59.6	5.48	0	56.9	5.40

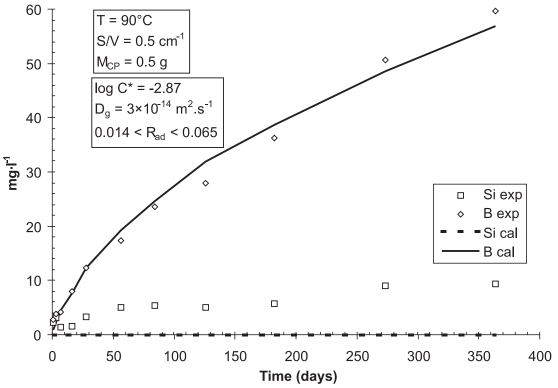

Fig. 2. Experimental and calculated silicon and boron concentrations versus time during glass alteration in the presence of 0.5 g of NS24 steel corrosion products.

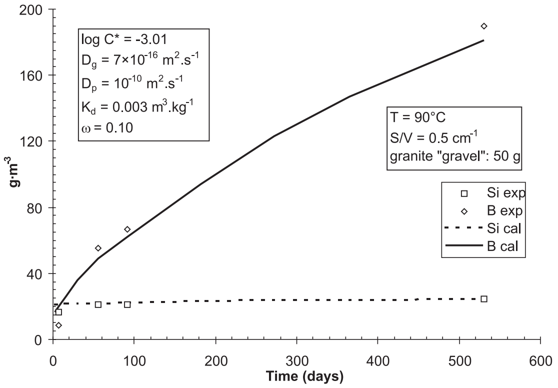

Fig. 3. Experimental and calculated silicon and boron concentrations versus time during glass alteration in the presence of crushed granite ('gravel' size fraction).

space; the internal porosity at grain boundaries was negligible (about 1%). The porosity of the 'gravel' layer was estimated at 0.10. The silicon concentration in the water in the intergranular porosity was determined by leaching crushed granite in the presence of deionized water; steady-state silicon concentrations were obtained between 2 and 530 days, allowing C^0_{EM} to be determined equal to 15, 18 and 20 g m^{-3} for 'gravel', 'sand' and 'silt', respectively.

The following parameter values were used for the simulations based on the operating conditions:

- $S = 14.5$ cm^2,
- $V = 30$ cm^3,
- $L = 1$ cm,
- $\rho = 2700$ kg m^{-3},
- $C^0_{\mathrm{EM\,'gravel'}} = 15$ g m^{-3},
- $C^0_{\mathrm{EM\,'sand'}} = 18$ g m^{-3},
- $C^0_{\mathrm{EM\,'silt'}} = 20$ g m^{-3}.

The test results for the 'gravel' size fraction are indicated in Table 3. We used the estimated porosity value of 0.10 for ω. The best fit with the experimental results was obtained with the following values: $C^* = 10^{-3.01}$ mol l^{-1}, silicon diffusion coefficient in the gel interstitial water $D_g = 7 \times 10^{-16}$ m^2 s^{-1}, silicon diffusion coefficient in the granite pores $D_p = 10^{-10}$ m^2 s^{-1}, and distribution coefficient $K_d = 0.003$ m^3 kg^{-1}. As shown in Fig. 3, these parameters satisfactorily accounted for the experimental glass alteration results.

The tests with the granite 'sand' and 'silt' size fractions were simulated using the same parameter values as for the 'gravel' test, except for the porosity ω. The diffusion coefficient D_p was maintained constant for all three tests (the variable was the effective diffusion coefficient $D_e = \omega\ D_p$); similarly, the distribution coefficient K_d remains constant for a given environmental material. We also chose to maintain the same C^* and D_g values, as the alteration films were formed under identical environmental conditions and with identical silicon concentrations in all three tests. Only the EM porosity varied: ω diminished with the granite size fraction. The test results are shown in Table 4 and Fig. 4 for the 'sand' fraction, and in Table 5 and Fig. 5 for the 'silt' fraction. The closest fit with the experimental results was obtained with a ω value of 0.065 for the 'sand' and 0.05 for the 'silt'; both values show a logical evolution with respect to the 'gravel' porosity.

All three test simulations satisfactorily accounted for the experimental glass alteration results while conserving the same parameter values for the glass (C^* and D_g) and for the granite (D_p and K_d): i.e., a single set of C^*, D_g, D_p and K_d parameter values was sufficient for all the simulated tests. Additional simulations with a constant porosity ($\omega = 0.10$) were also performed for the three size fractions with different D_p and K_d values, but were unable to account for the actual altered glass quantities. The three tests simulated using LIXIVER 2 thus confirm

Table 3
Glass alteration in the presence of crushed granite ('gravel' size fraction)

Time (days)	[Si] exp (g m^{-3})	[B] exp (g m^{-3})	pH$_{(90°C)}$ exp	[Si] calc (g m^{-3})	[B] calc (g m^3)	pH$_{(90°C)}$ LIX (imposed)
7	16.8	8.7	7.85	21.3	19.8	7.85
56	21.0	55.4	8.00	22.0	48.9	8.10
91	21.0	66.5	8.24	22.0	62.3	8.10
530	24.7	190	8.55	24.7	181	8.55

Table 4
Glass alteration in the presence of crushed granite (‘sand’ size fraction)

Time (days)	[Si] exp ($g\ m^{-3}$)	[B] exp ($g\ m^{-3}$)	$pH_{(90°C)}$ exp	[Si] calc ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	$pH_{(90°C)}$ LIX (imposed)
7	19.1	6.8	7.60	24.1	24.8	7.85
56	21.8	52.0	7.82	24.3	58.2	7.85
91	–	–	–	24.8	77.2	8.10
530	25.9	255	8.52	27.4	247	8.55

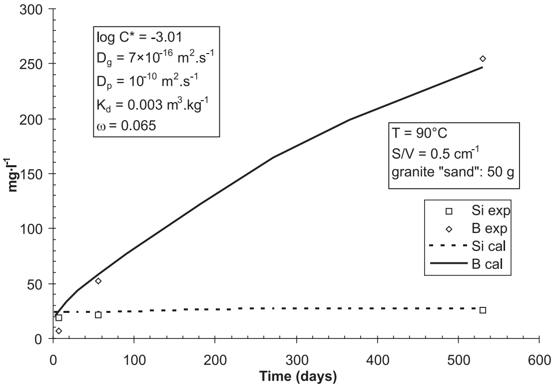

Fig. 4. Experimental and calculated silicon and boron concentrations versus time during glass alteration in the presence of crushed granite (‘sand’ size fraction).

that the basic model hypotheses (silicon diffusion and adsorption in the EM) correctly describe glass alteration in the presence of granite.

6. Simulated tests in the presence of clay

Several clays with different degrees of aggressiveness with respect to the glass were tested, notably smectite 4a (which is considered for use as a nearfield engineered barrier material for a geological radwaste repository), Boom clay (a site clay), and bentonite FB2 (which is much less aggressive for the glass than the other clays).

In view of the difficulties involved in recovering the leachate after leach tests with clay, the actual degree of glass alteration was determined by weighing the test coupons before and after leaching (the leached samples were scratched to remove the gel layer before weighing). The specimen mass loss was then used to determine the experimental boron concentration in solution (the quantity used by LIXIVER 2 to calculate the degree of glass alteration) according to formula (11)

$$[B]_{\text{exp}} = \frac{\Delta M \times 0.0435}{V} \quad (11),$$

with ΔM: mass loss (difference between the pristine sample and the sample after scratching to remove the gel formed during leaching) and 0.0435 is the boron content of glass.

The boron concentration calculated by the code was thus compared with the boron concentration calculated from the experimental mass loss. The experimental silicon concentrations could not be calculated from the mass loss, as the Si retention factor in the gel is unknown.

6.1. Glass alteration in the presence of smectite 4a

Two glass alteration tests were simulated with pure smectite 4a, and another with a mixture of smectite 4a and sand to verify whether the model hypotheses correctly describe the influence of the EM on glass alteration. The steady-state silicon concentration in the clay pore water was measured after maintaining equilibrium conditions for six months with deionized water in contact with the smectite, yielding a silicon concentration of 6 $g\ m^{-3}$. The following parameter values were then defined based on the physical characteristics of smectite 4a:

- $\omega = 0.3$,
- $\rho = 1800\ \text{kg m}^{-3}$,
- $C^0_{\text{EM}} = 6\ \text{g m}^{-3}$.

Table 5
Glass alteration in the presence of crushed granite (‘silt’ size fraction)

Time (days)	[Si] exp ($g\ m^{-3}$)	[B] exp ($g\ m^{-3}$)	$pH_{(90°C)}$ exp	[Si] calc ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	$pH_{(90°C)}$ LIX (imposed)
7	17.4	6.0	7.90	26.1	29.3	8.00
56	24.7	56.0	8.15	26.2	68.4	8.00
91	29.5	76.0	8.34	27.6	97.2	8.35
530	27.9	287	8.50	28.9	287	8.50

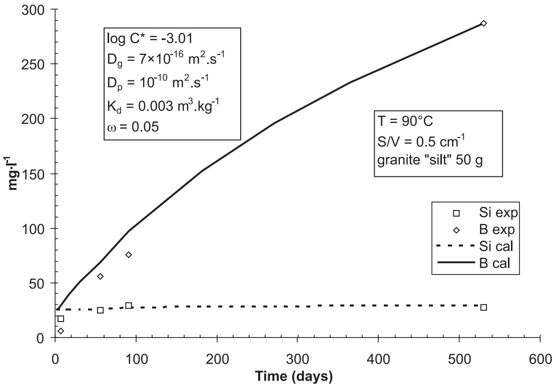

Fig. 5. Experimental and calculated silicon and boron concentrations versus time during glass alteration in the presence of crushed granite ('silt' size fraction).

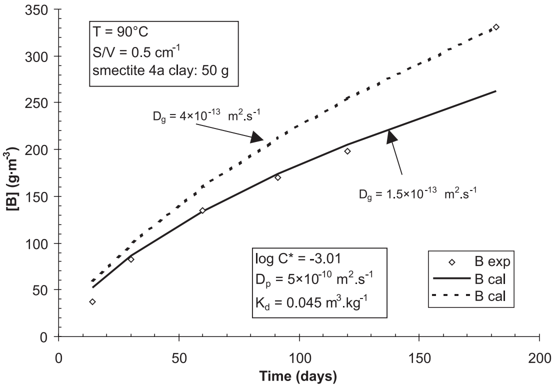

Fig. 6. Experimental and calculated glass alteration in static mode in the presence of 50 g of smectite 4a.

The results of a leach test at an S/V ratio of 0.5 cm^{-1} in contact with 50 g of smectite 4a are indicated in Table 6. The clay thickness on either side of the glass coupon was $L = 1.5$ cm. The simulations were performed with the default C^* value of $10^{-3.01}$ mol l^{-1}. The best fit was obtained for $D_p = 5\times10^{-10}$ m^2 s^{-1} and $K_d = 0.045$ m^3 kg^{-1}. Considering the scattered experimental results at 182 days compared with the other measurement intervals, we performed two simulations. One ($D_g = 1.5\times10^{-13}$ m^2 s^{-1}) provided a very close correlation between the calculated and experimental results except for the 182-day data point, while the other ($D_g = 4\times10^{-13}$ m^2 s^{-1}) correctly accounted only for the 182-day data point, as shown in Fig. 6. The most logical fit thus corresponds to $D_g = 1.5\times10^{-13}$ m^2 s^{-1}. It should be noted that both curves were calculated using the same smectite parameter values (D_p and K_d); the only difference was the protective property of the gel. A high D_p value was used here to account for the very fluid nature of the clay due to the quantity of water added.

The results of a second leach test at an S/V ratio of 0.79 cm^{-1} in contact with 37 g of smectite 4a are indicated in Table 7. The clay thickness on either side of the glass coupon was $L = 1.0$ cm. The best fit was obtained for $C^* = 10^{-3.01}$ mol l^{-1}, $D_g = 10^{-13}$ m^2 s^{-1}, $D_p = 10^{-10}$ m^2 s^{-1} and $K_d = 0.05$ m^3 kg^{-1}. As shown in Fig. 7, these parameters provided a satisfactory correlation between the calculated values and the scattered experimental results. The D_p value was five times lower than in the preceding simulation, but in this case the smectite 4a had a pasty consistency; logically, however, D_g and K_d were practically the same as before.

The results of a third leach test at an S/V ratio of 1.0 cm^{-1} in contact with a mixture of 10 g of smectite 4a and 10 g of sand are indicated in Table 8. The EM thickness around the glass in this case was $L = 0.8$ cm. Once again, a satisfactory correlation was obtained between the calculated and experimental results (Fig. 8). The best fit was obtained for $C^* = 10^{-3.01}$ mol l^{-1}, $D_g = 1.6\times10^{-13}$ m^2 s^{-1}, $D_p = 5\times10^{-10}$ m^2 s^{-1} and $K_d = 0.023$ m^3 kg^{-1} (the high D_p value logically corresponded to the consistency of the smectite–sand mixture, comparable to that of the first test). The adsorption capacity of sand is negligible compared with smectite 4a; logically, therefore, the distribution coefficient for a mixture of equal amounts of smectite and sand could be expected to be half the value determined for pure smectite. The simulation yielded a K_d value of 0.023 m^3 kg^{-1}, corresponding to exactly half the K_d value found for pure smectite during the two preceding tests.

The simulations satisfactorily accounted for the influence of smectite 4a on glass alteration. All the tests were correctly simulated using a single parameter set (C^*, D_g, D_p, K_d). Not unexpectedly, and despite minor

Table 6
Experimental and calculated glass alteration in static mode in the presence of 50 g of smectite 4a (D_g in m^2 s^{-1})

Time (days)	[B] exp (g m^{-3})	[B] calc (g m^{-3}) $D_g = 1.5\times10^{-13}$	[B] calc (g m^{-3}) $D_g = 4.0\times10^{-13}$	pH$_{(90°C)}$ LIX (imposed)
14	37	52	58	7.70
30	82	86	99	7.70
60	135	134	160	7.70
91	170	174	212	7.70
120	198	205	254	7.70
182	331	263	330	7.70

Table 7
Experimental and calculated glass alteration in static mode in the presence of 37 g of smectite 4a

Time (days)	[B] exp ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	$pH_{(90°C)}$ LIX (imposed)
30	76	96	7.60
91	162	184	7.60
182	358	273	7.60
273	341	343	7.60
364	400	402	7.60
455	500	454	7.60
546	465	501	7.60

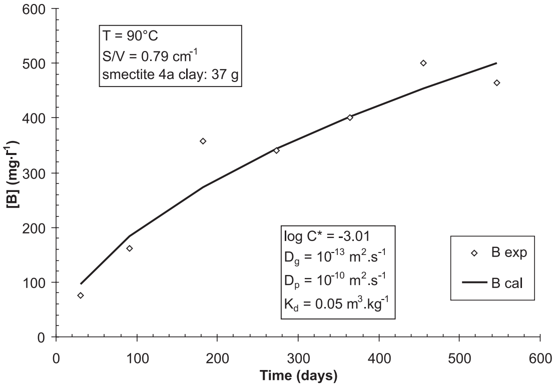

Fig. 7. Experimental and calculated glass alteration in static mode in the presence of 37 g of smectite 4a.

Table 8
Experimental and calculated glass alteration in static mode in the presence of 10 g of smectite 4a and 10 g of sand

Time (days)	[B] exp ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	pH exp	$pH_{(90°C)}$ LIX (imposed)
28	88	132	7.5	7.60
56	176	210	7.5	7.60
97	308	294	7.5	7.60
182	421	410	7.6	7.60
486	581	596	–	7.60

differences in the operating conditions, the simulations resulted in identical values for the gel parameters (C^* and D_g) in all three tests. The D_g values ranging from 1.0 to 1.6×10^{-13} $m^2\ s^{-1}$ indicate that the gel formed in the presence of smectite 4a is much less protective than the gel obtained under identical leaching conditions without clay. The D_p variation in these tests according to the consistency (fluid or pasty) of the clay was also predictable. All three tests also resulted in very similar K_d values (0.045, 0.05 and 0.046 after correction for pure smectite), for a mean value of 0.047 $m^3\ kg^{-1}$ (the simulated mean value is higher than the experimentally determined value [21] of 0.034 $m^3\ kg^{-1}$).

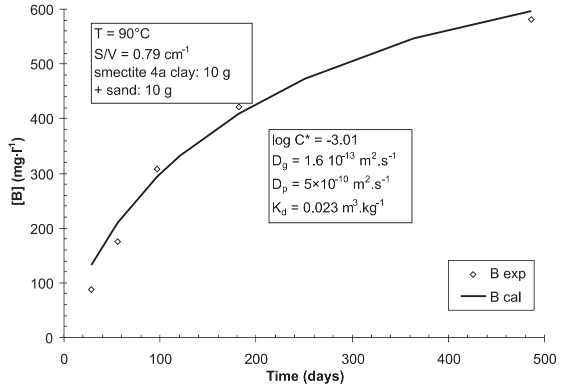

Fig. 8. Experimental and calculated glass alteration in static mode in the presence of 10 g of smectite 4a and 10 g of sand.

6.2. Glass alteration in the presence of Boom clay

A glass leach test was simulated at an *S*/*V* ratio of 0.82 cm^{-1} in the presence of 37 g of Boom clay, forming a layer 1 cm thick around the glass. The physical characteristics (ω and ρ) of Boom clay used for these simulations were experimentally measured values [22]. The steady-state silicon concentration in the Boom clay pores (30 $g\ m^{-3}$) was measured after maintaining equilibrium conditions for six months with deionized water in contact with the clay. The following parameter values were defined for simulation purposes:

- $S = 18.9$ cm^2,
- $V = 23$ cm^3,
- $L = 1.0$ cm,
- $\omega = 0.4$,
- $\rho = 1700$ $kg\ m^{-3}$,
- $C^0_{EM} = 30$ $g\ m^{-3}$.

The results of the leach test and the corresponding simulation are indicated in Table 9. The closest fit between the calculated and experimental results was obtained for $C^* = 10^{-2.70}$ mol l^{-1}, $D_g = 5\times10^{-13}$ $m^2\ s^{-1}$, $D_p = 5\times10^{-10}$ $m^2\ s^{-1}$ and $K_d = 0.018$ $m^3\ kg^{-1}$. This parameter set correctly accounted for the experimental glass alteration results, as shown in Fig. 9 (with the exception of the visibly aberrant data point at 455 days). The high D_p value was due to the fluidity of the Boom clay during this test.

As for the other tests, a single set of parameters (C^*, D_g, D_p, K_d) allowed the experimental alteration to be simulated correctly. The D_g value obtained in this way was relatively high, showing that the alteration gel formed in the presence of Boom clay is much less protective than the gel obtained under identical leaching conditions without clay. The simulated K_d value is slightly higher than the experimentally measured values [22], which ranged from 0.0053 to 0.0115 $m^3\ kg^{-1}$ with a mean of 0.0083 $m^3\ kg^{-1}$. Other measurements made on

Table 9
Experimental and calculated glass alteration in static mode in the presence of 37 g of Boom clay

Time (days)	[B] exp ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	pH exp	$pH_{(90°C)}$ LIX (imposed)
30	88	52	3.65	3.70
91	127	134	4.85	4.90
182	338	290	7.65	7.70
273	392	392	7.70	7.70
364	471	462	7.70	7.70
455	275	513	6.10	7.70
546	521	549	7.10	7.70

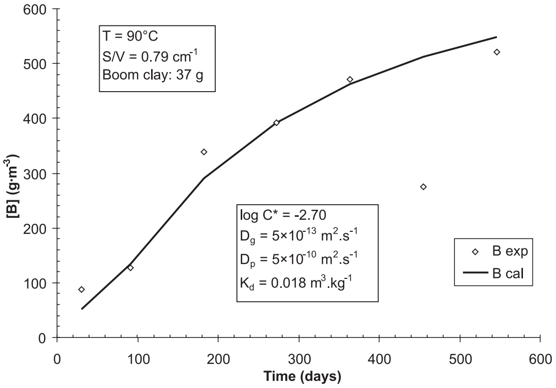

Fig. 9. Experimental and calculated glass alteration in static mode in the presence of 37 g of Boom clay.

batch experiments [23] lead to an average K_d value of about 0.03 $m^3\ kg^{-1}$. SON 68 glass alteration in a Boom clay medium as simulated by the GLADIS code [24] yielded K_d values ranging from 0.01 to 0.05 $m^3\ kg^{-1}$, confirming the overall agreement between the simulation results obtained with the GLADIS and LIXIVER 2 codes.

6.3. Glass alteration in the presence of bentonite FB2

A glass leach test was simulated at an *S*/*V* ratio of 0.5 cm^{-1} in the presence of a mixture of 7.5 g of bentonite FB2 and 7.5 g of sand, forming a layer 0.5 cm thick around the glass. The physical characteristics (ω and ρ) of bentonite FB2 used for these simulations were assumed identical to those of smectite 4a. The steady-state silicon concentration in the bentonite FB2 pores (44 $g\ m^{-3}$) was measured after maintaining equilibrium conditions for six months with deionized water in contact with the clay. The following parameter values were defined for simulation purposes:

- $S = 15\ cm^2$,
- $V = 30\ cm^3$,
- $L = 0.5\ cm$,
- $\omega = 0.3$,
- $\rho = 1800\ kg\ m^{-3}$,
- $C^0_{EM} = 44 g\ m^{-3}$.

The results of the leach test and the corresponding simulation are indicated in Table 10. The best fit between the calculated and experimental results was obtained for $C^* = 10^{-2.90}$ mol l^{-1}, $D_g = 10^{-15}$ $m^2\ s^{-1}$, $D_p = 10^{-10}$ $m^2\ s^{-1}$ and $K_d = 0.0015$ $m^3\ kg^{-1}$. This parameter set very satisfactorily accounted for the experimental glass alteration results, as shown in Fig. 10. It was possible to take leachate samples during this test to analyze the silicon concentration; the results were in good agreement with the predicted values. The D_p coefficient corresponded to the consistency of the clay/sand mixture used for this test; since the mixture consisted of equal amounts of clay and sand, the K_d coefficient for pure bentonite FB2 can be estimated at 0.003 $m^3\ kg^{-1}$ (disregarding the sand adsorption sites, which are negligible in comparison with the clay).

Bentonite FB2 is the least aggressive clay with respect to glass alteration. This was reflected during the simulations by a lower (~1 order of magnitude) distribution coefficient K_d for bentonite FB2 than for the other clays and by a much lower (two orders of magnitude) apparent silicon diffusion coefficient D_g in the gel interstitial water. The D_g value corresponds to a highly protective gel, with the same diffusion barrier properties as the gel obtained under static conditions with neither EM nor CP. This phenomenon may be attributable to the fact that bentonite FB2 is naturally saturated in amorphous silica (it is the clay with the highest initial pore silicon concentration C^0_{EM}).

The experiments done in the presence of three different clays show that bentonite is not agressive towards glass and that smectite and Boom clay lead to the formation of gels weakly protective, as indicated by the D_g values. Although the Boom clay D_g value is higher than

Table 10
Experimental and calculated glass alteration in static mode in the presence of 7.5 g of bentonite FB2 and 7.5 g of sand

Time (days)	[Si] exp ($g\ m^{-3}$)	[B] exp ($g\ m^{-3}$)	$pH_{(90°C)}$ exp	[Si] calc ($g\ m^{-3}$)	[B] calc ($g\ m^{-3}$)	$pH_{(90°C)}$ LIX (imposed)
28	49	9.3	8.45	47.1	9.9	8.50
56	45	10.0	8.45	47.5	12.0	8.50
84	41	10.0	8.40	47.7	12.7	8.50
112	45	13.1	8.40	47.7	13.0	8.50

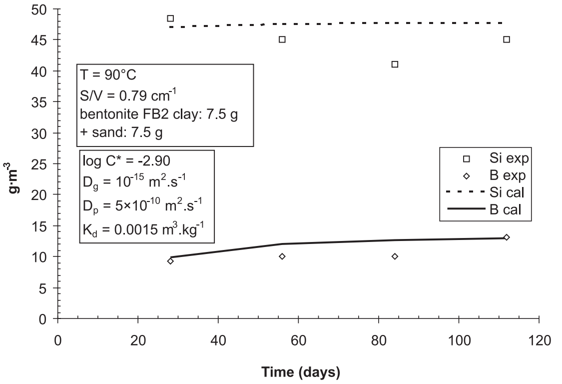

Fig. 10. Experimental and calculated glass alteration in static mode in the presence of 7.5 g of bentonite FB2 and 7.5 g of sand.

smectite one, this does not necessarily mean that Boom clay is more agressive than smectite towards glass. In fact, the gel layer formed in the presence of Boom clay does not correspond to the really altered glass thickness. So, the LIXIVER 2 code needs to take a higher D_g value for compensating the higher gel thickness that it takes into account for the calculations.

The K_d values show that Boom clay will be silicon saturated shorter than smectite because of its smaller K_d value.

7. Conclusion

Leach tests in the presence of CP or EM simulated using the LIXIVER 2 code satisfactorily accounted for the experimental alteration results obtained with non-radioactive specimens of the French SON 68 nuclear glass, even though the influence of these materials is modeled very simply. LIXIVER 2 includes five adjustable parameters: two related to the glass alteration kinetics (C^* and D_g), one to the CP (R_{ad}) and two to the EM (D_p and K_d). Despite the number of parameters involved, the best fit between the experimental findings and the simulation for a given test was obtained using a single set of parameters.

The evolution of the parameter values related to the EM logically followed the operating conditions and the nature of the test materials; the D_p value, for example, varied with the consistency (fluid or pasty) of the clay. The test results with different granite size fractions were successfully predicted simply by varying the porosity ω; this is also quite logical: the nature of the gel (i.e., C^* and D_g) and the nature of the granite (i.e., K_d) should not vary from one test to another, and this was confirmed by the simulations. The K_d values also varied logically according to the relative aggressiveness of the test clays with respect to glass alteration:

K_d (granite) $\approx$ K_d (bentonite FB2) $<$ K_d (Boom clay) $<$ K_d (smectite 4a).

Leach tests in the presence of CP, smectite 4a, or Boom clay resulted in the formation of gels with substantially lower protective properties ($D_g \approx 10^{-13}$ m^2 s^{-1}) than the gels that formed in the presence of granite, bentonite FB2, or pure water ($D_g \approx 10^{-15}$ m^2 s^{-1}). This again is corroborated by the actual altered glass quantities.

The K_d values obtained by simulation were slightly higher than the experimentally measured values. This may be attributable either to the fact that silicon adsorption on the EM was simulated by an oversimplified K_d (perhaps other adsorption isotherms should be used instead), or by a phenomenon other than adsorption (e.g., silicon precipitation).

Consequently, the consistent evolution of the adjustment parameters – notably those related to the CP and EM (R_{ad}, D_p, K_d) – confirms that these values can be used to estimate the lifetime of a vitrified radioactive waste package in a geological repository environment.

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