



LONG-TERM BEHAVIOR OF NUCLEAR GLASS: THE $r(t)$ OPERATIONAL MODEL

I. Ribet¹, S. Gin¹, Y. Minet¹, E. Vernaz¹, P. Chaix² and R. Do Quang³

¹Commissariat à l'Énergie Atomique, CEA Valrhô, DIEC/SEC, BP 17171, 30207 Bagnols-sur-Cèze, France

²Commissariat à l'Énergie Atomique, CEA Saclay, DPC/SCPA, 91191 Gif-sur-Yvette, France

³COGEMA, 1 rue des Hérons, Montigny-le-Bretonneux, 78/182 Saint Quentin en Yvelines, France

ABSTRACT

Predicting the long-term behavior of vitrified waste packages requires the development of models incorporating knowledge of the aqueous alteration mechanisms of nuclear glass. The $r(t)$ model allows for the formation of a protective gel layer during leaching, and is thus able to account for the major drops in the glass alteration rate that are observed experimentally. This article describes the model hypotheses, the methodology implemented to determine its three internal parameters, and the results obtained from about fifty leaching experiments performed under various conditions. The orders of magnitude of the internal parameter values are indicated according to the alteration conditions.

Keywords: nuclear waste glass, long-term behavior, modeling

1. INTRODUCTION

Borosilicate glass is used in France for containment of the fission product solutions produced by reprocessing spent nuclear fuel. Knowledge and understanding of the long-term behavior of nuclear glass under different environmental conditions are necessary to design facilities for long-term storage and to demonstrate their safety.

Vitrified waste packages basically comprise a well-characterized homogeneous matrix. This allows precise analysis of their long-term behavior, not only under closed-system conditions (typical of interim storage or of the operating phase of a repository) but also in the presence of water (typical of a geological repository following nearfield saturation and deterioration of the outer containers).

Water is by far the main vector of radionuclide release, and it is therefore important to study the mechanisms and kinetics of glass alteration in water-saturated media. The work accomplished over more than two decades to date in this area has shown that nuclear glass alteration begins by an ion exchange process (interdiffusion between protons and network-modifying alkali metal ions). The kinetics are subsequently limited by hydrolysis of the covalent bonds in the glass network; as long as the solution remains sufficiently dilute, the rate remains at its maximum value (i.e. the initial rate, r_0 , which depends only on the glass composition, the temperature and the pH). The rate then gradually diminishes by several orders of magnitude from the initial rate; this phenomenon is accompanied by a gradual rise in the solution concentrations, notably for silicon. The diminishing rate under saturation conditions was first interpreted in terms of an equilibrium between the glass and solution (Grambow's model [1]) or between the gel and solution (Bourcier's model [2]); more recently, it has been attributed to a diffusion barrier effect of the gel that forms by recondensation of a fraction of the hydrolyzed species [3]. From this phenomenological knowledge, we have developed a reliable and realistic model, $r(t)$, based on the protective effect of the gel.

This model is intended for use as an operational model, by which we mean a simple, robust and reasonably conservative model that focuses on the essential mechanisms controlling the long-term behavior of the glass package under the alteration conditions specified by the user.

2. DESCRIPTION OF THE $r(t)$ MODEL

The $r(t)$ model is based on the following hypotheses and equations.

1. Glass alteration leads to the formation of an alteration layer or "gel" between the glass and solution. Some of the glass constituent elements are retained inside the gel; others are completely released into solution, (e.g. boron, which can be used as a glass alteration tracer). The model assumes that radionuclide release is congruent with glass alteration, and thus overestimates the actual release rate.

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2. The transformation between the glass and gel is an iso-volume process. The dynamics of glass alteration are therefore described by the progression of the alteration front where the glass is transformed into a gel. The gel thickness at time t is designated $a(t)$, and the positions are identified by the distance x from the fixed gel/solution interface.
3. Glass alteration is controlled by silica. Key parameters include notably the silica concentration $C(x,t)$ at point x at time t , the concentration at the fixed gel/solution interface $C(t) = C(x=0,t)$, and the concentration at the mobile glass/gel interface $C(x=a(t),t)$.
4. At the alteration front, a fraction $(1 - f_{\text{Si}})$ of the hydrolyzed silica enters solution, while the remainder of the silica f_{Si} is retained to form the gel. The silica retention function f_{Si} reflects the balance between the hydrolysis kinetics and the recondensation kinetics. It is an increasing function of the silica concentration C in solution—recondensation increases as the concentration rises in solution (see below). Silica conservation at the silica front is expressed as follows:

$$-D_g \partial_x C(x=a(t),t) = [1 - f_{\text{Si}}(C(t))] C_g \partial_t a$$

where C_g is the silicon concentration of the glass.

5. The hydrolyzed silica entering solution is transported by diffusion through the gel, with a diffusion coefficient D_g . **D_g is the first parameter of the $r(t)$ model.** A fraction of this silica may then be removed in the surrounding media. Diffusive transport is expressed as follows:

$$\partial_t C(x,t) = D_g \partial_x^2 C(x,t)$$

The gel comprises the silica fraction that recondenses. Its structure—notably its porosity and diffusion coefficient D_g —therefore depends on the capability of the medium to remove silica from the reaction zone. The slower the rate at which silica is removed, the more compact and protective the gel (i.e. the lower the diffusion coefficient D_g).

6. The higher the silica concentration $C(x=a(t),t)$ at the alteration front, the lower the rate at which the reaction front advances. The model assumes a linear relation of the following type:

$$d_t a = r(t) = r_0 \left(1 - \frac{C(x=a(t),t)}{C^*} \right)$$

where C^* is a glass-gel-solution interaction parameter that can be interpreted as the concentration value $C(x=a(t),t)$ at the alteration front at which the glass-to-gel transformation ceases. **C^* is the second parameter of the $r(t)$ model.** It is important to note that this parameter is not an intrinsic property of the glass, but rather of the glass-gel system [3-5]. As with the silica diffusion coefficient in the gel D_g , C^* is thus a function of the silica removal behavior of the environment (cf. item (7)). The dependence of D_g and C^* on the silica removal behavior of the environment is indicative of the fact that the gel structure itself is dependent on this phenomenon.

7. The retention function $f_{\text{Si}}(C)$ and the dependence of the model parameters D_g and C^* are determined experimentally. The $f_{\text{Si}}(C)$ function follows a law of the following type:

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

α is the third parameter of the $r(t)$ model.

8. The silica conservation equation for an experiment carried out with a glass surface area S and a solution volume V renewed at a rate F is:

$$d_t C(t) = -D_g \left(\frac{S}{V} \right) \partial_x C(x=0,t) - FC(t)$$

The silica removal capability of the environment is thus characterized by the S/V ratio and the renewal flow rate F . The reciprocal of the S/V ratio is the water thickness adjacent to the glass available to accept silica released by glass alteration. The greater this thickness, or the higher the renewal rate, the greater the silica removal capability of the medium.

The $r(t)$ model is shown schematically in **Figure 1**.

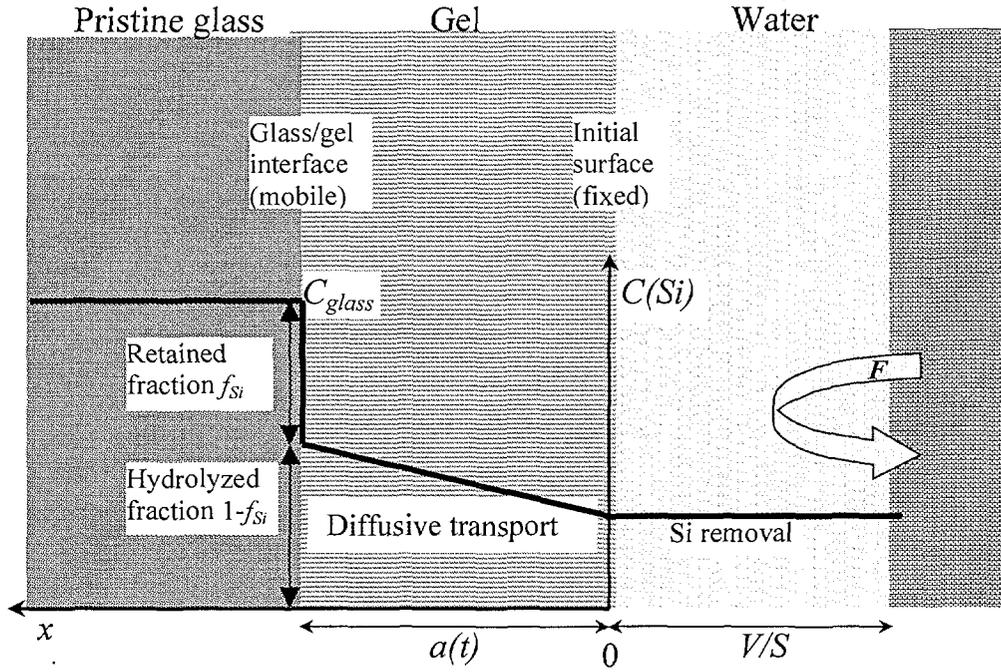


Figure 1. Conceptual schematic of the $r(t)$ model

3. DETERMINING THE D_g , C^* AND α PARAMETERS

The three internal parameters D_g , C^* and α depend on the environmental conditions under which glass alteration occurs. Their values must be known in order to use the model for glass source term predictions under specified alteration conditions. We chose to use the results of laboratory experiments to quantify these values and their uncertainty margins for a wide range of alteration conditions.

The methodology adopted to optimize the fit of each experimental result and to identify the range of values in which the experimental fit is satisfactory involves three steps:

1. Solve the model equation system for a parameter set, using a method based on an inversion program written in Mathematica and Excel.
2. Compare the concentration profiles for boron (alteration tracer) and silicon (kinetically limiting element) with the experimental values based on the norm adopted (see below), and iterate until a parameter triplet is optimized to minimize the norm.
3. Determine the parameter variability range around the optimum values (the limits indicated in this article for each parameter correspond to a 95% confidence interval).

An absolute norm was used to optimize the deviation between the calculated and experimental values according to a least-squares method. It combines the following two norms:

$$S_{Si}(\theta) = \sum |C_{Si}(t_i) - C_{Si}(t_i, \theta)|^2$$

$$S_B(\theta) = \sum |C_B(t_i) - C_B(t_i, \theta)|^2$$

where θ is the parameter triplet, $C_{Si}(t_i)$ and $C_B(t_i)$ are the measured silicon and boron concentrations at time t_i , and $C_{Si}(t_i, \theta)$ and $C_B(t_i, \theta)$ are the calculated silicon and boron concentrations at time t_i .

The boron and silicon concentration profiles may differ by several orders of magnitude depending on the experimental conditions. We therefore elected to minimize both curves by weighting them with a scale factor k representing the ratio between the mean silicon and boron concentrations:

$$S(\theta) = S_{Si}(\theta) + k^2 S_B(\theta)$$

This criterion maintains the long-term values predominant over the initial alteration values, and was considered more pertinent to a long-term behavior study.

The uncertainties on the parameter values are determined from the scattering of the experimental data points around the optimum curve. We thus determined a 95% confidence interval within which any parameter triplet is assumed to provide an acceptable fit with the experimental results. Projecting this interval on the three parameter axes defines the minimum and maximum limits for each parameter.

Figure 2 shows a typical inversion result for a glass powder sample from the R7T7 composition range, altered under static conditions at 50°C at unrestricted pH, with an S/V ratio of 75 cm^{-1} [6]. Graph (a) shows the experimental values and the calculated results for the optimum values of D_g , C^* and α as indicated in **Table I**, and illustrates the very close agreement between the model and reality. Graph (b) again shows the experimental results for the same experiment, together with the envelope curves for the acceptable model parameters, yielding the minimum and maximum values indicated in **Table I**.

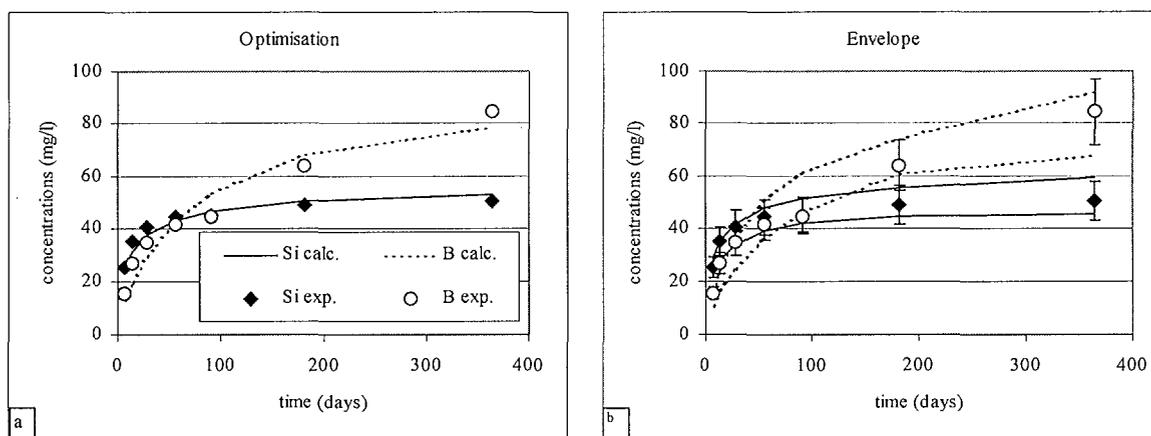


Figure 2. Typical calculated inversion. The experimental results and optimum calculated curves are plotted in graph (a); graph (b) shows the experimental results and the envelope curves for D_g , C^* and α within the limits indicated in **Table I**. The experimental uncertainty on boron and silicon concentrations (15%) is indicated on graph (b)

Table I. Optimum values and upper and lower limits for the D_g , C^* and α parameters corresponding to the experiment shown in **Figure 2**

Values	D_g ($\text{m}^2 \cdot \text{s}^{-1}$)	C^* (ppm)	α (ppm^{-1})
Optimum	1.0×10^{-18}	53.7	0.059
Minimum	6.7×10^{-19}	45.7	0.051
Maximum	1.8×10^{-18}	61.8	0.071

4. ASSIGNING MODEL PARAMETER VALUES

This article describes the initial phase of assigning parameters to the $r(t)$ model, corresponding to experiments carried out in initially pure water with no environmental materials. The inversion methodology described above was applied to forty-nine experiments (**Table II**). The objectives were to verify that the model is applicable to a large number of experiments, and to determine the model parameter variation ranges for variations in the alteration conditions (glass composition in the R7T7 range, alteration solution pH, temperature, S/V ratio, and leachate renewal rate). The results obtained will subsequently be used to propose values for the model parameters for source-term predictions.

The experiments taken into account during this phase of the parameter evaluation were carried out within the CEA between 1983 and 2001. Some have been described in published work [3-4,6-12], while others are documented in internal CEA reports.

Table II. Experiments taken into account for the inversion calculations

Glass	T (°C)	pH	S/V (cm ⁻¹)	F (d ⁻¹)	Glass	T (°C)	pH	S/V (cm ⁻¹)	F (d ⁻¹)
SON68	90	Free	50	0	SON68	90	Free	10	0
SON68	90	7	50	0	SON68	90	Free	50	0
SON68	90	8	50	0	SON68	90	Free	500	0
SON68	90	9.5	50	0	SON68	90	Free	2000	0
SON68	90	10	50	0	SON68	50	Free	1.25	0
SON68	90	10.5	50	0	SON68	90	Free	1.25	0
SON68	90	11	50	0	SON68	110	Free	1.25	0
SON68	90	11.5	50	0	SON68	150	Free	1.25	0
SON68	90	Free	1.25	0.048	SON68	150	Free	1.25	0
SON68	90	Free	1.25	0.122	R7T7 _{min}	90	Free	500	0
SON68	90	Free	1.5	1.24	R7T7 _{max}	90	Free	500	0
SON68	50	Free	50	0	25 compositions				
SON68	50	Free	200	0	from R7T7 range	50	Free	55–75	0

SON 68 glass is a nonradioactive reference glass with a composition similar to that of the R7T7 nuclear glass [13]. The R7T7_{min} and R7T7_{max} glasses are two extreme compositions from the R7T7 range calculated using a thermodynamic model to obtain the minimum and maximum initial alteration rates [12]. The 25 glasses from the R7T7 composition range were identified for use in an experimentation plan to quantify the effect of the composition on the initial rate in saturation conditions [6]. The term “Free pH” in **Table II** means that the experimental pH was not controlled by acid or base adjustment; the presence of boron in solution quickly buffered the pH to about 9.5 ± 0.5 .

A set of values was determined for the D_g , C^* , α parameters in each of these experiments, confirming that the $r(t)$ model suitably describes R7T7 glass alteration within the complete composition range and over a wide range of leaching conditions.

In these experiments, the inversion results for some experiments performed under the same composition, pH, temperature, S/V and flow rate conditions have been compared. So it has been verified that the model results are reproducible, i.e. the same values are obtained for D_g , C^* and α .

The variation ranges observed for the three model parameters were studied for variations in the leaching conditions. The variations of each parameter versus the S/V ratio (the parameter for which most extensive data are available) are plotted in **Figure 3**. The experiments are grouped according to the other parameters defining the alteration conditions (pH, temperature, composition, solution renewal).

4.1 Effect of Alteration Conditions on the Apparent Silicon Diffusion Coefficient in the Gel D_g

The apparent silicon diffusion coefficient, D_g , can be estimated within an order of magnitude, and ranges from $10^{-13} \text{ m}^2\text{s}^{-1}$ (comparable to the diffusion coefficients in porous media) to $10^{-21} \text{ m}^2\text{s}^{-1}$ (comparable to the diffusion coefficients in the solid glass) depending on whether the material is altered in a dilute medium with leachate renewal, or in a medium with very high silicon confinement. **Figure 3a** shows that when the temperature varies between 50 and 150°C, or when the renewal rate varies from 0 to 1.24 d⁻¹, or when the composition varies within the extreme limits of the R7T7 glass domain, the apparent silicon diffusion coefficient varies over about two orders of magnitude. A variation in the S/V ratio between 1 and 2000 cm⁻¹, however, results in a D_g variation of eight orders of magnitude. The confinement of the medium with respect to silicon is thus the parameter with the greatest effect on the protective properties of the gel.

These inversion results were recently confirmed by Valle [14], who measured the diffusion coefficient directly by isotopic tracing of the alteration solution, and showed that the measured D_g values were of the same order of magnitude as the values calculated by inversion. Moreover, the direct measurements confirmed that the diffusion coefficient diminishes by several orders of magnitude between flowing conditions and static conditions with saturated leachate.

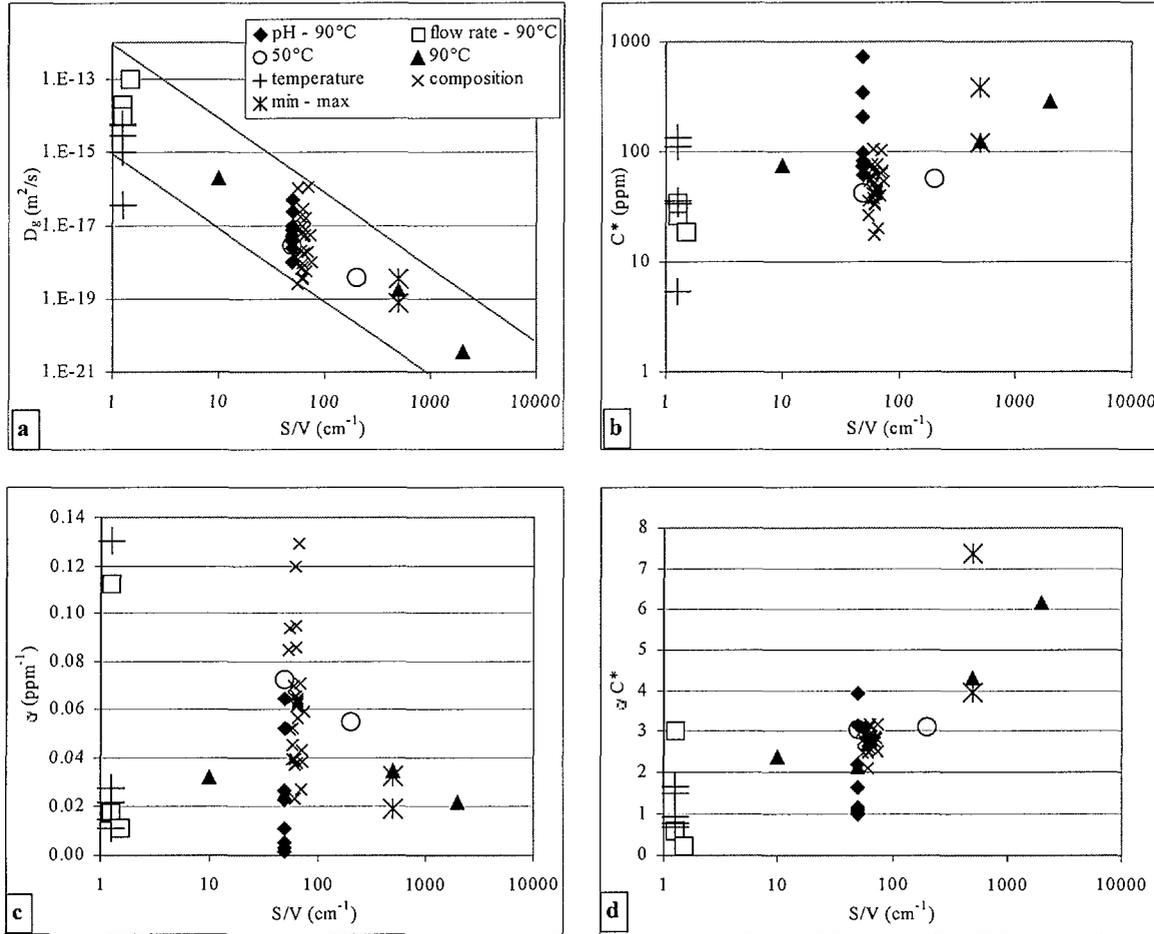


Figure 3. Variations of the three model parameters D_g (a), C^* (b) and α (c), and the product αC^* versus the S/V ratio, representing the degree of system confinement. The experiments from which these values were determined are grouped according to the other alteration parameters. The “pH - 90°C” series includes static tests in which the pH varied from 7.5 to 11.5. The “flow rate - 90°C” series includes dynamic tests at renewal rates ranging from 0.048 to 1.24 d^{-1} . The “50°C” and “90°C” series correspond to static tests at unrestricted pH. The “temperature” series includes static experiments at unrestricted pH at temperatures ranging from 50°C to 150°C. The “composition” series corresponds to static tests at 50°C at unrestricted pH for 25 different glass compositions selected within the R7T7 composition range. The “min/max” series includes static tests at 90°C and unrestricted pH for 2 extreme compositions ($R7T7_{min}$ and $R7T7_{max}$) inside the R7T7 range. The uncertainty is about 30% on C^* , 50% on α , and an order of magnitude on D_g .

4.2 Effect of Alteration Conditions on the C^* Parameter

Figure 3b shows that most of the C^* values lie between 10 and 100 ppm. Those exceeding 100 ppm correspond to “extreme” alteration conditions ($pH \geq 10.5$, temperature $\geq 150^\circ C$, $S/V \geq 500 \text{ cm}^{-1}$). The composition variations within the R7T7 composition range did not result in any C^* parameter variation above 100 ppm. As the $R7T7_{min}$ and $R7T7_{max}$ compositions were altered with an S/V ratio of 500 cm^{-1} , the fact that C^* exceeded 100 ppm for both glasses could be attributed either to the composition or to the S/V value.

Within the 10–100 ppm range, however, the C^* value depends both on the glass composition and on the alteration conditions (pH, temperature, flow rate, S/V ratio). These results confirm that C^* is not an intrinsic glass parameter [3-5]. Its order of magnitude is known (between 10 and 100 ppm for the composition range tested here), but the actual value depends on the alteration conditions.

4.3 Effect of Alteration Conditions on the α Parameter

No pronounced trend in the variation of the α parameter was observed with any of the alteration parameters (Figure 3c). It is thus arguably more reasonable to consider the product αC^* , which reflects the silicon retention factor in the gel: $f_{Si}(\alpha C^*) = 1 - \exp(-\alpha C^*)$ corresponds to the silicon retention factor in the gel when the concentration reaches C^* . When C^* is equal to $1/\alpha$, the long-term silicon retention factor in the gel is 63% (if $\alpha C^* = 2$, then $f_{Si}(C^*) = 86\%$; and if $\alpha C^* = 3$, then $f_{Si}(C^*) = 95\%$).

As shown in Figure 3d, αC^* was greater than 1 for most of the experiments, i.e. the silicon retention factor in the gel at advanced stages of reaction progress exceeded 63%, which is already the sign of a dense, protective gel. The only experiments for which the retention factor was below 50% were those combining high water renewal rates, low S/V ratios and temperatures below 100°C.

The silicon retention factor in the gel tended to increase with the S/V ratio, i.e. the greater the confinement of the medium, the denser the gel. Within the R7T7 composition range, moreover, the composition had no effect on the silicon retention factor. This observation is consistent with the results reported by Frugier [6].

4.4 Coupling between the Model Parameters (D_g , C^* and α)

The three parameters do not vary independently. As shown in Figure 4, low diffusion coefficients are associated with high retention factors and, conversely, high diffusion coefficients are associated with low retention factors. Figure 4 also shows that the degree of silicon confinement within the system is the primary determinant of the protective gel properties: irrespective of the other alteration conditions, the higher the S/V ratio, the lower the D_g coefficient and the higher the silicon retention factor in the gel. The other alteration conditions can be considered to exert a secondary role on the protective properties of the gel.

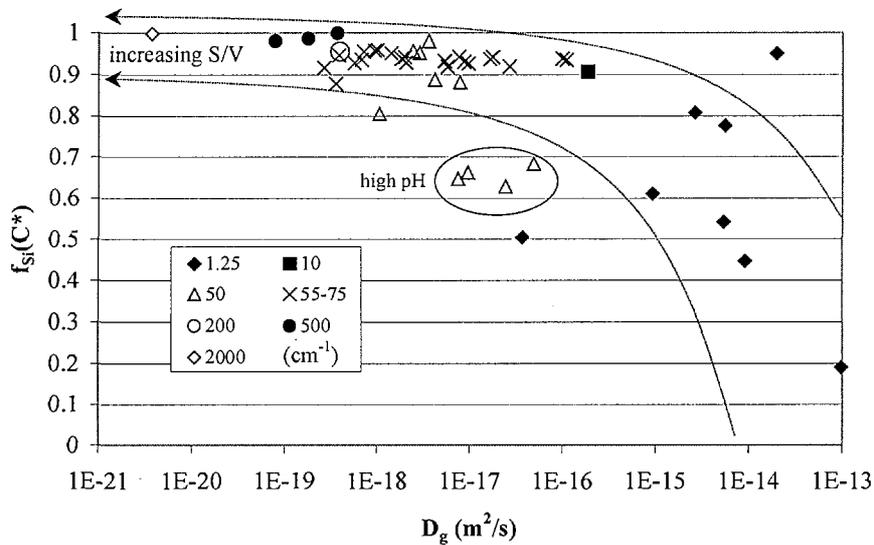


Figure 4. Maximum retention factor $f_{Si}(C^*) = 1 - \exp(-\alpha C^*)$ versus the apparent silicon diffusion coefficient D_g . The series of experiments were all carried out at the same S/V ratios, irrespective of the other leaching conditions (pH, temperature, renewal rate, composition).

5. CONCLUSION

The $r(t)$ model of glass alteration by water correctly accounts for the drop in the alteration rate observed during leaching of glasses from the R7T7 composition range under a variety of alteration conditions (pH, temperature, flow rate, S/V ratio). The methodology developed to determine the three internal parameters of this model (D_g , C^* and α) highlighted the following points:

- The apparent silicon diffusion coefficient, D_g , can be estimated within an order of magnitude, and ranges from $10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ to $10^{-21} \text{ m}^2 \cdot \text{s}^{-1}$ depending on whether the material is altered in a dilute medium with leachate renewal, or in a medium with very high silicon confinement.
- The silicon concentration C^* at which the glass ceases to be transformed into a gel is known within an order of magnitude. It ranges from 10 to 100 ppm under average alteration conditions (temperature below 100°C , pH between 7 and 10, renewal rate below 1.2 d^{-1} , and S/V ratio below 500 cm^{-1}).
- The silicon retention factor in the gel exceeds 50% when the water renewal rate is less than 0.05 d^{-1} , resulting in an αC^* product exceeding 1.

These trends will have to be confirmed under other experimental conditions, and in particular with radioactive glass specimens or in the presence of environmental materials such as canister corrosion products or engineered barrier clay, before the parameter values assigned to the $r(t)$ model can be considered complete.

Further consideration must also be given to a conservative manner of integrating the secondary phenomena affecting the long-term alteration rate, such as a possible residual rate or partial degradation of the gel, in order to obtain an "operational" model suitable for all possible alteration conditions. The results can then be used for predictive calculations of the glass source term under repository conditions.

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