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MODELLING OF THE SOLUTION RENEWAL WITH THE KINDIS CODE : EXAMPLE OF R7T7 GLASS DISSOLUTION AT 90°C

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MODELING OF SOLUTION RENEWAL WITH THE *KINDIS* CODE : EXAMPLE OF R7T7 GLASS DISSOLUTION AT 90°C.

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ABSTRACT

The deep underground environment that would correspond to a geological repository is a system open to fluid flow. It is therefore necessary to investigate the effects of solution renewal on the long-term behavior of glass in contact with water. These effects can now be simulated using the new version of the geochemical *KINDIS* model (thermodynamic and kinetic model).We tested the model at 90°C with an *SA/V* ratio of 400 m^{-1} at twelve renewal rates of pure water ranging from 200 to 0 vol% per day. With renewal rates between 200 and 0.065 vol% per day, steady-state conditions were obtained in the reaction system: i.e. the glass corrosion rate remained constant as did the concentrations of the dissolved species in solution (although at different values depending on the renewal rate). The ionic strength never exceeded 1 (the validity limit for the DEBYE-HÜCKEL law) and long term predictions of the dissolved glass mass, the solution composition and the potential secondary mineral sequence are possible. For simulated renewal rates of less than 0.065 vol% per day (27 vol% per year), the ionic strength rose above 1 (as in a closed system) before steady-state conditions were reached, making it critical to calculate long-term rates; A constant and empirical long-term rate, derived from laboratory measurement, have to be extrapolated. These calculations were based on a first order equation to describe the glass dissolution kinetics. The results obtained with the KINDIS code show discrepancies with some major experimental kinetic data (the long term rate must decrease with the « glass-water » reaction progress, under silica saturation conditions). This clearly indicates that a more refine kinetic relation is needed for the glass matrix.

INTRODUCTION

The general objective is to simulate aqueous corrosion of the French "R7T7" reference LWR nuclear waste containment glass over time as would occur following disposal in a geological repository. The time period (required by regulatory agencies) over which glass behavior in contact with water must be assessed is about 10,000 years [1,2]. Although the phenomenological and mechanistical aspects of glass-water interactions are extremely complex, solutions may be advanced using a model that is necessarily based on a simplified representation of the phenomena involved.

In order to predict the consequences of the interaction between glass and water, four types of phenomena must be taken into account in a model:

- *Glass corrosion reaction mechanisms.* The principal findings of experiments conducted over the last decade concern the importance of surface reactions [3, 4, 5]. They have also shown that ion exchange occurs by interdiffusion of glass network modifiers with protons or water, although this phenomenon has been found to be either transient or of secondary importance.

- *Reaction kinetics* measured and formalized by general and/or empirical laws. The dissolution kinetics of R7T7 glass are controlled primarily by the pH and dissolved silica concentration of the alteration solution [3, 4]. Control of the glass matrix corrosion kinetics by diffusion of aqueous species, especially the silicon, within the alteration films has also been reported [3, 6].

- *Behavior of glass chemical elements released into the liquid phase.* Among the components of a nuclear waste containment glass, special attention must be given to the behavior of the radionuclides (some of the important radionuclides for long-term predictions are Pu, Am, Np, Cm, Tc, Zr, Cs). However, this aspect cannot be separated from the overall assessment

of all the major chemical species with which various reactions occur: coprecipitation, adsorption, absorption, etc. A prerequisite to modeling these phenomena is to identify and quantify the processes by which elements are partitioned between the aqueous solution and the secondary alteration products (gel material and crystalline phases). Laboratory glass corrosion studies during the last decade have revealed the complexity of the processes by which alteration products form to constitute an alteration film on the glass surface [7, 8]. It is essential to note than in a dilute, oxidizing aqueous medium at neutral or basic pH, the alteration films exhibit strong containment of radionuclides such as the actinides [8, 9], as well as the rare earths and Zr [11]. Nevertheless, this is unquestionably the aspect of the problem that has been the least investigated to date.

- *Incidences on the glass behavior of environmental context.*The nature of the aqueous fluid in contact with the glass is first highly dependent on its interactions with the host rock, the engineered barrier and the canister. It is thus absolutely essential to develop a tool capable of predicting the effects of renewed alteration solution compositions on the long-term stability of the glass.

The scope of the present communication is to estimate with the *KINDIS* code the geochemical consequences of glass corrosion in initially pure water at 90°C, by taken into account the thermodynamics of chemical equilibria, the chemical kinetics and the leaching solution renewal.

THE *KINDIS* CODE.

Overview and current limitations.

The thermodynamic foundation for the *KINDIS* model is the *DISSOL* code [11]. The kinetic basis was added to *DISSOL* by MADE [12]. The program currently manages the following variables throughout the temperatures range from 0 to 300°C: 60 mineral phases, 3 solid solutions (with 2 pure poles) and 3 clay solid solutions (with 15 or 36 pure poles); 29 "basic" chemical elements (Al, K, Na, Ca, Mg, Fe2+, Fe3+, Mn2+, Mn3+, Sr, F, Li, Pb, Zn, Cu+, Cu2+, P, B, Si, N, NO3, S, C, CO3, Cl, O, H, H2O, e) and 145 aqueous species; A number of chemical elements found in R7T7 glass, notably Mo, the rare earths and the actinides, are not currently included in the *KINDIS* code.

The kinetic law of dissolution for the R7T7 reference glass [13] is as follows:

$$\vartheta = \frac{d\xi}{dt} = k^+ \frac{SA}{V}[H^+]^{-n}\left(1 - \frac{[H_4SiO_4{}^\circ]}{[H_4SiO_4{}^\circ]^*}\right) \tag{1}$$

where ϑ is the silicate dissolution rate, in $mole \cdot kg^{-1}{}_{H_2O}d^{-1}$; ξ is the reaction progress variable $(mole_{glass} \cdot kg^{-1}{}_{H_2O})$; k^+ is the dissolution kinetic constant, in $mole \cdot m^{-2}d^{-1}$; SA/V is the ratio between the reactant interface surface area and a unit solution mass, in $m^2 \cdot kg^{-1}$; $[H^+]$ is the proton activity in solution; $-n$ (-0.39 at 90°C) is the stoichiometric coefficient expressing the pH-dependence of k^+; $[H4SiO4^\circ]$ is the aqueous silica activity; $[H4SiO4^\circ]^*$ is the glass solubility product only based on silica $(10^{-3.009} mole.l^{-1}$ at 90°C).

The computer code operates by incrementing the time step and the dissolution of small amounts of glass into the aqueous phase, in order to calculate in time the molalities and activities of aqueous species, the molar quantities of potential secondary solid phases (any solid phases that are supersaturated are then precipitated), and the glass dissolution rate evolution. For each increment of time Δt, the variation of the concentration ΔC_i for the ith chemical element in solution is given by the following relation :

$$\frac{\Delta C_{i(n)}}{\Delta t} = \left(\left(-C_{i(n-1)} + C_i^{ren.sol.}\right) \times RR\right) + \left(\alpha_i \times \vartheta_{(n)}\right) \tag{2}$$

where n is the number of the time step (or increment of time); RR is the solution renewal rate, in volume % per day; C_i is the dissolved quantity for the ith chemical element in the reaction compartment, in $mole \cdot kg^{-1}$; $C_i^{ren.sol.}$ is the dissolved quantity for i in the renewal solution, in $mole \cdot kg^{-1}$; α_i is the number of mole of i in one mole of glass; $\vartheta_{(n)}$ is the glass dissolution rate.

Thus, for each simulation time step Δt, the system is pertubed by the irreversible kinetic dissolution of the glass *and* by solution renewal.
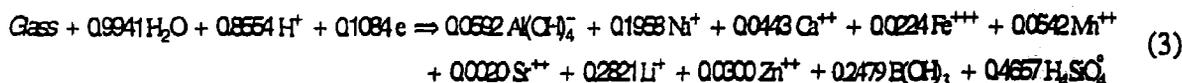
The extended DEBYE-HÜCKEL relation is used for activity coefficients calculations. However, it is valid only when the ionic strength does not exceed 1.

Our calculations do not account for the diffusion of silica species from the glass to the leaching solution through the alteration film, as the GLASSOL code [3] and the LIXIVER [6] code do.

Simulations : Temperature, SA/V ratio, Water Composition, Secondary phases.

Tests were conducted at 90°C, with an SA/V ratio of 400 m^{-1}. Glass corrosion was simulated in initially pure water at equilibrium with the carbon dioxide in the air ($pCO_2=10^{-3.5}$ atm.), and a pO_2 of 10^{-40} atm. A wide range of fluid renewal rates (RR) was tested, from 0 to 200 vol% per day (0, 0.05, 0.065, 0.075, 0.1, 0.25, 0.5, 2.5, 30, 50 and 200).

KINDIS does not currently allow for all the oxides found in R7T7 glass. The fission product oxides represent 11.24 wt% of the glass composition [14], but only SrO (0.33 wt%) is taken into account; the remainder (10.91 wt%) as well as all the actinide oxides (0.85 wt%), ZrO_2 from the glass frit and the metal fines suspension (1 wt%) and P_2O_5 (0.28 wt%) are replaced. MnO_2, Li_2O and ZnO oxides are substituted for them. This procedure maintains the correct concentrations and relative proportions of all the other major glass elements taken into account in the code (Si, B, Na, Ca, Sr, Fe and Al).The glass dissolution equation (for one mole) can therefore be determined as follows:

$$Glass + 0.9941H_2O + 0.8554H^+ + 0.1084e \Rightarrow 0.0692Al(OH)_4^- + 0.1958Na^+ + 0.0443Ca^{++} + 0.0224Fe^{+++} + 0.0542Mn^{++}$$
$$+ 0.0020Sr^{++} + 0.2821Li^+ + 0.0300Zn^{++} + 0.2479B(OH)_3 + 0.4657H_4SiO_4 \qquad (3)$$

Various potential secondary minerals (oxides, hydroxides, carbonates, tectosilicates and phyllosilicates) were selected and checked for saturation at each increment of the simulation (see ref.[13] for their solubility products). Appropriate solid phases able to constraint individual glass constituent release in the solution were widely discussed in reference [9].

MODELING GLASS CORROSION AT 90°C AND 400 m^{-1} IN STATIC MEDIA (RR=0% vol per day)

• Chemical Composition of Aqueous Solution Versus Time.

The simulated results are compared in figure 1 with the experimental data reported by GODON [15]. The calculated values for silica were closed to the measured values. The calculated boric acid concentrations over the first 100 days were well below the experimental values (by nearly a factor of 2), but approximated the measured results after 180 days. The pH measured after the experiments was higher than the calculated values by about 0.5 unit during the first 50 days, and similar thereafter. More generally, the higher experimental pH (notably during the first months) could account for the higher

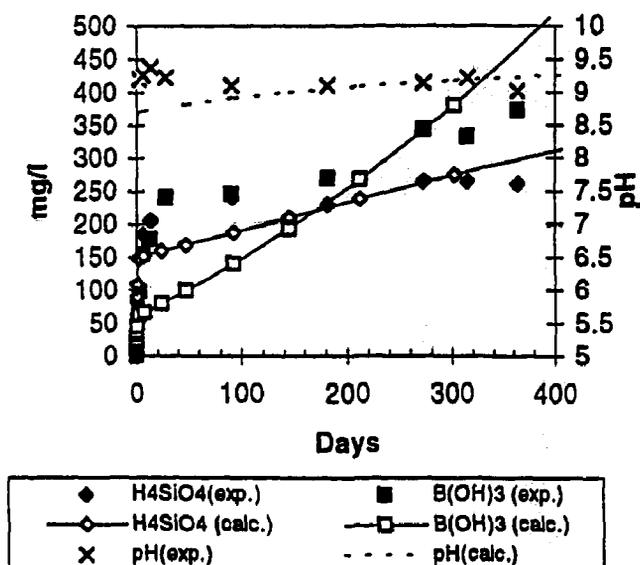| ◆ H4SiO4(exp.)	■ B(OH)3 (exp.)
—◇—H4SiO4 (calc.)	—□— B(OH)3 (calc.)
✕ pH(exp.)	- - - - pH(calc.)

Figure 1. Calculated versus experimental pH and concentrations of H4SiO4, B(OH)3. Aqueous corrosion of R7T7 glass for 1 year at 90°C, SA/V=400m-1.

dissolution rate, and therefore the higher $B(OH)_3$ and H_4SiO_4 concentrations measured during the experiments.The results for the minor elements (Al, Fe, Ca, Zn and Sr) between 1 day and 1 year were as indicated in the *table 1*. Except for Zn^{2+}, the experimental results for the "minor" elements were accounted for with relative success by the code (same order of magnitude).

• Secondary mineral equilibria (Figure 2)

Amorphous iron hydroxide quickly reached equilibrium (after 35 seconds). "TOT" clay began precipitating after 18 minutes, simultaneously eliminating iron hydroxide. Manganese and zinc hydroxides appeared respectively 1.5 and 2.4 hours after the beginning of the glass dissolution reaction, followed by strontium carbonate (strontianite: 3.8 hours) and calcium carbonate (calcite: 19 hours). After about 8 days, the minimum possible glass dissolution rate was reached due to precipitation of the metastable

Table I. Calculated versus experimental concentrations for minor elements. R7T7 glass corrosion for 1 year at 90°C, SA/V=400m-1.

Element	Experimental Concentrations (mg·l⁻¹)	Calculated Concentrations (mg·l⁻¹)
Al(OH)₄⁻	2.9 (σ= 0.7)	2.95 (σ= 0.85)
Fe²⁺	n.d.	2×10^{-12}
Ca²⁺	0.9(σ= 0.5)	1.5 (σ= 0.8)
Sr²⁺	0.03 (σ= 0.007)	0.05 (σ= 0.04)
Zn²⁺	0.07 (σ= 0.03)	0.34 (σ= 0.003)
Mn²⁺	–	0.006 (σ= 0.005)

siliceous compound SiO_2(m) controlling the orthosilicic acid activity in solution. The last mineralogical event was the formation of low-temperature albite after 50 days of interaction. After one year, the dominant silicate minerals were albite, metastable silica gel and « TOT » clay, which together accounted for about 60 wt% of the simulated alteration products.

• Glass Dissolution Rate versus Time

The minimum rate (8.67 × 10^{-3} $g \cdot m^{-2}d^{-1}$) was observed after 8 days when saturation occurred with $SiO_{2(m)}$ (Fig. 1 and 2). Precipitation of this compound at equilibrium determined the $H_4SiO_4^{\circ}$ activity of $10^{-3.01}$, preventing the system from reaching saturation with respect to the R7T7 glass (i.e. $10^{-3.009}$) that would have caused the dissolution to cease [3, 5, 9, 13]. Under experimental conditions, the minimum rate was 2.5 × 10^{-3} $g \cdot m^{-2}d^{-1}$ [16], and stayed at this value over a 1 year period. During the calculation, the pH of the alteration solution continued to increase slowly, and the glass dissolution rate increased again after about 100 days. This was primarily attributable to the very alkaline pH (> 9), which caused the $[H_4SiO_4^{\circ}]/[H_3SiO_4^-]$ ratio to drop and increased the product of the kinetic constant by the proton activity ($k^+ \cdot [H^+]^{-0.39}$). The calculation was interrupted after a simulated 25-year period, when the ionic strength reached 1 (above which the DEBYE-HÜCKEL law is no longer applicable for computing activity coefficients). These calculations thus show that an increasing reaction progress induces a slight increase in the dissolution rate under silica saturation conditions. This is however clearly inconsistent with experimental data where an increase in the SA/V ratios (i. e. an increase of the glass/water reaction progress) conducts to a decrease of the dissolution rate, under silica saturation conditions [16].

MODELING GLASS CORROSION AT 90°C AND 400 m-1, WITH A FLOWING, SLIGHTLY CARBONATED SOLUTION.

Among the wide range of flow rates which was tested, only the results for two very different renewal rates are discussed in detail, although the other results are summarized below. There are not yet experimental data (on a 1 year period) to compare with the simulated results.

Simulation with High Solution Renewal Rate (50 vol% per day)

The results obtained with a renewal rate of 50 vol% per day are illustrated in figure 3 (evolution of the solution chemistry) and figure 2 (evolution of the secondary minerals).

During the first four hours of the simulated interaction (log t = –0.8 day) the variations in the pH, the orthosilicic acid activity and the glass dissolution rate differed only slightly from the values obtained without solution renewal, although 8.3% of the solution volume had been replaced during that time. The differences gradually became evident, and after 24 simulated days (log t = 1.38 day) the system with solution renewal reached steady-state conditions : a total of 2.897 $g \cdot kg^{-1}_{H_2O}$ of glass had dissolved (the log of the number of moles dissolved was -1.382). Steady-state dissolution occured when the gains due to glass dissolution were offset by the losses due to solution renewal. The solution properties at that time are shown in the *table II*. After 24 days the alteration solution pH was 8.65, the orthosilicic acid activity was $10^{-3.086}$
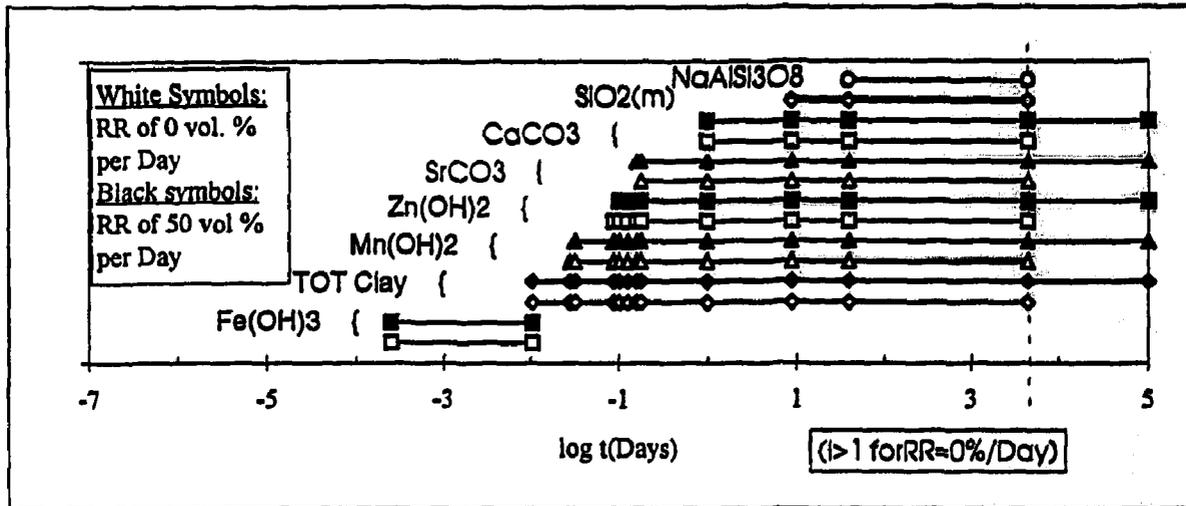
Figure 2. Evolution of secondary minerals with time during aqueous corrosion of R7T7 glass at 90°C, SA/V=400m-1, with 0 vol%/day and 50 vol%/day renewal of alteration solution.
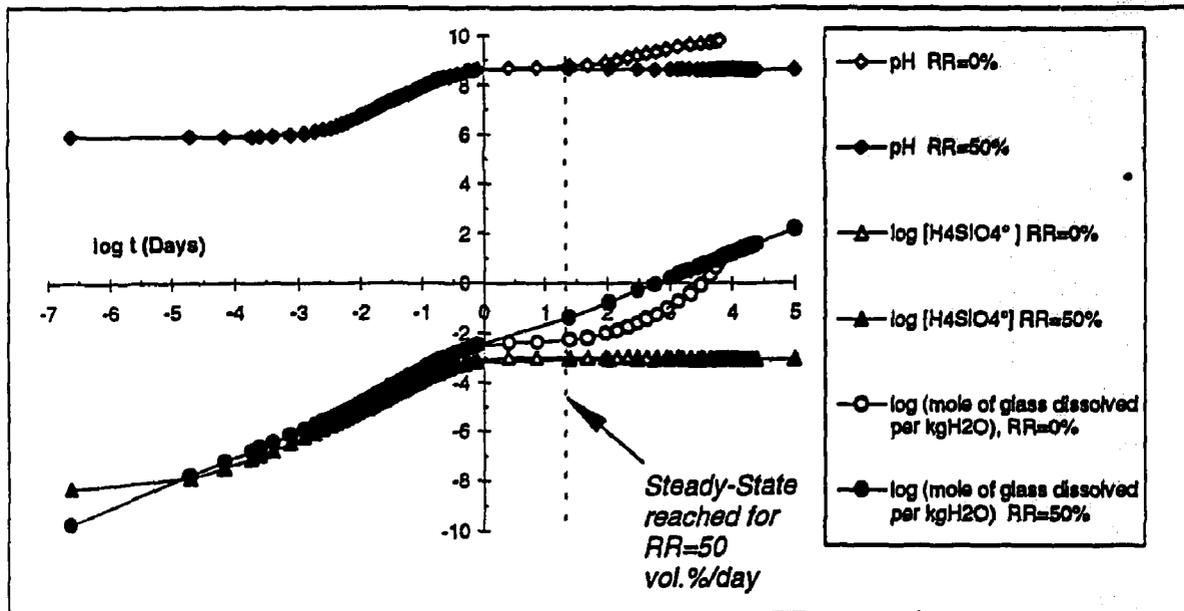

Figure 3. Calculated pH, concentrations of H4SiO4,and quantity of glass dissolved versus time. KINDIS code simulation results for aqueous corrosion of R7T7 glass at 90°C, SA/V=400m-1, with 0 vol% and 50 vol% renewal of alteration solution.

and the corresponding steady-state dissolution rate was 0.156×10^{-2} mole·kg^{-1}$_{H_2O}$d^{-1} (0.27 g·m^{-2}d^{-1}). Solution renewal by pure water thus increased the dissolved glass quantity after 1 year, compared with a closed system (Figure 3).The simulation was interrupted after 274 years. Once steady-state conditions are reached, however, and assuming the renewal solution composition, flow rate, temperature, and the SA/V ratio remain constant, the state of the "glass–water–secondary mineral" system is predictable regardless of the

Table II. Calculated rate and concentrations for major elements, at steady-state. 90°C, SA/V=400m^{-1}, with a solution Renewal Rate of 50 vol%/day.

H$_4$SiO$_4$ (mg·l^{-1})	120.1
B(OH)$_3$ (mg·l^{-1})	49.2
[H$_4$SiO$_4$$^\circ$]	10$^{-3.086}$
R (g·m^{-2}d^{-1})	0.2706
pH	8.65
Ionic strength	10$^{-2.767}$

time period, since the glass corrosion rate will remain constant at 0.27 g·m^{-2}d^{-1} (*Table II*).

Simulation with Low Solution Renewal Rate (0.5 vol% per day)

The results provided by *KINDIS* with a renewal rate of 0.5 vol.% per day (182 % per year) are illustrated in Figure 4. The variations of the pH, the orthosilicic acid activity and the dissolved
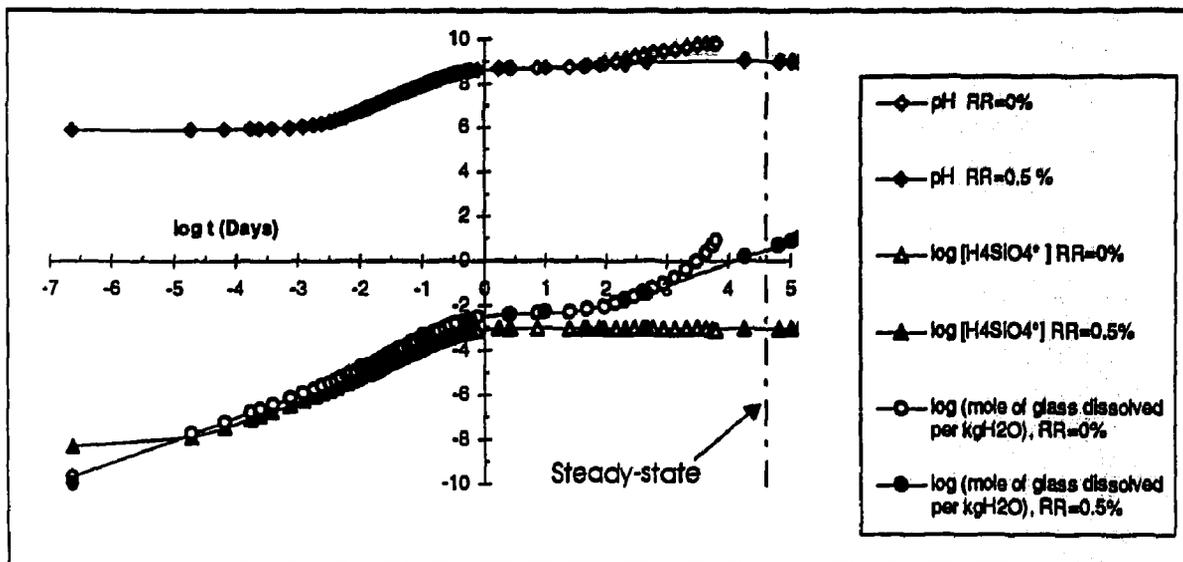
Figure 4. Calculated pH, concentrations of H4SiO4,and quantity of glass dissolved versus time. KINDIS code simulation results for aqueous corrosion of R7T7 glass at 90°C, SA/V=400m⁻¹, with 0 vol% and 0.5 vol% renewal of alteration solution.

glass quantity were very similar to those obtained without renewal up to about $10^{1.5}$ days (31.6 days), despite the fact that 15.8% of the alteration solution had been renewed by that time. The minimum dissolution rate for this low flow rate was obtained after about 2.7 days: 0.5×10^{-4} mole·kg⁻¹$_{H_2O}$d⁻¹ (8.67×10^{-3} g·m⁻²d⁻¹).

As already observed with a high renewal rate, the two systems then gradually diverged. However, in the same way as for the simulation without the flow term, the ratio of the [H₄SiO₄°] to [H₄SiO₃⁻]

Table III. Calculated rate and concentrations for major elements, under steady-state condition. Aqueous corrosion of R7T7 glass at 90°C, SA/V=400m⁻¹, with a solution Renewal Rate of 0.5 vol%/day.

H₄SiO₄ (mg·l⁻¹)	212.6
B(OH)₃ (mg·l⁻¹)	200.5
[H₄SiO₄°]	10⁻³·⁰¹¹
R (g·m⁻²d⁻¹)	1.16 × 10⁻²
pH	9.01
Ionic strength	10⁻²·²⁵

activities diminished as the pH rose to highly alkaline values (> 9). This caused the dissolution rate to increase after reaching a minimum, although the magnitude of the increase was lower than in the closed system: as shown in Figure 4, the curve plotting the number of moles of dissolved glass in the renewed system remained below the curve for the closed system. Steady-state conditions were finally reached after 182 years, at which time the alteration solution properties were as indicated in the table III. Lastly, it should be noted that the final secondary mineral association was identical with the results given by KINDIS without solution renewal (not shown here). All the potential secondary minerals reached equilibrium at virtually the same moment in both cases because their formation rate was very fast (a few minutes or hours) compared with the renewal rate.

Review and Discussion of Simulation Results for Various Renewal Rates.

The steady-state results of simulations with various flow rates at 90°C and 400 m⁻¹ are indicated in the table IV. Some rough calculations were also reported in columns 7 and 8, to estimate the long term stability of a cylindric glass block of 412 kg, 15.35 m² (fracturation rate of 9), and in contact with 38 kg$_{H_2O}$ (10.7 kg$_{glass}$ per kg$_{H_2O}$, or 0.4 m²$_{glass}$ per kg$_{H_2O}$). After 500 years, we estimated that the steady-state dissolution rates were 5 time lower than the values reported in column 6, in order to take into account the temperature decrease from 90°C to 50°C of the glass cylinder in time (the experimental final rates determined at 90°C and 50°C were respectively equal to 6×10^{-4} and 1.2×10^{-4} g.m⁻².d⁻¹ [4, 16]).

The higher the simulated renewal rates, the earlier steady-state conditions occurred in the reaction system. As could be expected, increasing the solution renewal rate (using pure water)

resulted in correspondingly lower pH and ionic strength values. Conversely, as soon as steady-state conditions were obtained, the corrosion rate and the solubilized glass quantity followed a « *parabolic relation* » dependent on the renewal rate (column 6 in *table IV*).

• For renewal rates (*RR*) of 200 to 1 vol% per day, the glass dissolution rate and dissolved glass quantity calculated over a 500 year period gradually diminished (columns 6 and 7, *table IV*). The reason is that, as *RR* decreased, the moment at which steady-state conditions were reached tended increasingly to coincide with the moment when the system reached the minimum possible glass corrosion rate. This fundamental trend is controlled by the increasingly high steady-state orthosilicic acid activity, which approaches the saturation value of the $SiO_2(m)$ compound $(10^{-3.01})$ as *RR* decreases.

*Table IV.KINDIS code simulation results of glass corrosion with various flow rates (of pure water) at 90°C and 400 m-1, under steady-state conditions. An asterisk * indicates that silica saturation was reached (the molar weight of R7T7 glass is 69.39).*

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
RR (vol% per day)	pH	log [$H_4SiO_4°$]	log (I)	Mineralogical Association	Dissolution Rate ($mol·kg^{-1}d^{-1}$)	Dissolved Glass Mass after 500 Years at 90°C ($kg·kg^{-1}_{H2O}$)	Mass% of the initial glass cylinder corroded after 10^4 years
200	8.51	−3.11	−2.96	TOT Clay + Mn(OH)₂ + Zn(OH)₂ + SrCO₃	0.383×10^{-2}	48	100%
50	8.62	−3.086	−2.77	TOT Clay + Mn(OH)₂ + Zn(OH) + SrCO₃ + CaCO₃	0.156×10^{-2}	19	100%
30	8.67	−3.058	−2.72	(same as above)	0.106×10^{-2}	8.5	100%
2.5	8.70	−3.013	−2.68	(same as above)	0.100×10^{-3}	1.3	56%
1	8.78	−3.011*	−2.58	(same as above) + SiO₂(m) + albite	0.537×10^{-4}	0.7	30%
0.5	9.01	−3.011*	−2.25	(same as above)	0.670×10^{-4}	0.9	39%
0.25	9.28	−3.011*	−1.81	(same as above)	0.919×10^{-4}	1.2	52%
0.1	9.57	−3.013*	−1.07	(same as above)	0.177×10^{-3}	2.3	100%
0.075	9.66	−3.016*	−0.71	(same as above)	0.369×10^{-3}	4.7	-
0.065	9.68	−3.023*	−0.59	(same as above)	0.486×10^{-3}	6	-
0.05	⁊	< −3.02*	> 0	(same as above)	-	-	(see text)
0	⁊	< −3.02*	> 0	(same as above)	-	-	(see text)

• At renewal rates of 1 vol% per day or less, the metastable $SiO_2(m)$ compound reaches saturation and the orthosilicic acid activity is therefore maximal. Nevertheless, the glass corrosion rate and the quantity of glass dissolved in 500 years increase as *RR* continues to decrease. At renewal rates of 1 to about 0.25 vol% per day, the corrosion rate is controlled mainly by the steady-state pH; at lower *RR* values, the increase in the steady-state glass corrosion rate results from the combined effects of the pH rising to highly alkaline values (because of passive accumulation of boron, sodium and lithium in solution) and the diminishing orthosilicic acid activity in solution (attributable to strong dissociation forming $H_3SiO_4^-$). We may however consider, as already discussed for the static media, that such « parabolic trend » is inconsistent with some general experimental evidences. Indeed, diminishing the flow rate conducts to an enclosed aqueous media. In static media, the rate decreases with time (i.e. the reaction progress): the larger the glass reaction progress, the lower the glass dissolution rate [16]. The simulated data reported in the *table IV* (columns 6 and 7) are on this point inconsistent, for the lowest renewal rates (1 to 0.065 vol%). Thereby, the values reported in column 8 are highly questionable. So, we may conclude that a kinetic relation for the glass, only based on pH and orthosilicic activity, is in part inconsistent to reproduce experimental observations. The relevance for long term simulation results is directly dependent on these inconsistencies.

- The validity limit of the DEBYE-HÜCKEL law $(I > 1)$ is reached after a few hundred years, when the renewal rate drops below 0.065 vol% per day (24 vol% per year) at a temperature of 90°C and an SA/V ratio of 400 m^{-1}. Direct predictions by the code over long term period are then critical, except a constant « long term rate » [3], extracted from laboratory experiments, is considered (6×10^{-4} g.m^{-2}.d^{-1} at 90°C and 1.2×10^{-4} g.m^{-2}.d^{-1} at 50°C [4, 16]). In this case, about 1.9 mass% of the initial glass block should be dissolved after 10000 years. This last value should be regarded as the most relevant for a closed media.

CONCLUSIONS.

Renewal of the glass alteration solution by a pure water solution allows the reaction system to reach steady-state conditions.The qualitative and potential quantitative effects of the flow term on a kinetic simulation of R7T7 glass at 90°C and 400 m^{-1} were estimated for a wide range of simulated flow rates (200 to 0 vol% per day). Several significant conclusions may be drawn from this work:

- With renewal rates between 200 and 0.065 vol% per day, steady-state conditions are obtained in the reaction system and predictions are theoretically possible over a period of 10 000 year.

- For simulated renewal rates of less than 0.065 vol% per day (27 vol% per year), the ionic strength rises above 1 before steady-state conditions are reached (as under static conditions). It is therefore impossible to establish long-term predictions, unless a constant «final rate » is retained. In this case, 1.9% of the initial glass block could be corroded after 10000 years.

- The calculations revealed a parabolic relation between the rate and the quantity of glass dissolved after 10 000 years and the daily solution renewal volume percentage. This ratio diminishes for renewal rates of 200 to 1 vol% per day, but increases for lower renewal rates. The minimum dissolved glass quantity was obtained for a daily solution renewal rate of 1 vol%, and not for a lower value. However, our calculations show that major uncertainies remain on the long term rates. The relevance for long term simulation is directly dependent on a more refined kinetic relation for the glass.

Finally, a daily solution renewal of several vol% per day is very high, and would no doubt be considered unrealistic for a nuclear waste repository (values lower than 0.01vol% per day could be more realistic). We may also note that different SA/V ratios and aqueous solution compositions may lead to completely different conclusions.

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