

ENHANCEMENT OF THE GLASS CORROSION IN THE PRESENCE OF CLAY MINERALS: TESTING EXPERIMENTAL RESULTS WITH AN INTEGRATED GLASS DISSOLUTION MODEL.

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ABSTRACT

Recent glass dissolution experiments, conducted at 90°C in the presence of potential backfill materials, indicate remarkably faster glass corrosion in the presence of clay, compared to tests where the glass is leached either alone or with alternative backfill materials. This effect correlates with the clay content in the backfill, and may be attributed to the removal of silica from solution. Sorption, or dissolution with reprecipitation of a silica-rich clay, have been proposed as possible mechanisms for the silica consumption.

The results of some experiments have been tested against a glass dissolution model, in which a widely used kinetic equation for glass corrosion is coupled with diffusive silica transport through a single porosity, linearly sorbing medium, which represents the backfilling. Because the glass corrosion rates imposed by the kinetic equation are inversely proportional to the silicic acid concentration of the leachant contacting the glass, the model predicts enhanced glass dissolution if silica is sorbed by the porous medium.

The experimental data proved to be consistent with the predicted enhancement of the glass dissolution. Moreover, the model-estimated distribution coefficients for silica sorption (K_d) fall within the range of values extracted from available literature data, thus supporting the hypothesis that the observed high corrosion rates are due to sorption of silica on the clay mineral surfaces.

INTRODUCTION

Synthetic borosilicate glass is one of the most promising materials for high-level radioactive waste (HLW) immobilization [1] and will probably serve as matrix for spent nuclear fuel in many countries, including Switzerland and France. Studies of glass corrosion kinetics are essential in determining a source-term function for the release of radionuclides from the waste matrix. A vast literature exists on this topic, including experimental as well as model studies [2]. One of the most widely accepted results emerging from the experimental data, is that glass corrosion depends on the silicic acid concentration according to a first-order equation of the form [3]:

$$R = k^+ \left(1 - \frac{[H_4SiO_4]}{K} \right) \quad (1)$$

where: R	is the normalized glass corrosion rate	$[\text{kg m}^{-2} \text{s}^{-1}]$
k^+	is the corrosion rate in Si-free solutions	$[\text{kg m}^{-2} \text{s}^{-1}]$
$[H_4SiO_4]$	is the activity of orthosilicic acid in the solution contacting the glass surface	[-]
K	is an empirically derived constant	[-]

A similar equation is used by the Commissariat à l'Énergie Atomique (CEA) in France [4]. Equation (1) imposes a linear decrease of the corrosion rate with increasing silicic acid con-

centration in the leachant. This concentration, however, cannot increase indefinitely. Instead, it reaches a limiting value (saturation concentration) at which glass corrosion apparently proceeds at a minimum rate usually called *saturation rate* or *long-term rate* (R_{sat}). The saturation concentration is probably determined by the precipitation of an unidentified siliceous compound. It is usually assumed, but not proven, that glass dissolution in the saturated solution will continue indefinitely at the saturation rate.

Recently, a model was developed which combines the glass corrosion equation formulated above with the effects of diffusive transport and silica sorption in a porous backfill for a setup with cylindrical geometry roughly similar to that foreseen in the Swiss HLW repository [6]. It neglects, however, the influence of precipitating or dissolving silicates, as the kinetics and even the identity of such reactions are virtually unknown. The model is formalized in a Fortran code called GLADIS.

The model has not yet been tested against suitable experimental data. An opportunity is now given by a set of experiments conducted recently at CEA Marcoule. In this study, the results of such experiments are compared against appropriate calculations performed with GLADIS, in order to check whether the simple model assumptions are sufficient to explain satisfactorily the results of the mentioned experiments.

MODEL DESCRIPTION

The formalism on which the model is based was thoroughly discussed in a previous paper [6]. Essentially, the following equations are solved numerically:

$$\frac{\partial c}{\partial t} = \frac{D_p}{R} \left(\frac{\partial^2 c}{\partial r^2} + \frac{\partial c}{r \partial r} \right) \quad (2)$$

$$\alpha [1 - \beta c(r_1, t)] = \epsilon D_p \frac{\partial c}{\partial r}(r_1, t) \quad (3)$$

$$c(r_2, t) = c_0 \quad (4a)$$

$$\text{or: } \frac{\partial c}{\partial r}(r_2, t) = 0 \quad (4b)$$

where:

$c(r, t)$	is the dissolved bulk silica concentration as a function of the radial position (r) and of time (t)	$[\text{mol.m}^{-3}]$
D_p	is the pore diffusion coefficient for silica	$[\text{m}^2.\text{s}^{-1}]$
R	is the retardation factor	$[-]$
ϵ	is the bentonite porosity	$[-]$
α	is the net silica flux of Si from the glass into bentonite in silica free solutions, i.e. when $c(r_1, t) = 0$	$[\text{mol.m}^{-2}.\text{s}^{-1}]$
β	is a factor accounting for the Si speciation in solution	$[-]$
r_1	is the radial position at the glass/bentonite interface	$[\text{m}]$
r_2	is the radial position at the bentonite outer boundary	$[\text{m}]$
c_0	is the dissolved Si concentration in the host-rock	$[\text{mol.m}^{-3}]$

Equation (2) is the basic transport equation in cylindrical geometry for purely diffusive transport of dissolved silica through a linearly sorbing, water-saturated bentonite. The assumption of linear (i.e. concentration independent) sorption is implicitly incorporated in the retardation factor, which is a function of the bentonite porosity and of the *distribution coefficient* (K_d , [$\text{kg}\cdot\text{m}^{-3}$]). The K_d defines a constant ratio between sorbed and dissolved silica concentrations within the porous medium.

Equation (3) specifies the inner boundary condition (glass/bentonite interface) by requiring the net flux of silica due to glass dissolution to match Fick's 1st law. The left-hand term of equation (3) is a modified form of the previously discussed corrosion equation (1). The modifications account for: a) the retention of a fraction of the silica liberated from the glass on the surface alteration layer [4], b) the increase of the surface area exposed to corrosion due to cooling-induced glass fragmentation, and c) the dissociation of silicic acid at alkaline solution pHs. The factor β includes a term relating the *bulk* silica concentration to the silicic acid activity through a simple speciation model, which accounts for the dissociation to H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$ at alkaline pH values. This term is a function of pH and of the dissociation constants, and enables the transformation of equation (1) in terms of bulk silica concentration rather than of silicic acid activity. This transformation is needed to formulate equation (3) in a way consistent with the transport laws, since the gradient in the right-hand term refers to the bulk dissolved silica, not just to the silicic acid concentration.

Finally, equations 4a) and 4b) define two alternative boundary conditions at the outer bentonite edge (bentonite/host-rock interface). In the first case, a constant dissolved silica concentration (c_0) is assumed, which corresponds to the silica concentration in the pore water permeating the host-rock. In the second case, diffusion into and out of the bentonite outer boundary is forbidden by requiring a zero concentration gradient. Such a condition applies to closed systems, as are the experimental setups of the modeled CEA experiments, where the outer boundary is defined by the walls of the reaction vessels. All model calculations presented in this paper used therefore equation (4b) as outer boundary condition.

DESCRIPTION AND INTERPRETATION OF THE EXPERIMENTS

Recently, glass leaching experiments simulating repository conditions were carried out at CEA, Marcoule (France). Detailed descriptions of the experiments and their results can be found in [7, 8].

Experiments with 11 backfill materials (3 smectites, 3 bentonites, 3 illites, sand, and a granite) showed that glass corrosion is markedly faster in the presence of backfill materials containing clay than in the presence of clay-free materials or with no backfill at all. A unique exception was a peculiar bentonite, which differs from the others by the presence of minute, easily soluble opal spherules (diameter less than $0.1 \mu\text{m}$). Apparently, the opal dissolved rapidly, leading rapidly to high silica concentrations in the leachant and consequently to very low glass corrosion rates. This effect, however, may be transitory, since opal could be replaced in the long term by quartz, a more stable and less soluble SiO_2 modification, which would lead to glass corrosion rates an order of magnitude higher.

The detrimental effect of most clay materials on the glass performance may be explained by assuming specific adsorption of silica on the edge surfaces of disrupted clay

particles [7,8]. Yariv and Cross [9] showed that silica sorption on mineral surfaces reaches a maximum at $\text{pH} = \text{pK}$ of silicic acid, i.e. in the region buffered by most borosilicate glasses used for the immobilization of radioactive waste ($\text{pH} \sim 9-10$).

Among the various experiments performed, the Moist Clay Tests (MCT) were judged to be the most suitable for a comparison with the GLADIS model. In the first place, the enhancement of the glass corrosion rate was stronger, since a pure smectitic clay was used instead of diluted sand/clay mixtures. Secondly, the MCT experiments were carried out under static conditions, in agreement with the model assumptions, whereas other potentially suitable experiments required considerable exchange of leachant (thus simulating an advective flux). In the MCT experiments, small wafers of RT17 glass ($25 \times 25 \times 3$ mm) were leached in a clay paste saturated with granitic water. The tests were carried out in steel vessels of 50 ml volume, containing 30 ml of leachant and 50 g of backfill material. The total amount of glass corroded per unit surface area (NL_{glass}) was estimated by measuring the net mass loss of the glass specimen. This is a minimum estimate, as the measured weight loss does not include the weight of the corrosion products retained on the surface alteration layer of the glass. Thus, the raw data were corrected by a factor of about 40%, estimated from the thickness of the altered layer.

MODELING RESULTS

When modeling the MCT experiments, we had the following objectives in mind: (1) to find out whether these data can be modeled successfully assuming silica sorption on the clay surface; and, if the answer to (1) is affirmative: (2) to estimate a range of distribution coefficients (K_d) for silica from the modeling results, and (3) to check it for consistency with the available literature data.

The modeled data stem from a 2 year experiment performed with an inactive version of the RT17 glass. The raw and the corrected data are reported graphically on Figure 1, along with model curves obtained by varying the distribution coefficients for silica from zero (no sorption) to infinity (corrosion proceeding at the maximum possible rate, $R = R_0$). The plots report the mass losses of the glass per unit exposed surface area (NL_{glass}) as a function of time. The open circles (raw data) represent the net mass losses measured at the conclusion of the experiments, while the solid circles represent the same data corrected for the weight of the alteration layer. A list of the input parameters used in the calculations is shown on Table 1.

Figure 1 clearly demonstrates that the experimental data cannot be interpreted without assuming a mechanism removing silica from solution, like sorption by the backfill material. If the raw data are used to derive a minimum estimate of K_d , a value of $0.005 \text{ [m}^3/\text{kg]}$ is required. The corrected data are compatible with values up to $0.5 \text{ [m}^3/\text{kg]}$ for reaction times up to half a year. If the 2 year measurement is considered, a much narrower range (0.005 to $0.01 \text{ [m}^3/\text{kg}]$) appears to be a more reasonable extrapolation. Most measurements were made at times where the curves are linear and poorly discriminated. More accurate results would be obtained if both time scale of the experiment and frequency of the measurements in the region where the curve smooths out could be increased, and if the amount of solid alteration products precipitating on the glass could be determined precisely. Long-time experiments would cover the region where the mass loss vs. time functions display a characteristic curvature due to a substantial reduction of the corrosion rate (Figure 2), allowing a better check for con-

sistency of the model with the analytical data. In that sense, the GLADIS model could be used as a tool to plan future experiments, as it can predict the times at which the curves start to bend. For instance, all the mass loss curves which are still linear and close to each other after 1 year (see Figure 1) are clearly discriminated after 5 years (compare with Figure 2). Thus, a 5 year experiment with the same configuration would lead to more accurate results.

Table 1 - Key parameters for model calculations. The values stem from CEA internal laboratory data.

initial corrosion rate	R_0	1.5×10^0	$[\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}]$
saturation rate	R_{sat}	1.0×10^{-2}	$[\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}]$
temperature	T	9.0×10^2	$[^{\circ}\text{C}]$
pH	pH	8.5×10^0	$[\text{pH units}]$
fraction of Si retained on glass surface	p	3.0×10^{-1}	$[-]$
porosity of backfill material	ϵ	5.0×10^{-1}	$[-]$
pore diffusion coefficient in backfill	D_p	1.0×10^{-9}	$[\text{m}^2/\text{s}]$
thickness of backfill	$r_2 - r_1$	1.5×10^{-2}	$[\text{m}]$
radius of equivalent glass cylinder	r_1	1.5×10^{-3}	$[\text{m}]$
distribution coefficient of silica	K_d	0.0 to 0.5	$[\text{m}^3/\text{kg}]$

Table 2 reports the distribution coefficients (K_d) for silica in montmorillonite and bentonite suspensions, as determined from three experimental studies carried out at 25 °C, at neutral to alkaline pHs. The comparison shows that the K_d values from the literature are roughly consistent with those determined by modeling the CEA experiments, as the corrected model values lie within the range defined by the experimental values. Further, a simple calculation shows that the modeled distribution coefficient are comparable with data on the site density of hydrous oxide surfaces. The surface site occupancy was calculated for $K_d = 0.5$ $[\text{m}^3/\text{kg}]$, assuming a specific surface area of 5.5×10^5 $[\text{m}^2/\text{kg}]$ for the smectite backfill [10], and a silica dissolved concentration of 2.5×10^{-3} $[\text{mol/l}]$ (the saturation concentration of the glass at pH=9). The result was a surface coverage of about 2.3×10^{-6} $[\text{mol}/\text{m}^2]$, which is slightly less than the maximum site density of 3.84×10^{-6} $[\text{mol}/\text{m}^2]$ recommended by Davis and Kent for oxide mineral surfaces [11]. Thus, a K_d of 0.5 $[\text{m}^3/\text{kg}]$ is still consistent with the limits imposed by the chemical structure of mineral surfaces, although it should be regarded as an overconservative value.

Table 2 - Distribution coefficients of silica on montmorillonites and a bentonite, calculated from literature data.

MATERIAL	LEACHANT	pH	K_d $[\text{m}^3/\text{kg}]$	REFERENCE
Montmorillonite	seawater	8.4	0.018-0.057	[12]
Montmorillonite	seawater	9.0	0.066-0.148	[12]
Montmorillonite	Si+dist.water	6-9	0.014-0.018	[12]
Wyoming bentonite	Si+dist.water	9.0	0.166	[13]
Montmorillonite	Si+dist.water	7.0	0.500	[14]

There are, however, some inconsistencies which limit the application of the GLADIS model to the MCT experiments. For instance, the model assumes cylindrical geometry and linear sorption. Neither requirement is strictly satisfied, as the glass specimens used in the experiments are not cylindrical (thin wafers), and silica sorption on clays has been shown to be to some extent non-linear [12].

Figure 1 - Comparison of model calculations with the MCT tests, in which a wafer of inactive R7T7 glass was leached by granitic water in a pure smectite paste. Open circles represent raw data, while solid circles are the same data corrected for the estimated weight of the glass surface alteration products.

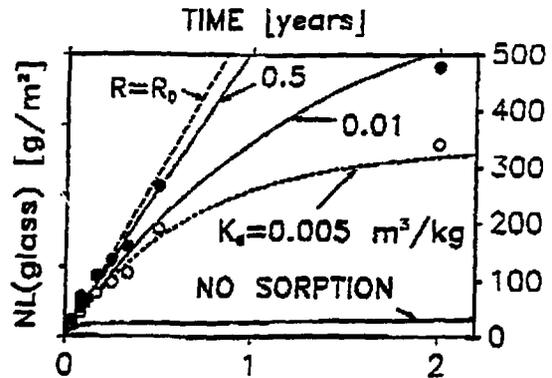
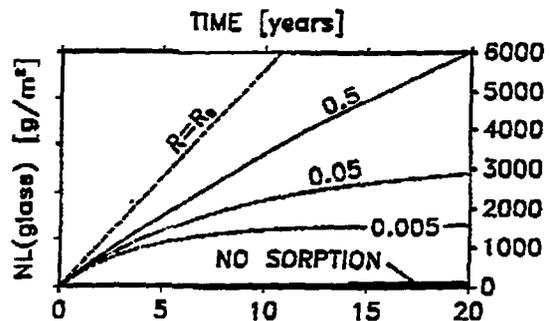


Figure 2 - Extended graph of model curves, labeled with the assumed K_d for Si sorption on bentonite in $[m^3/kg]$. This plot shows that discrimination among the different NL_{glass} vs. time isotherms improves with time. The characteristic "bending" of the curves, which occurs when silica saturation is approached, is visible on this figure also for large distribution coefficients.



CONCLUSIONS

(1) The enhanced glass corrosion observed in the MCT experiments cannot be predicted by the model if the backfilling is assumed not to sorb silica at all.

(2) The model reproduces the MCT results reasonably well, if distribution coefficients between 0.005 and 0.5 m^3/kg are assumed. The best fit is obtained for $K_d = 0.01 m^3/kg$, which is a value frequently extrapolated from literature data on sorption of silica on montmorillonites and bentonites.

(3) The GLADIS model is a promising tool for predicting the potential damages to the repository performance due to silica sorption in the backfilling, and can be used to plan future glass leaching experiments simulating repository conditions.

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