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First-order dissolution rate law and the role of surface layers in glass performance assessment

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Abstract

The first-order dissolution rate law is used for nuclear waste glass performance predictions since 1984. A first discussion of the role of saturation effects was initiated at the MRS conference that year. In paper (1) it was stated that "For glass dissolution A^* (the reaction affinity) cannot become zero since saturation only involves the reacting surface while soluble elements still might be extracted from the glass" [B. Grambow, J. Mater. Res. Soc. Symp. Proc. 44 (1985) 15]. Saturation of silica at the surface and condensation of surface silanol groups was considered as being responsible for the slow down of reaction rates by as much as a factor of 1000. Precipitation of Si containing secondary phases such as quartz was invoked as a mechanism for keeping final dissolution affinities higher than zero. Another (2) paper [A.B. Barkatt, P.B. Macedo, B.C. Gibson, C.J. Montrose, J. Mater. Res. Soc. Symp. Proc. 44 (1985) 3] stated that "… under repository conditions the extent of glass dissolution will be moderate due to saturation with respect to certain major elements (in particular, Si, Al and Ca). Consequently, the concentration levels of the more soluble glass constituents in the aqueous medium are expected to fall appreciable below their solubility limit." The formation of dense surface layers was considered responsible for explaining the saturation effect. The mathematical model assumed stop of reaction in closed systems, once solubility limits were achieved. For more than 15 years the question of the correctness of one or the other concept has seldom been posed and has not yet been resolved. The need of repository performance assessment for validated rate laws demands a solution, particularly since the consequences of the two concepts and research requirements for the long-term glass behavior are quite different. In concept (1) the stability of the 'equilibrium surface region' is not relevant because, by definition, this region is stable chemically and after a potential mechanical destruction it will be reformed instantaneously. The same is true for radiation damage. The dissolution of silica from the surface in this concept is considered as rate limiting for the release of soluble elements from the glass. After surface stabilization by local solid/solution equilibrium the release of soluble radionuclides continues with lower rates, but this is considered as resulting from parallel leaching mechanism. In fact, the deconvolutions of the overall leach mechanism into individual parallel and sequential rate limiting steps (not necessarily elementary reactions) is fundamental to this concept. In concept (2) surface stability as well as surface morphology are fundamental. A fracture in the protective surface would increase glass corrosion. The protective effect is based on the low diffusivities of radionuclides and other glass constituents in this layer. However, a true relation between layer thickness and rates is seldom observed. Diffusion coefficients are considered to vary with time as well as with the surface area to solution volume S/V ratio. Sometimes, extremely low diffusivities in extremely thin layers are invoked to explain experimental data. The two concepts are not so different from each other and one is tempted to think of a problem of semantics. In fact, there are two alternative ways by which the protective layer concept can be coupled to the saturation concept: (a) the layer may be formed by solubility effects as proposed in [loc.cit] and/or (b) the layer plays the role of a silica diffusion barrier limiting glass dissolution rates according to the first-order rate law at the interface between the pristine glass and the surface layer. However, the mathematical models based on these conceptual models yield quite different long-term predictions, even though the models may equally well fit a given set of experimental data. The models are also different with respect to the

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number of interrelated parameters. In the case of a model based on a surface layer slowing down glass network dissolution, the numerical value of the diffusion coefficient of silica, the layer thickness and the saturation concentration of dissolved silica are interrelated. Often, none of the parameters are measured directly. As a consequence this leads to not-sufficiently constrained models with poor predictive capacity. Recent research has indicated that there might be problems with the applicability of the first-order rate law [C. Jegou, thesis, University of Montpellier II, 1998]. Fresh glass or pre-altered glass samples were put in solutions over-saturated with silica. A decrease in reaction rates by as much as a factor of 10 was observed, but the rates remained much higher than predicted from a first-order rate law. It was argued that none of the kinetic models based on the notions of 'chemical affinity' and 'deviation from an equilibrium' is adapted to describe the kinetics of glass corrosion. In contrast, the formation of a surface gel and condensation of silanol groups are considered responsible for the decrease in reaction rates. The present communication argues against this view. Based on recent results of Monte Carlo calculations [M. Aertsens, Mater. Res. Soc. Symp. Proc. 556 (1999) 409] it is shown that some time of surface restructuration is necessary before saturation effects become fully effective in controlling long-term release of soluble glass constituents. The formation of a gel layer is not opposed to an affinity based kinetic concept, but it is in contrast a manifestation of this concept. It is the belief of the authors that much of the confusion related to the first-order rate law results from the fact that glass network dissolution is not considered as only one of a series of reaction mechanism and that glass network hydration and alkali ion exchange were ignored as parallel leaching mechanism. Our experimental results show that glass network hydration and ion exchange are important in short-term laboratory tests and in certain cases (closed system) also in the long term.

1. The model

Previous model development [1,8] was extended by combining ion exchange and matrix dissolution. The model is consistent with the observation that the initial surface modification in the glass/water reaction is diffusion controlled glass hydration accompanied by alkali/H^+ ion exchange. Matrix dissolution is considered in the model to occur as a parallel reaction implying that the rate of water diffusion/ion exchange is initially faster and decreases with the square root of time until it becomes equal to the rate of matrix dissolution. Under these steady-state conditions the rate becomes constant with time and a stationary water/alkali diffusion profile of constant depth is established at the corroding glass surface.

A similar steady state with constant rates and diffusion profiles would also result from surface transformation in the absence of surface dissolution. If sufficient network bonds are hydrolyzed, a transformed layer [3] (gel) is formed, often with a clear phase boundary to the glassy phase. The transformed surface layers are porous [4], containing molecular water [5,6], and allowing for high ionic mobility [7] as well as high water mobility. Thus, water transport in this gel layer cannot be rate limiting. The rate limiting diffusion step is in a thin diffusion layer at the interface between the pristine glass and the gel layer. Mathematically, in the context of the present model, the in situ transformation of the surface layer is equivalent to a matrix dissolution process, if a large quantity of the silica content of the dissolved glass is retained in the surface gel. The matrix dissolution front then is the interface between the water/alkali diffusion profile and the transformed layer.

Traditional glass corrosion models try to quantify the release of glass constituents associated to either of matrix dissolution and ion exchange. Here an alternative viewpoint is introduced. The model describes the penetration of water into the glass network assumed to be a prerequisite for both reactions. The penetration of water into the glass is described by an advection/dispersion/reaction equation, typically used for mass transfer calculation of reactive contaminant transport in porous media:

$$\frac{\delta C_{\mathrm{H_2O,gl}}}{\delta t} = D_{\mathrm{H_2O,eff}} \frac{\delta^2 C_{\mathrm{H_2O,gl}}}{\delta x^2} - U(t) \frac{\delta C_{\mathrm{H_2O,gl}}}{\delta x} - k\, C_{\mathrm{H_2O,gl}}, \tag{1}$$

where $C_{\mathrm{H_2O,gl}}$ is the space and time-dependent concentration of free *mobile* water molecules in the glass, x is the distance variable ($x = 0$ denotes the position of the original glass surface prior to the start of the glass water reaction. The relation between the concentration of *mobile* water and *total* water entering the glass is discussed further below (see Eq. (10)). Boundary conditions are $C_{\mathrm{H_2O,gl}} = 0$ for $x > 0$ and $t = 0$, and $C_{\mathrm{H_2O,gl}} = \text{const.}$ at $x = 0$ at all times), $D_{\mathrm{H_2O,eff}}$ is the effective diffusion coefficient of water molecules in the dry glass, $U(t)$ is the time-dependent matrix dissolution rate in m/s and k is a rate constant describing the potential immobilization of water molecules by the formation of hydroxyl groups attached to the glass network (silanol groups). The constant interfacial boundary concentration $C_{\mathrm{H_2O,gl}}$ at $x = 0$ can be expressed in various units. In thermodynamic context, relevant to the driving force of the transport process, it would be equal to the water activity in the adjacent aqueous phase, hence in non-saline solutions it is close to 1, whereas in concentration units (measurable by solid state analyses of total water content) it may be considered equal to the molar concentration of water in the aqueous phase (e.g. 55.45 mol/l in diluted systems) multiplied by the maximal fractional porosity of the glass phase. The maximal fractional porosity of the glass phase is the threshold porosity beyond which the glassy state is lost (glass/gel transition). This value is not known, a value of 0.2 is assumed. In weight fraction units $C_{\mathrm{H_2O,gl}}$ would represent the weight fraction of water filled maximal pore volumes.

The hypothesis that the transport of H_2O molecules is rate limiting for the release of alkali ions and boron is a simplification. In reality, water inward-diffusion is expected to be coupled by an inter-diffusion process to the outward-diffusion of alkali ions and boron in a rather complex way, where each component flux, in general, depends on the gradients of all the components. This results from spatial requirements where water diffusion is hindered by alkali ions if the large alkali ions are not removed. Since water diffusion and alkali diffusion are two processes in series, the slowest of the two would be rate limiting. The consideration of water molecules as a key diffusing species is equal to the hypothesis of a strong asymmetry in the diffusion couple water/alkali characterized by water diffusion being much slower than the subsequent diffusion of alkali and boron. This seems reasonable since in the opposite case one would expect large differences in the release properties of alkali ions and of B, in contrast to the congruent release which is often observed, even in domains of the leaching mechanism where ion exchange is the dominant process.

Eq. (1) is solved by a finite difference representation, using a forward time space centered algorithm:

$$C_{t+1,j} = \left(\frac{C_{t,j}}{\Delta t} + D_{\mathrm{H_2O,eff}} \frac{C_{t,j+1} - 2C_{t,j} + C_{t,j-1}}{\Delta x^2} - U_t \frac{C_{t,j+1} - C_{t,j-1}}{2\Delta x} - kC_{t,j} \right) \Delta t. \tag{2}$$

In the present paper, we will only consider sorption equilibrium, and thus Eq. (2) is only evaluated with the reaction constant k equal to zero. The corrosion and the diffusion terms of Eqs. (1) and (2) are described.

1.1. The corrosion rate U

The term 'corrosion' is used in the present context to denote all processes which lead to the loss of the glassy state by the interaction with water. This comprises particularly the dissolution of glass matrix constituents as well as the neoformation of solid reaction products and gel layer formation but it does not comprise glass hydration and alkali ion exchange which are considered to occur by maintaining the glassy state. In Eq. (1) the corrosion rate U is a function of time and environmental variables, so we first focus on determining $U(t)$. It is this part of the nuclear waste glass dissolution mechanism where most modeling work has been focussed on. It involves the question of the validity of the first-order dissolution rate law, the effect of protective surface layers, acting as silica transfer barriers etc. A model has been outlined recently [8] describing the effect of temperature, time, solution volume, and of growing protective surface layers. The base of the model is the well-known affinity/transition state theory-based interfacial reaction equation [9]:

$$r_{\mathrm{glass}} = \frac{\mathrm{d}\xi_r}{s_r \mathrm{d}t} = k_r \prod_i a_i^{-v_i} \left[1 - \exp\left(-\frac{A_r}{\sigma_r RT} \right) \right], \tag{3}$$

where the indices r and i denote the rth dissolution reaction and the ith species. The activity in the reaction forming the rate limiting activated surface complex is denoted a raised to the power of its stoichiometric coefficients, ξ denotes reaction progress, A affinity $A = -RT\,\ln(Q/K)$, R the gas constant, T the absolute temperature, Q the ion activity product and K the equilibrium constant of the dissolution reaction, s the surface area, and k_r the rate constant. The coefficient σ relates the stoichiometry of the activated complex to that of the dissolving solid. In this equation the overall rate r of the dissolution reaction is implicitly related to a series of sequential elementary hydrolysis reactions by the affinity term (parallel elementary reactions require a different mathematical treatment) (contextual affinity [10]). The global glass dissolution affinity

$$A_{\mathrm{tot}} = \sum_j v_j A_j$$

can be measured calorimetrically, and may be estimated by solid solution representations of the glass phase, but the empirical saturation affinity term A_r is not to be related to this value. Instead saturation of a silica end member plays a decisive role in slowing down glass corrosion rates ($A_r \approx A_{\mathrm{SiO_2}}$) and the rate law often takes the simple form of a first-order dissolution rate law characterized by a forward rate constant k_+ (unit: $\mathrm{kg_{glass}/(m^2\ s)}$), the activity of dissolved silicic acid a_{Si} and a corresponding saturation constant $K_{\mathrm{SiO_2}}$ at the dissolving glass surface. The rate r_{glass} of the corrosion reaction is given in simplified manner by

$$r_{\mathrm{glass}}(T) = k_+(T) \left[1 - \frac{Q}{K(T)} \right] = k_+(T) \left(1 - \frac{a_{\mathrm{Si}}}{K_{\mathrm{SiO_2}}(T)} \right). \tag{4}$$

A collective response of soluble elements such as Na and B to silicic acid saturation effects exists (tendency towards 'congruent dissolution') indicating that also the release of these elements is controlled by $r_{\mathrm{glass}}(T)$. At Si-saturation, the release rate of the soluble elements slows down by some orders of magnitude. If initially dissolved silica becomes reincorporated into solid reaction products, a selective release of Na and B can be the result, with release rates much faster than those of Si.

The dependency on temperature T of the forward rate constant is given by an Arrhenius equation with an activation energy E_a, the temperature dependency of K by a van't Hoff equation with an enthalpy of reaction ΔH.

The effect of potentially protective surface gel layers of solid alteration products is directly related to Eq. (4). It is assumed that the transport of dissolved silica through the growing layer is hindered. This implies (a) that the dissolving glass surface is the interface between the surface layer and the glass beneath and (b) that the interfacial concentration of dissolved silica (in general the interfacial Q value) is higher than that of the bulk aqueous solution or for example that of the inflowing groundwater. This protective effect is clearly different from the effect of water diffusion described above in Eqs. (1) and (2). The effect results from the mass balance constraint requiring that the mass flux of dissolved material from the glass surface equals the mass transfer across the transport barrier (analog to [11]):

$$-\phi D_{\mathrm{Si}}\left(\frac{\partial m_{\mathrm{Si}}}{\partial L}\right)\rho_{\mathrm{sln}} = k_+ \,\mathrm{FS}\,\beta\left(1-\frac{m_{\mathrm{Si,int}}\,\gamma_{\mathrm{Si}}}{K_{\mathrm{SiO_2}}}\right), \tag{5}$$

where D_{Si} is the pore diffusion coefficient of silicic acid in the layer of thickness L and porosity ϕ, m_{Si} and $m_{\mathrm{Si,int}}$ are the molalities of dissolved silica in bulk solution and that at the glass/solution interface, γ_{Si} is the activity coefficient of dissolved silica (in order to account also for solutions of pH > 8 m_{Si}, $m_{\mathrm{Si,int}}$ and γ_{Si} should only refer to the species H_4SiO_4, not to total dissolved silica), the dimensionless factor $\beta = s_r/s$ characterizes the ratio of the total interfacial surface area s_r (including surface roughness) to the cross-sectional surface area s perpendicular to mass transport direction (this factor is necessary because diffusive mass transfer is normalized to s, while glass corrosion rates are related to s_r) and ρ_{sln} is the solution density, necessary to convert molality units into volumetric concentration units. The factor FS (unit: mol/kg) describes the conversion of reaction rate units from $\mathrm{kg_{glass}}/(\mathrm{m^2\ s})$ to $\mathrm{mol_{Si}}/(\mathrm{m^2\ s})$

$$\mathrm{FS} = \frac{f_{\mathrm{Si}}(1-f_{\mathrm{ret}})}{\mathrm{MG_{SiO_2}}}, \tag{6}$$

where $\mathrm{MG_{SiO_2}}$ is the molecular weight of silica and f_{Si} is the weight fraction of silica in the pristine glass. Retention of silica in the surface alteration products is accounted for by using the factor f_{ret} describing the weight fraction of initially dissolved silica which became incorporated into secondary alteration products or sorbed on the glass surface. In general, the value of f_{ret} would depend on the concentration of silicic acid in solution. An equation $f_{\mathrm{ret}} = a + b \cdot m_{\mathrm{Si}}/K_{\mathrm{SiO_2}}$ ($a < 1;\ b < 1$) was used to fit experimental data. It was found that the quality of the fit was not improved by considering a concentration dependency. Hence, f_{ret} was considered to be constant.

In general, both L and the concentration gradient are functions of time. However, in case of glass corrosion under repository conditions the concentration of silicic acid in the groundwater may be considered constant at some distance of dissolving glass surface, due to a sufficient fast advective groundwater flow, due to concentration controls by silicate minerals or due to the establishment of a steady-state dissolved silica gradient in the near field. In this case, constant concentration boundary models (CCB) [11] can be applied, implying a stationary state concentration gradient:

$$\frac{\partial m_{\mathrm{Si}}}{\partial L} = \frac{m_{\mathrm{Si,CCB}} - m_{\mathrm{Si,int}}}{L}. \tag{7}$$

For a given layer thickness L, the effect of diffusion on the affinity law or on the first-order rate law (Eq. (4)) can be derived by combining Eqs. (4)–(6) to yield the equation [8]

$$r_{\mathrm{glass}}(T) = k_+(T)\left(1-\frac{k_+(T)\,\mathrm{FS}\,\beta L + \phi\, D_{\mathrm{Si}}(T)\, m_{\mathrm{Si,CCB}}\,\rho_{\mathrm{sln}}}{K_{\mathrm{SiO_2}}(T)\,\phi\, D_{\mathrm{Si}}(T)\,\rho_{\mathrm{sln}} + k_+(T)\,\mathrm{FS}\,\gamma_{\mathrm{Si}}\,\beta L}\gamma_{\mathrm{Si}}\right). \tag{8}$$

Depending on the choice of the appropriate parameters L, D and ϕ, two cases of silica transport controls can alternatively be described by the same rate equation: transport control by the surface layer (protective effect) and transport control in the porous media surrounding the glass. The slowest of both transport processes will be rate controlling.

1.2. Numerical approach to the corrosion rate U

In order to adapt the corrosion rate model to various static or dynamic experimental and/or disposal site conditions, a numerical approach was chosen. The overall reaction time of interest was divided into a sequence of time steps Δt_i and for each step first the reaction rate r_i was calculated with Eq. (8). The step size is selected sufficiently small as not to be of influence on the results.

The parameter L can either remain constant or vary with each time step. In case that the mass transfer resistance of the gel layer for dissolved silica is small when compared with that of the engineered or geo-engineered barriers in the near field, L and D_{Si} can represent for example the thickness and diffusion coefficients of a bentonite barrier. In this case L is considered to remain constant with time. In contrast, for the case of rate control by protective surface gel layers, the transport barrier thickness L is growing with time. This is considered in the numerical by using a very low initial $L(0)$ value (e.g. 10^{-10} m); then with the given rate r_i, a value

$$\Delta L_i = r_i \Delta t_i / \rho_{\text{glass}} \quad \text{and} \quad L = \sum \Delta L_i$$

is calculated for each time step i (ρ_{glass} is the glass density).

The numerical approach also allows one to apply Eq. (8) in case of non-validity of the constant silica concentration boundary (CCB) condition, for example for a static corrosion test performed in the laboratory or for the void volume of a corroding glass canister under disposal conditions. Here $m_{\text{Si,CCB}}$ is replaced by $m_{\text{Si,bulk}}$, the molality of silicic acid in the bulk solution. For each time step a new bulk silicic acid concentration is calculated by the corresponding rate term (Eq. (8)).

To allow modeling of a dynamic open system of a waste glass disposal site or of an experimental dynamic test, a combination of the constant concentration boundary approach with the static approach is implanted. Close to the waste glass surface, corrosion in the void volume of the canister (fracture space in glass bloc, free plenum in canister...) may be approximated by a static corrosion scenario with the dissolved silicic acid molality $m_{\text{Si,bulk}}$ increasing with time. However, at a certain distance from the glass the hydrogeological environment will become dominant, hence there will reappear a CCB. Transport processes from the void volume in the glass canister to the CCB could be of advective or dispersive nature. Dispersive (diffusion control) mass transfer across the engineered barrier system can be described directly with the help of Eq. (8) as discussed above (constant L).

In case of advective transport of dissolved silica the effect of a volumetric flow rate F (m^3/year) on the bulk silica concentration $m_{\text{Si,bulk},i}$ is given at each time step i by

$$m_{\text{Si,bulk},i} = r_{\text{glass},i}\text{FS}\,\Delta t \frac{s \cdot \beta / V}{\rho_{\text{sln}}} - F\,\Delta t \frac{m_{\text{Si,bulk},i-1} - m_{\text{Si,CCB}}}{V \rho_{\text{sln}}} + m_{\text{Si,int},i-1}, \tag{9}$$

where V is either the water filled void volume of a disposed glass canister including its close surrounding or the solution volume in a static or dynamic dissolution test. The maximum value of $m_{\text{Si,bulk}}$ is given by $K_{\text{SiO}_2}/\gamma_{\text{Si}}$. In each time step i the rate r_i is again calculated with Eq. (8) by replacing $m_{\text{Si,CCB}}$ in this equation by the $m_{\text{Si,bulk},i-1}$ value calculated in the previous time step by Eq. (9). In practice Eq. (9) is also used for static tests, simply setting $F = 0$.

After having calculated by Eqs. (3)–(9) a matrix of corrosion rate values for n time steps this matrix is converted from surface normalized rates r (unit: kg/(m^2 s)) to rates U in units of m/s ($U = r/\rho_{\text{glass}}$). These values are introduced in Eq. (2) to assess the effect of water diffusion.

1.3. Water diffusion

Molecular water is not an inert diffusing species but it reacts with the glass network. Principal reactions are:

$\vec{\text{A}}_1$	$(\equiv\text{Si{-}O}^{\delta-}\text{Na}^{\delta+}) + \text{H}_2\text{O(gl)} \rightarrow (\equiv\text{Si{-}OH}) + \text{OH}^-(\text{gl}) + \text{Na}^+(\text{gl})$
$\vec{\text{A}}_2$	$\text{OH}^-(\text{gl}) + (\equiv\text{Si{-}O{-}Si}\equiv) \rightarrow (\equiv\text{Si{-}OH}) + (\equiv\text{SiO}^-)$
$\overleftarrow{\text{A}}$	$(\equiv\text{Si{-}O}^-) + \text{Na}^+(\text{gl}) \rightarrow (\equiv\text{Si{-}O}^{\delta-}{-}\text{Na}^{\delta+})$
B	$(\equiv\text{Si{-}O}^-) + \text{H}_2\text{O(gl)} \rightarrow (\equiv\text{Si{-}OH}) + \text{OH}^-(\text{gl})$
C	$(\equiv\text{Si{-}O})_y\text{B}^{(3-y)-}(y-3)\text{Na}^+ + 3\text{H}_2\text{O(gl)} \rightarrow \text{H}_3\text{BO}_3(\text{gl}) + 3(\equiv\text{Si{-}OH}) + (y-3)(\equiv\text{Si{-}ONa})$
$\vec{\text{D}}$	$(\equiv\text{Si{-}O{-}Si})\equiv + \text{H}_2\text{O(gl)} \rightarrow 2(\equiv\text{Si{-}OH})$
$\overleftarrow{\text{D}}$	$2(\equiv\text{Si{-}OH}) \rightarrow (\equiv\text{Si{-}O{-}Si}\equiv) + \text{H}_2\text{O(gl)}$
E	$\text{Na}^+(\text{gl}) + \text{H}^+(\text{aq}) \Longleftrightarrow \text{Na}^+(\text{aq}) + \text{H}^+(\text{gl})$

where 'gl' indicates a mobile phase in the slightly porous hydrated glass. There are significant differences in reactions A and C. The mobile boric acid produced by hydrolysis of triangular ($y = 3$) or tetrahedral ($y = 4$) coordinated B in reaction C can diffuse out of the hydrated glass into solution. This is only true for a fraction n of Na which may become released as NaOH ion pair (provided this ion pair is at all stable in the mobile phase of the hydrated glass). Due to electroneutrality constraints, $\equiv\text{SiO}^-$ groups are unstable in the hydrated glass (in contrast to their function as surface charge carriers at the glass water interface). Neutralization can be achieved either by back reaction A or by the competing reaction B. A significant quantity of Na is immobilized by back reaction A in the hydrated glass and cannot diffuse out. Due to the high reactivity of $\text{OH}^-(\text{gl})$ with the silica network, the mobile fraction of $\text{OH}^-(\text{gl})$ could be considered to be close to zero, and the fraction of Na necessary to balance $\equiv\text{SiO}^-$ groups would be close to one, if there were no competing reaction B.

The net result of both partial forward reactions A_1 and A_2 and the back reaction A is the hydrolysis of siloxane bonds. The hydrolysis of bridging bonds via reaction A_2 is probably much faster than that via the forward reaction D, hence very little Na is released by the overall reaction A. However, with increasing acid concentration in the interfacial solution (aq), the alkali ions become more mobile, due to ion exchange. This is described by reaction E coupled to the last part of reaction A.

This allows Na ions to diffuse out and, hence, reaction E competes with the back reaction of A. The alkali/H^+ ion exchange may be governed either by the electroneutrality-coupled (inter)diffusion coefficients of alkali ions and H^+ ions in opposite direction, with the lower mobility of H^+ or H_3O^+ ions [12,13] normally being rate controlling. Or, alternatively, the rate limiting reaction may be the diffusion of water molecules into the glass network [14,15], i.e. the hydration of the glass network. Based on findings that the pH-response of glass electrodes is essentially determined by exchange equilibria of outermost surface species with solution species, it may be concluded that transport processes of H^+ and alkali ions are fast compared to water diffusion. If ion exchange would instead be driven by electrochemical potential differences between charged surfaces species and the bulk glass [16], the electromigration of H^+ and Na^+ in the surface layer would lead to electrical fields much stronger than those observed between the surface and the glass [17]. Hence, in the model, ion exchange equilibrium is assumed to be established instantaneously and only water molecules are considered in transport control in the overall water diffusion/ion exchange process. The proposed coupling of ion exchange and water diffusion is closely related to the ideas forwarded by Ernsberger [18], having the consequence that the liberation of hydroxyl groups leads to instantaneous dissolution of network siloxane bonds.

The detailed reactions A–E are not yet used in the model, because many data for a quantification are not yet known. Therefore, the influence of the reaction of water molecules on the diffusion process within the glass network is treated only in a qualitative fashion, to allow discussion of the experimental results. If one defines C_{tot} as the total concentration of water in the glass ($C_{\mathrm{tot}} = C_{\mathrm{H_2O,gl}} + C_{\mathrm{SiOH,gl}}$), its temporal evolution is related to the divergence of the flux of mobile water molecules by the equation

$$\frac{\partial C_{\mathrm{tot}}}{\partial t} = D_{\mathrm{H_2O,gl}} \frac{\partial^2 C_{\mathrm{H_2O,gl}}}{\partial x^2} - U(t) \frac{\partial C_{\mathrm{H_2O,gl}}}{\partial x}. \tag{10}$$

The temporal evolution of the concentration profile of mobile H_2O in the glass has been described in Eq. (1) by an effective diffusion coefficient (analog diffusion of H^+ in metals with trapping: see [19])

$$\frac{\partial C_{\mathrm{H_2O,gl}}}{\partial t} = D_{\mathrm{H_2O,eff}} \frac{\partial^2 C_{\mathrm{H_2O,gl}}}{\partial x^2} - U(t) \frac{\partial C_{\mathrm{H_2O,gl}}}{\partial x}$$

with (11)

$$D_{\mathrm{H_2O,eff}} \equiv \frac{D_{\mathrm{H_2O,gl}}}{1 + \partial C_{\mathrm{SiOH,gl}} / \partial G_{\mathrm{H_2O,gl}}}.$$

This equation implies that $D_{\mathrm{H_2O,eff}} < D_{\mathrm{H_2O,gl}}$. Eq. (10) also implies that the total water uptake of the glass is governed by the mobility of the mobile water (i.e. by $D_{\mathrm{H_2O,gl}}$), independent of its reactivity with the glass network. $D_{\mathrm{H_2O,gl}}$ thus corresponds to a pore diffusion coefficient. This is a simplification. In reality, due to the formation of a more open glass structure, the $D_{\mathrm{H_2O,gl}}$ value will increase when more silanol groups are formed. No experimental data (e.g. concentration profiles of mobile water) are available for nuclear waste borosilicate glass, which would allow one to quantify $D_{\mathrm{H_2O,gl}}$ directly. In contrast, the *total* water penetration depth is indirectly accessible from the release data of boron and alkali ions from the hydrated glass. We know from nuclear waste glass for alkali ion and boron as well as from natural analogue basaltic glass for alkali ions that the hydrated glass is depleted with respect to these ions [20]. We know from this work that the depletion depth of boron and the alkali ions is about equal to the hydration depth. This justifies one to consider in first approximation the concentration of boron and alkali ions from the hydrated glass as being correlated to the *total* water concentration at a given depth from the glass/gel-layer interface, hence, $D_{\mathrm{H_2O,eff}}$ can be estimated from boron release data.

The partial derivative $\partial C_{\mathrm{SiOH,gl}} / \partial C_{\mathrm{H_2O,gl}}$ can be solved by describing the concentrations of formed silanol groups for a given concentration of mobile water by an equilibrium distribution ratio governed by the immobilization of molecular water by hydrolytic reactions A–E as well as the regeneration of molecular water by condensation of silanol groups or other reactions. A Langmuir sorption isotherm was used for this purpose:

$$C_{\mathrm{SiOH,gl}} = K_{\mathrm{d}} \frac{C_{\mathrm{H_2O,gl}}}{1 + K_{\mathrm{d}} \cdot C_{\mathrm{H_2O,gl}} / C_{\mathrm{max,SiOH}}}, \tag{12}$$

where K_{d} is the distribution ratio valid at low water concentrations. The maximum value for 'sorbed' H_2O, i.e. the maximum concentration of silanol groups, is denoted $C_{\mathrm{max,SiOH}}$. In the application to experimental data, in few cases (data not shown here) an arbitrary very large K_{d} value was used, leading to $C_{\mathrm{SiOH,gl}} = C_{\mathrm{max,SiOH}}$, whereas in most calculations K_{d} was set to zero ($C_{\mathrm{tot}} = C_{\mathrm{H_2O,gl}}$; 'non-reactive H_2O transport'). Using Eq. (12) to solve the partial derivative,

$$D_{\mathrm{H_2O,gl}} = D_{\mathrm{H_2O,eff}} \left(1 + K_{\mathrm{s}} \frac{C^2_{\mathrm{max,SiOH}}}{\left(C_{\mathrm{max,SiOH}} + K_{\mathrm{d}}\, C_{\mathrm{H_2O,gl}} \right)^2} \right); \tag{13}$$

the diffusion coefficient $D_{\mathrm{H_2O,gl}}$ could be obtained from $D_{\mathrm{H_2O,eff}}$, however, since fitted $D_{\mathrm{H_2O,eff}}$ and $C_{\mathrm{max,H_2O}}$ are correlated and since $D_{\mathrm{H_2O,gl}}$ is concentration independent only at low concentrations of $C_{\mathrm{H_2O,gl}}$ (see Eq. (13)), no effort was made to obtain $D_{\mathrm{H_2O,gl}}$ from the experimental data.

The maximum value for the concentration of silanol groups $C_{\mathrm{max,SiOH}}$ can be estimated from reactions A–C and E if the forward reaction D is slow. Reactions A and E for example yield after coupling in case of equilibrium

$$\begin{aligned}\vec{\mathrm{A}}_{1+2} + \mathrm{E}\quad &(\equiv\mathrm{SiO}^{\delta-}\mathrm{Na}^{\delta+}) + \mathrm{H_2O(gl)} + (\equiv\mathrm{Si{-}O{-}Si}\equiv)\\ &+ \mathrm{H^+(aq)} \Longleftrightarrow 3(\equiv\mathrm{Si{-}OH}) + \mathrm{Na^+(aq)}\end{aligned}$$

with the equilibrium constant K_{EX} for ion exchange

$$K_{\mathrm{EX}} = \frac{[\equiv\mathrm{Si{-}OH}]^3 \cdot [\mathrm{Na^+(aq)}]}{[\equiv\mathrm{Si{-}O}^{\delta-}\mathrm{Na}^{\delta+}] \cdot [\mathrm{H_2O(gl)}] \cdot [\equiv\mathrm{Si{-}O{-}Si}\equiv] \cdot [\mathrm{H^+(aq)}]}. \tag{14}$$

This corresponds to the formation of three silanol groups per released alkali ion. However, in glass /water interactions typically only between 1 and 3 protons (silanol or molecular water) are taken up by the glass per released alkali ion [21]. The reason for lower proton uptake is the recondensation of silanol groups by the inverse reaction D. Therefore, for alkali silicate glasses the concentration of molecular water is often higher than that of silanol groups. The mechanism of proton transport into the glass network can be very fast and can be described by a mechanism by which the identity of the diffusing proton is changed permanently. This mechanism is associated to the presence of a continuous chain of water molecules within the glass network:

$$\begin{aligned}&\mathrm{H^+} + \|\mathrm{OH_2}\cdots\mathrm{OH_2}\cdots\mathrm{OH_2}\cdots\\ &\quad\to \|\mathrm{HOH_2^+}\cdots\mathrm{OH_2}\cdots\mathrm{OH_2}\cdots\\ &\quad\to \|\mathrm{HOH}\cdots\mathrm{HOH_2^+}\cdots\mathrm{OH_2}\cdots\end{aligned}$$

Since a significant fraction of initially formed silanol groups will recondense to produce molecular water and siloxane bonds, it has been postulated that the alkali and boron release are correlated to total water concentration which has been entered into the glass, implying that surface concentration profiles of alkali ions or of boron at the glass/gel-layer interface can be calculated from the total water diffusion profile $C_{\mathrm{tot}}(x)$. The following equation was used to calculate for example the concentration of boron ($C_{\mathrm{B}}(x)$) as a function of depth x from the outer surface of the glass via the gel layer and the glass/gel interface into the glass:

$$C_{\mathrm{B}}(x) = \frac{C_{\mathrm{H_2O,gl}}(x=0) - C_{\mathrm{tot}}(x)}{C_{\mathrm{H_2O,gl}}(x=0)} C_{\mathrm{B}}(x=\infty). \tag{15}$$

The diffusion coefficient of water in the glass varies with depth in the glass. It is expected to be some orders of magnitude higher in the gel-layer than in the pristine glass. Modeling essays with a concentration-dependent diffusion coefficient failed, due to numerical instability. Therefore, an indirect decision method was chosen: the position of the gel/glass interface L was calculated for each time step i by

$$L = \sum_i U_i \Delta t_i.$$

Once sufficient reaction time has passed, saturation of the bulk solution will be achieved under static conditions. Under these conditions, the position of the gel/glass interface does not move anymore with time, independent of how long water diffusion goes on. The gel/glass interface for this situation may be defined as L_{sat} being the position in the glass, so that (1) at larger positions, silica has not (and will not) dissolve anymore, (2) at smaller positions, silica has dissolved and partly been retained. In dynamic open systems L_{sat} will grow with time. The diffusion coefficient of water was considered to be very large if the sum of space increments $\sum_j \Delta x_j$ at a given time step i was smaller than L and a concentration-independent value for $D_{\mathrm{H_2O,eff}}$ was determined by a fit to experimental data, if it was larger than L. This implies that the concentration of water at the gel/glass interface is equal to that in bulk solution, hence, gel layer has a non-significant mass transfer resistance for water molecules, whereas it may be a transport barrier for dissolved silica. To avoid numerical instability, not the diffusion coefficient $D_{\mathrm{H_2O,eff}}$ but the numerical procedure was altered. In the finite difference representation of diffusion in Eq. (2). The approach chosen is mathematically equivalent to the establishment of a second space coordinate system x^2 where the position $x^2 = 0$ is always positioned at the glass/gel interface.

$$D_{\mathrm{H_2O,eff}} \frac{C_{t,j+1} - 2C_{t,j} + C_{t,j-1}}{\Delta x^2}$$

was replaced by

$$D_{\mathrm{H_2O,eff}} \frac{C_{t,j+1} - 2C_{t,j} + C_{t,x=0}}{\Delta x^2} \tag{16}$$

$$\text{for } L \leqslant \sum_{j=0}^{j} \Delta x_j.$$

For solving Eq. (2) the choice of space and time step sizes was made considering the following criteria for numerical stability:

$$\sigma = U_1 \frac{\Delta t}{\Delta x}, \quad \lambda = 2D_{\mathrm{H_2O,eff}} \frac{\Delta t}{(\Delta x)^2}, \qquad \text{with } \sigma^2 < \lambda < 1.0.$$

2. Experimental data for the application of the model

This model was applied to well-controlled static nuclear waste borosilicate glass dissolution experiments, performed at 50°C in deionized water at $S/V = 1000\ \mathrm{m^{-1}}$ and pH values controlled between 2.5 and 9 by a computer-assisted pH-Stat method. The WAK glass was used for this test (for composition see Table 1, the composition is close to that of the well-known glass R7T7).

Table 1
Composition of the WAK glass studied

	wt%	wt%
Frit	84	
SiO_2		50.4
B_2O_3		14.8
Al_2O_3		2.6
Li_2O		2.9
Na_2O		10.3[a]
MgO		1.8
CaO		4.5
TiO_2		1.0
HLW-oxide	16	

[a] Including 4.3% Na_2O from HLW.

During the tests of each 90–100 days the pH electrodes were left permanently in the reaction vessel, with the exception of short regular interruptions (at least once per week) for recalibration. Fluctuations in pH during the tests were considered to be less than 0.05 pH units, except at pH 5 to 6 where fluctuations as high as 0.2 pH units were encountered. Temperature was controlled to ±0.1°C using a water bath. Glass powder with an average grain size of 100 μm was used for the tests. The specific surface area was determined by the BET method. The experiments were performed under conditions of equilibrium with CO_2 of the air. Solutions were permanently stirred, thus avoiding cementation of the glass powder. Reaction progress was monitored both by analyses of the leach solutions for major and trace elements and by acid (base) consumption as a function of time. About five solution analyses and 1000 acid consumption data are available at each pH. In order to convert acid consumption data to normalized mass loss of boron, the solution analyses results were used as input to the geochemical code PHREEQC to obtain the speciation (hydrolysis of cations and carbonate equilibria) for each leached element and to determine whether a given glass constituent is leached congruent with boron or to which degree it is retained at the glass surface. Based on these data, the contribution to the overall charge balance was calculated; hence from the known acid consumption data, the concentration of elements in solution can be calculated, and from these concentrations the elemental mass loss values even for time increments, where no solution analyses were available. Glass constituents which did contribute to the charge balance were the alkali and molybdate ions (all pH) aluminum (pH 3 only), calcium (pH 3–9), silica and boron (pH 8–11 only). The results are given in Fig. 1 for acid consumption and in Fig. 2 for the normalized boron release (normalization to glass composition and to surface area).

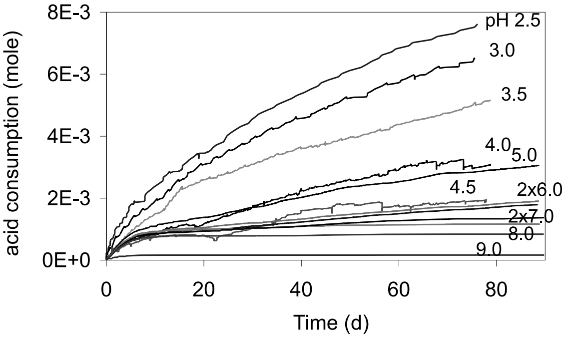

Fig. 1. Monitoring of the reaction progress of WAK borosilicate glass at 50 ± 0.1°C and $S/V = 1000\ \mathrm{m}^{-1}$ as a function of time and pH by the quantity of acid (0.01 m HCl) necessary to compensate the alkali release from the glass to keep the pH at various pre-selected values.

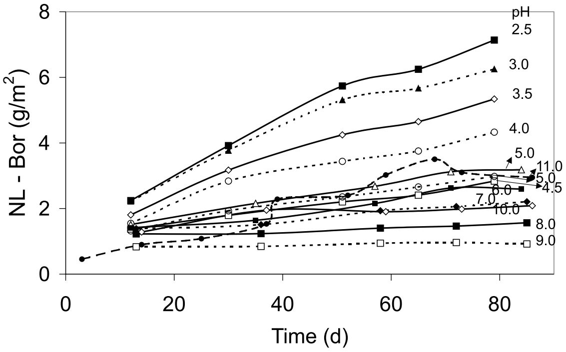

Fig. 2. Monitoring by the release of boron the extent of corrosion of WAK borosilicate glass at 50 ± 0.1°C and $S/V = 1000\ \mathrm{m}^{-1}$ as a function of time and pH. The pH is kept constant by pH stat titration (NL-boron = release of boron normalized to surface area and glass composition, indicates the quantity of glass to be dissolved to account for measured boron concentrations).

The data for acid consumption and solution analyses gave quantitatively consistent results. The silica concentration in solution reached constant values (saturation) after few days in all tests below pH 11. The saturation concentration was found to be independent of pH for pH < 10 but it increased at pH 11 due to the hydrolysis of dissolved silica in solution. In contrast to silica, the concentrations of alkali and boron continued to rise in all cases. The release rates of these glass constituents decreased, once silica saturation was attained. The ratio of normalized release values of Li to B was 1.0 ± 0.2 without any clear variation either with pH or with time. Hence, any of the two elements can be used to represent the other and both elements represent the progress of the glass water reaction. The ratio of normalized Ca to B releases is shown in Fig. 3. As for Li/B for pH values <5 also the normalized Ca/B ratio is 1.0 ± 0.2. However, with increasing pH the ratio decreases. This can be attributed to sorption processes in

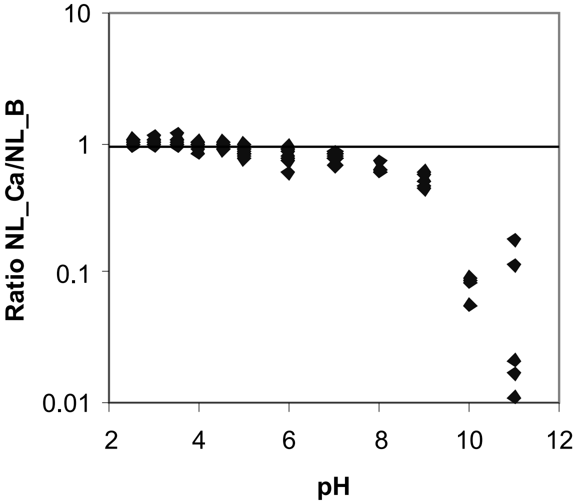

Fig. 3. Ratio of the normalized mass loss values of Ca to those of B as a function of pH.

the pH range 5–8 and to the precipitation of calcite at higher pH [22]. These data indicate that there is a tendency for congruent release of glass constituents as far as sorption and precipitation can be ruled out. There does not appear to be a selective release of alkali elements when compared to network former elements such as B. Still, in terms of the above-described model, overall glass network corrosion has already ceased under these high S/V conditions and the only process controlling the apparent congruent release of certain glass constituents is water diffusion.

Considering now B as indicator for glass/water reaction progress (or the extent water diffusion), the glass/water reaction rate was highest at pH 2.5 and decreased with increasing pH. Minimum release rates were observed at pH 9. Release rates increased again at pH 10 and 11, at pH 11 directly related to the increased release of silica, hence to glass matrix corrosion and not to water diffusion.

3. Data interpretation by model application

The model was applied to all experimental data, using the four parameters:

- forward rate constant k_+,
- Si-saturation constant K_{SiO_2},
- the effective diffusion coefficient of water in glass $D_{H_2O,eff}$,
- adsorbed fraction f_{ret} of silica in the surface layer (the parameters a and b were not used)

as adaptable in a fit. Parameters which where kept constant are the surface to volume ratio (S/V 1000 m^{-1}), the water flow rate (F 0.0 ml/d), the density of the solution (ρ_{sln} 1.00 g/cm^3) and of the glass (ρ_{gl} 2.7 g/cm^3), the maximum porosity of the gel (20%), the initial silica concentration ($m_{Si,CCB}$ 0.0 mol/kg$_{H_2O}$), the pore diffusion coefficient of dissolved silica in the gel (D_{Si} 3×10^{-13} m^2/s), the solid to flow surface conversion factor (β 1.0), the initial gel layer thickness ($L(0)$ 10^{-10} m) and the activity coefficient of dissolved silica (γ 1.0).

The forward rate constant was obtained from early acid consumption data. The results are given in Fig. 4. The forward rate constant varied only little as a function of pH. Also the Si-saturation constant was found to remain constant with changing pH at $9 \geqslant pH > 3$. The Si-saturation constant is given by the measured long-term silica concentrations which were found to be constant after a few days. The present experimental data were found insensitive to effects of silica diffusion in the growing surface layer, because a necessary (not a sufficient) condition for silica transport (protective layers) as a rate limiting reaction step is that silica has not been attained in bulk solution saturation ($m_{Si,bulk} \ll K_{SiO_2}/\gamma_{Si}$) whereas, due to the high S/V ratio, silica saturation in bulk solution ($m_{Si,bulk} = K_{SiO_2}/\gamma_{Si}$) was attained in our experiments in only few days.

As an example for model application, results for pH 3 and 7 are given in Figs. 5 and 6. Model results for Si and B are compared with acid consumption and analyzed B and Si release values. The most pronounced effect of pH was observed for the values of the effective diffusion coefficient (fit by non-reactive transport model) of water molecules (Fig. 7) and for the sorption constants of silica in the surface gel (Fig. 8). An attempt was made to explain the observed dependency of the diffusion coefficient. In case of non-reactive transport, sorption of water in the glass was ignored and the effective

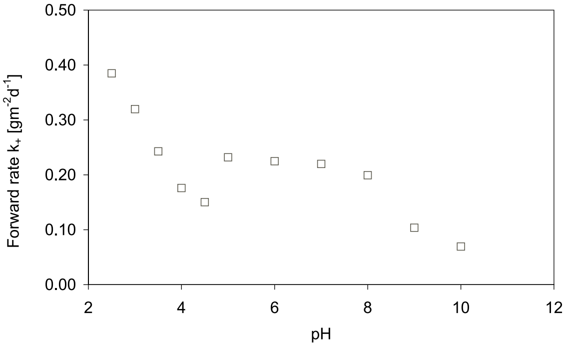

Fig. 4. Forward rate constant k_+ as a function of pH. Data deduced from the acid initial values of acid consumption, assuming that the relation between acid consumption and release of boron observed for longer time periods of >10 days (i.e. under the influence of saturation effects) is also valid at early times. There are large errors associated to the correlation of acid consumption and B release at pH > 9, and the apparent decrease in the forward rate constant may be an artifact.

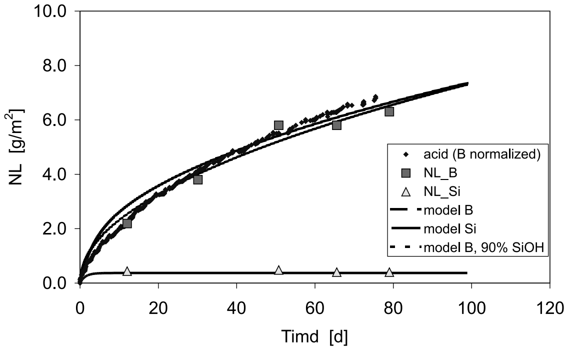

Fig. 5. Corrosion of glass WAK in deionized water (50 ± 0.1°C, pH 3.0 ± 0.05 and $S/V = 1000\ \mathrm{m}^{-1}$). Comparison of model results with experimental data (normalized elemental mass loss of soluble glass constituents deduced either from acid consumption or B analyses). Model parameters for total water transport are $D_{\mathrm{H_2O}} = 5.5 \times 10^{-19}\ \mathrm{m}^2/\mathrm{s}$, $f_{\mathrm{ret}} = 0$, $k_+ = 0.27\ \mathrm{g/m}^2$ day (k_+ is without influence on model results), $\log K_{\mathrm{SiO_2}} = -2.64$.

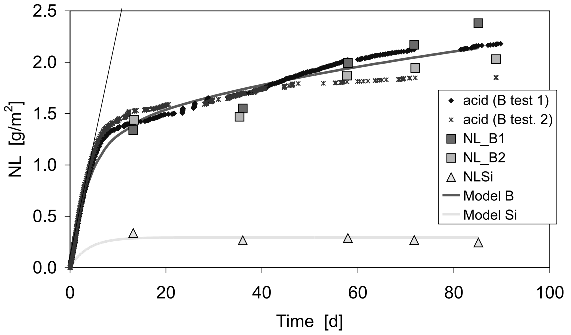

Fig. 6. Corrosion of glass WAK in deionized water (50 ± 0.1°C, pH 7.0 ± 0.1 and $S/V = 1000\ \mathrm{m}^{-1}$). Comparison of model results with experimental data of two parallel tests (normalized elemental mass loss of soluble glass constituents deduced either from acid consumption or B analyses). Model parameters for total water transport are $D_{\mathrm{H_2O}} = 1.8 \times 10^{-20}\ \mathrm{m}^2/\mathrm{s}$, $f_{\mathrm{ret}} = 0.7$, $k_+ = 0.27\ \mathrm{g/m}^2$ day, $\log K_{\mathrm{SiO_2}} = -2.94$. The straight line between zero and 15 days represents the initial rate.

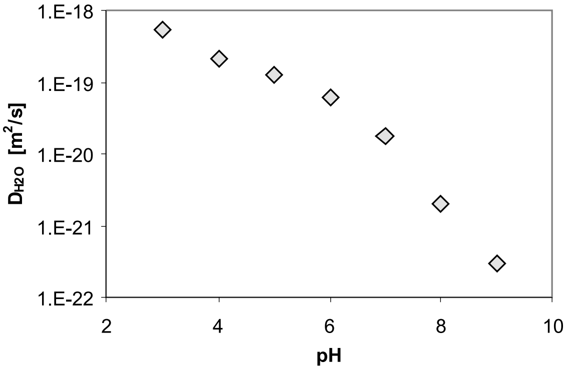

Fig. 7. Diffusion coefficients for water molecules in the glass network as a function of pH.

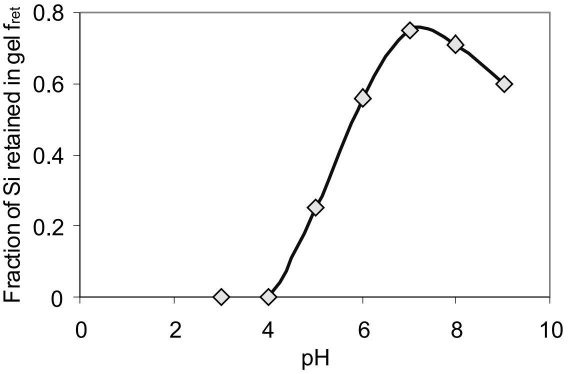

Fig. 8. Sorption of Si in the surface gel as a function of pH.

diffusion coefficient of water was obtained by direct fit to the experimental data. In contrast, in the case of reactive transport, the effective diffusion coefficient was kept constant in the pH range 3–7 and only $C_{\mathrm{max,SiOH}}$ was varied. Results from the second approach are not shown, due to the arbitrary character of the fixed $D_{\mathrm{H_2O,eff}}$ value, but the approach shows that the pH dependency of $D_{\mathrm{H_2O,eff}}$ in the non-reactive transport calculations could be explained in part by reaction of water molecules with the glass network.

Retention of silica in the surface gel layer appears to be at a maximum value at pH 7 and decreases both at higher as well as at lower pH. This decrease may be attributed to the increasing solubility of clay minerals as typical solid reaction products of glass dissolution reactions. At pH lower than 4, Si-retention approaches zero. High Si-contents of surface layers at these pH values then are attributable not to formation of Si-containing surface reaction products but to the formation of a Si-rich hydrated glass, depleted by ion exchange of alkali and alkali earth elements, and possibly (at pH 3) even of Al.

Surface concentration profiles calculated with the model are given in Fig. 9 for the case of pH 7 (model parameters as in Fig. 6). The first 300 nm of the outer glass surface exhibit corrosion features characterized by a total release of alkali and boron, a water activity equal to the solution phase and a certain reduction of silica content. Water diffusion and alkali and boron depletion profiles extend from the interface of this layer to a depth of as much as 1.5 μm. The experimental data do not allow one to distinguish between reactive and non-reactive transport. More work is necessary on the speciation of water in the glass in order to distinguish between these cases.

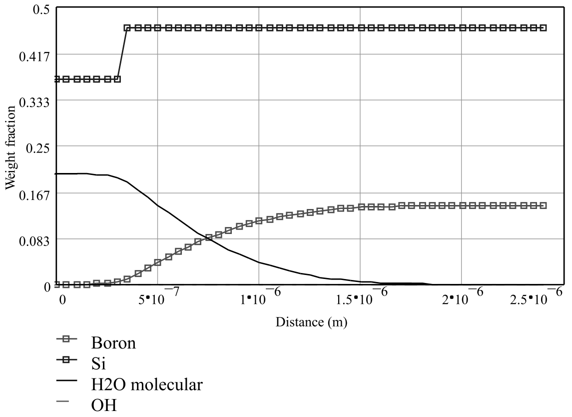

Fig. 9. Concentration profiles for H_2O, B (valid for alkali as well) and for Si at the glass surface, calculations based on parameters used in Fig. 4 (50 ± 0.1°C, pH 7.0 ± 0.1, $S/V = 1000\,\mathrm{m}^{-1}$, $D_{H_2O} = 1.8\times10^{-20}\,\mathrm{m}^2/\mathrm{s}$, $f_{\mathrm{prec}} = 0.7$, $k_+ = 0.27\,\mathrm{g/m}^2$ day, $\log K_{SiO_2} = -2.94$), for total transport of water molecules.

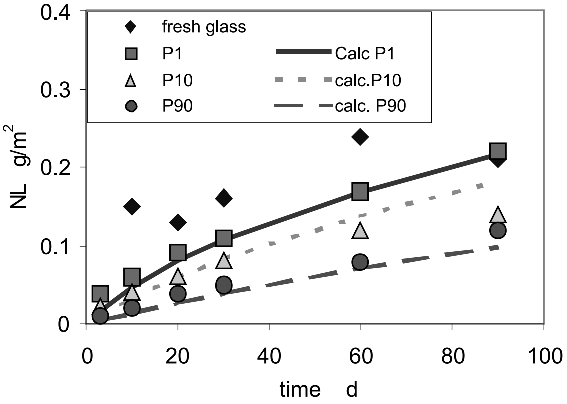

Fig. 10. Effect of pre-alteration times (P1 = 1 day, P10 = 10 days, P90 = 90 days) on the corrosion resistance (normalized mass loss NL) of R7T7 glass in aqueous solutions ($S/V = 1000\ \mathrm{m}^{-1}$, $D_{H_2O} = 7\times10^{-21}\ \mathrm{m}^2/\mathrm{s}$). The solutions were saturated prior to the test by leaching of glass powder (the glass powder was removed prior to the test shown here). Experiments reported by Jegou [2]. Comparison of experimental and modeling results (Calc).

4. Model application to literature data

The model may also be used to resolve some of the recent doubts in the validity of the first-order dissolution rate law for nuclear waste glass dissolution. In the experiments performed by Jegou [2] fresh and pre-altered glass was exposed to solutions which were previously in another powder glass dissolution test saturated with dissolved glass constituents. A simple first-order dissolution rate law would assume that the glass water reaction should stop, because the solution is saturated. Instead, it was observed that glass corrosion rates were initially high and reaction rates were a function of pre-alteration time. The observed continuation of the reaction after saturation of the solution with dissolved glass constituents is in accordance with previous modeling effort by one of the authors [1] and was previously explained by the fact that there is no true equilibrium between the glass phase and the solution. The observed saturation effect was considered to apply only to equilibria between the solution and a surface region, while a thermodynamic driving force for continued reaction does remain. However, in this modeling pre-alteration was never considered. The final thermodynamic affinity for long-term reaction is a necessary condition for long-term corrosion, but it is an insufficient explanation for the variation of corrosion rates with pre-alteration times.

The experimental results from [2] are given in Fig. 10. The fit of the model to the experimental data was done with a unique set of parameters and particularly a unique effective diffusion coefficient of water in the glass for all experiments. Pre-alteration was considered in the model in the following way. Pre-alteration was interpreted by the model as a continuous experiment with a discontinuous interpretation of model results. If for example the effect of 10-day pre-alteration on 90-day glass alteration under saturated conditions were to be calculated, one would make a calculation for 100 days and subtract from the 100-day result the initial 10-day result (this method works only under silica-saturated conditions; in diluted solutions, pre-alteration would demand a re-saturation of the solution). The agreement of model and experiment shows that water diffusion in the glass is a possible explanation for the observed effect of pre-alteration. The lower rate at 90-day pre-alteration can be explained by a larger thickness of the water diffusion zone.

5. Validity of the first-order rate law in the long term

If the above interpretation can be confirmed by a detailed experimental analyses of diffusion profiles of water into the glass it would imply that the reported [2] deviation of initial glass dissolution rates from the first-order rate law are short-term effects. Initial reaction rates measured during a period of few days were found to respond only very little on the initial silica concentration in solution, in contrast to expectations from a pure first-order rate law [2]. However, this may result also from the fact that water diffusion is not depending on silica concentration. In the short term, water diffusion distances are short and reaction rates are high. Using the full model, Fig. 11 shows the calculated effect of the initial silica concentration ($m_{\mathrm{Si,CCB}}$) on the corrosion rate after 3 days at 50°C and $S/V = 1000\ \mathrm{m}^{-1}$ as a function of pH. The model parameters ($D_{\mathrm{H_2O,eff}}$, $K_{\mathrm{SiO_2}}$, k_+, f_{ret}, fixed parameters) were used as determined above as a function of pH for the WAK glass. Resulting effects on reaction rates are expressed as a ratio of the calculated normalized rates of release of a soluble element (boron or alkali ions) in an initially silica containing solution ($m_{\mathrm{Si,CCB}} > 0$) to the respective rate calculated for $m_{\mathrm{Si,CCB}} = 0$. Depending on pH a reduction of rates by only a factor of 5 or much less is predicted to occur in saturated solutions. At pH 4 (not shown) almost no reduction of the reaction rate with increasing silica concentration is predicted to occur. A similar pH dependency was reported as experimental observation by Jegou [2] and it was concluded that an affinity-based rate law is not applicable to glass dissolution. However, the calculations were repeated for a total reaction time of 1 year. Much larger effects are predicted. The corrosion rate for example at pH 8 is predicted by the model to be more than a factor of 100 lower than the initial rate and it continues to decrease with time.

In an open system, the rates cannot decrease to zero but a constant final rate will be established, governed by a steady state between the rate of glass corrosion and the rate of removal of corroded glass constituents from the glass surface either by the slowly flowing groundwater or by diffusion into a finite or infinite porous media. This minimal rate is identical to that calculated for the conditions of validity of an affinity-based rate law (e.g. first-order rate law). The time necessary to reach this minimum rate law depends on water diffusion coefficients as well as on diffusive and advective groundwater transport processes. This indicates that an affinity-based rate law may be more valid in the long-term than in short-term tests.

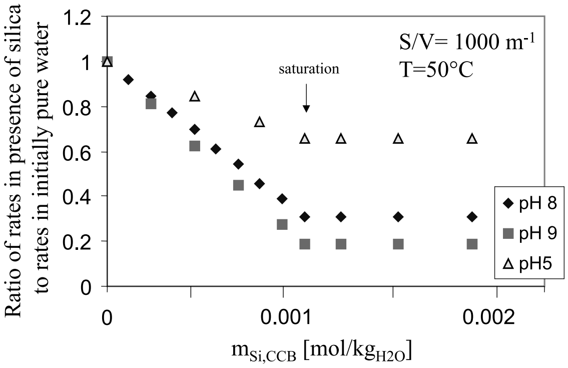

Fig. 11. Calculated effect of initial solution concentrations of silica ($m_{\mathrm{Si,CCB}}$) on the WAK glass corrosion rates after 3 days at $S/V = 1000\ \mathrm{m}^{-1}$ and 50°C as a function of pH. Effects on reaction rates are expressed as a ratio of the calculated normalized rates of release of a soluble element (boron or alkali ions) in an initially silica containing solution ($m_{\mathrm{Si,CCB}} > 0$) to the respective rate calculated for $m_{\mathrm{Si,CCB}} = 0$. The pH-dependent parameter f_{ret}, $D_{\mathrm{H_2O}}$ and $K_{\mathrm{SiO_2}}$ were used as determined from the experiments.

6. Conclusions

A model has been developed, describing nuclear waste glass corrosion both for experimental conditions and for a dynamic repository environment. The model combines the effect of glass hydration by water diffusion with ion exchange and affinity-controlled glass network corrosion both for static and dynamic corrosion environments. The potential protective effect of growing surface gel layers is represented by a mass transfer resistance for silica of this layer. At the interface between the pristine glass and the gel layer, a second 'layer' of hydrated glass is assumed to be formed as part of the glass phase with diffusion profiles for water molecules and alkali ions and boron in opposite directions. If this layer is thin, high reaction rates are expected even under conditions of a very low glass corrosion affinity.

The model allows one to test and to compare various hypotheses on long-term glass corrosion by parameter variation within a single overall model: rate control by an affinity term, by retention of silica in alteration products, by protective effects of surface gels, by water diffusion etc.

The principal results of the application of the model to experimental data of a nuclear waste glass dissolution were:

- The effective diffusion coefficient of water molecules for glass hydration and ion exchange decreases with an increase in the pH. This is coherent with the general observation that ion exchange is more important in acid than in alkaline solutions. The pH dependency in the effective diffusion coefficient of water molecules may in part be explained by an enhancement of water diffusion by the formation of silanol groups creating a more open glass structure.
- When simulating short-term experiments, it was found that the first-order dissolution rate law was not rate controlling at pH < 4 but it was rate controlling at higher pH. The extrapolation to the long-term considering open system flow through conditions has shown, that the first-order rate law is also important at pH < 4.
- A low corrosion affinity ('silica saturation', $m_{\mathrm{Si,bulk}} = K_{\mathrm{SiO_2}}/\gamma_{\mathrm{Si}}$) is a necessary but not a sufficient condition for the long-term decrease in glass dissolution rates (release rates of soluble species such as alkali or boron). The other condition is that a hydrated surface region is formed, constituting a diffusion barrier against the penetration of water molecules into the glass network.

- In contrast to the gel layer, this diffusion barrier (hydrated glass) is not a surface layer (a phase separate from the glass) but can be considered as part of the glass phase. The gel layer is a new phase replacing the glass phase.
- Under closed system conditions glass hydration continues in the long term and the glass corrosion rate is expected to decrease continuously, provided no secondary silica consuming phase is formed. In case of formation of silica-rich secondary alteration phases (zeolites, quartz,...) a steady state between glass hydration and phase formation could become established. Then glass corrosion would become controlled by the rate of secondary phase formation.
- In an open dynamic system, another steady state is established where the rates of glass hydration and of ion exchange are becoming equal to the network corrosion rate, the latter being controlled by an affinity-based rate law. If this affinity-based dissolution rate law would remain applicable in the long term, extremely low long-term dissolution rates would be expected. Long-term persistence of low glass dissolution rates would then depend neither on transport properties nor on the mechanical or chemical long-term integrity of a surface gel layer but on the intrinsic non-avoidable presence of the hydrated glass region. However, more work is necessary to experimentally validate water diffusion mechanisms in the glass. The validity of an affinity-based rate law as a necessary condition for low glass corrosion rates implies also that certain silica-consuming reactions could potentially be detrimental to long-term stability. Observed examples include the adsorption on bentonite backfill or on metallic overpack materials. These detrimental effects may be of transitory nature, but more research is necessary to quantify the potential impact on the long-term glass performance.

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