SIMULATING BY A MONTE CARLO METHOD THE PROTECTION BY A SURFACE LAYER IN GLASS DISSOLUTION

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The presented Monte Carlo method solves the mathematics of transition state theory and describes the glass dissolution process on a microscopic scale. In the model, the glass is considered as a random mixture of a slowly dissolving, solubility limited component and a fast dissolving component. As the model parameters are similar to those in the Grambow model, the parameters of both models can be compared with each other, as well as with experimental values. The Monte Carlo method is used to investigate recent experimental results according to which the protection provided by the gel should be the major factor determining the glass dissolution rate. Although these results contradict the Grambow model, they are consistent with the presented simulations: protection by the gel is indeed important in glass dissolution. On a qualitative level, the simulation results agree with experimental observations. In particular, protective surface layer is expected(1) in static tests, (2) at high surface to volume ratios and (3) at long leaching times.

INTRODUCTION

Although the basic reactions responsible for glass corrosion (dissolution) are known, there are still no reliable models that allow to predict the corrosion behavior of the glass as a function of time, the glass composition and the glass environment. Several kinds of models describing glass dissolution exist, but they mostly focus on just one aspect of the dissolution process. New computation techniques, emerging because of the large increase in computation power in recent years, should be able to remedy this. Molecular dynamics is an example of such a technique. It has the capability to describe most aspects of the dissolution process, but, unfortunately, it only allows to describe glass dissolution on extremely small time scales. Therefore, we try another method that, although less accurate than molecular dynamics, should allow to describe glass dissolution on experimentally more relevant time scales (hours, days). In this paper, we explain the basics of this method, as well as some results. In this stage of development of the technique, we still focus on reproducing qualitatively experimentally observed phenomena. Of course, reproducing these observations also quantitatively is the final goal.

PRESENTATION OF THE MODEL

We first discuss how we represent the glass. We start by dividing all glass components in two classes: (1) easily dissolving components and (2) slowly dissolving, solubility limited components. Examples of the first class are sodium (in fact Na_2O) and boron (in fact B_2O_3). For simplicity, we call all such components 'sodium' (instead of sodium oxide). Similarly, because silica (SiO_2), which is the major glass component, belongs to the second class, we call all these components 'silica'. Next, we consider the glass as a random mixture of 'silica' and 'sodium'. Another approximation is that we suppose that all glass components are on a lattice. This assumption is not crucial, but it makes it easy to find neighboring particles and to include volume exclusion in the model. We choose a diamond lattice because (1) it is three dimensional and (2) a coordination number of four represents best the tetrahedral silica network. Apart from the 'two component (glass)' version, that we just described, we also performed simulations with only one glass component. In this 'one component' version, we assume that all sodium has already leached out at zero time. So, initially, the 'one component' glass is the 'two component' glass, in which we have replaced all sodium particles with water particles. In this paper, we present results of (1) the dissolution of a semi-infinite 'two component' glass in a semi-infinite water volume and (2) the dissolution of a finite 'one component' glass (since the sodium has already leached out, one could also call this a 'gel') in a finite water volume. For the second case, the width of the glass (gel) and the water volume are chosen so that the glass (gel) contains considerably more silica than needed for saturating the water volume.

We now explain how we simulate the dissolution of silica. Like Dove [1], we assume that the silica dissolution reaction $SiO_2 + 2H_2O \rightarrow Si(OH)_4$, is the sum of four elementary reactions, where in each elementary reaction a Si-O-Si bond is broken by a neighboring water particle. Because in each elementary reaction, a Si-O-Si bond is broken, it is a good approximation that all these elementary reactions have the same reaction parameters. A chemical reaction can be characterized

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by two parameters, for instance (1) the free energy difference between both sides of the reaction (which is usually converted into the equilibrium constant) and (2) the initial reaction rate. In our model, we [2] convert both reaction parameters into microscopic probabilities: a probability P^+ for the forward (dissolution) reaction and a probability P^- for the backward (condensation) reaction. Next, Si-O-Si bonds in the system are broken and restored according to these probabilities. If a silica particle has no remaining Si-O-Si bonds anymore, it is dissolved. Then, it diffuses onto water bearing sites with a probability P_{diff}. Because diffusion in water is much faster than the breaking and restoration of Si-O-Si bonds, the probability P_{diff} should be much higher than both P^+ and P^-. The diffusion of a dissolved silica particle stops, when it is trapped again (with probability P^-) by a neighboring silica particle. For a good understanding of the simulation results, it is important to know that the dissolution behavior in the model is mainly determined by the ratios of the three probabilities P^+, P^- and P_{diff}. Indeed, the ratio P^+/P^- determines the equilibrium constant of the silica dissolution reaction and thus also the silica solubility. Therefore, we introduce the notation $J = -\ln(P^+/P^-)$, with J the free energy difference between both sides of an elementary silica dissolution reaction (we simply call the J the (Si-O-Si) 'bond strength'). Similarly, the probability that a dissolved (and thus diffusing) silica particle is trapped again by a neighboring silica particle, is mainly determined by the ratio P_{diff}/P^-. With both the ratios P^+/P^- and P_{diff}/P^- fixed, the choice of an absolute value for one of these probabilities (for instance P^+) determines the time scale of the simulation. We estimate the parameter values for simulating a real experiment in the next way: (1) a value for P^+ can be obtained from the initial silica dissolution rate, (2) a value for P^- can be calculated from the silica saturation concentration and P^+, and (3) a value for P_{diff} results from $D_{water} \approx 0.7\ 10^{-7}\ m^2\ s^{-1}\ P_{diff}$ with D_{water} the diffusion coefficient of silica in water. This last relation is found numerically from the relation $X^2 = 6\ D\ t$ with X^2 the mean square displacement of a diffusing particle, D its diffusion coefficient and t time. The calculations are simple: (1) choose an origin, where you put a dissolved silica particle, (2) simulate the diffusion of this particle (in water), (3) calculate the mean square displacement X^2 as a function of time, and (4) after a sufficiently large number of time steps, the ratio $X^2/6t$ is a reliable estimate for the diffusion coefficient D_{water}.

Simulating sodium dissolution (for the two component glass) is similar as simulating silica dissolution. For the dissolution of sodium, we consider the ion exchange reaction: glass-Na + H^+ → glass-H + Na^+. Because in the present system, we have only silica, sodium and water particles, we simulate ion exchange by exchanging a sodium particle with a water particle (instead of a hydrogen particle). By introducing ion exchange, we would need three additional parameters: P_{ex}^+, P_{ex}^- and $P_{ex,diff}$. We reduce this amount of parameters by assuming that the diffusion probabilities for silica and sodium are the same ($P_{diff} = P_{ex,diff}$). Another possible simplification could be to consider ion exchange as a pure diffusion reaction, which would imply that $P_{ex}^+ = P_{xe}^-$. (= P_{ex})

With this last simplification, the parameters are:

P^+	probability to break a Si-O-Si bond
P^-	probability to restore a Si-O-Si bond
P_{diff}	probability for diffusion
P_{ex}	probability for ion exchange.

RESULTS

We start by discussing the choice of our parameter values. Apart from the already discussed parameters, we also need a parameter ρ, which is the probability that initially, a site in the glass contains a sodium particle ($0 \leq \rho \leq 1$). Concerning the other parameters, we have already explained how the forward probability P^+ (and similarly P_{ex}^+) and the diffusion probability P_{diff} can be related to experimentally measurable values. For estimating the bond strength J from the silica saturation concentration, we performed one component simulations for several values of the bond strength J and determined for each simulation the silica saturation concentration. Fitting of the silica saturation concentration as a function of bond strength leads to

$$\gamma^* = 2.6 \exp(-1.95\ J) \qquad (1)$$

with γ^* the probability that a site of the water volume contains a dissolved silica particle. The values of the fit parameters in (1) differ slightly from those mentioned in a previous paper [3], because we have included in the present fitting also newly obtained simulation results. It remains also possible that the silica saturation concentration depends slightly on the sodium density ρ, but our data are not precise enough for a definitive conclusion. According to Vernaz [4], the experimentally measured silica saturation concentration at 90 °C is of the order of 10^{-3} mole/Liter, which we [3] convert to $\gamma^* \approx 1.8\ 10^{-5}$. Substituting this value in (1) leads to $J \approx 6.1$. So, we largely know which values to choose for the silica dissolution parameters for having the real experimental values. Nevertheless, we have performed most of the simulations with other parameter values. One reason is that at this stage of development of the model, we still want to know how the simulation results behave when we vary the model parameters. Besides, we also try to choose our parameters so that (1) they should lead to the same phenomena as in the real system and (2) they lead to lower computation times. As an example, if we would use the real values for P^+, P^- and P_{diff}, almost all the computation time would be spent on the diffusion in solution of very few dissolved silica particles. In Aertsens [3], it is shown that, for a sufficiently high value of P_{diff}, the simulation results depend only weakly on P_{diff}. This allows to obtain representative results by using a lower P_{diff} value, which requires less computation time. It is also for saving computation time, that we introduced the one component glass as an approximation of the two component glass.

Using our simulations, we study the protection provided by the gel to glass dissolution. During the last decade, the most widely used glass dissolution model is the Grambow model [5]. According to this model, the dissolution rate of the glass is mainly determined by the concentration in solution of dissolved silica. Recent experimental results by Gin [6] and Jégou [7] contradict this: the protection provided by the gel should be the crucial factor determining the glass dissolution rate. In most experiments, the glass dissolution rate is estimated by the boron leach rate. Besides, experiments by Van Iseghem [8] and Grambow [9] indicate that the long term glass dissolution rate is diffusion controlled. In most experiments, the glass dissolution rate is estimated by the boron leach rate. According to the basic assumptions of our model, this means that we must observe during our simulations the amount of released sodium. We did this for (1) a solution containing no silica and a silica saturated solution, and (2) two values for the ratio P_{diff}/P^- ($P_{diff}/P^- = 500$ and $P_{diff}/P^- = 5$). In

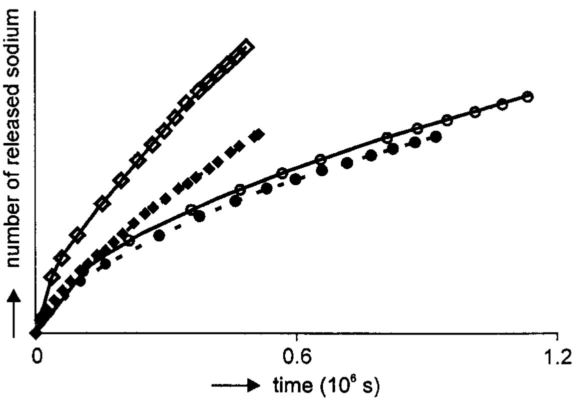

Figure 1. Amount of leached sodium as a function of time for $J = 4$, $\rho = 0.4$, $P_{ex} = 5P^-$ and $P_{ex} = 2.7\ 10^{-14}$. More sodium is released when the solution contains no silica.
◊ – no silica in solutions, $P_{diff}/P^- = 500$; o – no silica in solutions, $P_{diff}/P^- = 5$; ♦ – silica saturated solution, $P_{diff}/P^- = 500$; • – silica saturated solution, $P_{diff}/P^- = 5$.

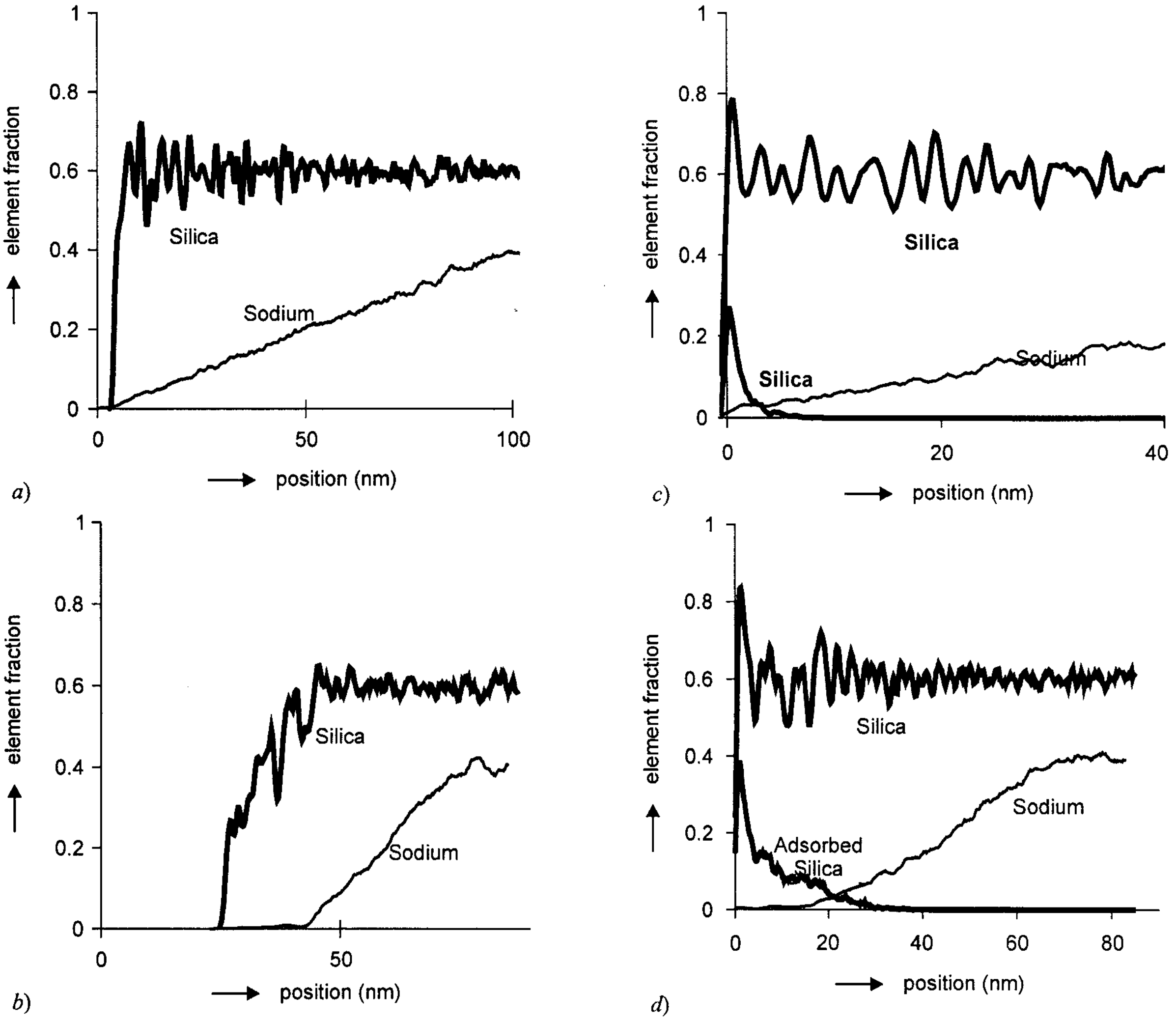

Figure 2. Element profiles for $J = 4$, $\rho = 0.4$, $P_{ex} = 5P^-$ and $P_{ex} = 2.7\ 10^{-14}$. The initial glass/water surface is at zero position.
a) - no silica in solutions, $P_{diff}/P^- = 1$, 12.3 days; *b*) - no silica in solutions, $P_{diff}/P^- = 100$, 4.6 days; *c*) - silica saturated solution, $P_{diff}/P^- = 1$, 9.4 days; *d*) - silica saturated solution, $P_{diff}/P^- = 100$, 5.7 days.

figure 1, we show for these four cases the amount of released sodium as a function of time. One clearly observes that (1) more sodium is released in a solution containing no silica than in a silica saturated solution, and (2) the difference of the released amount of sodium between the no silica solution and the saturated solution is larger for the largest ratio $P_{diff}/P^{-} = 500$. An explanation of this behavior can be given from the element profiles in the glass, computed at the end of the simulations (see figure 2). For the silica saturated solutions, one clearly observes a peak in the silica content close to the glass/water surface. This peak is due to 'adsorbed' silica: dissolved silica coming from the solution, which is captured again by the glass (gel). If the P_{diff}/P^{-} ratio increases, silica can diffuse further in the gel before being trapped. So, this peak is wider for higher P_{diff}/P^{-} values (see figure 2). If there is no silica in solution, there is no peak. Instead, we observe an important depletion of silica near the glass/water surface for high P_{diff}/P^{-} ratios. Again, this is easy to explain because for large P_{diff}/P^{-} ratios, a dissolved silica particle can reach the solution before being trapped again by the gel. For smaller P_{diff}/P^{-} ratios, this is not anymore the case and thus we do not observe such an important depletion. Because sodium can only leach out of the glass by diffusing on water bearing sites, it is obvious (1) that a silica peak at the surface limits sodium leaching and (2) that silica depletion at the surface enhances sodium leaching. Hence, the sodium leach rate should be smaller for a silica saturated solution than for a silica solution containing no silica. Similarly, the difference in leach rate between a silica saturated solution and a solution without silica should increase with larger P_{diff}/P^{-} ratios.

Another simulation result that illustrates the importance of the ratio P_{diff}/P^{-} in the protection provided by the gel is given in figure 3 (one component glass simulation). For a ratio $P_{diff}/P^{-} = 50$, silica particles coming from solution are trapped very close to the surface of the glass/water surface. The result is a peak of silica particles near the surface, so high that at positions around 170 Angstrom, almost 100 % of the sites bear a silica particle. In this case, it is impossible that particles that are behind this peak can leach into the solution. This structure is clearly very protective. On the other hand, for $P_{diff}/P^{-} = 5000$, dissolved silica particles from solution can reach almost any site in the gel before being trapped. In this case, the distribution of adsorbed silica particles in the gel is almost homogeneous. There is no peak and the surface layer is not very protective.

DISCUSSION

We start by comparing our model with other types of models: the Grambow model, solid state diffusion models and thermodynamic models. Like the Grambow model [5], our model is based on transition state theory. Contrary to the Grambow model, we consider five posible silica states and apply transition state theory microscopically at the transition between each of these states. So, it is not surprising that the results of our model [3] are not always consistent with those of the Grambow model. Our model results also show that the formation of a protective layer is consistent with transition state theory. Thus, applying transition state theory does not mean that the dissolution rate of a glass should be a function of the

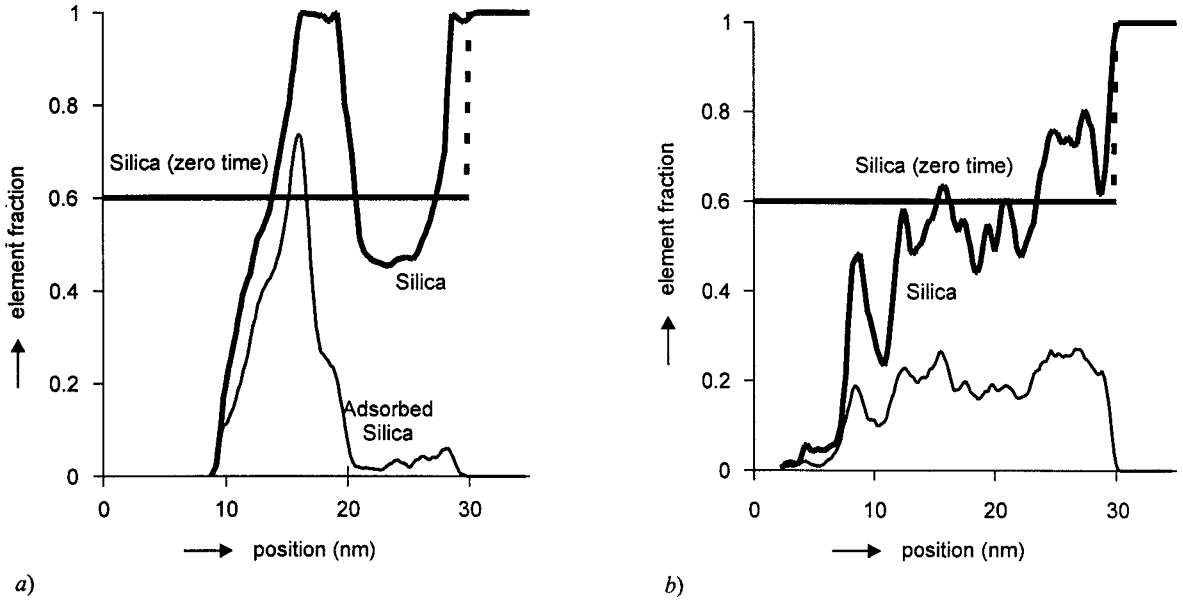

Figure 3. Element profiles for $J = 6$, $\rho = 0.4$ and $P^{-} = 4\ 10^{-4}$ and a (initial glass) surface (*SA*) to (water) volume (*V*) ratio $SA/V = 5000\ m^{-1}$. Initially the glass (gel)/water surface is at zero position.
a) -$P_{diff}/P^{-} = 50$, 160 days, *b*) - $P_{diff}/P^{-} = 5000$, 1.2 days.

concentration in solution of the glass components, like in the rate law derived by Aagaard and Helgeson [10]. Solid state diffusion models are based on the diffusion of water or hydrogen in the glass (or a component like sodium out of the glass). It seems evident that the basis of such models is consistent with our two component glass simulations. In thermodynamic models [11], a chemical reaction is characterized by only one parameter: the equilibrium constant. If the activation energy of the dissolution reaction of each glass component can be neglected, those models could be consistent with our simulations as well.

It is also evident that the protection provided by the gel against leaching of sodium at silica saturation, depends in the first place on the sodium density ρ (by a percolation phenomenon) [2, 12]. Obviously, sodium leaching is more difficult for low sodium densities than for higher sodium densities.

The final test for every model is consistency with experiments. Deruelle [13] observes that the gel pore size of R7T7 glass is larger in pseudo-dynamic mode than in static mode. Although we did not measure the pore size in our simulations, it seems logical that the pore size is larger for a silica depleted gel (no silica in solution in our simulations) than for a gel where the silica concentration shows a peak (silica saturated solution in our simulations). Since in general the silica concentration is higher in static than in dynamic tests, the result of Deruelle [13] is consistent with our simulation results of Figure 2. Similarly, Lee [14] reports that the surface layers in dynamic tests are more porous, and thus less protective, than those in static tests. Delage [15] interprets his fit results with the Lixiver code in the same way: the density of the gel increases (1) when one changes from dynamic to static tests, and (2) when the (dissolved) silica concentration (in the gel) rises. Xing [16] took two glasses with similar composition. He had both glasses been leached first. Then, he placed them in a renewed solution and found that the protection is highest for glass which had leached most. Similar tests by Gin [6] also show that glass samples which have leached longer, show a higher protection against leaching than pristine glass. Both these results agree with our interpretation of the simulation results. In our simulations, silica saturation is a pseudo stationary state, in which the fluxes of dissolving and adsorbing particles are (at least approximately) equal. During this pseudo stationary state, silica particles try to find their lowest energy state. This energy state corresponds to sites with many silica neighbors, and thus a compact, protective surface. Being longer at silica saturation should allow more silica particles to find such a favorable energy state, and thus a more compact, protective surface layer. However, what really matters is not time, but the product of (1) time and (2) the rate of the silica adsorption/dissolution process. If the activation energy of this process is small, then its rate is high and silica particles will find a favorable energy state much sooner than for a higher activation energy. Ab initio calculations by Xiao [17] as well as experiments by Advocat [18] and Knauss [19] show that at high *pH*, the activation energy for silica dissolution is small. Because in general a large surface to volume (*SA/V*) ratio leads to high *pH* values (e.g. Feng [20]), we expect the fast formation of a protective gel layer in this case. Another, more intuitive argument for protective surface layers in this case, is that, assuming that the bond strength J and the probability P_{diff} do no change as function of pH, a lower activation energy leads to a lower ratio P_{diff}/P^{-} and thus a more protective surface layer (see figure 3). These reasonings could explain the up to now not understood phenomenon that at low *SA/V*, Chick and Pederson [21] report a small protective effect, while for the same glass at much higher SA/V, Xing [16] finds a strong protective effect. Similarly, Vernaz [4] measures final rates of dissolution, which are much lower at higher *SA/V* than at lower *SA/V*. This is also consistent with a more protective gel layer at large *SA/V*. For avoiding all confusion, at high pH, the silica in solution starts dissociating and will lead to more glass dissolution than at low *pH* value. What we mean here, is that at high *pH*, the gel layer will be protective at the end of the dissolution process. We do not say anything about the start of this process.

CONCLUSIONS

We have presented a Monte Carlo method which (1) describes glass dissolution on a microscopic scale and (2) which is consistent with transition state theory. The simulation results show that protection by the gel is indeed an important phenomenon in glass dissolution. This also shows that transition state theory does not need to lead to a glass dissolution rate that depends on the concentration in solution of all glass components (an 'affinity term'). Our simulation results agree qualitatively with experimental observations. We expect a protective surface layer (1) in static tests, (2) at high *pH* (high surface to volume ratio) and (3) after sufficient long leaching times.

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MATEMATICKÁ SIMULACE ROZPOUŠTĚNÍ SKLA S OCHRANNOU POVRCHOVOU VRSTVOU METODOU MONTE CARLO

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Presentovaná metoda Monte Carlo simuluje neustálený proces rozpouštění skla. Model uvažuje sklo jako směs pomalu a rychle se rozpouštějících složek. Parametry modelu byly porovnány s parametry Grambowova modelu a s experimentálními daty. Metoda Monte Carlo byla použita ke zpracování dřívějších experimentálních výsledků, podle kterých je ochrana gelovou vrstvou hlavním faktorem ovlivňující rychlost rozpouštění skla. Výsledky odporující Grambowově modelu jsou ve shodě s naším modelem; ochrana skla gelovou vrstvou je důležitým faktorem. Tvorba vrstvy se předpokládá zejména ve statických testech, při vysokém poměru povrch/objem a při dlouhých loužících časech.