Monte Carlo modeling of the corrosion of SiO_2-B_2O_3-Na_2O glasses

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This work is concerned with the modeling of simple oxide glasses dissolution. These ternary glasses (Si-B-Na) are plunged in low basic buffered solutions (pH~8.5) at constant temperature (90 °C). Numerical simulations are performed within a classical Monte Carlo (MC) approach which respects the local chemistry of glasses. This modeling is able to reproduce the experimental conditions of alteration. The alteration by water leads to the formation of a restructurated silica layer between the solvent and the unaltered glass. This layer may become protective or not, depending on the glass composition and the conditions of alteration. In the first case all the soluble species (B, Na) are extracted until the alteration is blocked as a consequence of the structural rearrangement of the silica network. This behavior strongly depends on the initial choice of the MC parameters, which could be determined either by quantum chemistry calculations or by fitting the representative experimental data.

1. Introduction

Glass leaching strongly depends both of the glass composition and on the leaching solution. These two factors are not independent, since glass alteration modifies the leaching solution. Many mechanisms are involved in the corrosion phenomena, such as hydration and hydrolysis, ion-exchange, silica-water reaction, or still diffusion. The complexity of the whole glass system needs strong hypothesis to be reasonably studied. Grambow model[i], based on the transition state theory, is one of the major analytical glass dissolution model in use. Analytical models and recent computer achievements make it possible to treat this complex system efficiently. Aertsens et al[ii,iii] introduced Monte Carlo simulations for glass dissolution. They divided reactive species into two classes depending of their solubility (highly- and moderately- soluble). These studies have been performed either in cubic or in tetraedric geometries. Atoms dissolution processes bond after bond, and diffusion is taken into account. The results globally agree with Grambow first order kinetic law, but above all, they showed that in certain conditions the alteration layer, usually called the gel, can be protective with respect to further corrosion. MC simulations proposed by Devreux et al[iv,v] emphasize on the mechanisms which control the blocking of corrosion, and on the evolution of the morphology of the surface layer. In its initial form, atoms were set on a cubic lattice, their reactivity was modelized in term of site configuration, contrasting with Aertsens's bond approach. This model recently evolves toward a more realistic representation of the local chemistry of borosilicate glasses.

The description of this MC model for glass alteration is developed in section 2. Section 3 is devoted to the evaluation of the parameters of the MC model by a preliminary quantum chemistry approach. The correspondence between real and numerical glasses is discussed in section 4. Finally, section 5 summarizes the main conclusions of the present study.

2. Models and methods

This MC modelisation tries to respect as much as possible the local chemistry of the borosilicate glasses. At first, the glass is built, respecting some inputs (chemical composition, initial volume of solution and active surface). Then, for each step of simulation, solid atoms may be dissolved while atoms in solution may reprecipitate. One can check periodically the glass morphology and the solution composition.

2.1. Structural model

We start with a cristobalite crystal with the silicon atoms at the vertices of the lattice. Boron is introduced by random substitution of silicon. It is known that boron may exist in two coordinations in silicate glasses[vi], either 3-coordinated (B^{III}) or 4-coordinated (B^{IV}). In the former case, this implies breaking one Si-O-B bond and compensating the non-brindging oxygen by a sodium ion. In the latter case, the sodium ion is used as a charge compensator for BO_4^- unit. As our reactivity model (see below) does not distinguish in its present state between the behavior of B^{III} and B^{IV}, these two situations are equivalent. Pairs of sodium may also be introduced as network modifiers by breaking Si-O-Si bonds.

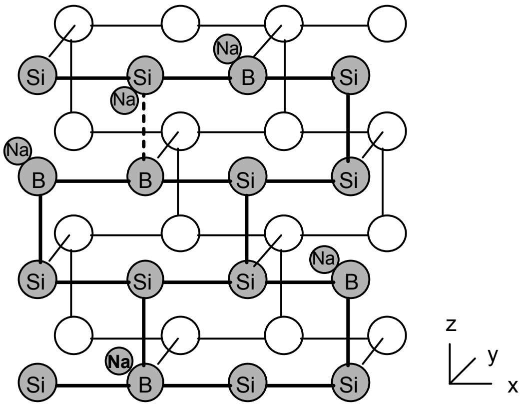

Fig. 1 : The cristobalite network. Boron atoms are used in substitution of silicon atoms. Doted lines represent broken bonds. Sodium atoms compensate either BO_4^- units or non bridging oxygen bound to silicon. Oxygen are implicitly set in the middle of the bonds bridging two successive cations.

2.2. Reactivity model

We assumed that boron and sodium, well-known to be easily soluble, are instantaneously dissolved when they are in contact with water, and cannot reprecipitate once solubilized. Silicon dissolution is determined after the connectivity of its coordination tetrahedron. Since the strength of the Si-O-B bonds are neglected compared to that of a siloxane bond, it remains three parameters, which correspond to the Q^1, Q^2, Q^3 species[1] of the ^{29}Si-NMR (Q^n means that the current silicon atom is involved in n siloxane bonds). Silicon condensation is accounted by a single parameter, arguing that the deposition rate is simply proportional to the concentration of solubilized silicon. This parameterization is equivalent to a first order kinetic law. Actually, if $w_d(i)$ represents the dissolution rate of silicon in the site i of the glass-water interface, c_{Si} the concentration dissolved silicon and w_{rd} the redeposition proportionality constant, the rate of dissolved silicon (N_{Si}) results from the competition between dissolution and recondensation fluxes. It can be written as :

$$\frac{dN_{Si}}{dt} = \sum_{surface\ site\ i} \left(w_d(i) - w_{rd} c_{Si}\right) \qquad (1)$$

It may be remarked that silicon concentration in water is supposed homogeneous in agreement with the hypothesis that diffusion is infinitively fast in solution. On the contrary, solid diffusion is neglected, and thus this MC modeling cannot pretend to reproduce the long time glass behavior. The silicon saturation concentration is obtained in the stationnary state from eq. (1), where the quantity between brackets corresponds to the dissolution rate averaged over all the interface :

$$c_{Si}^{stat} = \frac{\langle w_d(i) \rangle}{w_{rd}} \qquad (2)$$

3. Quantum chemical calculations

Quantum chemistry calculations are a powerful tool for the understanding of the system. Indeed if one considers the reversible reaction of a Q^n silicon with water :

$$(\equiv SiO)_n Si(OH)_{4-n} \quad + \quad n\, H_2O \quad \overset{w_d(Q^n)}{\underset{w_{rd}}{\rightleftarrows}} \quad (\equiv SiOH)_n \quad + \quad Si(OH)_4$$

According to the detailed balance principle, the ratio of the dissolution to condensation rates reads :

$$\frac{w_d(Q^n)}{w_{rd}} = \exp\left(-\frac{\Delta H_r(n)}{k_B T}\right) \qquad (3)$$

where $\Delta H_r(n)$ is the reaction enthalpy. Several calculations based on semi-empirical (AM1 method) geometry optimization were performed on small silica clusters, typically a cristobalite unit cell-like ($Si_{14}O_{40}H_{24}$) where hydrogen were used to limit the cluster extension and to maintain the electrical neutrality. The choice of this semi-empirical method is a compromise between accuracy and duration of the calculation. Calculations confirm two hypothesises of section 2.2 : (a) the enthalpy of reaction is practically independent of the configuration beyond the second coordination sphere, (b) the strength of the Si-O-B bond, tested on clusters including boron, is much weaker than that of the Si-O-Si one, justifying not to consider boron cations in the reactivity of silicon. Table 1 presents the typical values obtained for the reaction enthalpies and for the dissolution to condensation ratio deduced from equation (3).

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[1] The Q^4 parameter does not appear at the interface.

	ΔH_r (kcal.mol^{-1})	**w_d/w_{rd}**
Q^1	12	$1\ 10^{-7}$
Q^2	19	$2\ 10^{-11}$
Q^3	> 20	$< 2\ 10^{-12}$

Table 1 : Mean value of enthalpies of reactions and corresponding probabilities calculated for several silicon configurations at 90°C.

Quantum calculations strongly suggest a hierarchy between the Q^n : the more a silicon is bound, the harder to dissolve it is, which result is qualitatively satisfying. However, according to eq. (2), the values in Table 1 would lead to a silicon saturation concentration less than 10^{-0} (molar fraction), which is much lower than the experimental values, typically 10^{-4} (150 Si mg.l^{-1}) at 90°C and neutral pH. This disagreement may come either from the method of calculation (representativity of clusters, no solvatation accounted) or from kinetic effects (accessibility on the interface, partial charge influence).

4. Experimental comparison : results and discussion

Thus, as these quantum calculations cannot be used directly to set the MC parameters, the latter were fitted by comparison with experimental data.

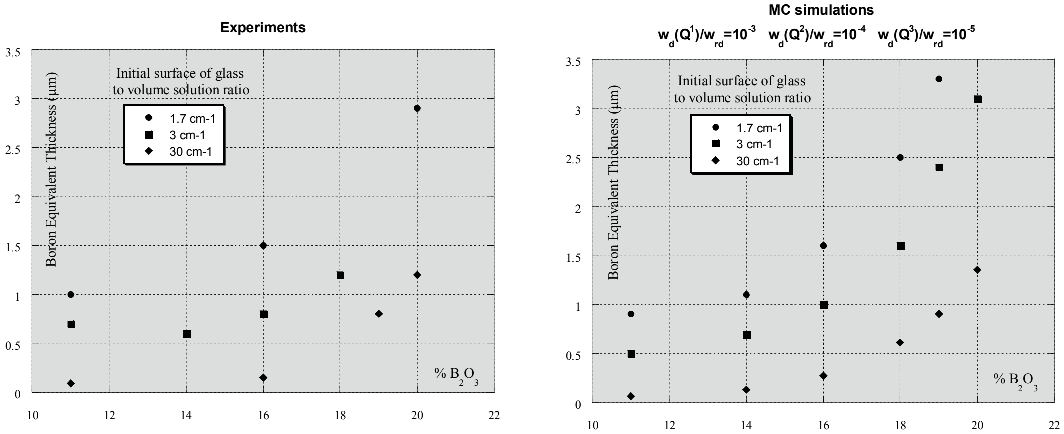

Fig. 2 : experimental and MC simulations equivalent boron leached thickness. Glasses molar composition is $(SiO_2)_{100-2x}(B_2O_3)_x(Na_2O)_x$.

4.1. Fit of parameters

Powdered borosilicate glasses have been leached in buffered water (pH 8.6). In this paper we discuss the effect of the content in boron and sodium, as well as the effect of the ratio S/V of the initial surface area of the glass S to the solution volume V. The elements released in the solution were titrated by conventional chemical techniques (colorimetry for silicon and boron, flame photometry for sodium). The Monte Carlo model has been used to simulate the same experiments. The initial rate of leaching and the saturation concentration in silicon or its equivalent for boron, the thickness of the altered layer, were used to adjust the parameters. Figure 2 presents a comparison of the equivalent leached thickness in boron as obtained in experiments (left) and in simulations (right) for different glass composition and S/V ratio. The same set of parameters gives also good agreement for the other experimental outputs, like concentrations evolution or kinetics of leaching.

4.2. Morphological influence of the parameters

NMR spectra and MC simulations were also found in good agreement. MC simulations confirm the predominance of Q^3 configuration in unaltered glass and the Q^4 predominance in the gel, as observed in experiments[vii]. Furthermore, simulations confirm that the parameters hierarchy, suggested by quantum calculations (section 3), is necessary : with such a choice, simulations lead to a protective gel that leads to a freezing of the leaching in static tests. Otherwise, one would obtain a swollen alteration layer which is not protective : the whole soluble species are extracted from the glass, even though their composition is far below the percolation threshold of the soluble lattice.

5. Conclusion

Although this MC modeling is based on very simple hypothesis and parameterization, it leads to interesting results for understanding the alteration of borosilicate glasses. With an optimized adjustment of MC parameters, one is able to reproduce the alteration of real glasses as a fonction of glass composition and S/V ratio. The evolution of gel morphology is qualitatively well accounted for. Redeposition model should be improved and compared to SAXS and NMR experiments in order to predict the evolution of porosity. *Ab-initio* calculations are in development to complete the study of the microscopic mechanism. In the near future, we will introduce aluminum in the chemical composition of the glasses and intend to distribute the MC parameters to modelize the topologic disorder.

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