Corrosion of Glass

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Abstract

The paper reviews the different models describing interaction between glasses and aqueous solutions. It is shown the development of kinetic and thermodynamic models (Rana & Douglas, Hlaváč & Matěj, Isard et al., Boksay & Doremus, Strachan, Grambow, Conradt, Aagaard & Helgeson). The models are compared from the point of view of different mechanisms and partial processes considered during model development. Model based on combination of Boksay & Doremus and Strachan models is shown, considering the glass corrosion as a combination of three simultaneous processes:

1. Glass matrix dissolution with two subsequent steps (surface reaction and surface reaction products transport through the precipitated layer and/or through solution layer adjacent to the glass surface)
2. Leaching of moveable ions (A^+) due to interdiffusion of H_3O^+ - A^+
3. Precipitation of dissolved glass components and/or solution components on the glass surface.

Finally, the outlook for future development of glass corrosion modelling is suggested, based on combination of Boksay & Doremus, Strachan, Conradt and Aagaard & Helgeson approach.

Introduction

Glass corrosion as both technically a scientifically interesting process is intensively studied since the second half of 20th century. Many mathematical and physico-chemical descriptions were suggested and developed in order to describe and predict the durability of glasses of different compositions in aqueous solutions and

under different conditions as solution volume (V) in contact with glass surface (S), solution flow rate (F) etc. Although the basic partial processes of glass corrosion and mechanisms were published by Hench [1] in 1977, there is no generally accepted and used mathematical model yet. The first description was published by Rana & Douglas [2] based on the assumption of two main processes of transfer of glass components into the solution: diffusion and glass matrix dissolution. This model, although based on consideration of basic partial processes, is often used for semi-empirical description of experimental data only, neglecting the physical meaning of model parameters. Later on, kinetic models by Hlaváč & Matěj [3] and by Boksay & Doremus [4] were developed, characterising corrosion by interdiffusion coefficient of moveable ions from glass and hydroxonium ions from solution in glass surface region (D_A) and by the constant rate of glass-solution boundary movement (a). The influence of solution saturation on this rate was published by Strachan [5]. Joining Boksay & Doremus with Strachan model, the more general description was published by Helebrant et al. [6]. In this model also back precipitation of dissolved glass components was considered.

The classical thermodynamic approach for glass dissolution rate prediction was presented by Grambow [7]. The thermodynamic principles were more accurately used by Conradt [8], who used so called constitutional approach emphasizing the glass character and surface composition and structure. The model combining both thermodynamic and kinetic approach can be based on the Aagard & Helgeson considerations [10].

The aim of this paper is to review existing models of glass corrosion and to suggest new possibilities of its description using their combination.

Basic mechanisms

The glass corrosion is the complex interaction between the glass surface and solutions. As the result of such interaction, three main effects can be observed:

1. Congruent dissolution of glass
2. Selective leaching of some glass components
3. Forming of secondary layers on the glass surface

The proportion of these changes depends on many factors, as glass and solution composition, pH, temperature, solution volume and flow rate. Qualitatively, the different forms of interaction were sorted by Hench [1] into 5 categories. In order to

describe the kinetics and mechanisms of glass corrosion we have to regard these changes as consequences of three simultaneous partial processes:

1. Dissolution of silicate matrix, consisting of two subsequent steps – a) surface reaction itself and b) transport of surface reaction products from the glass surface into bulk solution. This transport is usually described as diffusion through the precipitated layer and/or through the solution boundary layer adjacent to the solid/solution interface.

2. Interdiffusion of moveable ions (alkalis, alkaline earth, lead ions) and hydroxonium ions in the glass surface.

3. Precipitation of solution components on the glass surface and/or precipitation of formerly dissolved glass components.

Kinetic models

Model of Rana & Douglas [2]

Although model published by Rana & Douglas is usually used as semiempirical one, it can be explained considering main partial processes involved in the interaction under simplifying conditions. The amount Q_i (in g.m^{-2}) of dissolved glass components i is according to [2] either

$$Q_i = u + s\sqrt{t} \quad \text{or} \qquad (1)$$

$$Q_i = u + wt \qquad (2)$$

The model is often used without real understanding of the physical meaning of the constants u, s and w. For compounds creating glass network, as SiO_2, the total amount in the solution is given by (1) when non-steady diffusion in the solution controls the dissolution and

$$s \equiv 2(c_s - c_{l0})\sqrt{\frac{D}{\pi}} \qquad (3)$$

assuming D is the SiO_2 diffusion coefficient in the solution, c_s is SiO_2 saturated concentration and c_{l0} actual concentration in the solution. If the surface reaction or steady diffusion through the solution layer adjacent to the glass surface controls the corrosion, the Q_{Si} is given by (2) and

$$w = k(c_s - c_{l0}) \qquad (4)$$

Rate constant k then equals to surface reaction rate constant k^+ or to D/h (h is the thickness of solution boundary layer), respectively.

In the case of selective leaching due to interdiffusion A^+-H_3O^+, the amount of moveable ion is given by (2). In this case, however, the meaning of s is different:

$$s = 2(c_{A0} - c_{Asur}) \sqrt{\frac{D_A}{\pi}} \tag{5}$$

where c_{A0} and c_{Asur} are moveable ion concentrations in uncorroded glass and at glass surface, respectively, and D_A is interdiffusion A^+-H_3O^+ coefficient in glass.

The meaning of u in all cases means the amount of component i present in the solution at $t=0$, e.i $u=Q_{i(t=0)}$.

The model is only valid for the large systems with $V \to \infty$ where $c_{i0} \to$ constant. This model also neglects interferences between partial processes and can be therefore used only under strictly defined experiments, where either only congruent dissolution or only interdiffusion without matrix dissolution occurs.

Model of Hlaváč & Matěj [3]

The first model assuming some interference between the glass matrix dissolution and A^+-H_3O^+ interdiffusion was published by Hlaváč & Matěj [3]. They supposed the constant rate of the glass matrix dissolution a (in $m.s^{-1}$). Under this assumption

$$a = \frac{w}{\rho x_{Si}} \tag{6}$$

where ρ is glass density and x_{Si} SiO_2 mass ratio in glass, w is given by equation (4). Q_{Si} is then given by equation (2). As another simplifying condition, the linear dependence of c_A was assumed in the glass surface layer of thickness l and $c_{Asur}=0$. This thickness was considered as changing with time $l=f(t)$. The amount Q_A of moveable components dissolved is then

$$Q_A \cong c_{A0}at + \frac{1}{2}lc_{A0} \tag{7}$$

Assuming the 1st Fick's law and comparing it with time derivation of (7), dependence $l=f(t)$ is

$$t = \frac{1}{2a^2}\left[D_A \ln\frac{1}{1-al\,/\,D_A} - al \right] \tag{8}$$

For $t \to \infty$, the steady state was supposed with constant l. Then from (8) $l=D_A/a$ and

$$Q_{At \to \infty} = c_{A0}\left[at + \frac{1}{2}\frac{D_A}{a} \right] \tag{9}$$

Later on, Isard et al. [9] modified previous model considering that the glass matrix dissolution rate can increase due to the transfer of alkalis into the solution and consequent pH increase. Than Q_{Si} is given by

$$Q_{Si} = r_2 Q_A + \rho x_{Si} at \qquad (10)$$

The second term on the right side of (10) gives the part of dissolved SiO_2 at original pH, the first term with empirical constant r_2 characterises the influence of increasing pH. The time dependence of diffusion layer thickness l is then given by

$$\ln\left(1 - \frac{la}{D_A\left(1 - \frac{r_2}{r_1}\right)}\right) = -\frac{a}{D_A\left(1 - \frac{r_2}{r_1}\right)}(2at + l) \qquad (11)$$

Model of Boksay & Doremus [4]

More precise model was proposed by Boksay and modified by Doremus [4]. Despite of Hlaváč & Matěj, they did not suppose the linear concentration profile of moveable components, but determined this profile from the generalised 2nd Fick's law. Assuming the moving glass-solution boundary and co-ordinate system connected with the glass-solution boundary with $y=0$ at actual glass surface, the c_A is

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial y}\left(D_A \frac{\partial c_A}{dy}\right) + a\frac{\partial c_A}{dy} \qquad (12)$$

For constant dissolution rate a, amount of moveable ions is then

$$Q_A = c_{A0}\left[at + \frac{D_A}{a}\left(erf\frac{\sqrt{\tau}}{2} + \tau ierfc\frac{\sqrt{\tau}}{2}\right)\right] \quad where \quad \tau = \frac{a^2 t}{D_A} \qquad (13)$$

For $\tau \gg 1$

$$Q_A = c_{A0}\left[at + \frac{D_A}{a}\right] \qquad (14)$$

Comparing the steady state solution of Boksay & Doremus (eq.14) with the one of Hlaváč & Matěj (eq.9), the only difference is factor ½. It was shown in [11] that this factor is consequence of the presumption of linear concentration profile of moveable component A in glass surface.

Model of Strachan [5]

All above models were mostly concentrated on the moveable components transfer into the solution, assuming constant rate of glass matrix dissolution. However, such

constant rate was observed only under particular conditions – fast solution flow rate (F) and/or low glass surface to solution volume (S/V) ratio, when saturation effect can be neglected. Strachan [5] derived the model considering this effect. If the initial glass matrix dissolution (in $g(SiO_2).m^{-2}.s^{-1}$) is R_0, then SiO_2 solution concentration c

$$c = \frac{1}{1\,c_s + F\,R_0 S}\left[1 - \exp\left(-\left(\frac{R_0 S}{c_s V} + \frac{F}{V}\right)t\right)\right] \tag{15}$$

In Strachan's model, the congruent dissolution was expected.

Model of Helebrant et al. [6]

The approach of Boksay & Doremus and the one of Strachan were connected into the new model published in [6] and [12]. The rate a from equation (12) is supposed to be time dependent

$$a = k\frac{k^+ D/h}{k^+ + D/h}\frac{c_s - c}{\rho x_{Si}} \tag{16}$$

where k^+ is the surface reaction rate constant, c is given by the SiO_2 mass balance in the solution and is function of interaction time:

$$\frac{dc}{dt} = \frac{S}{V}\left(1 - k^-\right)\frac{k^+ D/h}{k^+ + D/h}\left(c_s - c\right) - \frac{F}{V}c \tag{17}$$

The D is diffusion coefficient of surface reaction product in the precipitated layer of thickness h or in the solution layer adjacent to the glass surface. In this model, not only selective leaching and glass matrix dissolution was assumed as in the previous ones, but also the back precipitation of dissolved glass components was considered. The parameter k^- is the ratio of the precipitated and dissolved SiO_2 amount. The ideally stirred solution and the instantaneous precipitation were supposed deriving equation (17).

Q_{Si} and Q_A values are then given by equations

$$\frac{dQ_{Si}}{dt} = \left(1 - k^-\right)\frac{k^+ D/h}{k^+ + D/h}\left(c_s - c\right) \tag{18}$$

$$Q_A = c_{A0}\int_0^t a\,dt + c_{A0}x - \int_0^x c_A dy \tag{19}$$

where x is the distance from glass surface where $c_A = c_{A0}$.

In general case, the model must be solved numerically. Some analytical solutions for simplified cases were published in [13]. Many of solutions lead to the general equation

$$Q_{Si} = \frac{B}{k}[1-\exp(-kt)] + wt \tag{20}$$

where B, k, and w are functions of both glass durability characterising parameters (D, k^+, k^-, c_s) and experimental arrangement parameters (S, V, F).

The model is based on the partial kinetic processes and could generally described glass corrosion under broad variety of conditions. On the other hand, the weakness of so far discussed models is the number of not known characteristic parameters, which are to be estimated from the experiment [6]. Then the kinetic model can be used for prediction of glass corrosion under different experimental conditions.

Thermodynamic models

The development of thermodynamic approach to the glass corrosion was described in the study of Conradt [8]. In this study, the classical approach of Grambow [7] is described and also new concept of thermodynamically based model of glass corrosion is suggested.

The model of Grambow was based on the assumption that the glass composition can be described as a physical mixture of metasilicates and oxides. The rate of dissolution is then proportional to the total change of Gibbs' energy of hydration of these compositional units. This approach was tested on the broad scale of silicate glasses and allowed to compare the probable glass durability in water.

Conradt [8] suggested improved theoretical thermodynamic treatment of multi-component glasses based on constitutional approach. In this concept, the glass composition is represented in terms of their crystalline reference state plus energy of vitrification. Again, the rate of glass dissolution $r=dQ_S/dt$ (in $g.m^{-2}.s^{-1}$) is proportional to the total change of Gibbs' energy of hydration of these constitutional units

$$\ln r = A + B\Delta G_{hydr} \tag{21}$$

Taking into account also the coverage of glass surface by charged groups, especially by H^+ and OH^-, the Conradt's model can explain also the pH dependences of dissolution rates.

The transition state theory (TST) formulated by Aagard & Helgeson [10] was employed by numerous authors for the purposes of glass dissolution modelling. The general form of the rate law is

$$\frac{dQ_i}{dt} = k_0 v_i e^{\frac{-E_a}{RT}} a_{H^+}^n \left[1 - \left(\frac{Q}{K}\right)\right]$$ (22)

where v_i is the stoichiometric coefficient for element i, E_a is the activation energy, R is the gas constant, T is the absolute temperature, a_{H^+} is the hydronium activity, n is the reaction order with respect to a_{H^+}. The final square bracketed term describes the thermodynamic reaction affinity, where Q is the activity product of the rate-limiting reaction and K is the equilibrium constant for this reaction. The main advantage of this model is that the solution saturation is not given by the experimentally obtained value of c_s. Jiřička [14] has observed on model glasses from the system MeO-Na$_2$O-SiO$_2$ that for Q in equation (22), the activity product $a_{Me2+}^p.a_{SiO2}^q$ can be used, where p and q are the molar ratios of Me and SiO$_2$ in glass. Considering this, it seems that the glass matrix dissolution is driven by the reaction between the dealkalised surface layer and the solution. The actual values of activities can be obtained for example using PHREEQC geochemical code [15]. This code together with enclosed databases also allows theoretical estimation of precipitation process. Similarly as in Helebrant's model, the instantaneous precipitation is supposed and the amount of glass components transferred into the solution can be corrected by deduction of precipitated amount.

The main disadvantage of TST based model is the fact that the pH dependence characterised by n has to be determined experimentally. In fact, it is empirical parameter again. Usually, it has different value and sign for acid and basic solutions [14]. In this case, it seems plausible to combine the TST based model with the Conradt's model, obtaining the intrinsic rate of dissolution and its pH dependence using approach of Conradt and the dependence on the solution composition from the TST model. Another constraint of thermodynamic models is that they do not describe the selective leaching. For this reason, the rate of glass matrix dissolution obtained using thermodynamic approach should be used in modified model of Boksay & Doremus. For practical reason, it would be helpfull to find the direct dependence between the hydrodynamic conditions (S/V, F) and saturation effect defined using thermodynamic reaction affinity. This will need the combination of

Aagard and Helgeson approach with the kinetic one, based on combination of models of Boksay & Doremus and Strachan.

Summary and outlook

The kinetic and thermodynamic models of glass corrosion were reviewed. For the next development, the mathematical description based on the Aagard & Helgeson approach seems to be the right way. Nevertheless, the combination with other models would be interesting. The intrinsic initial dissolution rate and its dependence on solution pH should be determined rather using Conradt's model then the Aagard and Helgeson semi-empirical method. Also the combination with kinetic models considering external system parameters as solution volume, solution flow rate and glass surface would be helpful for evaluation and comparison of glass corrosion behaviour under different conditions. The kinetics of secondary precipitated layers and the prediction of their real composition remain the challenge for the future model development.

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