

# KINETICS OF CORROSION OF SILICATE GLASSES IN AQUEOUS SOLUTIONS

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## INTRODUCTION

The term glass corrosion is used for a complex interaction between glass surface and solution. As a consequence of this interaction irreversible changes both in glass and in solution can be observed: transfer of glass components into the solution, changes of glass surface composition, especially the depletion of alkali and alkali earth ions contents and creation of secondary precipitated layers on the glass surface. Although the glass is a stable material, already small changes mentioned above could be important considering the wide extent of glass containers used in pharmaceutical and food industry, the possibility of nuclear waste storage in glassy form or weathering of historical stained windows. In order to describe the changes mentioned above, several mathematical models were derived. These models were reviewed in [1]. They can be divided into three groups. The empirical models describe the experimental data well and can be used for exact interpolation. On the other hand, they cannot be used for prediction of glass corrosion under different conditions. The models based on thermodynamics, e.g. [2,3], describe satisfactorily final stages of corrosion process. However, thermodynamic models are based on hardly accessible databases of thermodynamic data and cannot describe the initial stages of corrosion when equilibrium in solution is not achieved. In order to describe the corrosion both at initial and at final stage the models based on kinetics of the processes involved in glass corrosion have to be used. In our previous works [4,5] the model was derived and verified assuming that glass corrosion involves three simultaneous processes: 1) SiO<sub>2</sub> matrix dissolution; 2) precipitation of solution species or the species transferred into the solution from glass on the glass surface; 3) moveable ions - H<sub>3</sub>O<sup>+</sup> interdiffusion in glass. This model is based on model of Boksay and Doremus [6]. In contrary to Boksay and Doremus, model published in [4] considers the time dependent rate of glass matrix dissolution.

The aim of this paper is to review the kinetics and mechanisms of processes involved in glass corrosion using the above mentioned kinetic model.

## Glass dissolution

The glass matrix dissolution is characterised by the rate  $a$  at which the glass - solution boundary moves toward the bulk glass. The overall time dependence of  $a$  (m s<sup>-1</sup>) can be usually described using equation

$$a = (a_0 - a_n) \exp(-Kt) + a_n \quad (1)$$

where indices 0 and  $n$  denotes initial and final value, respectively,  $K$  is the rate constant (s<sup>-1</sup>).

Possible variations of glass dissolution rate are shown in figure 1. If  $a = a_0 = a_n$  then glass dissolves by constant rate (curve 1). If  $a_n = 0$  then the dissolution rate decreases to zero (curve 2). General time dependence is given by curves 3a ( $a_n > a_0$ ) and 3b ( $a_n < a_0$ ). Although the equation (1) could be used as semiempirical equation, assuming that the overall process of glass dissolution is the first order process, it can be explained on theoretical basis, too. The glass matrix dissolution in-

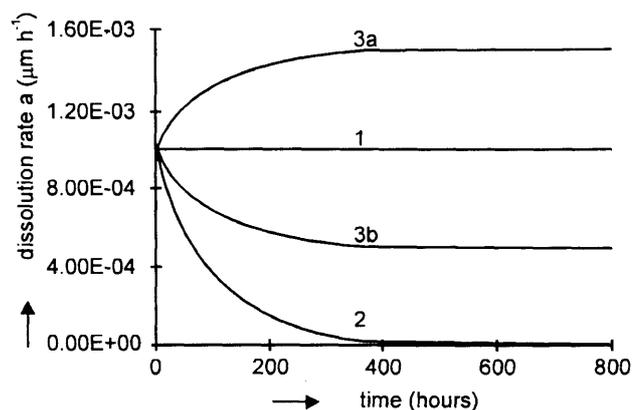


Figure 1. Possible time dependencies of glass dissolution rates. 1 - Constant dissolution rate. ( $D/h \rightarrow \infty$ ,  $F \rightarrow \infty$  and/or  $S/V \rightarrow 0$ ). 2 - Dissolution rate decreases to zero ( $F=0$  and/or  $(D/h)_n \rightarrow 0$ ). 3 - General time dependence of glass dissolution rate according to equation (1) a)  $a_n > a_0$ ; b)  $a_n < a_0$ .

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volves two steps: a) surface reaction between glass matrix and water and/or OH<sup>-</sup> ions and b) transport of reaction products through the precipitated layer or through the layer of solution adjacent to the glass surface (figure 2). The first step is characterised by surface reaction rate constant  $k^+$ , the second by the ratio between diffusion coefficient of reaction product in precipitated layer  $D$  and layer thickness  $h$ . From the mass balance of SiO<sub>2</sub> in the solution follows that time dependence of SiO<sub>2</sub> concentration  $c$  is given by

$$\frac{dc}{dt} = \frac{S}{V} (1-k^+) k(c_s - c) - \frac{F}{V} c \quad (2)$$

In equation (2)  $c_s$  represents saturated SiO<sub>2</sub> concentration,  $S$  is glass surface,  $V$  and  $F$  are solution volume and solution flow rate, respectively. The dimensionless parameter  $k$  represents the ratio between precipitated and dissolved SiO<sub>2</sub>.

Assuming that the surface reaction can be described as a first order process and concentration profile of surface reaction products in precipitated layer is linear

$$a = k \frac{c_s - c}{x_{Si} \rho} \quad (3)$$

where

$$k = \frac{k^+ \frac{D}{h}}{k^+ + \frac{D}{h}} \quad (4)$$

$\rho$  is glass density,  $x_{Si}$  is SiO<sub>2</sub> mass fraction in glass. Generally, the values of  $k^+$ ,  $D/h$ ,  $c_s$  and  $c$  depend on time.

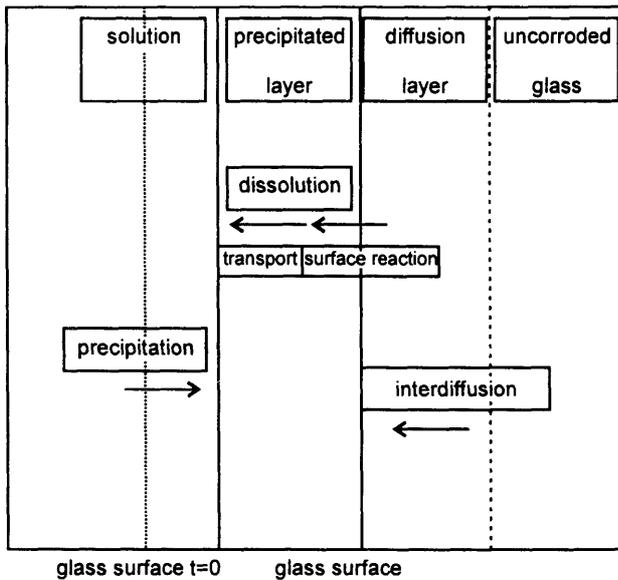


Figure 2. Schematic representation of processes involved in glass dissolution.

If the values of  $k^+$ ,  $D/h$ ,  $c_s$  are constant and only SiO<sub>2</sub> concentration in solution changes with time, the values of parameters  $a_0$ ,  $a_n$  and  $K$  are given by following equations [7]:

$$a_0 = k \frac{c_s}{x_{Si} \rho} \quad (5)$$

$$a_n = a_0 \frac{F}{S(1-k^+)k + F} \quad (6)$$

$$K = \frac{S(1-k^+)k + F}{V} \quad (7)$$

According to the equation (1) the rate of dissolution decreases with time due to saturation effect (figure 1, curve 3b). Only if solution flow rate  $F \rightarrow \infty$  and/or glass surface to solution volume ratio  $S/V \rightarrow 0$ , the value of SiO<sub>2</sub> concentration  $c \rightarrow 0$ . Consequently the value of  $a$  remains constant (figure 1, curve 1). Assuming that no back precipitation of SiO<sub>2</sub> occurs,  $k = k^+$ ,  $k^- = 0$  and  $D/h \rightarrow \infty$ . The equation (1) is then simplified to the model of dissolution published by Strachan [8].

However, the decreasing rate of dissolution was also observed under such experimental conditions when saturation effect was excluded [8, 9]. Such behaviour could be explained by the growth of precipitated layer on glass surface. As this layer grows and becomes less permeable, the mass transfer coefficient of surface reaction products ( $D/h$ ) decreases. The assumption of constant  $D/h$  value made in previous part is fulfilled under some conditions only: 1) no precipitation occurs and consequently  $D/h \rightarrow \infty$ ; or 2) the precipitation reaction is very fast and takes place only at the beginning of the process. Under normal conditions the time dependence of  $D/h$  cannot be neglected. The empirical time dependence

$$\frac{D}{h} = \left[ \left( \frac{D}{h} \right)_0 - \left( \frac{D}{h} \right)_n \right] \exp(-mt) + \left( \frac{D}{h} \right)_n \quad (8)$$

was found to be suitable for description of experimental data [4]. Theoretically, if the  $D/h$  value is at any time much smaller than  $k^+$  value, the diffusion through the precipitated layer controls the glass dissolution. Assuming that  $c \rightarrow 0$ , the values of parameters  $a_0$ ,  $a_n$  and  $K$  are given by equations (9-11):

$$a_0 = \left( \frac{D}{h} \right)_0 \frac{c_s}{x_{Si} \rho} \quad (9)$$

$$a_n = \left( \frac{D}{h} \right)_n \frac{c_s}{x_{Si} \rho} \quad (10)$$

$$K = m \quad (11)$$

The situation discussed above when the value of  $(D/h)_0 \ll k^+$  is not very probable. At the beginning of the

corrosion process the value of  $h = 0$  and therefore  $(D/h)_0 \rightarrow \infty$ . However, if the layer grows fast and/or if the permeability of this layer decreases rapidly, the rate of dissolution could be described by equation (1) using the approximate values of  $a_n$  and  $K$  given by equations (10) and (11) and the value of  $a_0$

$$a_0 = k^+ \frac{c_s}{x_{\text{Si}}\rho} \quad (12)$$

The dissolution rate is then represented by curve 2 in figure 1 if  $(D/h)_n \rightarrow 0$  or by curve 3b if  $(D/h)_n \neq 0$ .

The  $a_0$ ,  $a_n$  and  $K$  values given by equations (9-11) could also be used in the case when no precipitation on the glass surface occurs and the surface reaction products have to diffuse through the layer of solution adjacent to the glass surface [9]. Then the  $D/h$  value represents the mass transfer coefficient in the solution layer of thickness  $h$  adjacent to the glass surface.

If the values of  $D/h$  and  $k^+$  are comparable, the time dependence of  $a$  is more complex than the one given by equation (1). If no saturation effect takes place ( $c \rightarrow 0$ )

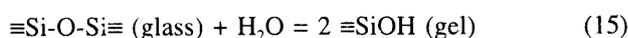
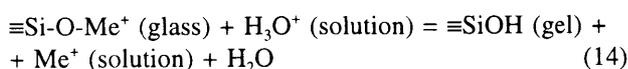
$$a = k \frac{c_s}{x_{\text{Si}}\rho} \quad (13)$$

where  $k$  is defined by equations (4) and (8).

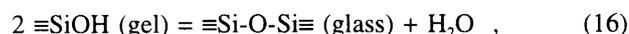
The general equation (3) has to be used if both saturation effect takes place and  $D/h$  value is time dependent. The  $\text{SiO}_2$  concentration in solution is given by equation (2), which has to be solved numerically.

The other factor influencing the time dependence of glass dissolution is solution  $pH$ . The total equilibrium activity of the soluble forms of  $\text{SiO}_2$  ( $\text{H}_4\text{SiO}_4$ ,  $\text{H}_3\text{SiO}_4^-$ ,  $\text{H}_2\text{SiO}_4^{2-}$ ) in solution and consequently the  $c_s$  value remains constant to the  $pH = 8-9$  and then increases fast [9]. If solution  $pH$  increase during the corrosion to this range, the time dependent  $c_s$  value has to be taken into account in equation (3). The increase of  $pH$  can occur due to the transfer of alkali and alkali earth ions into the solution both by matrix dissolution and by interdiffusion  $\text{Me}^{n+} - n\text{H}_3\text{O}^+$ .

At last, the time dependence of surface reaction constant  $k^+$  can influence the overall dissolution rate. Of course this value depends on solution  $pH$ . However, even if  $pH$  value remains constant,  $k^+$  can change during the corrosion. This dependence could be explained by the chemical and structural changes in glass surface. Due to the reactions



a gel-like layer is created in glass surface. This layer is more soluble than the original glass surface and the rate constant of surface reaction increases. Such behaviour is represented by curve 3a in figure 1. On the other hand, if recombination of Si-O-H groups occurs



a more durable layer of glass with high content of  $\text{SiO}_2$  is created and  $k^+$  value decreases (figure 1., curve 3b). Considering the similar time dependence of  $k^+$  as for  $D/h$  value

$$k^+ = (k_0^+ - k_n^+) \exp(-wt) + k_n^+ \quad (17)$$

Neglecting other factors influencing dissolution rate, the parameters  $a_0$ ,  $a_n$  and  $K$  are

$$a_0 = k_0^+ \frac{c_s}{x_{\text{Si}}\rho} \quad (18)$$

$$a_n = k_n^+ \frac{c_s}{x_{\text{Si}}\rho} \quad (19)$$

$$K = w \quad (20)$$

In general case all effects mentioned above, i.e. saturation effect, precipitated layer growth and surface reaction rate constant changes, take place. The dissolution rate is then given by equations (2), (3), (4), (8) and (14). The  $\text{SiO}_2$  concentration in the solution  $c$  given by equation (2) to be solved numerically.

Very interesting is the question of influence of organic compounds in solution on the dissolution process. Unfortunately, there is a lack of experimental data in this field. Therefore the effect of organic compounds is not quantitatively described yet. From experiments made by Rybařková and Kouřilová [10] it follows that the organic compounds accelerate glass dissolution in neutral and alkaline area. Creation of soluble organic complexes and compounds could be responsible for this behaviour. On the other hand, Ahmed and Youssof [11] reported the decreased dissolution of soda-lime-silica glass in organic acids in comparison with HCl and water. The decreasing solubility of  $\text{SiO}_2$  was attributed to the formation of organic complexes with silica, which cover the glass surface.

The temperature dependence of dissolution rate can be described by Arrhenius equation. The apparent activation energy is in the range 40-70 kJ mol<sup>-1</sup> [12, 13].

#### Precipitation

The kinetics of the precipitated layer growth is not described exactly yet. This fact is connected with the

character of the layer. There is a lack of experimental data about the time dependence of layer thickness. The determination of its character, composition and thickness requires complex analytical methods. The poor crystallinity of the layer complicates the determination of precipitated product. Therefore the mathematical description of this part of glass corrosion is based on semiempirical equations.

The problem of precipitation could be divided into two parts: 1) the back precipitation of species originally contained in glass and 2) the precipitation of solution species.

The first case occurs for example during the glass corrosion in distilled water. If glass contains alkaline earth ions, it is probable that the layer of poor soluble silicate is created on the glass surface. The thermodynamic probability of  $MgSiO_3$  and  $CaSiO_3$  precipitation was discussed in [14]. The layer rich on Mg and Si was found in [14] also experimentally by ESCA method (Electron Spectroscopy for Chemical Analysis) on surface of float glass after corrosion in distilled water. There are two possible mechanisms of creation of this layer. First mechanism considers that due to the glass dissolution and interdiffusion the ion activity products in respect to mentioned silicates exceeded their solubility products. The precipitated layer is then created "through the solution". Second possibility assumes the direct reaction of Ca and Mg ions in gel layer on glass surface created due to reactions (14) and (15).

The rate of precipitation can be for both mechanisms described as linear proportional to the rate of dissolution

$$R_p = k \rho x_{Si} a \quad (21)$$

The dimensionless parameter  $k$  represents the ratio between precipitated and dissolved  $SiO_2$  and is in interval  $<0;1>$ . In other way, the equation (21) means that the part  $k$  of dissolved  $SiO_2$  precipitates immediately after the dissolution. Then the total amount of  $SiO_2$  transferred into the solution  $Q_{Si}$  is given by equation

$$\frac{dQ_{Si}}{dt} = (1 - k) \rho x_{Si} a \quad (22)$$

The validity of equations (21) and (22) was verified indirectly in [4] by comparison of experimental time dependence of  $SiO_2$  for glasses of different composition with solution of equation (22).

During the corrosion in concentrated solutions, the precipitation of solution species can be observed. This process occurs for example during the interaction between bioactive glasses with simulated body fluids, when hydroxyapatite precipitates on glass surface. The precipitation of hydroxyapatite was observed also on glasses containing no phosphorus [15]. The equations

(21) and (22) cannot be used in this case. According to Mann et al. [16] the precipitation rate can be described as a function of supersaturation in respect to the precipitated compound

$$R_p = k_p [(IAP/K_s)^{1/j} - 1]^n \quad (23)$$

The value of exponent  $n$  is the function of precipitation mechanism,  $j$  is the number of ions in precipitated compound. The determination of ion activity product (IAP) could be difficult in complex solutions. Also the precise value of solubility product ( $K_s$ ) is not known for many compounds. The thickness of precipitated layer was successfully described assuming first order kinetics [17]:

$$h = h_n(1 - \exp(-k_n t)) \quad (24)$$

It was shown that the value of rate constant  $k_n$  is very similar for different glasses and glass-ceramics. The value of  $h_n$ , i.e. the final layer thickness, can be used for comparison of bioactivity of studied materials.

#### Interdiffusion

The moveable ions -  $H_3O^+$  interdiffusion is characterised by the interdiffusion coefficient  $D_A$ . Considering that the glass surface moves at rate  $a$ , the mass balance of diffusing species leads to extended 2<sup>nd</sup> Fick's law [6]

$$\frac{\partial x_A}{\partial t} = \frac{\partial}{\partial y} \left( D_A \frac{\partial x_A}{\partial y} \right) + a \frac{\partial x_A}{\partial y} \quad (25)$$

where  $x_A$  is concentration of moveable ion,  $y$  is the perpendicular distance from glass surface. The amount of moveable ions transferred into the solution is then given by equation

$$Q_A = \int_0^t D_A \left( \frac{\partial x_A}{\partial y} \right)_{y=0} dt \quad (26)$$

The solutions of both (25) and (26) assuming constant rate of glass dissolution  $a$  were published by Doremus [6]. In general case, however,  $a$  is time dependent according to equation (3). Then the equation (25) has to be solved numerically, e.g. by finite difference method or by finite elements method. The estimation of concentration gradient at glass surface  $(\partial x_A / \partial y)_{y=0}$  is not very exact using numerical methods. Therefore it is better to use equation

$$Q_A = \rho \left( \int_0^z x_A dy \right)_{t=0} - \rho \left( \int_0^z x_A dy \right)_t + \rho x_{A0} \int_0^t a dt \quad (27)$$

where  $x_{A0}$  is mass fraction of moveable ion in uncorroded glass

The first two terms on the right side represent the amount transferred into the solution by interdiffusion, the last term represents the contribution of glass dissolution (figure 3).

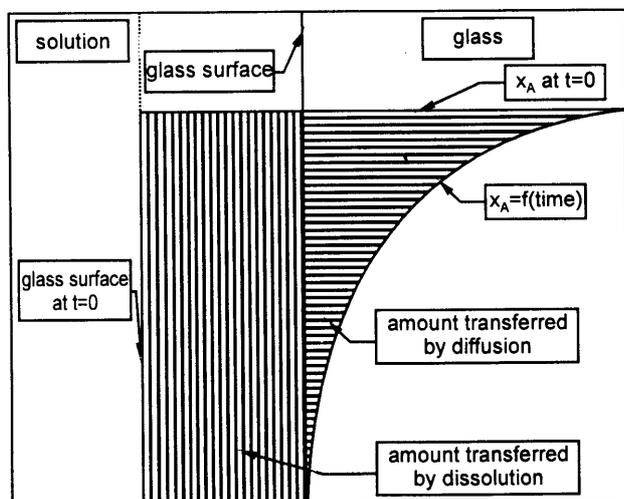


Figure 3. Schematic representation of amount of moveable glass species transferred into the solution.

From the comparison of theoretical equations with experimental results it follows that the value of diffusion coefficient is often time dependent, especially in acid solutions [12, 13, 18]. This fact can be explained either by concentration dependence of  $D_A$  or by structural changes in glass surface during corrosion process. The content of moveable ions in glass surface decreases with time according to equation (25). The diffusion coefficient decreases usually with decreasing content of diffusing species. The structural changes could influence the value of  $D_A$ , too. Due to the reactions (14-16) the layer is created in the glass surface, which is less permeable than the uncorroded glass. In contrary, if only the reactions (14) and (15) take place, the more permeable gel-like layer is created and interdiffusion coefficient increases.

Similarly as in the case of glass dissolution rate, the temperature dependence of  $D_A$  is given by Arrhenius equation. Apparent activation energy is in the range 60-100 kJ mol<sup>-1</sup> [8, 14].

### CONCLUSION

The aqueous corrosion of silicate glasses involves three simultaneous processes: glass dissolution, precipitation on glass surface and moveable ions - H<sub>3</sub>O<sup>+</sup> interdiffusion. The complex interaction can be described considering the kinetics of partial processes. Glass dissolution rate changes with time due to saturation effect

and due to the protective function of precipitated layer. The dissolution rate could be also influenced by structural changes in glass surface. The rate of precipitation can be described in diluted solution as linear proportional to the dissolution rate. The interdiffusion process is described by extended 2<sup>nd</sup> Fick's law assuming the moving glass-solution boundary.

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