

Analytical solutions of the diffusion differential equation

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Abstract

The water diffusivity in silica is affected by swelling stresses in the surface region which are caused by the silica/water reaction. Since the diffusivity is a function of stress, the consequence is a diffusivity that depends on the local water concentration. Then the solution of the diffusion equation is complicated and makes numerical computations necessary.

Disadvantage of numerical computations is the fact that the used extend of the depth range must be finite and, consequently, the semi-infinite body can only be approximated. In the following considerations we will give exact and semi-analytical solutions for diffusion problems in the half-space.

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1 Analytical solution of the diffusion equation for constant diffusivity

The partial diffusion differential equation for the uniaxial case is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left[D(C) \frac{\partial C}{\partial z} \right] \quad (1.1)$$

Here C is the water concentration, t the time, z the depth coordinate, and D the diffusivity that may depend on the water concentration.

For water vapour as the environment, the surface condition is

$$\frac{dC}{dz} = \frac{h}{D}(C - C_0) \quad \text{at } z=0, \quad (1.2)$$

where C_0 is the concentration of molecular water reached at $z=0$ for $t \rightarrow \infty$.

The equations (1.1) and (1.2) can be solved numerically as was done in [1, 2]. Disadvantage of numerical computations is the fact that the used extend of the z -range must be finite and, consequently, the semi-infinite body can only be approximated. In the following considerations we will give exact and approximate solutions of the diffusion differential equation (1.1) for the half-space.

First, let us consider the case of constant diffusivity. As shown by Carslaw and Jaeger ([3], Section 2.7), the concentration profile, $C(z)$ resulting from the boundary condition for a semi-infinite body is given by

$$C(z, t) / C_0 = \operatorname{erfc} \left[\frac{z}{2\sqrt{Dt}} \right] - \exp \left[\frac{h}{D} z + \frac{h^2}{D} t \right] \operatorname{erfc} \left[\frac{z}{2\sqrt{Dt}} + h\sqrt{\frac{t}{D}} \right] \quad (1.3)$$

At the surface, $z=0$:

$$C(0, t) / C_0 = 1 - \exp \left[\frac{h^2}{D} t \right] \operatorname{erfc} \left[h\sqrt{\frac{t}{D}} \right] \quad (1.4)$$

For reasons of simplicity, we introduce a normalized dimensionless time τ and normalized depth coordinate ζ , defined by

$$\tau = \frac{h^2}{D_0} t; \quad \zeta = \frac{z}{\sqrt{D_0 t}} \quad (1.5)$$

Equations (1.3) and (1.4) then read

$$\frac{C(\zeta, \tau)}{C_0} = \operatorname{erfc} \left[\frac{\zeta}{2} \right] - \exp[\zeta \sqrt{\tau} + \tau] \operatorname{erfc} \left[\frac{\zeta}{2} + \sqrt{\tau} \right] \quad (1.6)$$

and
$$C(0, \tau)/C_0 = 1 - \exp[\tau] \operatorname{erfc}[\sqrt{\tau}], \quad (1.7)$$

For the ratio $C(\zeta, \tau)/C(0, \tau)$

$$\frac{C(\zeta, \tau)}{C(0, \tau)} = \frac{\operatorname{erfc}\left[\frac{\zeta}{2}\right] - \exp[\zeta\sqrt{\tau} + \tau] \operatorname{erfc}\left[\frac{\zeta}{2} + \sqrt{\tau}\right]}{1 - \exp[\tau] \operatorname{erfc}[\sqrt{\tau}]} \quad (1.8)$$

two limit cases are of special interest. At very short times, we obtain by a series expansion with respect to τ that by setting $\tau \rightarrow 0$ reads

$$\frac{C(\zeta, 0)}{C(0, 0)} = \exp\left[-\frac{\zeta^2}{4}\right] - \frac{\sqrt{\pi}}{2} \zeta \operatorname{erfc}\left[\frac{\zeta}{2}\right] \quad (1.9)$$

At very long times $\tau \rightarrow \infty$, only the first term on the right-hand side of eq.(1.6) remains finite. Consequently, we obtain the well-known solution for constant surface concentration:

$$\frac{C(\zeta, \infty)}{C(0, \infty)} = \operatorname{erfc}\left[\frac{\zeta}{2}\right] \quad (1.10)$$

These limit cases are plotted in Fig. 1a. The depths at which these limit distributions decrease to $C(\zeta, \tau)/C(0, \tau) = 1/2$ are

$$\begin{aligned} \zeta_{1/2} &= 2 \operatorname{erf}^{-1}\left[0, \frac{1}{2}\right] = 0.6695 \quad \text{for } \tau \rightarrow 0 \\ \zeta_{1/2} &= 0.9538 \quad \text{for } \tau \rightarrow \infty \end{aligned} \quad (1.11)$$

(erf^{-1} is the inverse error function). The areas under the curves define the water uptake in normalized time and depth units

$$m_c(\tau) = \int_0^\infty C(\zeta, \tau) d\zeta = C(0, \tau) \times \begin{cases} \frac{\sqrt{\pi}}{2} & \text{for } \tau \rightarrow 0 \\ \frac{2}{\sqrt{\pi}} & \text{for } \tau \rightarrow \infty \end{cases} \quad (1.12)$$

or in usual units with $\sqrt{(D_0 t)} = b$

$$m_c(t) = \int_0^\infty C(z, t) dz = C(0, t) \times \underbrace{\sqrt{D_0 t}}_b \begin{cases} \frac{\sqrt{\pi}}{2} & \text{for } t \rightarrow 0 \\ \frac{2}{\sqrt{\pi}} & \text{for } t \rightarrow \infty \end{cases} \quad (1.12a)$$

For etching tests it is of advantage to know the amount of water Δm_c , when a layer of thickness δ has been removed from the surface. In this case it holds

$$\begin{aligned} \Delta m_C(\delta, \tau) &= -\int_0^\delta C(\zeta, \tau) d\zeta = \\ &= -m_C(\tau) \begin{cases} \frac{1}{\sqrt{\pi}} \delta \exp[-\frac{1}{4} \delta^2] + \operatorname{erf}[\frac{1}{2} \delta] - \frac{1}{2} \delta^2 \operatorname{erfc}[\frac{1}{2} \delta] & \text{for } t \rightarrow 0 \\ (1 - \exp[-\frac{1}{4} \delta^2]) + \frac{\sqrt{\pi}}{2} \delta \operatorname{erfc}[\frac{1}{2} \delta] & \text{for } t \rightarrow \infty \end{cases} \quad (1.13) \end{aligned}$$

The results from (1.13) are shown in Fig. 1b. For the thickness removal d in normal thickness unit we have to replace δ by $d/\sqrt{(D_0 t)}$.

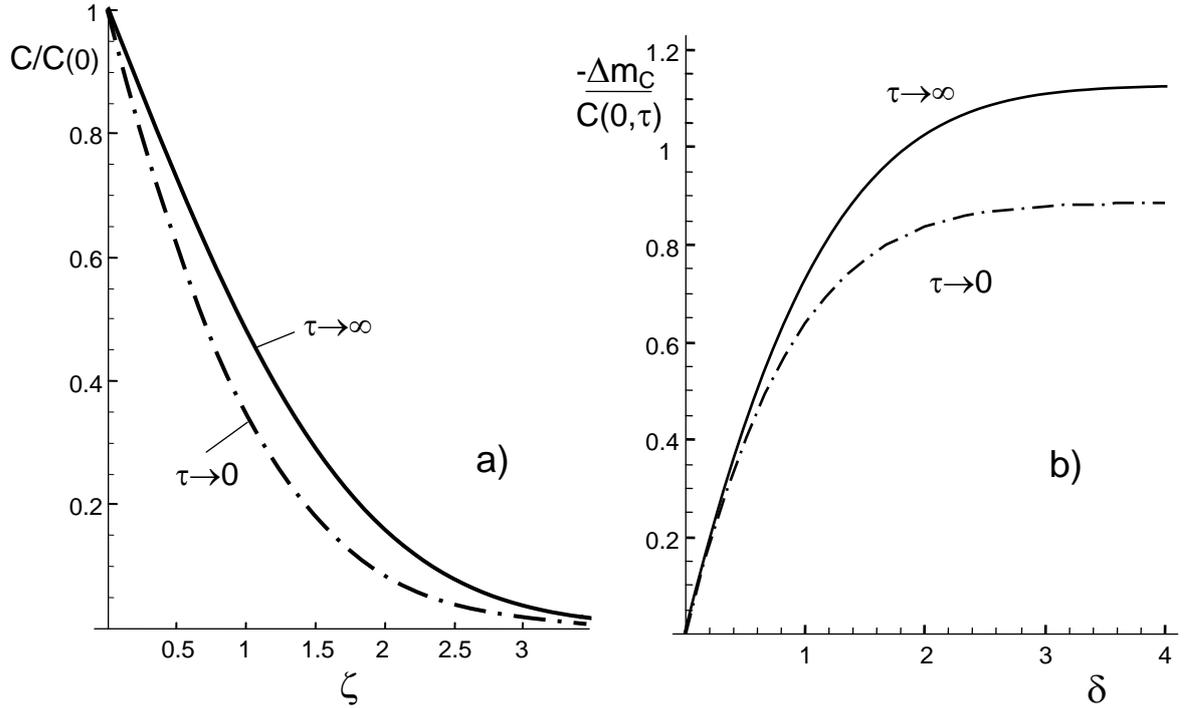


Fig. 1 a) Concentration profiles for limit cases derived from the analytical solution of diffusion, eq.(1.12) with constant diffusivity, $D=D_0$. b) Water uptake according to eq.(1.13). The negative sign at Δm_C stands for the *decrease* of the water content.

2 Solutions under swelling conditions

2.1 Stress enhanced diffusion

The diffusivity as a function of stress is commonly expressed by the hydrostatic stress component, σ_h . The diffusivity for the case of stress-enhanced diffusion is given by the following equation [4]

$$D = D_0 \exp \left[\sigma_h \frac{\Delta V_w}{RT} \right] \quad (2.1)$$

where D_0 denotes the value of the diffusivity in the absence of a stress. T is the absolute temperature in K ; ΔV_w is the activation volume for stress-enhanced diffusion and R is the universal gas constant.

The hydrostatic stress term caused by *swelling stresses* is

$$\sigma_h = -\frac{2 \kappa E}{9(1-\nu)} k C, \quad \kappa \cong 0.97, \quad (2.2)$$

where E is Young's modulus, ν Poisson's ratio, and k is the equilibrium constant of the silica/water reaction given for temperatures $<500^\circ\text{C}$ by $k=S/C$ (C =molecular water concentration, S =hydroxyl concentration).

According to eq.(2.2) the swelling stress depends linearly on the water concentration, $\sigma_h \propto C$. The saturation value of $\sigma_{h,sw}$ for $C=C_0$ is in the following considerations denoted as $\sigma_{h,0}$. In order to allow short expressions, the exponential term in eq.(2.1) may be abbreviated by

$$\sigma_h \frac{\Delta V_w}{RT} = \sigma_{h,0} \frac{\Delta V_w}{RT} \frac{C}{C_0} \equiv \alpha C, \quad \alpha \equiv \frac{\sigma_{h,0}}{C_0} \frac{\Delta V_w}{RT} \quad (2.3)$$

2.2 Solution based on a perturbation set-up by Singh

By use of the Boltzmann substitution

$$\lambda = \frac{z}{2\sqrt{t}} \quad (2.4)$$

an ordinary differential equation results

$$2\lambda \frac{dC}{d\lambda} + \frac{d}{d\lambda} \left[D \frac{dC}{d\lambda} \right] = 0 \quad (2.5)$$

Singh [5] showed that this equation can be solved if the diffusion coefficient fulfills an exponential relation

$$D = \exp(\alpha C + \beta) \quad (2.6)$$

with constant coefficients α and β . This result is used in bottom mechanics [6] where the diffusivity depends on the water concentration, too. The solution based on a perturbation ansatz reads

$$D = c_1 \frac{\sqrt{\pi D_0}}{2} \operatorname{erf} \frac{\lambda}{\sqrt{D_0}} + c_2 \quad (2.7)$$

For the swelling problem the condition (2.6) is fulfilled since

$$D = D_0 \exp(\Delta V_w \sigma_h / RT) = D_0 \exp(\alpha C), \quad (2.8)$$

$$\beta = \ln D_0, \quad \alpha C = \frac{\Delta V_w \sigma_h}{RT} \quad (2.9)$$

Combining eqs.(2.7) and (2.8) yields

$$c_1 \frac{\sqrt{\pi D_0}}{2} \operatorname{erf} \frac{z}{2\sqrt{D_0 t}} + c_2 = D_0 \exp(\alpha C) \quad (2.10)$$

and from this the water concentration results as a function of depth z and time t

$$C = \frac{1}{\alpha} \ln \left(c_1 \frac{\sqrt{\pi / D_0}}{2} \operatorname{erf} \frac{z}{2\sqrt{D_0 t}} + \frac{c_2}{D_0} \right) \quad (2.11)$$

For $z \rightarrow \infty$ it must hold $C \rightarrow 0, D \rightarrow D_0$. This condition gives with $\operatorname{erf}[\infty]=1$

$$c_1 \frac{\sqrt{\pi / D_0}}{2} + \frac{c_2}{D_0} = 1 \Rightarrow c_2 = D_0 - c_1 \frac{\sqrt{\pi D_0}}{2} \quad (2.12)$$

Replacing c_2 in eq.(2.11) results in the solution

$$C = \frac{1}{\alpha} \ln \left(c_1 \frac{\sqrt{\pi / D_0}}{2} \operatorname{erf} \frac{z}{2\sqrt{D_0 t}} + 1 - c_1 \frac{\sqrt{\pi / D_0}}{2} \right) \quad (2.13)$$

or with the complementary error function $\operatorname{erfc}(x)=1-\operatorname{erf}(x)$:

$$C = \frac{1}{\alpha} \ln \left(1 - c_1 \frac{\sqrt{\pi / D_0}}{2} \operatorname{erfc} \frac{z}{2\sqrt{D_0 t}} \right) \quad (2.14)$$

2.2.1 Increasing surface concentration (mass-transfer condition)

A solution for the surface conditions by eq.(1.2) cannot result from Singh's procedure. This can even be seen from the application of the Boltzmann substitution. In terms of the normalized time and depth coordinate by (1.5), the substitution λ is only dependent on the depth coordinate ζ and not the time τ since

$$\lambda = \frac{z}{2\sqrt{t}} = \frac{\sqrt{D_0}}{2} \frac{z}{\sqrt{D_0 t}} = \frac{\sqrt{D_0}}{2} \zeta \quad (2.15)$$

Consequently the applicability is strongly restricted. Nevertheless, this solution is only appropriate for treating the limit case $\tau \rightarrow \infty$, i.e. for the condition of fixed surface concentrations.

2.2.2 Constant surface concentration

For very long diffusion times, the surface water concentration, $C(0)$, tends asymptotically to the saturation value C_0 . In order to compute the limit case for $t \rightarrow \infty$ specimen soaked in water vapour for very long times are assumed to show constant surface water concentration $C(z=0)=C_0$. In this case we obtain from (2.14)

$$C_0 = \frac{1}{\alpha} \ln \left(1 - c_1 \frac{\sqrt{\pi/D_0}}{2} \right) \quad (2.16)$$

the constant c_1 as

$$c_1 = 2\sqrt{D_0/\pi}(1 - \exp[\alpha C_0]) \quad (2.17)$$

The result for the concentration is then

$$C = \frac{1}{\alpha} \ln \left(1 - (1 - \exp[\alpha C_0]) \operatorname{erfc} \frac{z}{2\sqrt{D_0 t}} \right) \quad (2.18)$$

or

$$\frac{C}{C_0} = \frac{1}{\alpha C_0} \ln \left(1 - (1 - \exp[\alpha C_0]) \operatorname{erfc} \left[\frac{\zeta}{2} \right] \right) \quad (2.19)$$

Water profiles computed via eq.(2.19) are shown in Fig. 2a for different parameters αC_0 . Figure 2b shows a comparison of the analytical solution eq.(2.19) as the black curve and the numerical results according to [2] as the red curve, both for $\alpha C_0 = -3$. The small differences may be the consequence of the finite depth interval that had to be used in the numerical program *NDSolve* by *Mathematica* [7].

The depth $\zeta_{1/2}$ at which the distributions of Fig. 2a decreases to $C(\zeta)/C_0=1/2$ is

$$\zeta_{1/2} = 2 \operatorname{erf}^{-1} \left[\infty, -\frac{1}{1 + \exp[\frac{1}{2}\alpha]} \right] \quad (2.20)$$

or numerically

$$\zeta_{1/2} = \begin{cases} 0.6963 & \text{for } \alpha C_0 = -1 \\ 0.4861 & \text{for } -2 \\ 0.3262 & \text{for } -3 \\ 0.2121 & \text{for } -4 \end{cases} \quad (2.21)$$

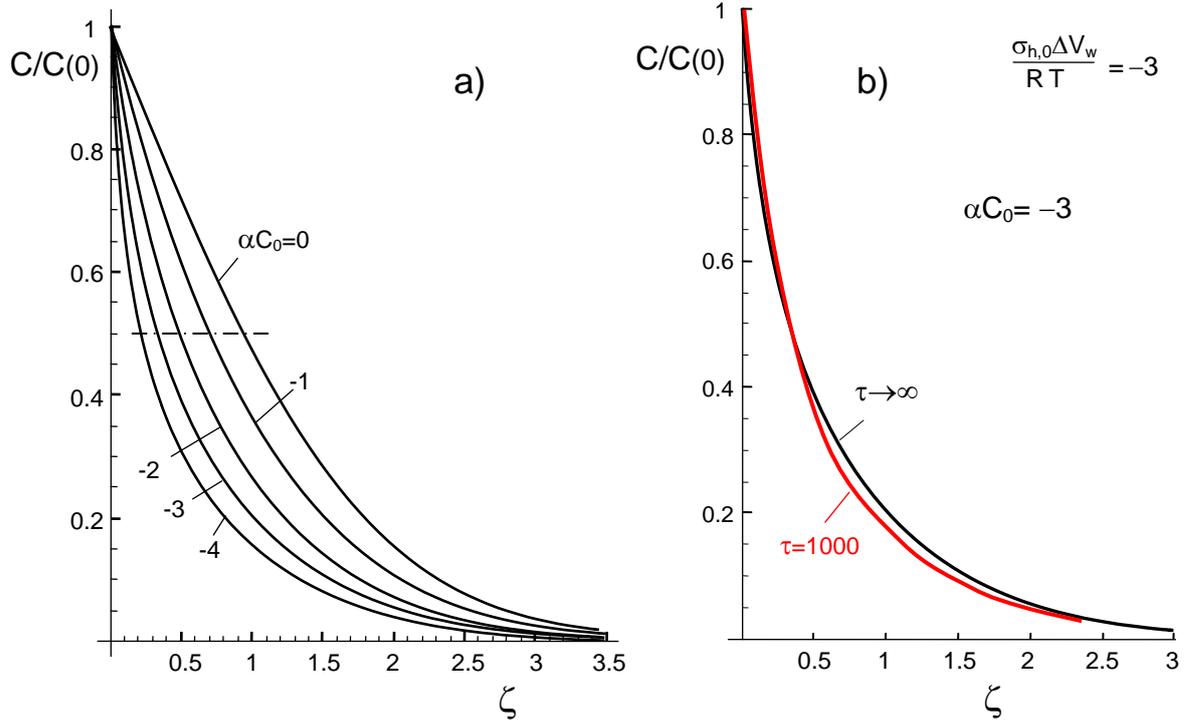


Fig. 2 a) Effect of swelling on the water profiles, b) comparison of eq.(2.19) with numerical solution from [2], given by the black and red curve, respectively.

Finally, we determined water uptake by integrating the swelling profiles of Fig. 2a numerically with the result

$$m_c(\tau) = \int_0^{\infty} C(\zeta, \tau) d\zeta = C(0, \tau) \times \begin{cases} 0.9115 & \text{for } \alpha C_0 = -1 \\ 0.7319 & \text{for } -2 \\ 0.5904 & \text{for } -3 \\ 0.4823 & \text{for } -4 \end{cases} \quad (2.22)$$

or

$$m_c(t) = \int_0^{\infty} C(z, t) dz = C(0) \underbrace{\sqrt{D_0 t}}_b \times \begin{cases} 0.9115 & \text{for } \alpha C_0 = -1 \\ 0.7319 & \text{for } -2 \\ 0.5904 & \text{for } -3 \\ 0.4823 & \text{for } -4 \end{cases} \quad (2.22a)$$

The value for $\alpha C_0 = 0$ is $2/\sqrt{\pi} \approx 1.128$ as given by eq.(1.12a).

The decrease of the water by surface removal δ is shown in Fig. 3. The depths at which half of the water content is removed, $\delta_{1/2}$, is given in (2.23) for a few values of αC_0 .

$$\delta_{1/2}(\tau) = \begin{cases} 0.6994 & \text{for } \alpha C_0 = 0 \\ 0.6036 & \text{for } -1 \\ 0.5323 & \text{for } -2 \\ 0.4846 & \text{for } -3 \\ 0.4558 & \text{for } -4 \end{cases} \quad (2.23)$$

Table 1 compiles all the data.

αC_0	$\zeta_{1/2}=z_{1/2}/\sqrt{D_0\tau}$	$m_C(\tau)/C(0)$	$\delta_{1/2}=d_{1/2}/\sqrt{D_0\tau}$
0	0.9538	$2/\sqrt{\pi}$	0.6994
-1	0.6963	0.9115	0.6036
-2	0.4861	0.7319	0.5323
-3	0.3262	0.5904	0.4846
-4	0.2121	0.4823	0.4558

Table 1 Data of water profiles and water uptake obtained for saturation conditions, $\tau \rightarrow \infty$.

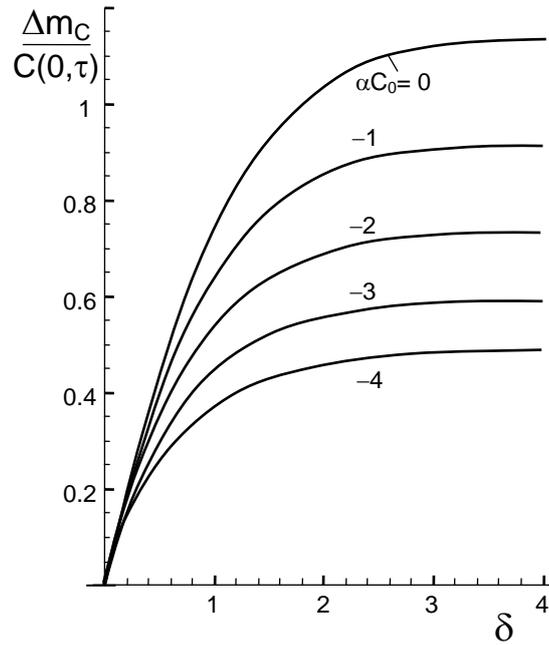


Fig. 3 Change of water uptake with surface removal δ delta as a function of swelling parameter αC_0 .

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