Karlsruher Institut für Technologie

Anisotropic Swelling for different Stress States

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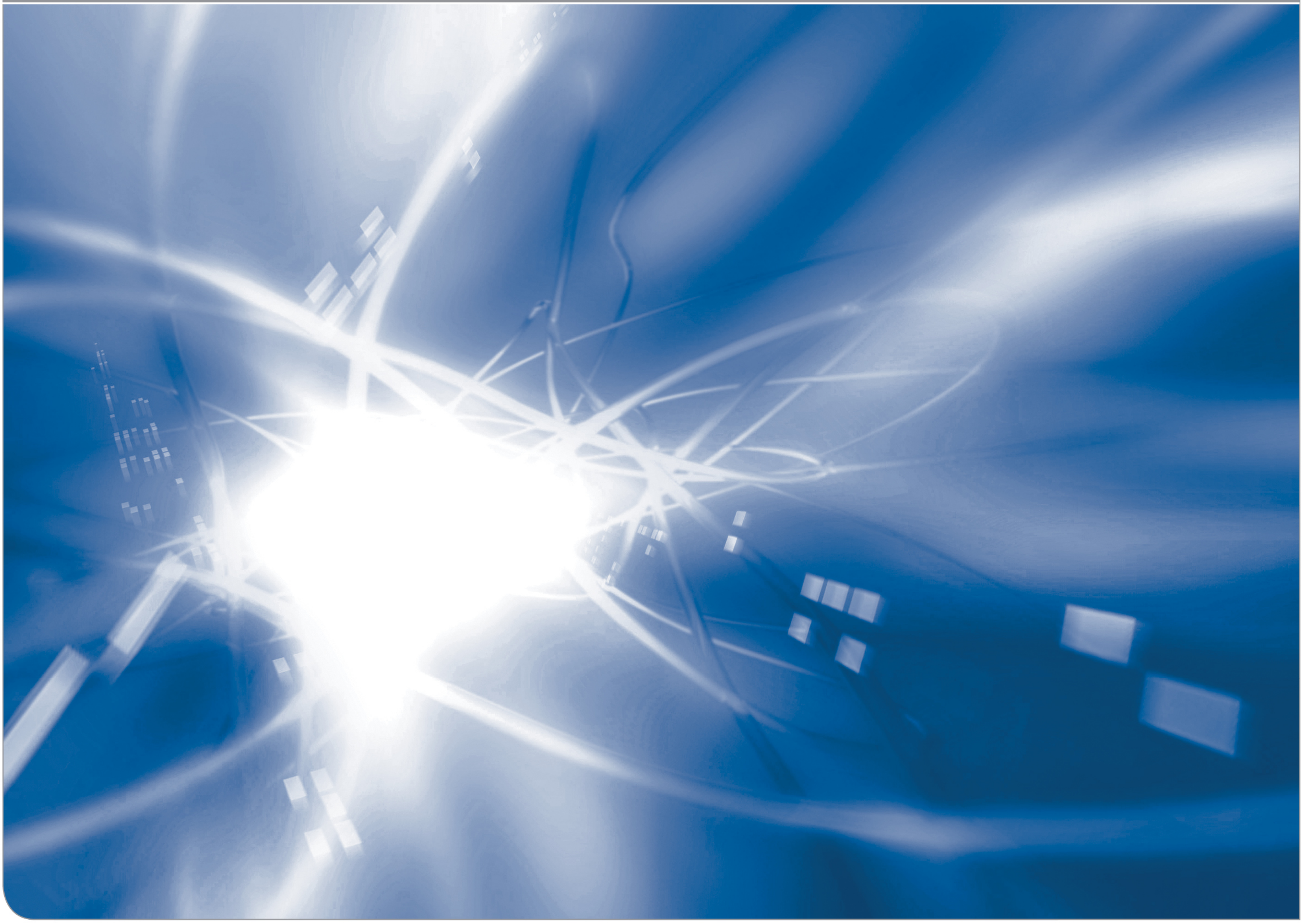

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Abstract

Water reacting with silica causes the generation of hydroxyl SiOH accompanied by a volume or swelling expansion. The principle of LeChatelier ensures that the hydroxyl concentration increases with increasing externally applied stresses. From the analysis in [1] it becomes obvious that

a) the hydroxyl concentration must depend on the multi-axiality of the applied stresses, and

b) that the swelling effect is anisotropic.

On the basis of the results in [1] it will be shown that under torsion loading the strongest effects should occur.

Contents

1 Motivation for anisotropic swelling

Strongly different stress states can result in the same hydrostatic stress term σ_h. An example for this fact is illustrated in Fig. 1 where the hydrostatic stress disappears completely, $\sigma_h=0$. This is trivial when all stress components disappear, Fig. 1a. In the case of Fig. 1b where the transversal stresses are half of the longitudinal stress with inverse sign, it is according to

$$\sigma_h = \tfrac{1}{3}(\sigma_x + \sigma_y + \sigma_z) = 0$$

The same holds for torsion loading, $\sigma_y=-\sigma_z$, Fig. 1b'. It is hardly imaginable that the high tensile stresses *in* bond direction should have no effect on bond fracture. It has to be expected that the reaction in tensile direction should produce swelling even for the hydrostatic stress state $\sigma_h=0$.

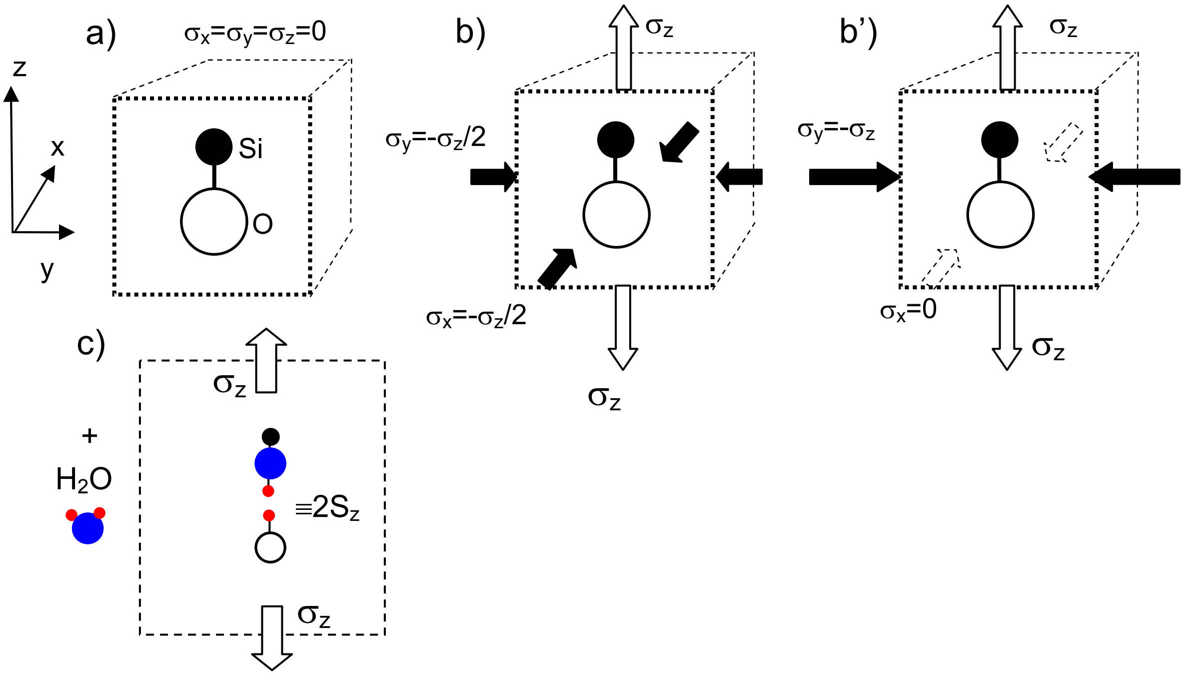

Fig. 1 a) b) Three stress states acting on a Si-O-bond exhibiting the same disappearing hydrostatic stress $\sigma_h=0$: a) isotropic swelling is expected, for b), b') swelling in *z*-direction should dominate as illustrated by c), case b') describes torsion loading, c) water molecule reacting with a stressed bond oriented in *z*-direction, producing two hydroxyls, $2S_z$.

Figure 2 shows the load-displacement curves for bond breaking. Perpendicular to the loading direction the necessary energy for splitting the bond is *U* and must be delivered by thermal vibrations.

The portion N_x (subscript *x* means the bonds oriented in *x*-direction in which no stress acts) of opened bonds results from the Boltzmann equation as

$$N_x \propto \exp\left(-\frac{U}{RT}\right) \tag{1.1}$$

The same equation holds for the y-direction

$$N_y \propto \exp\left(-\frac{U}{RT}\right) \tag{1.2}$$

The potential barrier U belongs to the case when no stresses are present or when the bond is perpendicular to the stress, Fig. 2a.

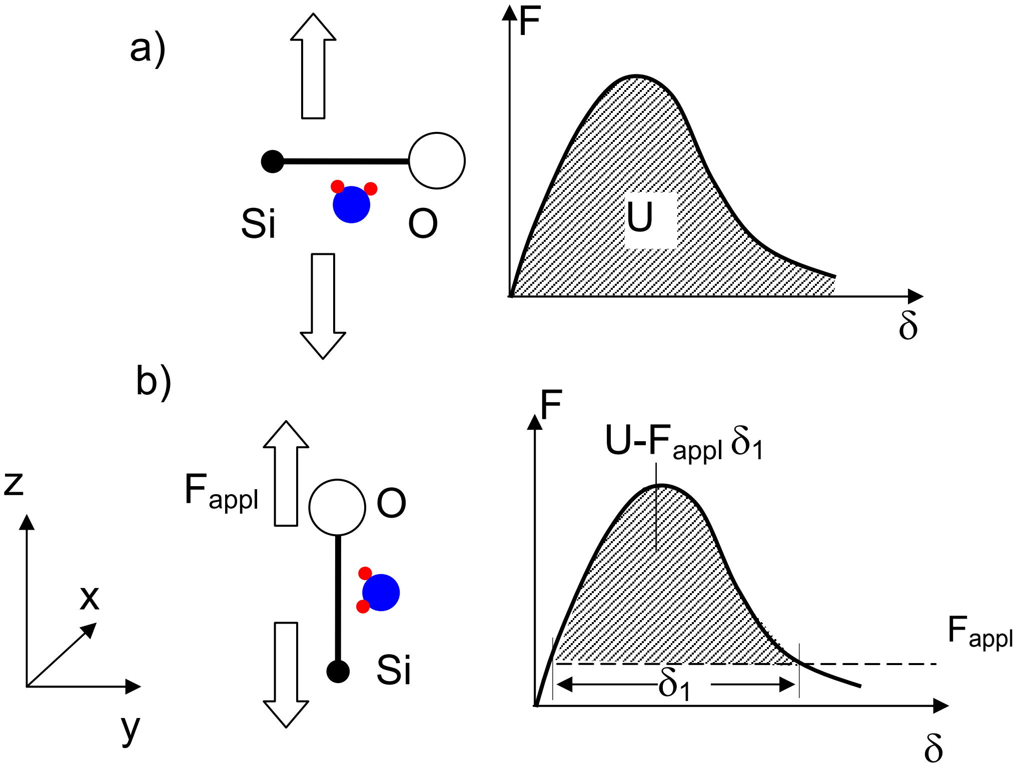

Fig. 2 Energy conditions for bond breaking.

Under action of a force F in bond-direction, Fig. 2b, the potential barrier is reduced to U-$F\delta_1$. Consequently, the occurrence of opened bonds in z-direction is increased

$$N_z \propto \exp\left(-\frac{U-\sigma_z V}{RT}\right) \tag{1.3}$$

where V is an activation volume. In the following considerations, it will be shown that the strongest anisotropy effect has to be expected for the torsion loading case.

For the computations on anisotropic swelling let us follow the derivations made in [1]. The stress effect on the equilibrium constant for reaction $SiO_2+H_2O \leftrightarrow 2\ SiOH$ can be derived from Eq.(6) of the article by de Boer [2]. Following the procedure in the review article by Hamann [3], we obtain the following equation for the equilibrium constant:

$$RT\ln k = \mu_{0,\mathrm{H2O}} - 2\mu_{0,\mathrm{SiOH}} + 2\Delta W + 2\Delta U\ , \tag{1.4}$$

where $\mu_{0,\mathrm{H2O}}$ and $\mu_{0,\mathrm{SiOH}}$ are the chemical potentials for molecular water and hydroxyls, respectively in the <u>unstressed state</u>; ΔW represents the work <u>per mol</u> of SiOH done by the mechanical stresses; and ΔU is the change of the elastic strain energy <u>per mol</u> due to a reduction of material stiffness as a consequence of the water reaction.

The work term ΔW in Eq. (1.4) is for loading in 3 directions σ_x, σ_y, σ_z

$$\Delta W / V_0 = \sigma_z \varepsilon_{sw,z}^{(1)} + \sigma_y \varepsilon_{sw,y}^{(1)} + \sigma_x \varepsilon_{sw,x}^{(1)} \tag{1.5}$$

with the Cartesian components of swelling strains $\varepsilon_{\mathrm{sw,i}}$, the glass volume, V_0, conveniently chosen as the molar volume of dry glass, and the superscripts $^{(1)}$ standing for 1 mole of S. The total swelling volume is in general the sum of the components

$$\varepsilon_v = \varepsilon_{sw,x} + \varepsilon_{sw,y} + \varepsilon_{sw,z} \tag{1.6}$$

Consequently, it holds for 1 mole of S

$$\varepsilon_v^{(1)} = \varepsilon_{sw,x}^{(1)} + \varepsilon_{sw,y}^{(1)} + \varepsilon_{sw,z}^{(1)} \tag{1.6a}$$

The change of strain energy is for uniaxial loading by $\sigma_z = \sigma_{appl}$

$$\Delta U / V_0 = -\tfrac{1}{2} \varepsilon_{appl}^2 \Delta E \tag{1.7}$$

where ΔE is the change in the Young's modulus as a consequence of the material damage by hydroxyl generation.

Due to the reaction between water and silica, a stiffness reduction of the SiO_2-structure, $\Delta E/\Delta S$, must occur since the interaction forces between the two S-groups are lower than the forces between the silicon atoms of the original Si-O-Si bond. The reduction in stiffness results in a change in the quantity of elastically stored energy, which in turn, contributes to the driving force of the reaction [4]. Since $\Delta E \leq 0$, the contribution ΔU has the same sign as ΔW. In the following evaluation, the energy term, ΔU, will be neglected assuming that $\Delta E/\Delta S$ is small due to the low hydroxyl concentrations in our calculations. Hence, we use the undamaged Young's modulus in all equations having in mind that the results of our computations are <u>lower limits</u>.

Equations (1.4) and (1.5) now yield

$$k = k_0 \exp\left[2V_0 \frac{(\sigma_z \varepsilon_{sw,z}^{(1)} + \sigma_y \varepsilon_{sw,y}^{(1)} + \sigma_x \varepsilon_{sw,x}^{(1)})}{RT} \right], \tag{1.8}$$

where k_0 includes all of the terms that are independent of stress ($\mu_{0,\mathrm{SiOH}}$, $\mu_{0,\mathrm{H2O}}$ and $\ln[C]$). The molar volume for glass is V_0=27.27 cm^3/mol. For one mole of hydroxyl with the mass m_{OH}=17g/mole in the volume V_0 we obtain the hydroxyl concentration in weight units (mass S/mass SiO_2)

$$S^{(1)} = \frac{m_{\mathrm{OH}}}{M_{\mathrm{glass}}} = \frac{17\ \mathrm{g/mole}}{60\ \mathrm{g/mole}} = 0.283 \tag{1.9}$$

with the related volume strain according to [1]

$$\varepsilon_v^{(1)} = \kappa S^{(1)} = 0.274 \tag{1.10}$$

Then it holds for $V_0\varepsilon_v^{(1)}$

$$V_0\varepsilon_v^{(1)} = 27.27 \times 0.274 \cong 7.5\ \mathrm{cm^3/mole} \tag{1.11}$$

2 Hydroxyl concentrations for special loading cases

2.1 Hydrostatic stress state as limit case

Combining eqs.(1.8) and the equilibrium constant $k{=}S^2/C$ (with the concentration of the hydroxyl $S = [\equiv\mathrm{SiOH}]$ and that of the molecular water $C = [H_2O]$) yields the stress-enhanced hydroxyl concentration for the *most general stress state*

$$S = S_0 \exp\left[V_0 \frac{(\sigma_z \varepsilon_{sw,z}^{(1)} + \sigma_y \varepsilon_{sw,y}^{(1)} + \sigma_x \varepsilon_{sw,x}^{(1)})}{RT} \right] \tag{2.1}$$

In the case of a purely equi-triaxial stress state

$$\sigma_x = \sigma_y = \sigma_z \tag{2.2}$$

the hydrostatic tensile stress σ_h is trivially given as

$$\sigma_h = \tfrac{1}{3}(\sigma_x + \sigma_y + \sigma_z) = \tfrac{1}{3}(3\sigma_z) \tag{2.3}$$

Then eq.(2.1) reads:

$$S = S_0 \exp\left[\sigma_h \underbrace{(\varepsilon_{sw,z}^{(1)} + \varepsilon_{sw,y}^{(1)} + \varepsilon_{sw,x}^{(1)})}_{\varepsilon_v^{(1)}} \frac{V_0}{RT} \right] = S_0 \exp\left[\sigma_h \varepsilon_v^{(1)} \frac{V_0}{RT} \right] \tag{2.4}$$

When $\overline{V}$ denotes the partial molar volume for the hydroxyl S, (2.4) can be rewritten as

$$\frac{S}{S_0}=\exp\left(\frac{\sigma_h \overline{V}_S}{RT}\right)=\underbrace{\exp\left[\sigma_h \varepsilon_v^{(1)}\frac{V_0}{RT}\right]}_{\text{Eq.(2.4)}} \Rightarrow \varepsilon_v^{(1)} V_0=\overline{V}_S \tag{2.5}$$

2.2 Uniaxial tension

Under purely uniaxial tensile stresses $\sigma_z = \sigma_{appl} > 0$, $\sigma_x = \sigma_y = 0$, Fig. 3a, it results from (2.1) simply

$$S = S_0 \exp\left[V_0 \frac{\sigma_{appl}\varepsilon_{sw,z}^{(1)}}{RT}\right] \tag{2.6}$$

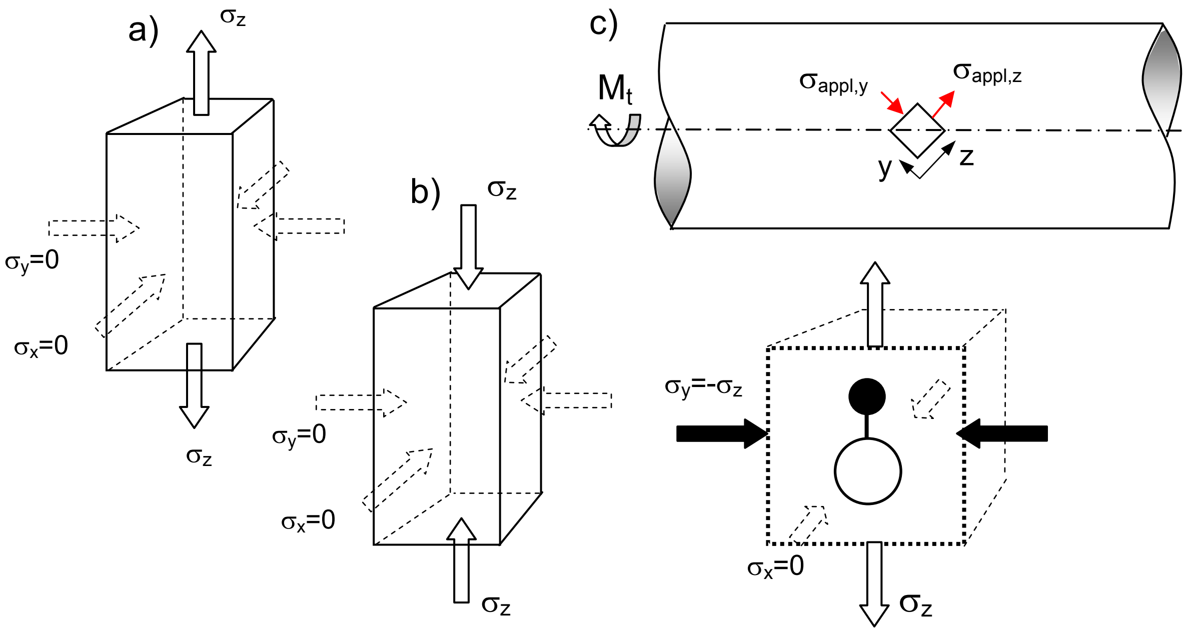

Fig. 3 Loading cases: a) uniaxial tension, b) uniaxial compression, c) cylinder under a torsion moment M_t.

In terms of the volume strain ε_v it is

$$S = S_0 \exp\left[V_0 \frac{\sigma_{appl}\,\varepsilon_v^{(1)}}{RT}\alpha\right] \tag{2.7}$$

where the ratio α is a measure for the anisotropy of swelling:

$$\alpha = \frac{\varepsilon_{sw,z}^{(1)}}{\varepsilon_v^{(1)}} \tag{2.8}$$

Symmetry in *x*- and *y*-directions yields $\varepsilon_{sw,x} = \varepsilon_{sw,y}$. This causes

$$\varepsilon_v = \varepsilon_{sw,z} + 2\varepsilon_{sw,x} \Rightarrow \varepsilon_{sw,x} = \tfrac{1}{2}(\varepsilon_v - \varepsilon_{sw,z}) \Rightarrow \frac{\varepsilon_{sw,x}}{\varepsilon_v} = \frac{\varepsilon_{sw,y}}{\varepsilon_v} = \tfrac{1}{2}(1-\alpha) \tag{2.9}$$

Since $\sigma_{\text{appl}}>0$, the hydroxyl concentration in pure tension increases, $S > S_0$.

2.3 Uniaxial compression

In a uniaxial compression test with $\sigma_z = \sigma_{\text{appl}} <0$, $\sigma_x = \sigma_y = 0$, Fig. 3b, it results from (2.1) simply

$$S = S_0 \exp\left[V_0 \frac{\sigma_{appl}\varepsilon_{sw,z}^{(1)}}{RT} \right] = S_0 \exp\left[V_0 \frac{\sigma_z \varepsilon_v^{(1)}}{RT} \alpha \right] \tag{2.10}$$

the same equation as in tension, but now with a negative applied stress and a different value α. The consequence is a reduction of the hydroxyl concentration $S<S_0$.

2.4 Biaxial stress state in a torsion test

Under torsion loading, the maximum and minimum principle stresses appear in a co-ordinate system turned by 45° with respect to the length axis. In this system, Fig. 3c, the “applied” stresses are

$$\sigma_{appl,y} = -\sigma_{appl,z}\ , \quad \sigma_{appl,x} = 0 \tag{2.11}$$

Under this load, eq.(2.1) reads

$$S = S_0 \exp\left[V_0 \frac{(\sigma_{appl,z} + \sigma_{sw,z})\varepsilon_{sw,z}^{(1)} + (\sigma_{appl,y} + \sigma_{sw,y})\varepsilon_{sw,y}^{(1)}}{RT} \right], \tag{2.12}$$

Introducing the ratio $\alpha=\varepsilon_{sw,z}/\varepsilon_v$, using (2.10) and replacing $\sigma_{appl,z}=\sigma_{appl}$

$$S = S_0 \exp\left[\alpha \frac{V_0 \varepsilon_v^{(1)}}{RT} \left(\sigma_{appl} \left\{ 1 - \frac{\varepsilon_{sw,y}^{(1)}}{\varepsilon_{sw,z}^{(1)}} \right\} + \sigma_{sw,z} + \sigma_{sw,y} \frac{\varepsilon_{sw,y}^{(1)}}{\varepsilon_{sw,z}^{(1)}} \right) \right] \tag{2.13}$$

Unfortunately, the ratio of strains $\varepsilon_{sw,y}^{(1)} / \varepsilon_{sw,z}^{(1)}$ is unknown and has to be determined experimentally. Simplification of (2.13) for moderate stresses is actually not possible. On the other hand, the torsion test would be an ideal tool to decide two closely connected points:

Under load the hydrostatic stress term disappears, $\sigma_h=0$. When swelling would be governed by the hydrostatic stress, not any enhanced hydroxyl concentration would be possible. Consequently, no swelling strains could occur, $\varepsilon_{sw,x} =\varepsilon_{sw,y} =\varepsilon_{sw,z} =\varepsilon_v=0$. The whole exponent in eq.(2.13) would then disappear with the consequence of $S=S_0$ $\neq$f(load). If even in torsion the hydroxyl concentration increases under load, the occurrence of anisotropy in swelling would be proofed. This had been derived and confirmed in [1].

The conclusions based on swelling effects under torsion load were:

a) The individual principal stresses affect the water/silica reaction differently.

b) The equivalent consequence to the non-symmetry of swelling strains: Swelling strains depend on the individual principal stresses.

Evaluation of experimental results by Agarwal et al. [5] and FE-computations show that the strain ratio $\alpha=\varepsilon_{sw,z}/\varepsilon_v$, representing anisotropic swelling, is in tension $\alpha=1.92$ [1] and $\alpha=2.06$ [6], respectively. Both values are a clear indication for anisotropic swelling.

3 Limit-case considerations

3.1 Orientation of reaction events

A volume element with a number of *N* Si-O bonds is shown in Fig. 4. In a statistical sense, the number of *N* arbitrarily oriented Si-O-bonds can be dismantled in "components" oriented in the *x*-, *y*-, *z*-directions of a rectangular coordinate system with *N*/3 single bonds in each direction.

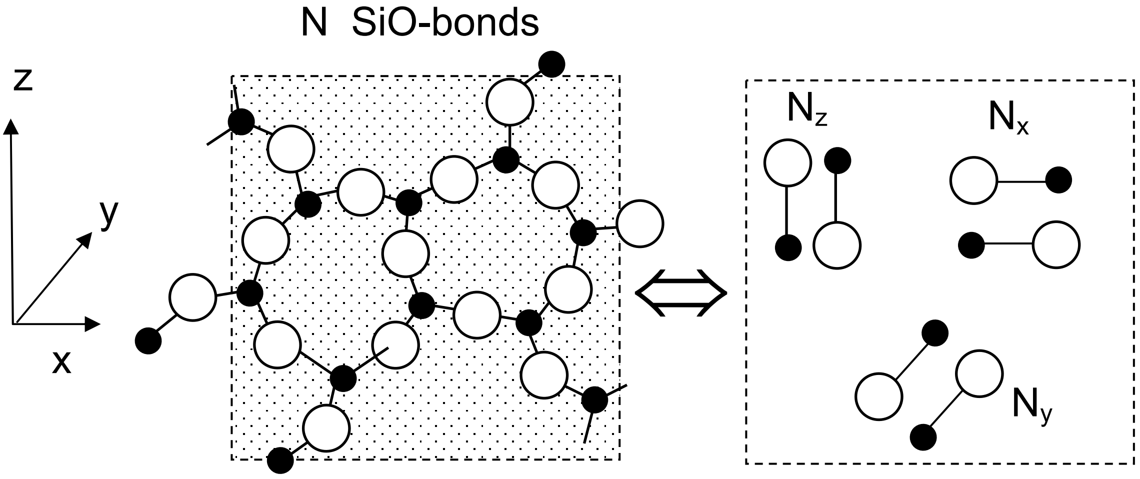

Fig. 4 Volume element containing a number of *N* Si-O bonds (2-dimensional representation) divided into each *N*/3 bonds oriented in *x*-, *y*-, and *z*-directions.

Under mechanical tensile stresses arbitrarily applied in *z*-direction, the probability of reaction events should be increased for the bonds N_z. The maximum swelling strain in *z*-direction should therefore result when all reactions occur at bonds N_z exclusively. In the FE-study made before, we considered this special case and looked for the maximum swelling strain $\varepsilon_{sw,z}$. Maximum anisotropy is reached if all stress-enhanced reaction events are located at bonds oriented in *z*-direction showing the probability P_z

$$P_z = \frac{N_z}{N_x + N_y + N_z} \tag{3.1}$$

or more general for the probability $P_i = P_{x,y,z}$

$$P_i = \frac{N_i}{N_x + N_y + N_z} \tag{3.2}$$

This probability is schematically shown in Fig. 5 for three limit cases. For high uniaxial stress in z-direction, $\sigma_z \to \infty$, the probability P_z tends to $P_z=1$, i.e. all reaction events are orientated in z-direction, (A) in Fig. 5.

Without an external stress $\sigma_x=\sigma_y=\sigma_z=0$ one would expect the expansion in all directions to be equal, $\varepsilon_x=\varepsilon_y=\varepsilon_z$. as shown as (B) in Fig. 5. The same has to be expected for an equi-triaxially loaded volume element with $\sigma_x=\sigma_y=\sigma_z\neq 0$.

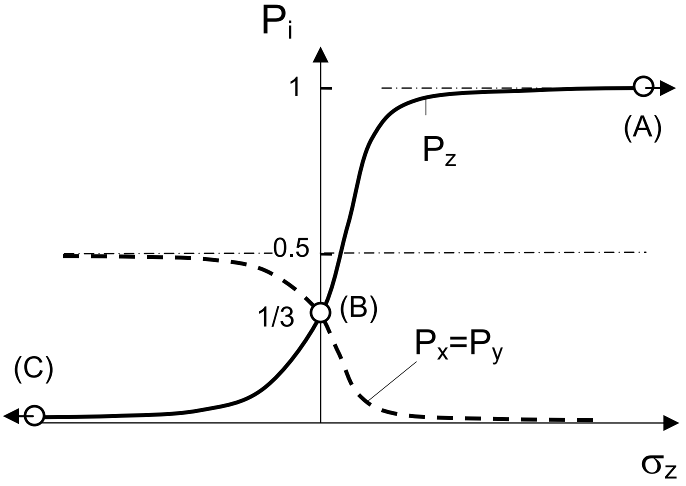

Fig. 5 Schematic representation of the "reaction probabilities" P_i on the stress acting in a volume element for the case of uniaxial loading (illustrated for the z-component σ_z).

For high compressive uniaxial stresses, $\sigma_z \to -\infty$, water molecules can only react in N_x- and N_y-directions. This case is in Fig. 5 introduced as (C). The same dependency shown in Fig. 5 for stresses in z-direction must trivially hold for the other two orientations x and y. It is self-evident that the FE-computation cannot provide further information on the detailed curve $P_z=f(\sigma_z)$. For this purpose, appropriate experiments or MHD-computations are necessary.

The solid curve in Fig. 5 may be represented by a hyperbolic tangent function

$$P_i = \tfrac{1}{2}(1 + \tanh[-a + b\sigma_z]) \tag{3.3}$$

with the fixed coefficient a=arctanh[1/3].

3.2 Special results for $\sigma \geq 0$ obtained by superposition

For simple problems with non-negative stresses involved, we can make predictions by superposition of tensile results.

In the case of uniaxial tension, $\sigma_z \rightarrow \infty$, the results from FE-computations are given in the first line of Table 1. As an example of application to a more complicated stress state, the second line shows results for the limit case of torsion equivalent to the biaxial stresses $\sigma_y = -\sigma_z$, $\sigma_x = 0$.

	σ_z	σ_y	σ_x	P_z	P_y	P_x	$\varepsilon_{sw,z}/\varepsilon_v$	$\varepsilon_{sw,y}/\varepsilon_v$	$\varepsilon_{sw,x}/\varepsilon_v$	$W/(V_0\,\varepsilon_v^{(1)}\,\sigma_z)$
Tension	$\rightarrow +\infty$	0	0	1	0	0	2.06	-0.53	-0.53	**2.06**
Torsion	$\rightarrow +\infty$	$-\sigma_z$	0	1	0	0				2.06−(−0.53) **2.59**

Table 1 Work W done under uniaxial tension and torsion loading (α=2.06).

Since the work under torsion, last column in Table 1, is larger than in uniaxial tension, we have to expect stronger stress enhancement in hydroxyl generation and swelling strains.

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