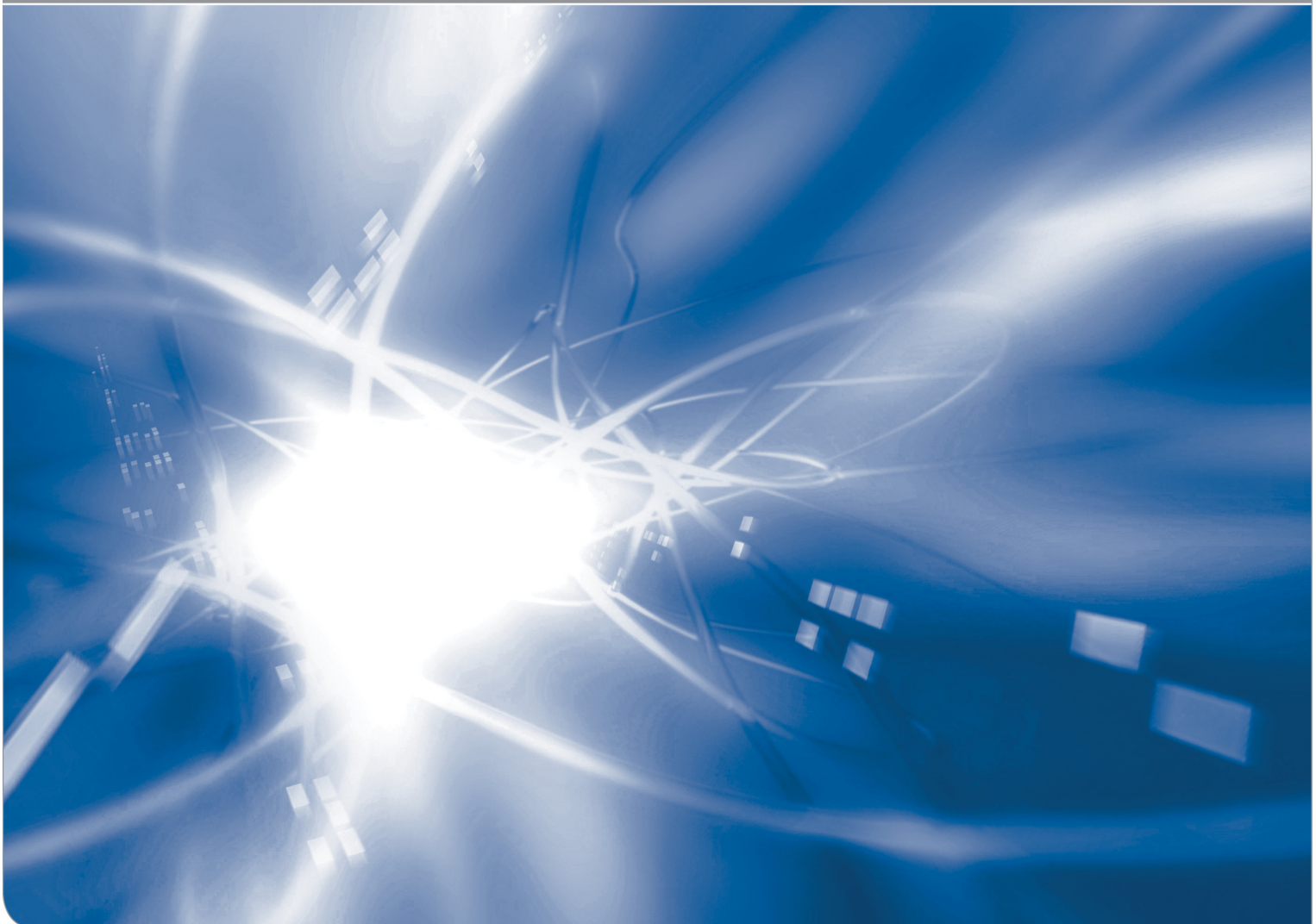


Stress-enhanced silica/water reaction under torsion loading

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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 [1,2] 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 [1,2] it will be shown that under torsion loading the strongest effects on stress-enhanced hydroxyl generation and swelling strains should occur, although this stress state shows a disappearing hydrostatic stress term.

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1 Motivation for anisotropic swelling

Water penetrated into silica reacts with the silica network according to



with the concentration of the hydroxyl $S = [\equiv\text{SiOH}]$ and that of the molecular water $C = [\text{H}_2\text{O}]$. The equilibrium constant of this reaction is at temperatures $\theta > 500^\circ\text{C}$

$$k = S^2 / C \quad (2)$$

Strongly different stress states can result in the same hydrostatic stress term σ_h . While in [1] arbitrary stress states were considered, here we concentrate on the special case of vanishing hydrostatic stress, $\sigma_h = 0$. An example for this fact is illustrated in Fig. 1 where the hydrostatic stress, given by

$$\sigma_h = \frac{1}{3}(\sigma_x + \sigma_y + \sigma_z) \quad (3)$$

disappears completely. This is trivial when all stress components disappear, $\sigma_i = 0$ (Fig. 1a). In the case of Fig. 1b where the transversal stresses are half of the longitudinal stress with inverse sign, it results from eq.(3), $\sigma_h = 0$.

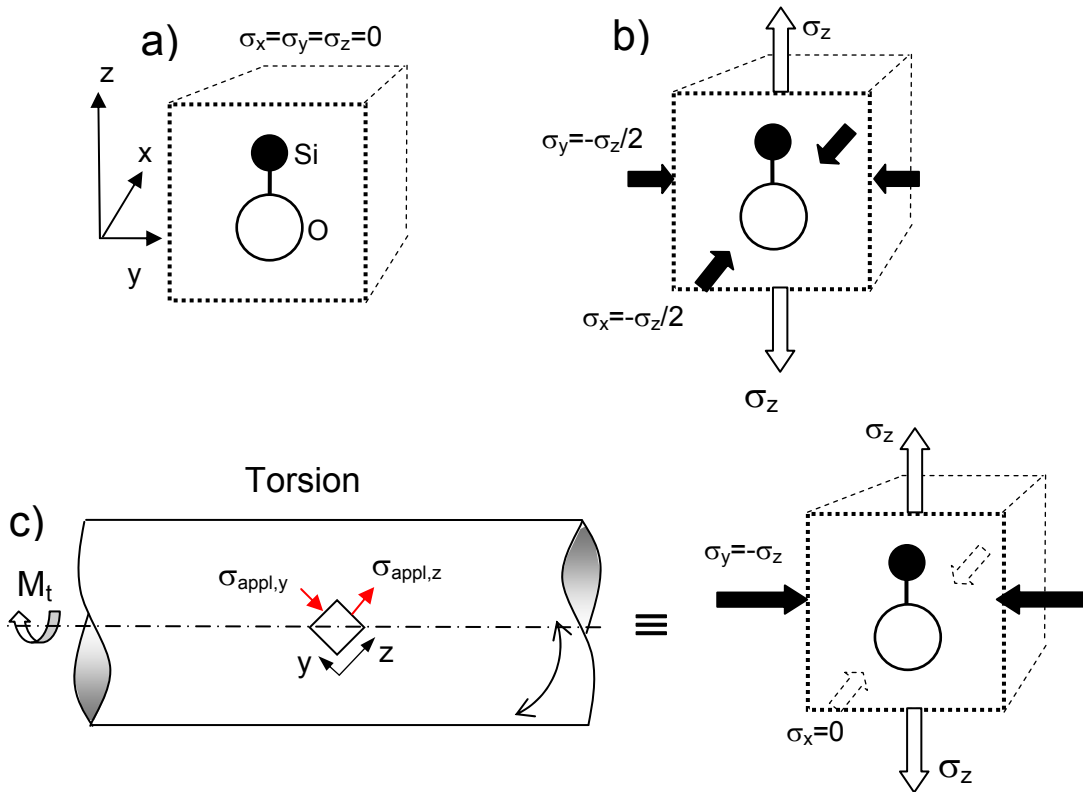


Fig. 1 a) b) Three stress states acting on a Si-O-bond exhibiting the same disappearing hydrostatic stress $\sigma_h = 0$: a) isotropic swelling is expected, for b) and c) swelling in z-direction should dominate.

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

Figure 2 illustrates the load-displacement curves responsible for bond breaking. Perpendicular to the loading direction the necessary energy for splitting the bond is U to be provided 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

$$N_x \propto \exp\left(-\frac{U}{RT}\right) \quad (4)$$

The same equation holds for the y -direction

$$N_y \propto \exp\left(-\frac{U}{RT}\right) \quad (5)$$

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

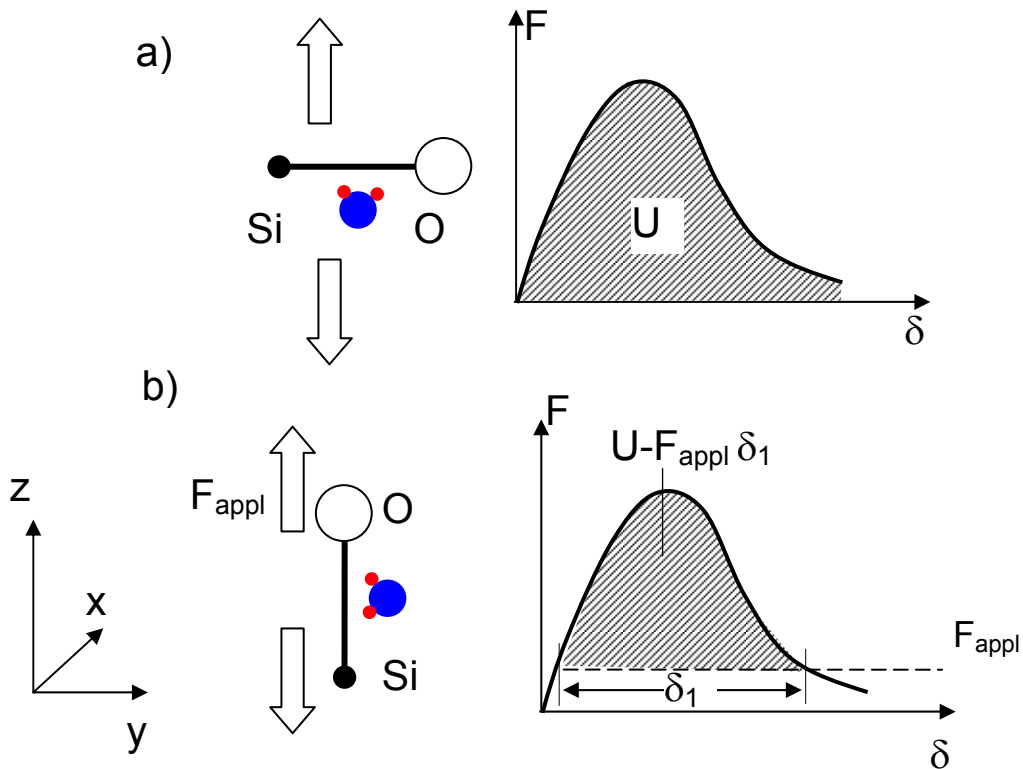


Fig. 2 Energy conditions for bond breaking (schematic).

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

$$N_z \propto \exp\left(-\frac{U - \sigma_z V}{RT}\right) \quad (6)$$

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 [2]. The stress effect on the equilibrium constant for reaction $\text{SiO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{SiOH}$ can be derived from Eq.(6) of the article by de Boer [3]. Following the procedure in the review article by Hamann [4], we obtain the following equation for the equilibrium constant:

$$RT \ln k = \mu_{0,\text{H}_2\text{O}} - 2\mu_{0,\text{SiOH}} + 2\Delta W + 2\Delta U, \quad (7)$$

where $\mu_{0,\text{H}_2\text{O}}$ and $\mu_{0,\text{SiOH}}$ are the chemical potentials for molecular water and hydroxyls, respectively in the unstressed state; ΔW represents the work per mol of SiOH done by the mechanical stresses; and ΔU is the change of the elastic strain energy per mol due to a reduction of material stiffness as a consequence of the water reaction.

The work term ΔW in Eq. (7) is for loading in 3 directions $\sigma_x, \sigma_y, \sigma_z$

$$\Delta W / V_0 = \sigma_z \varepsilon_{sw,z}^{(1)} + \sigma_y \varepsilon_{sw,y}^{(1)} + \sigma_x \varepsilon_{sw,x}^{(1)} \quad (8)$$

with the Cartesian components of swelling strains $\varepsilon_{sw,i}$, 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

$$\varepsilon_v = \varepsilon_{sw,x} + \varepsilon_{sw,y} + \varepsilon_{sw,z} \quad (9)$$

Consequently, it holds for 1 mole of S

$$\varepsilon_v^{(1)} = \varepsilon_{sw,x}^{(1)} + \varepsilon_{sw,y}^{(1)} + \varepsilon_{sw,z}^{(1)} \quad (10)$$

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

$$\Delta U / V_0 = -\frac{1}{2} \varepsilon_{\text{appl}}^2 \Delta E \quad (11)$$

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 [5]. 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 lower limits.

Equations (7) and (8) now yield

$$k = k_0 \exp \left[2V_0 \frac{(\sigma_z \varepsilon_{sw,z}^{(1)} + \sigma_y \varepsilon_{sw,y}^{(1)} + \sigma_x \varepsilon_{sw,x}^{(1)})}{RT} \right], \quad (12)$$

where k_0 includes all of the terms that are independent of stress ($\mu_{0,\text{SiOH}}$, $\mu_{0,\text{H}_2\text{O}}$ and $\ln[C]$). The molar volume for glass is $V_0 = 27.27 \text{ cm}^3/\text{mole}$. For one mole of hydroxyl with the mass $m_{\text{OH}} = 17 \text{ g/mole}$ in the volume V_0 we obtain the hydroxyl concentration in weight units (mass S /mass SiO_2)

$$S^{(1)} = \frac{m_{\text{OH}}}{M_{\text{glass}}} = \frac{17 \text{ g/mole}}{60 \text{ g/mole}} = 0.283 \quad (13)$$

with the related volume strain according to [2]

$$\varepsilon_v^{(1)} = \kappa S^{(1)} = 0.274 \quad (14)$$

($\kappa \cong 0.97$). Then it holds for $V_0 \varepsilon_v^{(1)}$

$$V_0 \varepsilon_v^{(1)} = 27.27 \times 0.274 \cong 7.5 \text{ cm}^3/\text{mole} \quad (15)$$

2. Hydroxyl concentration under stresses

Combining eq.(12) and the equilibrium constant $k = S^2/C$ (with the concentration of the hydroxyl $S = [\equiv\text{SiOH}]$ and that of the molecular water $C = [\text{H}_2\text{O}]$) yields the stress-enhanced hydroxyl concentration for the *most general stress state*

$$S = S_0 \exp \left[V_0 \frac{(\sigma_z \varepsilon_{sw,z}^{(1)} + \sigma_y \varepsilon_{sw,y}^{(1)} + \sigma_x \varepsilon_{sw,x}^{(1)})}{RT} \right] \quad (16)$$

Under purely uniaxial tensile stresses $\sigma_z = \sigma_{\text{appl}} > 0$, $\sigma_x = \sigma_y = 0$, it results from (16) simply [2]

$$S = S_0 \exp \left[V_0 \frac{\sigma_{\text{appl}} \varepsilon_{sw,z}^{(1)}}{RT} \right] \quad (17)$$

In terms of the volume strain ε_v it is

$$S = S_0 \exp \left[V_0 \frac{\sigma_{\text{appl}} \varepsilon_v^{(1)}}{RT} \alpha \right] \quad (18)$$

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

$$\alpha = \varepsilon_{sw,z}^{(1)} / \varepsilon_v^{(1)} \quad (19)$$

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

3 A Finite Element model for a single reaction event

Due to the reaction (1), a SiO-bond may fracture in the absence of externally applied stresses. The coordinate system is oriented so that the z -axis agrees with the direction in which the repulsive forces between the silanols act (Fig. 3a). The “nano-pore” defined by the dashed circle in Fig. 4a was modelled as a sphere of radius R in an “infinite body”. In a FE-study [6] we modelled the “infinite body” by a cylinder of radius $500 R$ and half height $500 R$, Fig. 3b. For the computations, we used ABAQUS Version 6.9 on a mesh of 1246 elements and 3880 nodes. Due to symmetry, only a 4th of the total body had to be modelled. Expansion of the pore is prescribed by a displacement δ_0 in z -direction. As the only material parameter of relevance we used the Poisson ratio of $\nu=0.17$. Figure 4 represents the displacement distribution for a cylinder contour with $h = \rho = 16 R$. The distance from the pore is large. On the other hand, the contour is small compared with the modelled body. Saint-Venant’s theorem ensures that no boundary effects and details of the pore shape can affect the results noticeably. The displacements are normalized on the maximum displacements present on the symmetry lines.

The volume changes in axial and radial directions, ΔV_z and ΔV_r , are given by

$$\Delta V_z = 2\pi \int_0^\rho \delta_z(r) r dr \quad , \quad \Delta V_r = 2\pi r \int_0^{h=\rho} \delta_r(z) dz \quad (20)$$

Since the cylinder volume is

$$V_0 = \rho^2 \pi h \underset{\rho=h}{=} \rho^3 \pi \quad (21)$$

the volume swelling strain results as

$$\varepsilon_v = \frac{\Delta V_z + \Delta V_r}{\rho^3 \pi} \quad (22)$$

Finally, the anisotropy ratio $\bar{\varepsilon}_{sw,z} / \varepsilon_v$ is obtained by:

$$\frac{\bar{\varepsilon}_{sw,z}}{\varepsilon_v} = \frac{\Delta V_z}{\Delta V_z + \Delta V_r} \quad (23)$$

A more detailed derivation of eqs.(20-23) is given in the Appendix and in [6]. The averages of strains are explained in more detail in the Appendix. For the cylinder contour of $\rho = h = 16 R$, the evaluation of eq.(23) results in

$$\frac{\bar{\varepsilon}_{sw,z}}{\varepsilon_v} = 2.06 \quad (24)$$

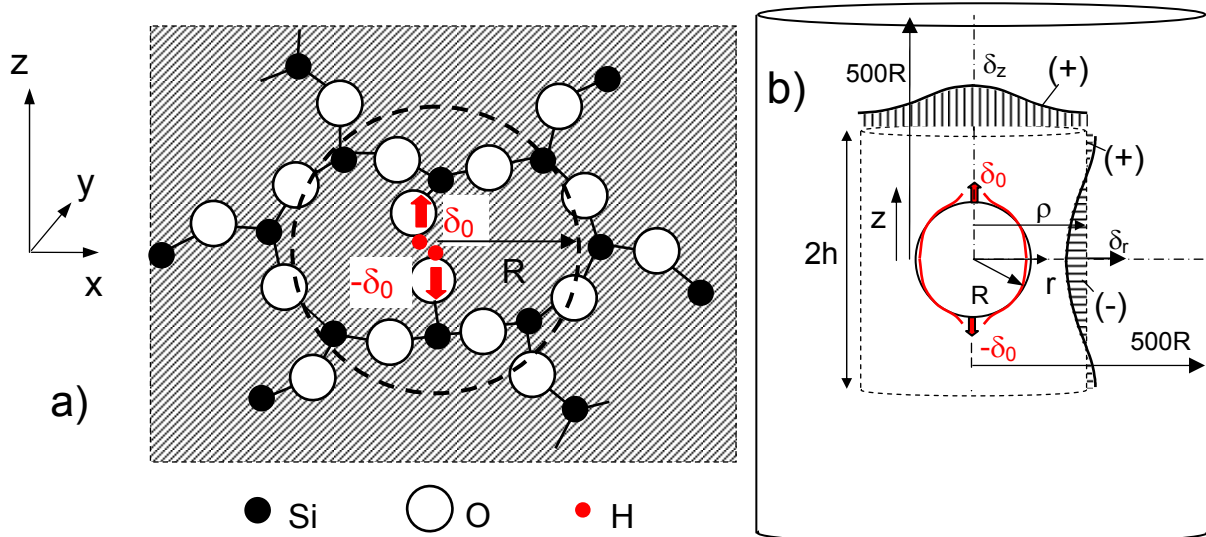


Fig. 3 a) Two-dimensional schematic drawing of bond breaking by water/silica reaction; the two hydroxyls yield an expansive displacement δ_0 in z -direction; the volume element in which the reaction occurred is represented by the dashed circle, b) Finite Element model of a “nano pore” (sphere of radius R) loaded by axial displacement δ_0 .

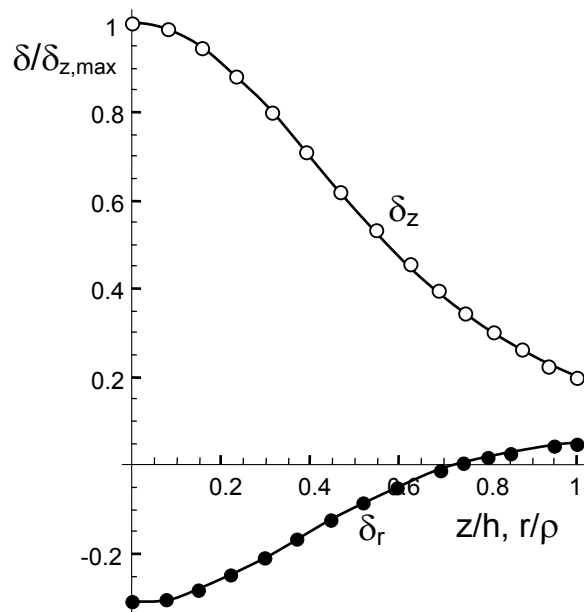


Fig. 4 Displacement distributions δ_z and δ_r at the cylinder contour in a distance of $h=\rho=16 R$.

Having in mind that the volume strain is

$$\varepsilon_v = \bar{\varepsilon}_{sw,x} + \bar{\varepsilon}_{sw,y} + \bar{\varepsilon}_{sw,z} = \bar{\varepsilon}_{sw,z} + 2\bar{\varepsilon}_{sw,r} \quad (25)$$

a ‘‘Poisson’s ratio $\bar{\nu}$ ’’ for swelling strains can be defined via

$$\bar{\nu} = -\frac{\bar{\varepsilon}_{sw,r}}{\bar{\varepsilon}_z} \quad (26)$$

From eqs.(24) to (26) we obtain

$$\frac{\bar{\varepsilon}_{sw,z}}{\varepsilon_v} = \frac{\bar{\varepsilon}_{sw,z}}{\bar{\varepsilon}_{sw,z} + 2\bar{\varepsilon}_{sw,r}} = \frac{1}{1 + 2\frac{\bar{\varepsilon}_{sw,r}}{\bar{\varepsilon}_{sw,z}}} = \frac{1}{1 - 2\bar{\nu}} = 2.06 \Rightarrow \bar{\nu} = 0.257 \quad (27)$$

resulting in a Poisson’s ratio as is usual for ceramics. The transverse swelling strains are

$$\frac{\bar{\varepsilon}_{sw,r}}{\varepsilon_v} = \frac{\bar{\varepsilon}_{sw,x}}{\varepsilon_v} = \frac{\bar{\varepsilon}_{sw,y}}{\varepsilon_v} = -0.53 \quad (28)$$

It has to be emphasized here once more, that the results from FE were obtained under the assumption that all stress-enhanced swelling strains are oriented in direction of the load. This is of course an upper limit case.

4 Hydroxyl concentrations for disappearing hydrostatic stress

4.1 Hydrostatic stress state as limit case

In the case of a purely equi-triaxial stress state

$$\sigma_x = \sigma_y = \sigma_z \quad (29)$$

the hydrostatic tensile stress σ_h is trivially given as

$$\sigma_h = \frac{1}{3}(\sigma_x + \sigma_y + \sigma_z) = \frac{1}{3}(3\sigma_z) \quad (30)$$

Then eq.(16) reads:

$$S = S_0 \exp \left[\sigma_h \underbrace{(\varepsilon_{sw,z}^{(1)} + \varepsilon_{sw,y}^{(1)} + \varepsilon_{sw,x}^{(1)})}_{\varepsilon_v^{(1)}} \frac{V_0}{RT} \right] = S_0 \exp \left[\sigma_h \varepsilon_v^{(1)} \frac{V_0}{RT} \right] \quad (31)$$

When \bar{V} denotes the partial molar volume for the hydroxyl S , (31) can be rewritten as

$$\frac{S}{S_0} = \exp \left(\frac{\sigma_h \bar{V}_S}{RT} \right) = \exp \left[\sigma_h \varepsilon_v^{(1)} \frac{V_0}{RT} \right] \Rightarrow \varepsilon_v^{(1)} V_0 = \bar{V}_S \quad (32)$$

4.2 Biaxial stress state in a torsion test

Under torsion loading, the maximum and minimum principle stresses appear in a coordinate system turned by 45° with respect to the length axis. In this system, Fig. 1c, the “applied” stresses are

$$\sigma_{appl,y} = -\sigma_{appl,z}, \quad \sigma_{appl,x} = 0 \quad (33)$$

Under this load, eq.(16) reads

$$S = S_0 \exp \left[V_0 \frac{(\sigma_{appl,z} + \sigma_{sw,z})\varepsilon_{sw,z}^{(1)} + (\sigma_{appl,y} + \sigma_{sw,y})\varepsilon_{sw,y}^{(1)}}{RT} \right], \quad (34)$$

Introducing the ratio $\alpha = \varepsilon_{sw,z} / \varepsilon_v$, using (33) and replacing $\sigma_{appl,z} = \sigma_{appl}$

$$S = S_0 \exp \left[\alpha \frac{V_0 \varepsilon_v^{(1)}}{RT} \left(\sigma_{appl} \left\{ 1 - \frac{\varepsilon_{sw,y}^{(1)}}{\varepsilon_{sw,z}^{(1)}} \right\} + \sigma_{sw,z} + \sigma_{sw,y} \frac{\varepsilon_{sw,y}^{(1)}}{\varepsilon_{sw,z}^{(1)}} \right) \right] \quad (35)$$

Under torsion load the hydrostatic stress term disappears, $\sigma_h = 0$. From this point of view, the torsion test seems to be an ideal tool to decide whether the individual stress components or the hydrostatic stress is responsible for the stress-enhanced reaction eq.(1) in a solid:

When swelling would be governed exclusively by the hydrostatic stress, not any enhanced hydroxyl concentration should be observable. The swelling strains would not depend on the coordinates x, y, z , resulting always in isotropic swelling, expressed by $\varepsilon_{sw,x} = \varepsilon_{sw,y} = \varepsilon_{sw,z} = \varepsilon_v$. Especially for $\sigma_h = 0$ it would then result $\varepsilon_v = 0$ and the whole exponent in eq.(35) would then disappear. The consequence is $S = S_0 \neq f(\text{load})$. If even in torsion the hydroxyl concentration increases under load, the occurrence of anisotropy in swelling would be proofed as had been derived and confirmed in [2].

Evaluation of experimental results by Agarwal et al. [7] and FE-computations show that the strain ratio $\alpha = \varepsilon_{sw,z} / \varepsilon_v$, representing anisotropic swelling, is in tension $\alpha = 1.92$ [2] from experiment and $\alpha = 2.06$ [6] from FE, respectively. Both values are a clear indication for anisotropic swelling since isotropic swelling would result in $\alpha = 1/3$.

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 torsion, the second line shows the result for the limit case of torsion equivalent to the biaxial stresses $\sigma_y = -\sigma_z$, $\sigma_x = 0$. The work ΔW , eq.(8), last column in Table 1, is larger under torsion even than in uniaxial tension. Consequently, we have to expect stronger stress enhancement in hydroxyl generation and swelling strains as can be concluded from eqs.(8) and (16) written in the common form

$$S = S_0 \exp \left[\frac{\Delta W}{RT} \right]$$

i.e. the larger the work ΔW is, the stronger is the hydroxyl increase.

	σ_z	σ_y	σ_x	$\varepsilon_{sw,z}^{(1)} / \varepsilon_v^{(1)}$	$\varepsilon_{sw,y}^{(1)} / \varepsilon_v^{(1)}$	$\varepsilon_{sw,x}^{(1)} / \varepsilon_v^{(1)}$	$\Delta W / (V_0 \varepsilon_v^{(1)} \sigma_z)$
Tension	$\rightarrow +\infty$	0	0	2.06	-0.53	-0.53	2.06
Torsion	$\rightarrow +\infty$	$-\infty$	0				≥ 2.06 $\approx 2.06 - (-0.53) = 2.59$

Table 1 Work ΔW , eqs.(8, 9), done under torsion loading, compared with uniaxial tension (for $\alpha=2.06$).

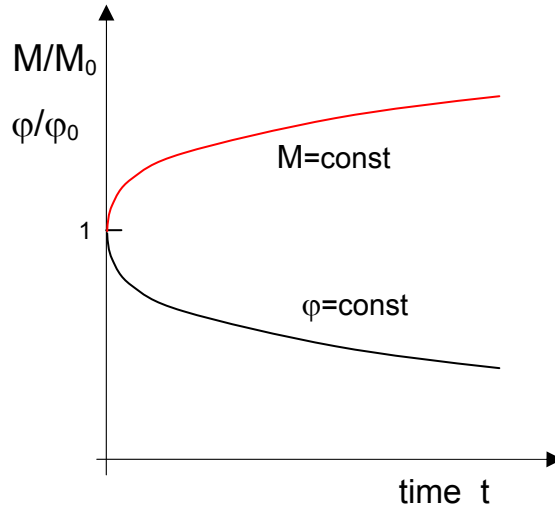


Fig. 5 Time dependence of twist angle (red curve) in a constant moment test and time dependent moment for twist angle kept constant (black curve)

Consequences for torsion tests:

In our study, we could show that the hydroxyl-enhancement in a torsion test is in the order of magnitude of uniaxial tensile tests. Measurable effects are expected. For thin water-affected surface layers of thickness $b=(Dt)^{1/2}$ (D =diffusivity, t =time) and $b \ll R$ (R =fiber radius),

1. the remaining S after the test would roughly be proportional to $S \times b \propto \sqrt{t}$, probably measurable by IR-spectroscopy,
2. in a test under constant twist angle (black curve in Fig. 5), the swelling stresses in the surface layer must decrease, resulting in a reduced torsion moment $M=M_0-\Delta M$ with $\Delta M \propto \varepsilon_{sw,z} \times b \propto \sqrt{t}$
3. in a constant moment test (red curve in Fig. 5), the reduced moment ΔM must be compensated, i.e. an additional twist angle $\Delta \phi \propto \sqrt{t}$ must appear, so that the instantaneously applied angle ϕ_0 is increased to $\phi_0 + \Delta \phi$.
4. After unloading a remaining twist angle $\Delta \phi$ should be observable.

For very short times, there has to be considered that the initial hydroxyl S_0 is not yet reached as has been outlined in [8]. Consequently, the time dependence will deviate from $\propto\sqrt{t}$ dependency for $t\rightarrow 0$.

Appendix: Displacements and strains from FE

According to [6] the relation between volume changes, displacements, and strains are outlined in in this Appendix. In terms of the geometric quantities of Fig. 3b, the volume change by the displacements in axial direction is given by

$$\Delta V_z = 2\pi \int_0^\rho \delta_z(r) r dr \quad (\text{A1})$$

In radial direction it holds

$$\Delta V_r = 2\pi r \int_0^{h=\rho} \delta_r(z) dz \quad (\text{A2})$$

On a cylinder contour with $\rho=h$ the average displacement in z -direction reads

$$\bar{\delta}_z = \frac{2}{\rho^2} \int_0^\rho \delta_z(r) r dr = \frac{\Delta V_z}{\rho^2 \pi} \quad (\text{A3})$$

Consequently, the average strain in z -direction is obtained as

$$\bar{\varepsilon}_z = \frac{\bar{\delta}_z}{h} \underset{\rho=h}{=} \frac{\bar{\delta}_z}{\rho} = \frac{\Delta V_z}{\rho^3 \pi} \quad (\text{A4})$$

Since the cylinder volume in the absence of swelling is

$$V_0 = \rho^2 \pi h \underset{\rho=h}{=} \rho^3 \pi \quad (\text{A5})$$

the volume welling strain results as

$$\varepsilon_v = \frac{\Delta V_z + \Delta V_r}{\rho^3 \pi} \quad (\text{A6})$$

The anisotropy ratio $\bar{\varepsilon}_z / \varepsilon_v$ is obtained by combining eqs.(A4) and (A6):

$$\frac{\bar{\varepsilon}_z}{\varepsilon_v} = \frac{\Delta V_z}{\Delta V_z + \Delta V_r} \quad (\text{A7})$$

A cylinder contour of $\rho = h = 16 R$ may be considered. In this case, the evaluation of eq.(A7) results in

$$\frac{\bar{\varepsilon}_z}{\varepsilon_v} \cong 2.06 \quad (\text{A8})$$

A Poisson's ratio ν for swelling strains can be defined via

$$\nu = -\frac{\bar{\varepsilon}_r}{\bar{\varepsilon}_z} \quad (\text{A9})$$

Since the volume strain is

$$\varepsilon_v = \bar{\varepsilon}_x + \bar{\varepsilon}_y + \bar{\varepsilon}_z = \bar{\varepsilon}_z + 2\bar{\varepsilon}_r \quad (\text{A10})$$

eqs.(A8) to (A10) yield

$$\frac{\bar{\varepsilon}_z}{\varepsilon_v} = \frac{\bar{\varepsilon}_z}{\bar{\varepsilon}_z + 2\bar{\varepsilon}_r} = \frac{1}{1 + 2\frac{\bar{\varepsilon}_r}{\bar{\varepsilon}_z}} = \frac{1}{1 - 2\nu} = 2.06 \Rightarrow \nu = 0.257 \quad (\text{A11})$$

The resulting Poisson's ratio is similar to those found for ceramics and metals.

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