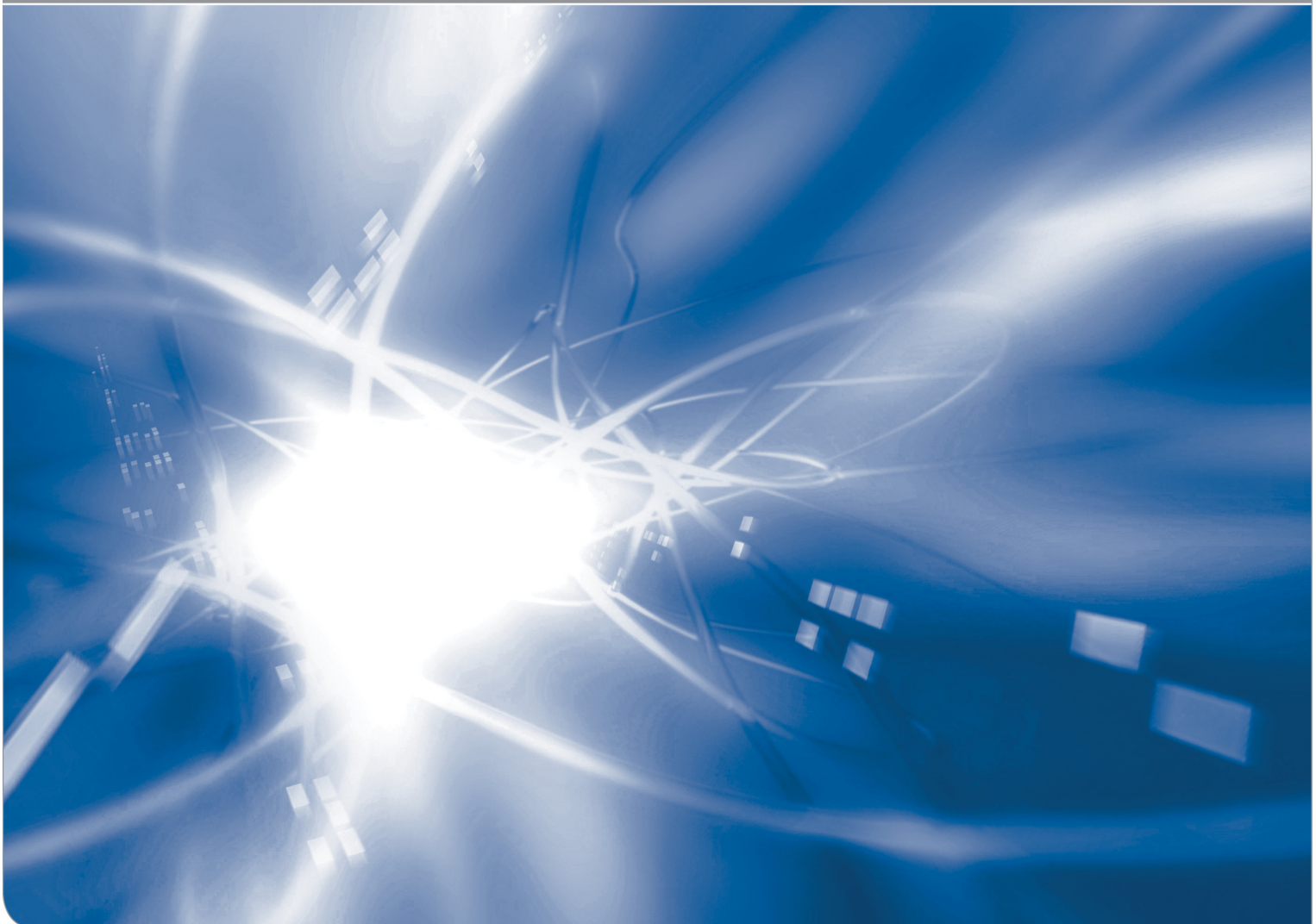


Swelling strains from gamma-irradiated silica - Evaluation of results by Shelby

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Abstract

Water introduced in silica reacts with the silica network under hydroxyl generation that causes a volume swelling. This effect has been discussed quantitatively in much detail in [1] for the case of water entrance by a heat treatment procedure. In the present Report we include also data by Shelby [8] obtained by in-situ generation of hydroxyl in gamma-irradiated silica. This procedure resulted in stronger density changes compared with the heat-treated material. Independent of this fact, we can show that the same volume swelling results for both methods. As an application of the results an estimation of the molar volume of hydroxyl is made.

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1 Previous results on swelling strains from density data

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 authors showed in a detailed analysis of literature results on density measurements [1] that volume swelling occurs by this reaction due to the hydroxyl generation. The principle effects of volume swelling in silica on mechanics and fracture mechanics properties were outlined in several papers, e.g. [2,3,4].

A swelling effect in water-containing silica at high temperatures was early reported by Brückner [5,6], Shackelford [7] and Shelby [8]. These authors showed that the density decreased by the reaction for a fictive temperature of $T_f=1100^\circ\text{C}$ according to

$$\frac{\Delta\rho}{\rho_0} = -\chi C_w, \quad C_w = \frac{m_w}{m_{\text{glass}} + m_w} \cong \frac{m_w}{m_{\text{glass}}} \quad (2)$$

where m_w is the total mass of water consisting of molecular and hydroxyl species and m_{glass} is the total mass of silica glass. C_w is the weight fraction of water. The literature data for a fictive temperature of $T_f=1100^\circ\text{C}$ are shown in Fig. 1 by the open symbols. The individual data for Brückner and Shelby were taken from the compilation by Shelby [8]. The data of Shackelford for fictive temperatures $T_f=1000^\circ\text{C}$ and $T_f=1100^\circ\text{C}$ were directly taken from the original paper [7] transforming the “water” content (wt% OH) in water content (wt% H₂O) using the factor (18/17)/2 where 18/17 reflects the different molar weights of OH and H₂O.

By a least-squares fit over all data points for $T_f=1100^\circ\text{C}$ exclusively, we obtain

$$\chi = 0.836 [0.739, 0.933] \quad (3)$$

with the 95%-Confidence Interval in brackets. The dependency given by this value is indicated in Fig. 1 as the dash-dotted line. In our former papers [2-4,9] we used the value of $\chi=0.84$ as was obtained simply as the average of the 3 values given in [8].

From the definition of the density as the quotient of mass $m=m_{\text{glass}}+m_w$ and volume V , $\rho=m/V$, it follows for the volume swelling strain ε_v

$$V = \frac{m}{\rho} \Rightarrow \varepsilon_v = \frac{\Delta V}{V} = \frac{\Delta m}{m} - \frac{\Delta\rho}{\rho} \quad (4)$$

Since only the water content m_w can change during water soaking, the mass change is

$$\Delta m = m_w = C_w m \quad (5)$$

for $m_w \ll m_{\text{glass}}$, and the volume swelling strain ε_v simply results from eqs.(2-5) as

$$\varepsilon_v = (1 + \chi) C_w \quad (6a)$$

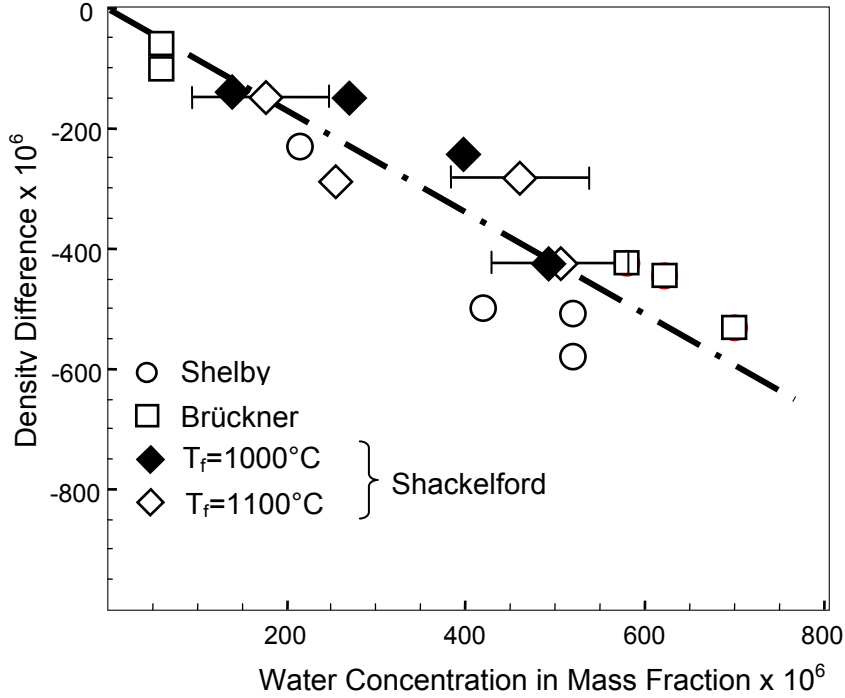


Fig. 1 Effect of water concentration on density of vitreous silica, results by Shelby [8], Brückner [5, 6], and Shackelford [7]. The dash-dotted line represents the value given in (3). The open symbols are for a fictive temperature of $T_f=1100^\circ\text{C}$ and the black symbols for $T_f=1000^\circ\text{C}$.

In the following, let us consider the case of swelling behavior for both the $\equiv\text{SiOH}$ and the molecular water that is present at low temperatures $<500^\circ\text{C}$. The total swelling strain ε_v is then composed of the individual contributions of the hydroxyl, ε_s , and the molecular water, ε_c , according to a molar “rule of mixture”:

$$\varepsilon_v = \frac{S/2}{C+S/2} \varepsilon_s + \frac{C}{C+S/2} \varepsilon_c \quad (6b)$$

So far, no reliable information on volume change is available for the strain ε_c by the molecular water species. We believe that the molecular water in the glass is located in molecular size holes in the silica glass network [10,9], where the water may not contribute to the volume change, i.e. we *assume* in the following considerations that $\varepsilon_c=0$. On the other hand, it is well known that molecular water at high temperatures of 1100°C is nearly absent. Under these circumstances, the volume swelling in [5-8] is due to hydroxyl generation by the water/silica-reaction, i.e. $\varepsilon_v=\varepsilon_s$. This may be con-

firmed and if necessary improved by future experiments of Molecular Dynamic (MD) computations.

In general C_w has to be converted to mole fraction of water, $x_{\text{H}_2\text{O}}$, in the glass via

$$x_{\text{H}_2\text{O}} = \frac{M_{\text{glass}}}{M_w} C_w = (60/18)C_w \quad (7)$$

Here we used the molar mass for water $M_w = 18\text{g/mole}$ and as an approximation $M_{\text{glass}} = 60\text{g/mole}$ for the molecular weight of the glass. For every water molecule that reacts with the glass, two SiOH are formed, therefore:

$$x_{\text{SiOH}} = 2x_{\text{H}_2\text{O}} \quad (8)$$

Combining (7) and (8) yields

$$x_{\text{SiOH}} = 2 \frac{60}{18} C_w \quad (9)$$

By assumption, the volume expansion is just due to the $\equiv\text{SiOH}$ formation.

The hydroxyl *mass concentration* S is

$$S = x_{\text{SiOH}} \frac{M_{\text{SiOH}}}{M_{\text{glass}}} = x_{\text{SiOH}} \frac{17}{60} \quad (10)$$

with molar mass of S , $M_{\text{SiOH}} = 17\text{ g/mole}$. Consequently, the volume swelling strain in terms of the water concentration C_w is

$$\varepsilon_v = (1 + \chi) C_w = 1.836 \times C_w \quad [1.739 \times C_w, 1.933 \times C_w] \quad (11)$$

Here it should be emphasized once more that this dependency holds for *small* water concentrations. This relation reads in terms of hydroxyl mass concentration S [1]:

$$\varepsilon_v = \frac{18}{17} (1 + \chi) \frac{S}{2} = \kappa \times S \quad (12)$$

Then

$$\kappa = 0.97 \quad [0.92, 1.02] \quad (13)$$

In (13) the numbers in brackets represent the 95% confidence interval. The value of $\kappa = 0.97$ is recommended to be used for “best” prediction, the lower boundary value of the CI, $\kappa = 0.92$, for “conservative” predictions. Our coefficient used so far [9], $\kappa = 0.92$, is located at the lower boundary of the 95%-CI.

The data by Shackelford for $T_f=1000^\circ\text{C}$ represented by the black solid symbols fit very well to the data for $T_f=1100^\circ\text{C}$. Therefore, we included these data in the analysis with the result of

$$\kappa = 0.965 [0.916, 1.014] \quad (14)$$

that is practically identical with the value of (13). To our actual knowledge we suggest use of $\kappa=0.97$.

2 Additional density results included

2.1 Results by Shackelford at $T_f=1200^\circ\text{C}$

Additional results for a fictive temperature of $T_f=1200^\circ\text{C}$ were reported by Shackelford [7]. These data are introduced in Fig. 2 by the red symbols. Including all the data for the fictive temperatures $T_f=1000^\circ\text{C}$, 1100°C , and 1200°C in the regression analysis gives

$$\kappa = 0.92 [0.86, 0.984] \quad (14a)$$

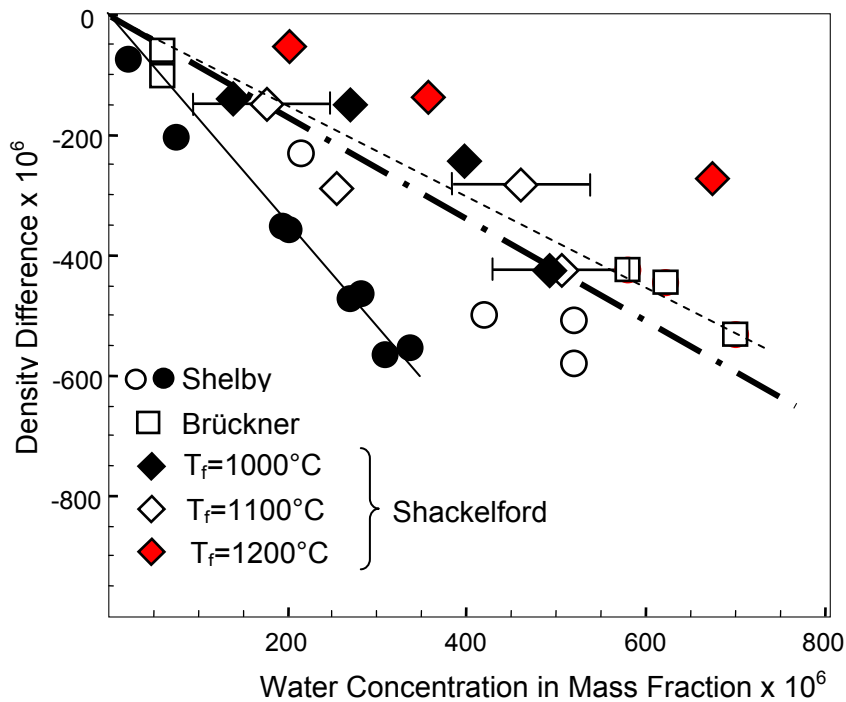


Fig. 2 Results from Fig. 1 plotted together with data from Shackelford [7] for a fictive temperature of $T_f=1200^\circ\text{C}$ (red symbols) and results by Shelby [8] with the water produced in silica saturated with hydrogen and then gamma-irradiated.

2.2 Results by Shelby on hydrogen infiltrated and gamma-irradiated silica

Shelby [8] generated water in the glass on a further way. He saturated the glass with hydrogen H_2 under gas pressures up to 70 kPa. The specimens were then gamma-

irradiated to doses of 1 to 15 Grads. In this way, SiOH was directly produced in the bulk material. The resulting density reduction by this procedure is shown in Fig. 2 by the solid circles. These results do strongly deviate by roughly a factor of two from all the other data. The regression analysis for this data gives

$$\frac{\Delta\rho}{\rho} = -\chi C_w, \quad \chi = 1.735 [1.60, 1.87] \quad (15)$$

For the computation of the volume strain it has to be taken into account that the resulting water has not been introduced from the environment, but was generated in situ with the oxygens taken from the SiO₂ network.

Unfortunately it is not clearly visible in [8] whether the initial density was measured before or after saturation by hydrogen. Therefore, we will perform two different evaluations:

Assumption 1: The initial density was measured *before* hydrogen infiltration. Consequently, the mass change is $\frac{2}{18} C_w$ since 2 hydrogen atoms were needed for each water molecule.

$$\Delta m = \frac{1}{9} C_w m \quad (16)$$

In this case, the volume strain results as

$$\varepsilon_v = \left(\frac{1}{9} + \chi\right) C_w \quad (17)$$

and according to (12) we obtain

$$\varepsilon_v = \frac{18}{17} \left(\frac{1}{9} + \chi\right) \frac{S}{2} = \kappa \times S \quad (18)$$

Introducing the result of eq.(15) yields

$$\kappa = 0.977 [0.906, 1.049] \quad (19)$$

Assumption 2: The initial density was measured *after* the hydrogen infiltration. In this case it is simply $\Delta m=0$ or $m_w = -m_{\text{glass}}$ and

$$\varepsilon_v = \frac{18}{17} \chi \frac{S}{2} = \kappa \times S \quad (20)$$

From this it yields

$$\kappa = 0.92 [0.847, 0.99] \quad (21)$$

Within the 95%-confidence intervals, also the results of (19) and (21) are in reasonable agreement with the results from heat-treated specimens.

Finally, the volume increase ε_v is plotted in Fig. 3a as a function of the water concentration C_w and in Fig. 3b versus the hydroxyl concentration S for all measurements in Fig. 2. The symbols in Fig. 3 are the same as given in Fig. 2. The straight line, introduced in Fig. 3b, represents the coefficient $\kappa=0.97$ according to (13). The good agreement with all the data is evident.

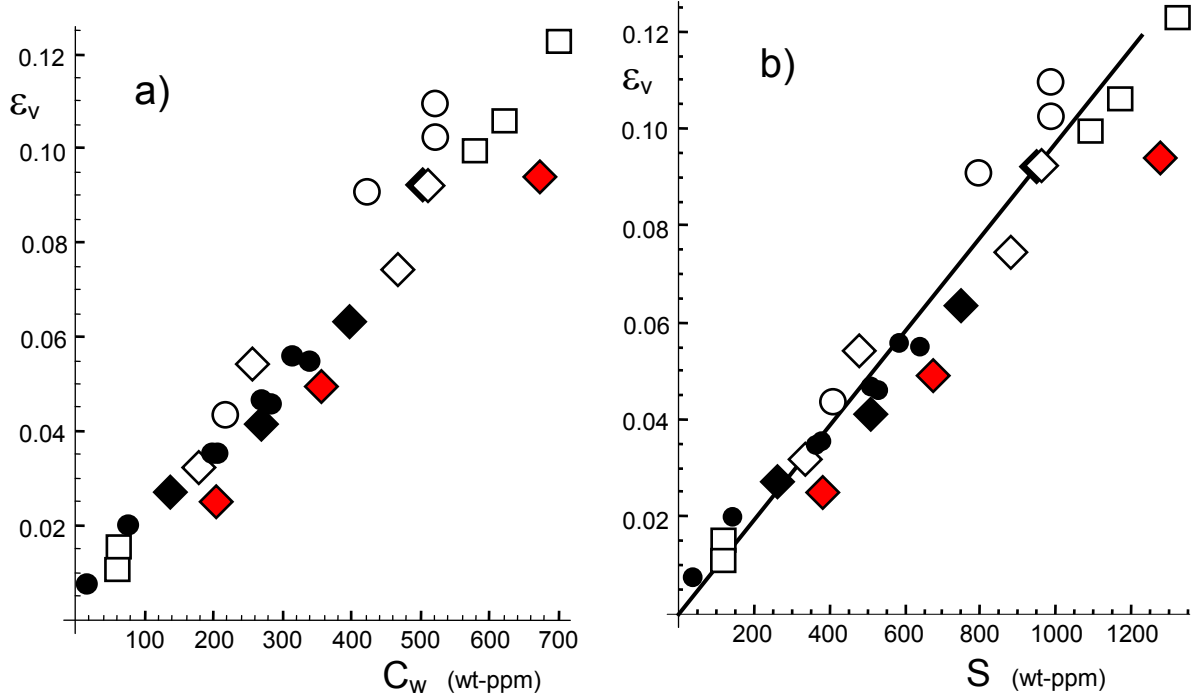


Fig. 3 a) Volume expansion strain vs. the water concentration, b) expansion vs. hydroxyl concentration S , (symbols as in Fig. 2), line: eqs.(20) and (21).

3. Application to molar volume \bar{V}_S

In calculating the reaction volume $\Delta\bar{V}$ from Shelby's data [8], we use eq.(12) to represent the volume expansion of silica with the addition of water to the glass. The molar volume of water-free silica glass is

$$V_0 = \frac{M_{glass}}{\rho_{glass}} = \frac{60 \text{ g / mole}}{2.2 \text{ g / cm}^3} = 27.27 \text{ cm}^3 / \text{mole} \quad (22)$$

($\rho_{glass}=2.2 \text{ g/cm}^3$).

The derivative $\partial V / \partial x_{SiOH}$ will give the partial molar volume of SiOH and this can be used to estimate the molar volume of the reaction.

$$\bar{V}_S = \partial V / \partial x_{SiOH} = 1.836 \times 4.09 = 7.51 \text{ cm}^3 / \text{mole} [7.11, 7.91] \quad (23)$$

For the silica/water reaction, eq.(1), the equilibrium constant is at high temperatures $\geq 500^{\circ}\text{C}$

$$K = \frac{S^2}{C} \quad (24)$$

This equation assumes a constant glass concentration $[\text{SiO}_2]=1$ that is correct for low water concentrations. At high S -concentrations, expected for instance at crack tips, a decrease of the glass-content has to be taken into account. By assumption, the volume expansion is just due to the $\equiv\text{SiOH}$ formation. Therefore, for every mole of water reacting with the glass, two moles of SiOH are formed; therefore, the molar volume of the reaction is

$$\Delta\bar{V} = 2\bar{V}_s = 15.03 \text{ cm}^3/\text{mole} \quad [14.22,15.8] \quad (25)$$

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