Water diffusion in cracked surface layers
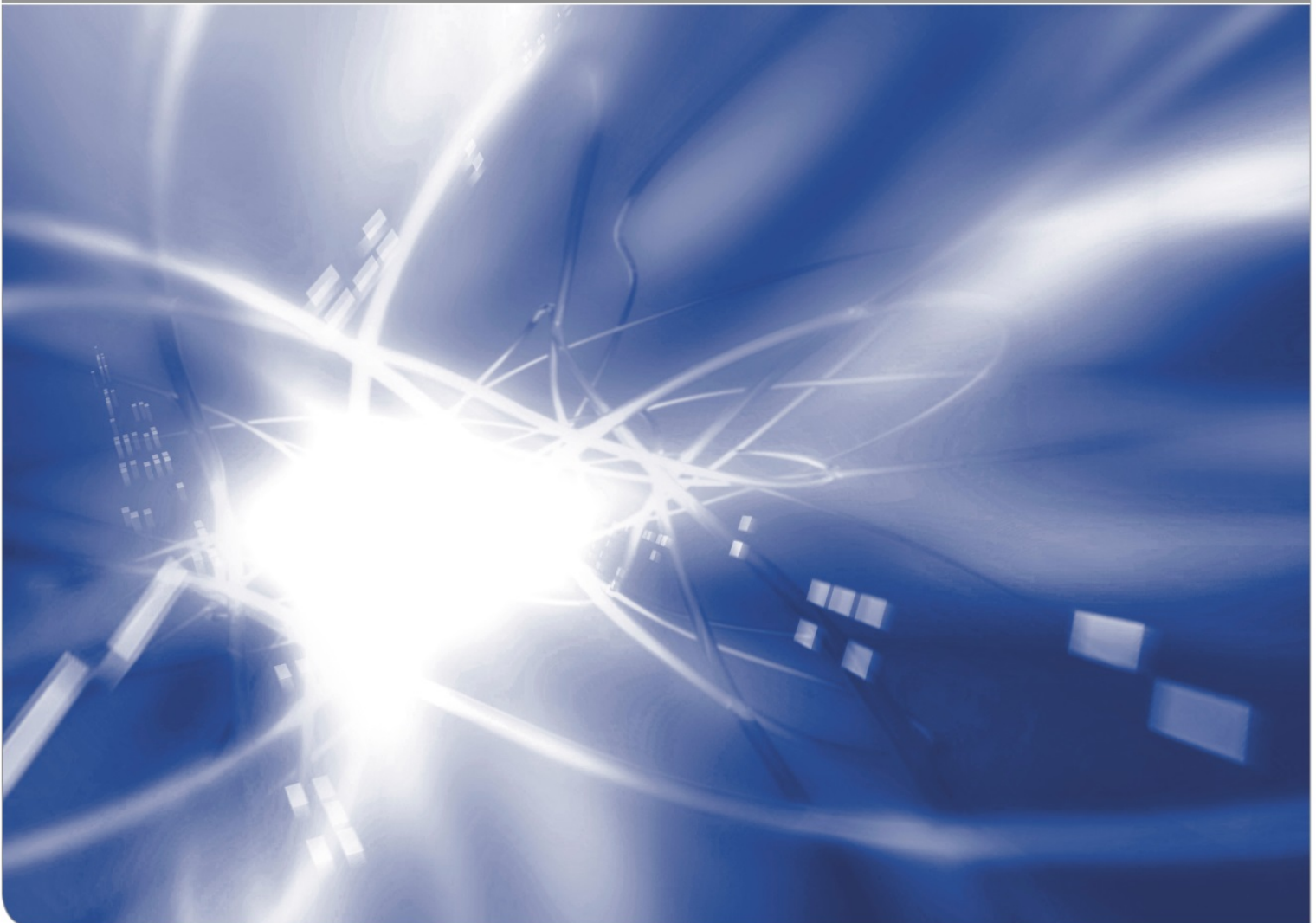
-Unloaded cracks

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Abstract

Water diffusion at the surface of a silica glass is increased when surface cracks are present which were inadvertently introduced by the surface treatment of samples. Due to the larger true surface exposed to the humid environment, an apparently increased diffusion constant must occur. With the help of a simple model the influence of the cracks for small water penetration depths is described. Simplified approximations are given which allow a continuous interpolation of two limit solutions over greater penetration depths or diffusion times.

In the present report we restrict our considerations on *unloaded* cracks.

Contents

1 Effect of surface cracks on the diffusion profile

1.1 Crack modelling

In ground silica surfaces cracks are present even in the case of finishing by mechanical polishing or chemical etching. This has been outlined by Suratwala et al. [1]. Such a surface state is schematically shown in Fig. 1a in side- and front view. The individual distributions of the depths a and the widths L are approximated in [1] by exponential distribution function.

For a simple explanation of the effect of such cracks on diffusion, let us replace the distributions of a and L periodically arranged cracks, Fig. 1c, of average crack surface

$$S = 2\langle a \times L \rangle \tag{1}$$

in the surface element of length A and width B, where the factor 2 counts for two crack faces of each crack.
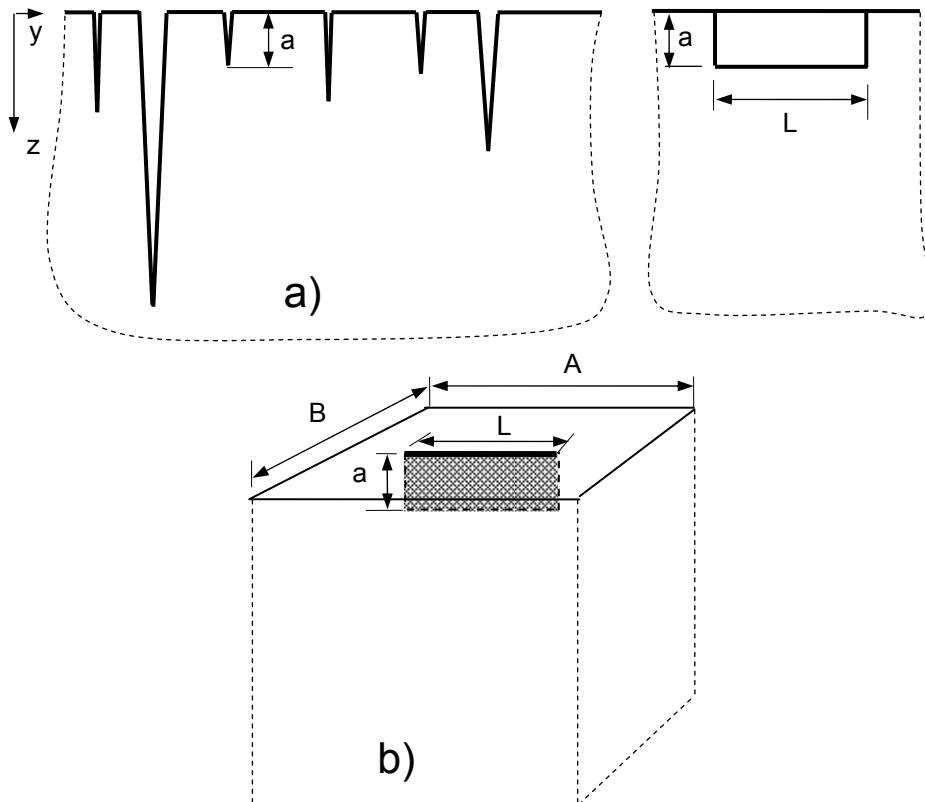

Fig. 1 a) Surface cracks due to surface treatment, front and side view, b) cracks of a) replaced by a periodical element with surface area $A \times B$ containing a single crack of mean crack surface S.

1.2 Diffusion profiles

When the "unit cell" in Fig. 1b is exposed to a humid environment, water can diffuse into the whole surface given by the original surface area $A \times B$ and the crack surface S,

$A{\times}B{+}S$, shown in Fig. 3a. The concentration of the water below the original surface, $C(z)$, is given by the complementary error function

$$C(z) = C_0 \operatorname{erfc}\left[\frac{z}{2b}\right] \tag{2}$$

with the concentration C_0 at the surface. The depth b, the diffusion length, at which the concentration decreased to 50%, depends on diffusivity D and time t via

$$b = \sqrt{Dt} \tag{3}$$

The water profile normal to the crack faces is the same with y instead of z in eq.(2). Deviations occur in the crack-tip region. In a FE-study [2], the diffusion problem for water-soaked specimens was solved.
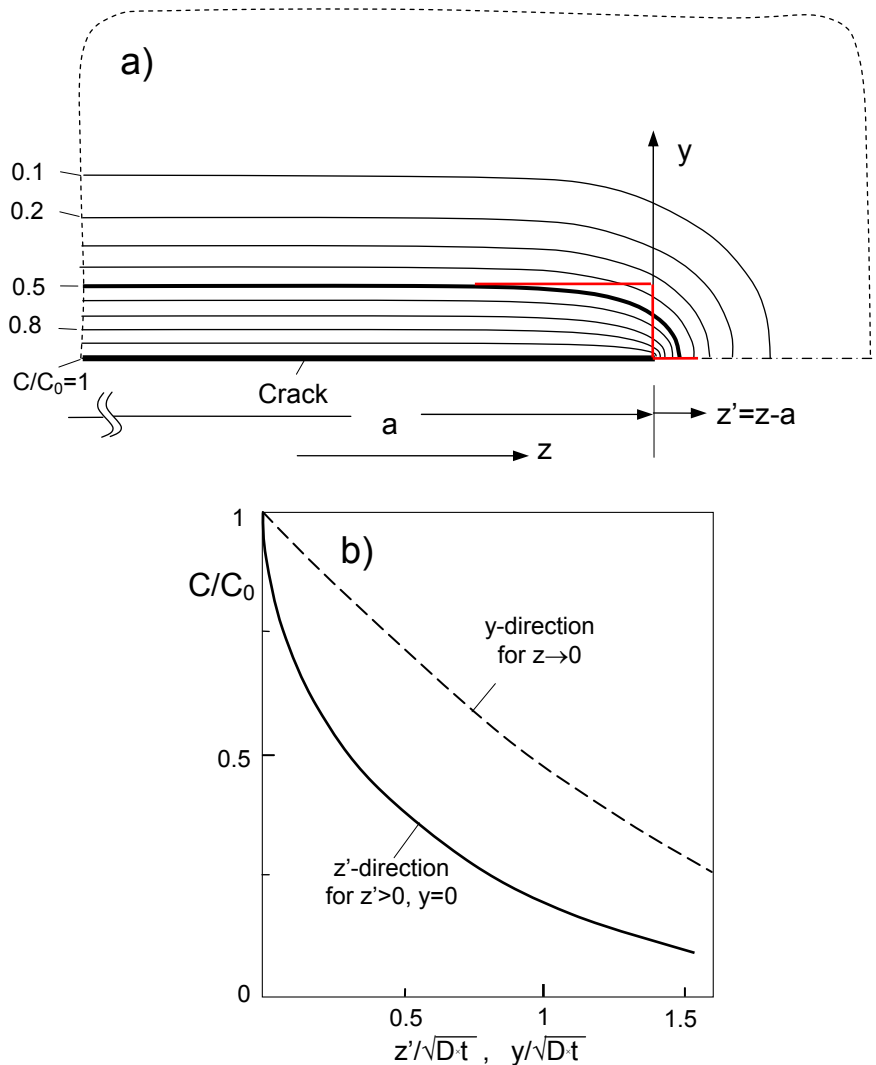
Fig. 2 Water diffusion through crack surfaces of a semi-infinite crack, a) contour lines for constant water concentration, b) concentration profiles in length and height directions.

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The water concentration contours are shown in Fig. 2a. It can be seen that the zone size ahead of the tip is reduced. In contrast to the profiles by eq.(2), there is also a height reduction visible near the tip.

Figure 2b gives the concentration profiles for the z-direction ahead of the crack tip and the profile by eq.(2) for larger distances behind the tip region. For reasons of simplicity we approximate the water distribution in the diffusion zone by a layer of thickness b and a constant water concentration C_0 as indicated by Fig. 2b. Near the crack tip, the missing water in y-direction is balanced by the water ahead the tip, resulting for $C/C_0=0.5$ in the red step-shaped distribution in Fig. 2a.

Figure 3a illustrates the water distribution in the unit cell after a short time with $b \ll a$.
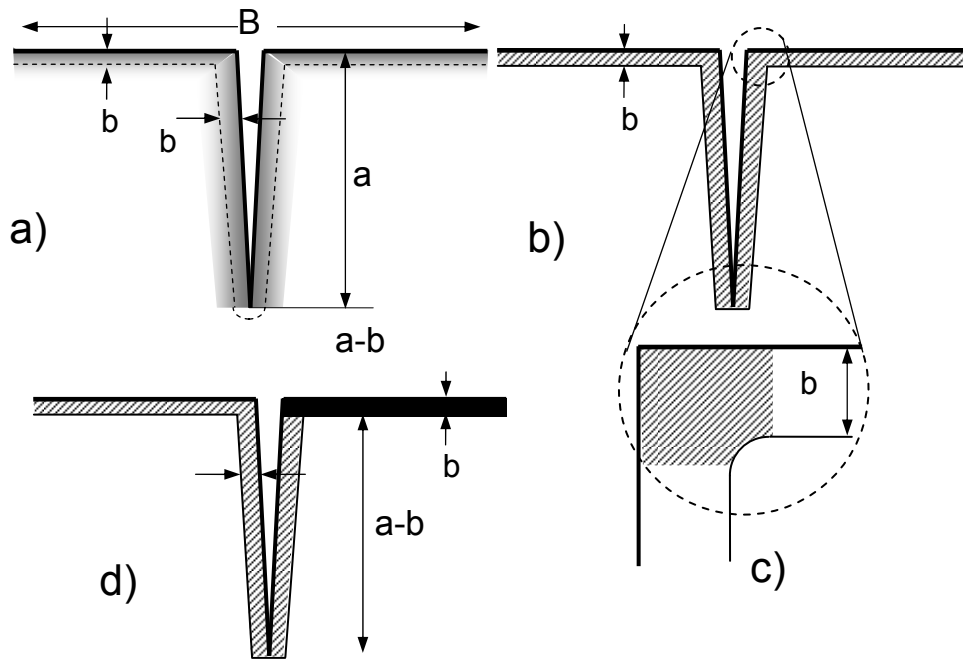

Fig. 3 Water diffusion into the crack surface containing a crack of depth a; a) water distribution for short times with diffusion zone $b \ll a$, b) water diffusion zone according to eq.(2) replaced by a zone of thickness b and constant concentration showing the same amount of water, c) interacting diffusion profiles near the crack mouth (schematic), d) separation of overlapping diffusion profiles.

The amount of water, penetrated into the glass is then approximated by a constant concentration of $C=C_0$ in a layer of thickness b, Fig. 3b. For very short times, the profiles from the surface and from the crack faces interact only at the crack mouth, Fig. 3c. As long as this region is small, i.e. for $b \ll a$, it holds for the total amount of water in the unit cell

$$m_C \cong C_0 b \left[AB + 2La \right] \qquad (4)$$

In terms of an apparent layer thickness b_{app} for very short time $t \to 0$, eq.(4) reads

$$b_{app,0} = b_{app,t\to0} = b\left(1 + \frac{<S>}{AB}\right) \tag{5}$$

For a not too large layer thicknesses, let say $b < 1/3\ \text{Min}(a, B/2)$, the moderate diffusion interactions may be separated in diffusion layers from the specimen surface over the whole width B and from the crack surface over the reduced distance of a-b as illustrated in Fig. 3d. In this case we obtain

$$b_{app} \cong b\left(1 + \frac{2L}{AB}(a-b)\right) = b\left(1 + \frac{<S>}{AB}(1 - b/a)\right) \tag{6}$$
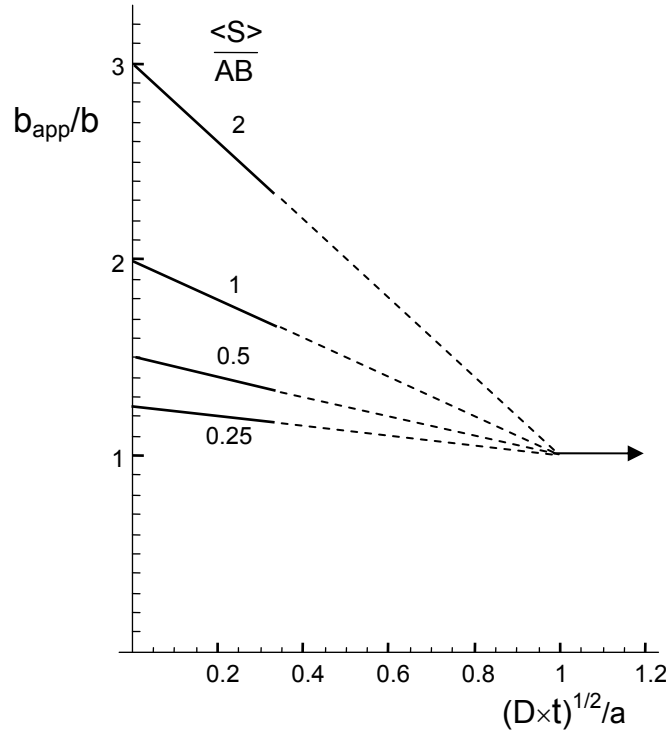
This dependency is shown in Fig. 4.

Fig. 4 Apparent diffusion layer thickness b_{app} as a function of time.

2. Apparent diffusivity

Equations (5) and (6) allow the determination of an apparent diffusivity D_{app}, defined via

$$b_{app} \overset{def}{=} \sqrt{D_{app}\, t} \tag{7}$$

This diffusivity is for $b < 1/3 \times \text{Min}(a, B/2)$

$$D_{app} \cong D\left(1 + \frac{<S>}{AB}\left(1 - \frac{\sqrt{Dt}}{a}\right)\right)^2 \tag{8}$$

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Two limit cases can be identified. For very short times, it results from eq.(8)

$$D_{app,0} = D_{app,t \to 0} = D\left(1 + \frac{<S>}{AB}\right)^2 \qquad (9)$$

For long times t and thick zones b, the limit diffusivity is trivially

$$D_{app,\infty} = D_{app,t \to \infty} = D \qquad (10)$$

Equation (8) makes clear that the apparent diffusivity resulting from measurements depends on time as is plotted in the representation of Fig. 5.
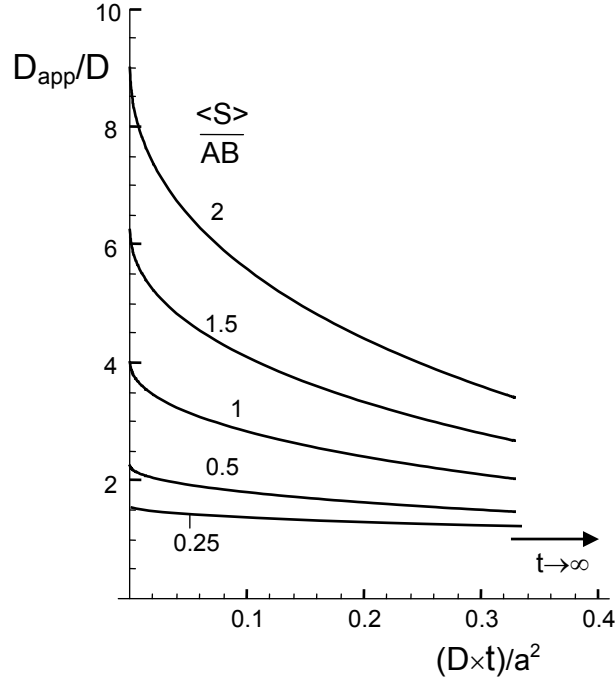

Fig. 5 Apparent diffusivity D_{app} as a function of time for several ratios of crack surface $<S>$ to specimen surface $A \times B$, arrow indicates the asymptotically reached diffusivity $D_{app} \to \infty$.

3. Interpolation of limit case solutions

Having in mind that the crack sizes and distances are continuously distributed [1], the results from Section 2 may be "smoothed" and expressed by interpolation relations. Usual descriptions by exponential functions result in our case in

$$b_{app} \cong b\left(1 + \frac{<S>}{AB} \exp(-b/a)\right) \qquad (11)$$

or

$$b_{app} \cong b\left(1 + \frac{<S>}{AB}(1 - \tanh(b/a))\right) \qquad (12)$$

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Figure 6a shows these interpolations for the case of $<S>/(AB)=2$. The straight lines are again the limit solutions for $t \to 0$ and $t \to \infty$. The dashed curve represents eq.(11) and the solid curve eq.(12). Use of (12) is recommended. Figure 6b shows the interpolations for different parameters $<S>/(AB)$. Finally, Fig. 6c gives the apparent diffusivity from eq.(12) as

$$D_{app} \cong b\left(1 + \frac{<S>}{AB}(1 - \tanh(\sqrt{Dt}/a))\right)^2 \qquad (13)$$
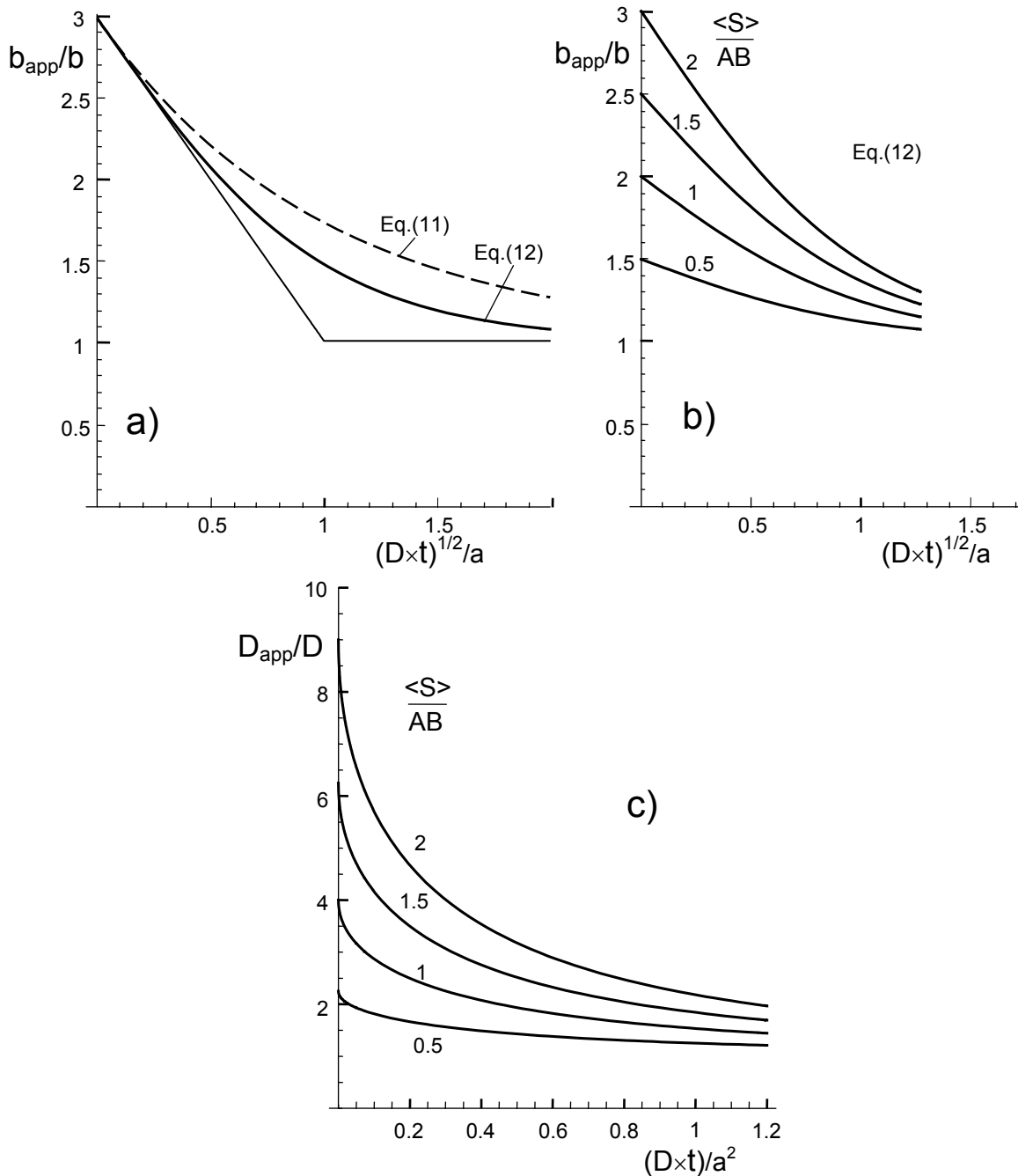

Fig. 6 a) Interpolation of limit solutions according to eqs.(11) and (12), b) interpolations for different crack parameters, c) related apparent diffusivities.

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4. Comparison with experimental results

Results of the diffusivity as a function of time are available in the literature. Profiles of time-dependent residual water content by stepwise surface removal were measured by Davis and Tomozawa [3] under water vapour pressure of 355mm Hg at 350°C. The results, Fig. 7a, showed reduced diffusion depths with increasing soaking time. This result is plotted again in Fig. 7b in terms of an effective diffusivity D_{eff} (red circles).
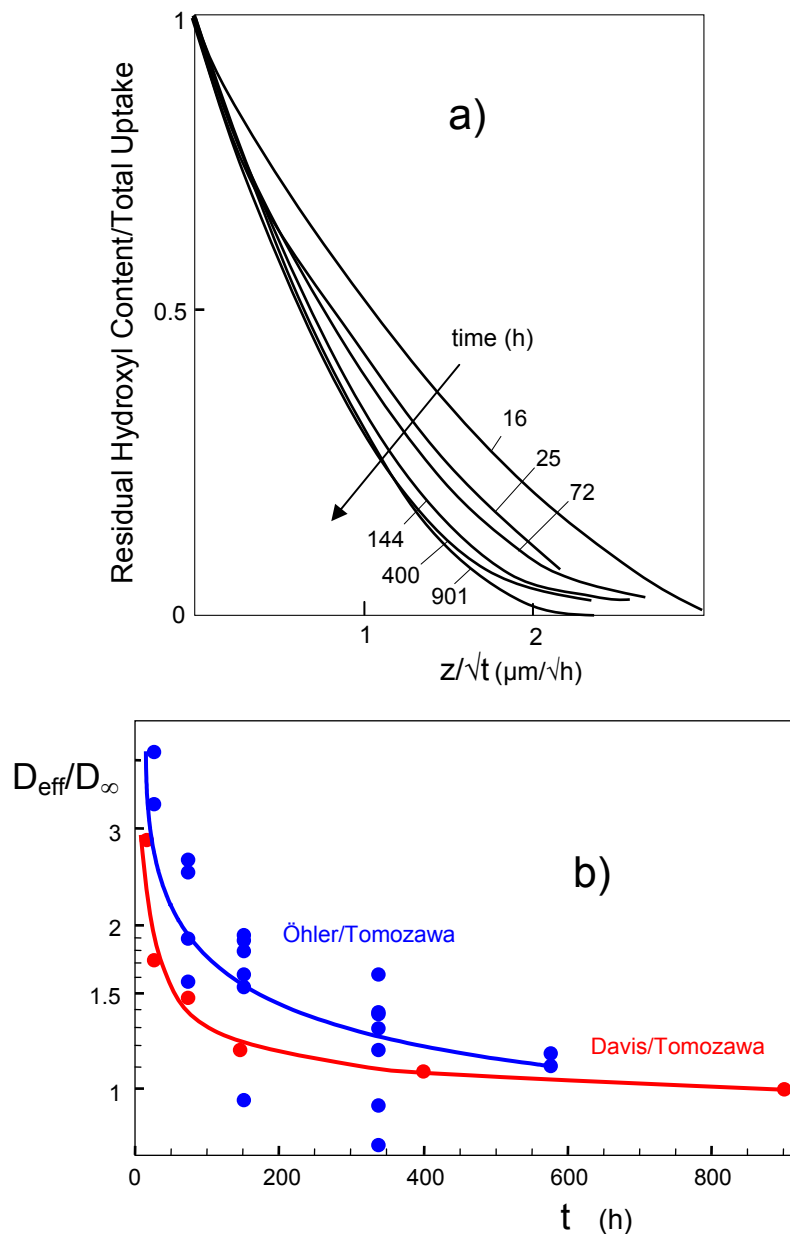

Fig. 7 a) Profiles of residual water content during stepwise surface removal by Davis and Tomozawa [3], b) effective diffusivities by Davis and Tomozawa [3] (red circles) and by Oehler and Tomozawa [4] at 250°C and 39 bar water vapour pressure (blue circles).

Measurements of effective diffusivities by Oehler and Tomozawa [4] at 250°C and 39 bar water vapour pressure are introduced by the blue circles. In both cases a clear decrease with time is evident. This effect was discussed in [5] in terms of swelling stresses. In the case of the results by Davis and Tomozawa [3] it has to be considered that under the rather low vapour pressure swelling stresses are not very high. As Fig. 6c shows, the curves in Fig. 7a may also be interpreted as the consequence of surface cracks. That will partially hold for the results in [4], too.

References

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