WATER ABSORPTION BY CORK

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ABSTRACT

A study of liquid water absorption by cork was carried out in which the anisotropy of cork was taken into account. The changes with time of the mass, volume, and linear dimensions were measured for different orientations of the sections in cork exposed to liquid water at room temperature (20 C) and at 90–100 C. Two regimes of water absorption were identified, namely, a period involving dimensional change and a period with only mass change. Diffusion coefficients at both temperatures were estimated using a special technique. There is a small anisotropy with a faster diffusion in the radial direction. Diffusion coefficients at 90 C are two orders of magnitude larger than at room temperature. Water absorption in the cell walls causes the expansion of cork, which (for the boiled specimens tested) is slightly smaller in the radial direction. The volume increase is proportional to the mass increase and ceases after relatively short immersion times. At this stage, the cell walls are apparently saturated with water. Further immersion results in penetration of water into the cells. The kinetics of absorption is rather slow at long times, but eventually the cells become full of water, the density increases above that of water, and the cork sinks.

Keywords: Cork, water absorption, dimensional change, diffusion.

INTRODUCTION

The characterization of water absorption by cork is of importance to many of its applications, as cork and cork products are frequently exposed to water and other liquids. Boards of reproduction cork (cork used for stoppers) are submitted, before industrial processing, to a boiling operation, which consists of immersion in boiling water for approximately one hour, followed by open air drying (Rosa et al. 1990). Cork stoppers are cut from boiled corkboards. In stoppers and when cork is used in floor covering and wall decoration, it is exposed to liquids, sometimes for long periods (e.g., in stoppers).

Among the exceptional properties of cork, its chemical stability and impermeability to liquids are often mentioned. Nevertheless, a quantitative study of water absorption by cork, which takes into account its anisotropy, has been lacking. This paper contains such a study.

The cellular structure of cork is well known (Gibson et al. 1981; Pereira et al. 1987; Rosa et al. 1990). The cells are rectangular prisms, packed base-to-base in columns parallel to the radial direction (see schematic diagram in Fig. 1). The cells in adjacent columns have their bases staggered. The cells are closed and hollow, probably containing air. Differences in dimensions occur in the same corkboard, between spring and autumn cells, the former being longer and having thinner walls. The spring cells are much more abundant than the autumn cells. Values of the cell height range be-

tween 10–30 μm and of the wall thickness be-
tween 1.5–3 μm. The average width of the
lateral cell walls is typically 10 μm. Because
the lateral cell walls (parallel to the radial di-
rection) are randomly oriented, cork is ap-
proximately a transversally isotropic material,
implying that all directions perpendicular to
the radial direction (including the axial and
tangential directions) are nearly equivalent.
Cork always contains lenticular channels (usu-
ally referred to as pores) which run parallel to
the radial direction, and therefore do not de-
stroy the cylindrical symmetry of this direc-
tion. The pores are usually hollow, but some
contain a powdery substance of unknown
chemical composition. The volume fraction of
pores varies considerably with cork type (be-
tween 5% and 30%) and is closely related to
its industrial quality.

The cell walls in cork are formed by various
lamellae symmetrically placed on each side of
a primary wall. The thickest lamella is the sec-
ondary wall, which is rich in suberin and waxes
(Sitte 1962). In addition to these constituents,
cork also contains cellulose and hemicellu-
loses, lignin and tannins (Pereira 1988). Su-
berin accounts for approximately 40% by
weight and is thought to be responsible for the
low permeability of the walls. Except for the
middle lamella, none of the cell-wall lamellae
in adjacent cells are connected, implying that
there is no continuous path for diffusion along
them.

The anisotropy of the cellular structure of
cork implies that properties such as diffusion
rates are also anisotropic. It is then necessary
to measure diffusion in the three principal di-
rections (radial, axial, and tangential; see Fig.
1), although, as explained above, the axial and
tangential directions are expected to behave
similarly. In this project, diffusion rates were
measured for the three principal directions at
room temperature and at 90–100 C. Water ab-
sorption causes dimensional changes in cork
and these were also measured. Most experi-
ments were carried out with good quality cork,
used for cork stoppers. In order to assess the
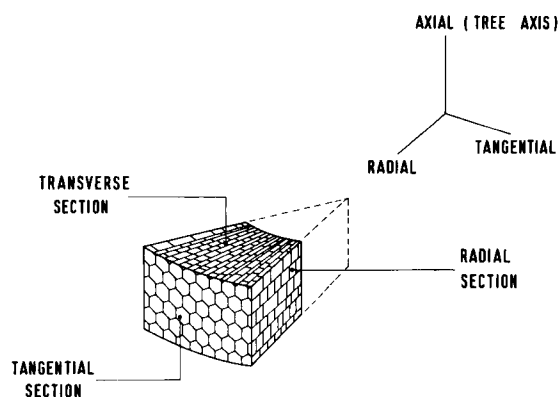effect of cork quality on water absorption, a

FIG. 1. Schematic representation of the cellular struc-
ture of cork, with indication of the nomenclature of di-
rections and sections. The cells are drawn as hexagonal
prisms, which is their average shape.

number of experiments were also done with
poor quality cork.

EXPERIMENTAL

The good quality cork used in most exper-
iments had previously been submitted to an
industrial boiling operation. The average den-
sity, measured after drying in an oven at 100
C to constant mass, was 150 kg m^{-3}. The esti-
mated volume fraction of pores in this cork
was 6%. The moisture content of the samples
after equilibration in the laboratory atmo-
sphere was 5%.

The absorption experiments were undertak-
en at two water temperatures: room temper-
ature (20 C) and 90–100 C. Two types of ex-
periments were conducted. In the first type,
which we term full-immersion experiments,
dried cork specimens were immersed in liquid
water, and dimensional and mass changes were
measured as a function of time. The specimens
used in the immersion experiments were of
two geometries: cubes and plates (slabs). The
edges parallel to each of the principal direc-
tions were identified in all specimens (cubes
and plates). The cubes (20 mm of edge) were
used essentially to measure the dimensional
changes due to water absorption. The plate
specimens had a thickness of 1 mm and 30
mm in the other dimensions. The large area
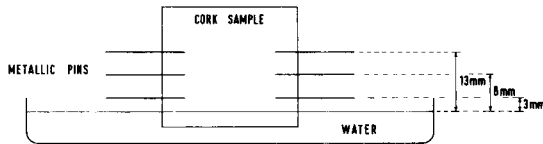surfaces were, in different specimens, parallel

FIG. 2. Experimental set-up used to measure diffusion coefficients of water in cork.

to each of the principal sections in cork, i.e., tangential, transverse, and radial (see Fig. 1), which are, respectively, perpendicular to the radial, axial, and tangential directions. Three specimens were tested in each case.

The specimens were periodically removed from water for measurement of the mass and linear dimensions. Before measurement, the specimens were gently touched with filter paper on their surface to remove attached water. Each linear dimension was measured at three different places in the specimens, and the average values were then used to calculate the volume change. After measurement, the specimens were re-immersed in water. Some of these experiments lasted for up to 1 year.

Full-immersion experiments were also done with cubes of a cork of higher porosity in order to assess the variability associated with cork quality in relation to water absorption. The dry average density and moisture content of this poorer quality cork were, respectively, 150 kg m^{-3} and 6%. The volume fraction of pores was around 10%.

A second type of experiment was carried out aimed at the determination of diffusion coefficients. In these experiments, cube specimens were only partly immersed in water in the way schematically shown in Fig. 2. Under these conditions, water diffuses into cork in the vertical direction, which was in different experiments parallel to a particular principal direction of cork. Pairs of metallic pins were placed at different levels in the specimen, and the electrical resistance between the pins in a pair was measured at various times. Two or more pairs of pins were in some cases placed at the same level but at different depths in a specimen. No wicking was detected. The resistance between a pair was found to drop strongly when water

reached the level of the pair. By measuring the time to the drop and the distance of the pair to the water level, it was possible to estimate diffusion coefficients. The direction of diffusion was varied to study anisotropy. The experiments were conducted at 20 C and 90 C (not 100 C because of experimental difficulties).

RESULTS

Results of full-immersion experiments

As already mentioned, most experiments were done with good quality cork. The results for this cork are indicated first. Those for the poorer quality cork are given at the end of this section.

Room temperature results. — In Fig. 3 the relative mass change $\Delta M/M_0$ as a function of time t, for plate specimens and for cube specimens is plotted. ΔM is the mass increase and M_0 the initial dry mass. The curves are average curves for the three specimens tested in each case. The absorption in the radial direction, i.e., for the tangential plates (curve R in Fig. 3), is faster than that for the other principal directions (curves T and A), i.e., for plates cut parallel to the radial direction. There is also evidence that absorption in the axial direction (A) is slightly faster than in tangential direction (T). The absorption curves for the cubes are below those for the plate specimens, which can be attributed to the lower specific area of the cubes. The plate specimens were found to sink after approximately 1 year. The measurements with the cubes were not carried out for such long times.

Figure 4 shows the relative volume change $\Delta V/V_0$ and the relative linear dimensional changes $\Delta L/L_0$ along the three principal directions of cork, as a function of time, for cube specimens. The conclusion is that the expansion of cork due to water absorption is far from being isotropic. The expansion in the radial direction is below the expansion in the other two directions, which behave similarly, although expansion is slightly larger in the axial direction. The volume stabilizes at values that
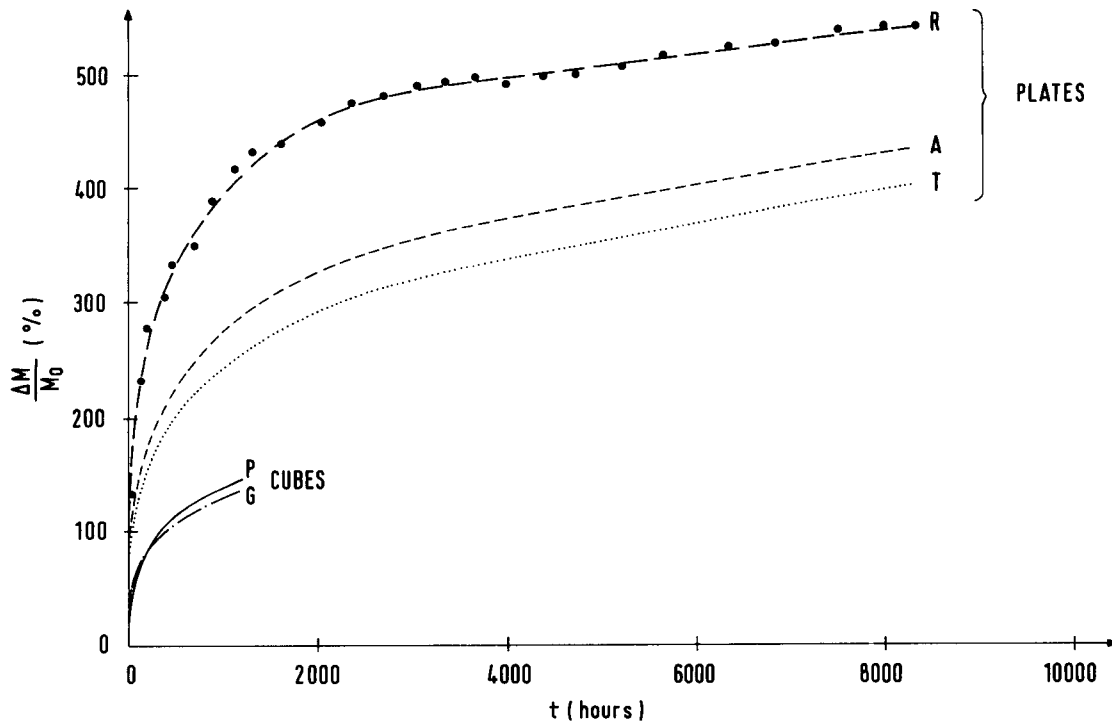
FIG. 3. Absorption curves, $\Delta M/M_0$ versus t, for plate specimens of good quality cork (three top curves) and for cube specimens (bottom curves) of good quality cork (G) and of poorer quality cork (P), immersed in water at room temperature. The direction of water movement through the plates is indicated: R—radial, A—axial, and T—tangential. Experimental points (average from 3 specimens) are indicated for the R-plate.

are indicated in Table 1, together with the corresponding times and mass changes. The standard deviation for the three specimens tested in each case is indicated in the table.

At the end of the immersion experiments at room temperature, the plate specimens were dried in an oven at 100 C to constant mass. The linear dimensional changes were measured, and the average values and standard deviations are indicated in Table 2. These re-

sults show that the final volume, after drying, is nearly the same as originally (reversibility) in the case of immersion at 20 C.

High temperature results. —Average absorption curves of plate specimens immersed in water at 100 C are shown in Fig. 5. The specimens immersed in water at 100 C were found to sink after relatively short times (~60 hours for the tangential plates and ~90 hours for the non-tangential plates). The relative dimen-

TABLE 1. *Maximum volume expansion ($\Delta V/V_0$), corresponding mass change ($\Delta M/M_0$) and time (t) to reach maximum dimensional change.*

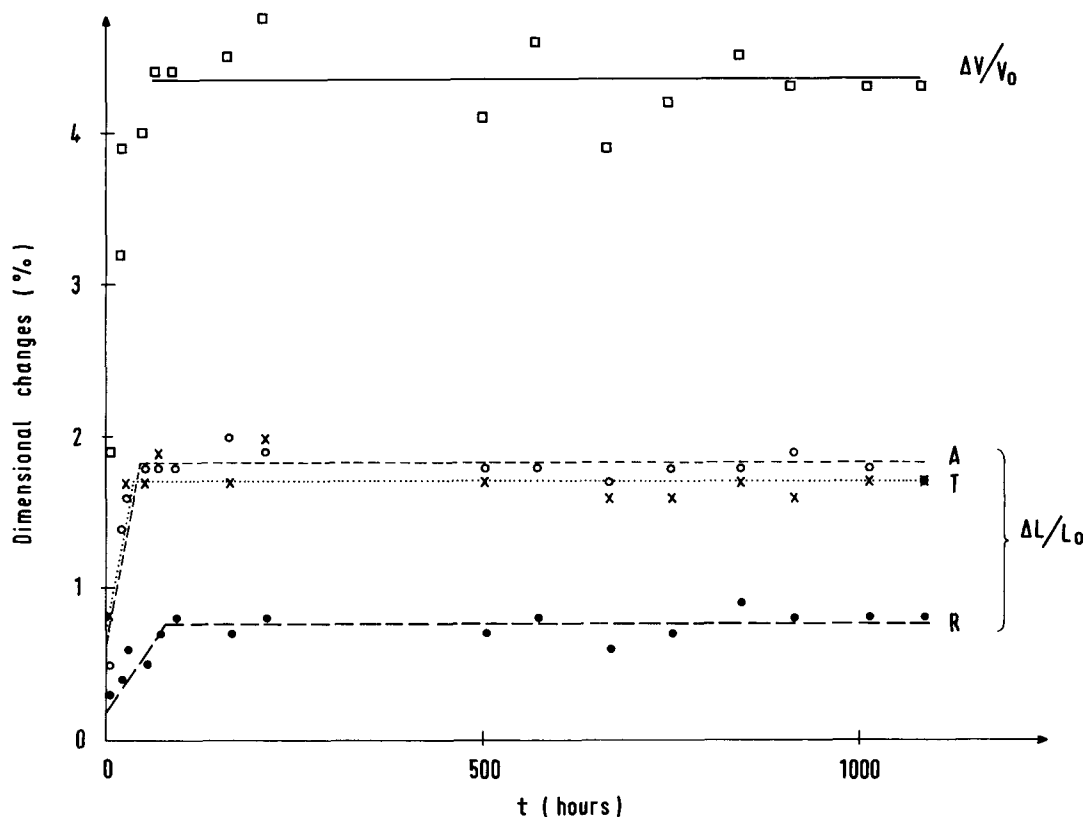| Cork quality	Water temperature (°C)	$\Delta V/V_0$ (%)	$\Delta M/M_0$ (%)	t (h)
Good	20	4.4 ± 0.3	58.2 ± 0.8	66 ± 10
	100	7.8 ± 1.2	200 ± 10	28 ± 2
Poor	20	6.0 ± 0.4	61.0 ± 1.0	120 ± 40
	100	14.8 ± 2.6	239 ± 13	33 ± 8

Fig. 4. Relative volume change $\Delta V/V_0$ and relative linear dimensional changes $\Delta L/L_0$ along the three principal directions of cork as a function of time t. R—radial, A—axial, and T—tangential.

sional changes with time show a variation that is similar to the changes at room temperature. The values at dimensional stabilization are given in Table 1. In Table 2 the dimensional and volume changes after drying in an oven at 100 C are indicated. The results in this table show that drying of cork with a high moisture content (~380%) causes large shrinkage, the final dimensions of the dried specimens being considerably smaller than the initial dimensions before immersion. A SEM photograph

of the tangential section of a specimen that was submitted to this treatment is shown in Fig. 6. The cork cell walls become heavily corrugated, due to shrinkage.

Other cork types.—Absorption curves obtained with cube specimens of a poorer quality cork are shown in Figs. 3 and 5, respectively, for room temperature and 100 C immersion. These results indicate that poorer quality cork tends to absorb a larger amount of water for the same time of exposure to water.

TABLE 2. *Dimensional ($\Delta L/L_0$) and volume changes ($\Delta V/V_0$) due to drying after water immersion.*

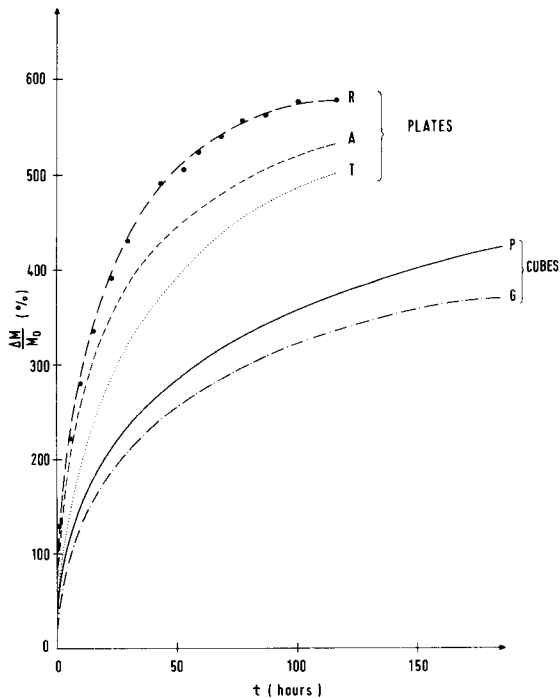| Cork quality	Water temperature (°C)	Immersion time (h)	$\Delta L/L_0$ (%)			$\Delta V/V_0$ (%)
			Radial	Axial	Tangential	
Good	20	~1,300	+0.3 ± 1.0	−0.2 ± 0.6	−0.4 ± 0.6	−0.4 ± 2
	100	~220	−8 ± 1	−10 ± 2	−14 ± 2	−29 ± 4
Poor	20	~1,300	+1 ± 1	+0.2 ± 0.7	−0.3 ± 0.6	1 ± 2
	100	~220	−5 ± 2	−10 ± 4	−15 ± 5	−27 ± 9

FIG. 5. Absorption curves, $\Delta M/M_0$ versus t, for plate specimens of good quality cork (three top curves) and cube specimens (bottom curves) of good quality cork (G) and of poorer quality cork (P), immersed in water at 100 C. The direction of water movement through the plates is indicated: R—radial, A—axial, and T—tangential. Experimental points (average from 3 specimens) are indicated for the R-plate.

FIG. 6. a) SEM image of the tangential section of cork dried after immersion in water at 100 C for a long time ($\simeq 220$ h). b) Idem, but before immersion.

The results of Table 1 show that, at room temperature, the volume expansion due to water absorption is similar for the two quality corks used in the experiments, but, at 100 C, the expansion is larger for the poorer quality cork.

After drying, the shrinkage is similar for the two cork types, as the results of Table 2 show.

Results of electrical resistance experiments

The electrical resistance between a pair of pins is abruptly reduced from the initial (virtually infinite) value to a measurable value. The times at which the drop occurs depend on the distance of the pins to the water level. For example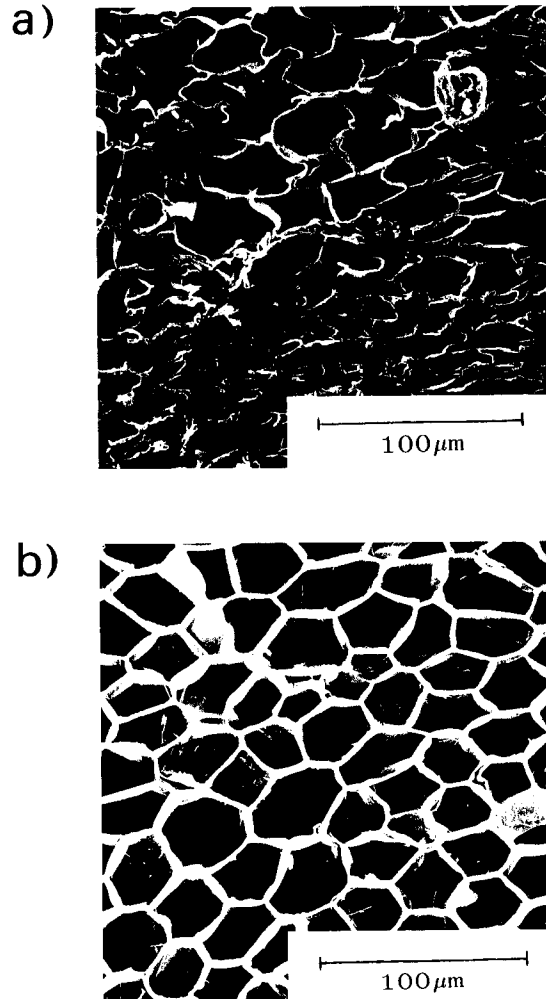, in one measurement at 20 C in the radial direction, the time was ~800 hours for pins at a distance of 8 mm from the water level. These experiments show that in general the water front is not planar, as would be the case if the material were homogeneous. In fact, when various pairs of pins are placed at the same level but at different depths, it is observed that the drop in resistance does not occur simultaneously, the differences in time amounting in some cases to 20%. Diffusion coefficients were estimated from the average times to reach successive levels, as will be discussed below.
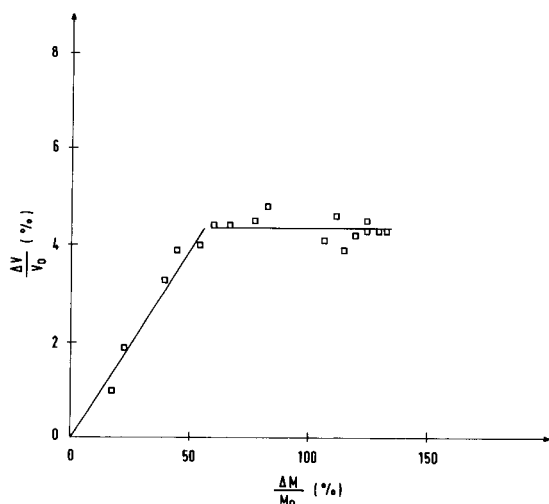
FIG. 7. Relative volume change $\Delta V/V_0$, due to water absorption at room temperature, as a function of relative mass change $\Delta M/M_0$, for good quality cork.

DISCUSSION

Dimensional changes

The results of Fig. 4 show that expansion in the radial direction is smaller than in the other two principal directions, which show comparable expansions. This is in contrast with the expansion produced in the boiling operation, which is larger in the radial direction (Rosa et al. 1990). In the case of wood, the expansion due to water absorption can be attributed (Bodig and Jayne 1982) to the occupation by the polar water molecules of empty space available in the cell walls. The fiber saturation point of wood is defined as the mass fraction of water required for saturation of the cell walls. Moisture changes below the fiber saturation point are always accompanied by dimensional changes. It is therefore likely that in cork stabilization of dimensions also corresponds to moisture saturation of the cell walls.

Figure 7 shows, for immersion in room temperature water, a plot of the volume change $\Delta V/V_0$ as a function of the mass change $\Delta M/M_0$ for good quality cork specimens. The variation is linear

$$\frac{\Delta V}{V_0} = k\frac{\Delta M}{M_0} \tag{1}$$

TABLE 3. *Values of the ratio k between volume and mass changes (Eq. 1).*

Cork quality	Water temperature (°C)	k
Good	20	0.08 ± 0.01
.	100	0.10 ± 0.05
Poor	20	0.11 ± 0.01
	100	0.10 ± 0.04

up to stabilization of dimensions. The values for the constant k are indicated in Table 3 and show that k is fairly independent of temperature and cork quality with an average value of 0.10.

Diffusion kinetics

The data obtained in the electrical resistance experiments can be used to estimate diffusion coefficients on the hypothesis (see below) that diffusion follows Fick's law. The diffusion coefficient D can be obtained from

$$x = \sqrt{\alpha Dt} \tag{2}$$

where x is the distance travelled by the water front in time t and α is a numerical factor of the order of unity that depends on the definition used to specify the water front, which is, of course, not sharp. The value $\alpha = 4/\pi$ results when the mass of water that enters through the surface of a semi-infinite specimen up to time t is taken as equal to the mass in a saturated layer of thickness x. Values of D can be calculated using Eq. (2) with $\alpha = 4/\pi$ from the time t at which the drop in resistance was detected in a pair of pins at a distance x from the water level. Average values of D for diffusion parallel (D_R) and perpendicular (D_{NR}) to the radial direction are given in Table 4, which also includes standard deviations. Diffusion coefficients at 90 C are about two orders of magnitude larger than those at room temperature. Assuming a unique thermally activated process responsible for diffusion, it is possible to obtain an activation energy around 62 kJ mol^{-1}. This value is comparable to that for polymeric materials (Woo and Piggott 1987). The scatter in the results does not allow

TABLE 4. *Diffusion coefficients (D) of water in a good quality cork. Diffusion parallel (R) and perpendicular (NR) to the radial direction.*

Water temperature (°C)	Electrical resistance experiments (m² s⁻¹)		Plate immersion experiments (m² s⁻¹)	
	R	NR	R	NR
20	$(1.9 \pm 0.2) \times 10^{-11}$	$(2.5 \pm 0.4) \times 10^{-11}$	$(1.2 \pm 0.4) \times 10^{-11}$	$(2.8 \pm 1.5) \times 10^{-12}$
90	$(2.9 \pm 0.7) \times 10^{-9}$	$(2.6 \pm 0.6) \times 10^{-9}$	—	—

drawing any conclusions on the anisotropy of diffusion. The two coefficients D_R and D_{NR} are not significantly different.

Further information on the diffusion coefficients can be derived by plotting $\Delta M/M_0$ obtained in the plate full-immersion experiments as a function of $t^{1/2}$. The plots are shown in Fig. 8 for the temperature of 20 C. There is an initial rapid increase, which can be attributed to water penetration in the open cells at the surface (an estimate, based on the volume of open cells per unit surface area, leads to a value of $\Delta M/M_0 \simeq 14\%$ due to this effect), followed by a fairly linear region. If water absorption at this stage is due mainly to diffusion, the linearity would indicate that Fick's law is followed. From the slope m of this linear region it is possible to obtain D from the equation (see, for example, Woo and Piggott 1987)

$$D = \frac{\pi}{16} m^2 h^2 \left(\frac{\Delta M}{M_0}\right)_s^{-2} \qquad (3)$$

provided $(\Delta M/M_0)_s$, the value of $\Delta M/M_0$ at cell-wall saturation, is known; h is the plate thickness. The value of $(\Delta M/M_0)_s$ can be taken at the stage when swelling ceases (see values in Table 1). It is apparent (see Fig. 8) that the slope m, and therefore D, are larger for radial diffusion. Using Eq. 3 we obtain values of D_R and D_{NR}, which are given in the 4th and 5th columns of Table 4, respectively. These values are consistent with those obtained in the electrical resistance experiments, but clearly show an anisotropy of the diffusion coefficient.

The faster diffusion in the radial direction can be due to a structural effect, in that for a given x (the displacement of the water front), the wall length traversed is smaller in the radial

direction, due to the alignment of the cell walls in this direction. In directions perpendicular to the radial direction, the path for diffusion is a zig-zag, the length of which is $\sim(\pi/2)x$ (because the average value of $\cos\theta$, for θ in [0, $\pi/2$] is $2/\pi$). Another contribution to faster diffusion in the radial direction can be related to the lenticular channels which are aligned in this direction.
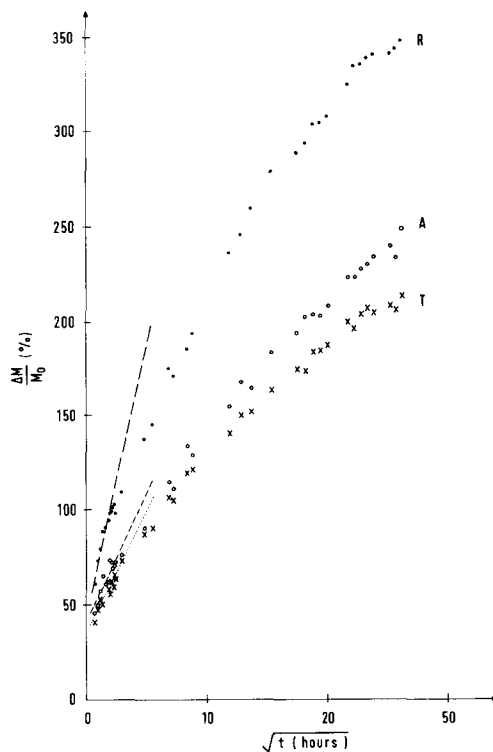

FIG. 8. Plot of $\Delta M/M_0$ as a function of $t^{1/2}$ for plate specimens of good quality cork immersed in water at room temperature. The direction of water movement through the plates is indicated: R—radial, A—axial, and T—tangential.

Penetration of water in the cells

In addition to absorption by the cell walls, water also penetrates into the closed cells, as if it were permeating through the cell walls. After saturation of the cell walls by diffusion, water penetration into the closed cells is the only contribution to the mass increase. However, before saturation both mechanisms (diffusion in the cell walls and water penetration in the cells) contribute to absorption of water. The regime of penetration continues until all cells are filled with water. This can be shown by the following simple calculation. If the volume expands from V_0 to λV_0, the limiting value of $\Delta M/M_0$ corresponding to all cells filled with water is

$$\left(\frac{\Delta M}{M_0}\right)_1 = \left(\lambda - \frac{\rho}{\rho_c}\right)\left(\frac{\rho_w}{\rho}\right) \qquad (4)$$

where ρ_c is the density of the cell walls and ρ and ρ_w are the densities of cork and water, respectively. This equation is derived by noting that the final volume of the water-full cells is $\lambda V_0 - V_c$, where V_c is the volume of the cell walls, which we assume not to vary due to water absorption. Using $\rho_c = 1.25$ (Flores et al. 1992), we obtain, for cork with density $\rho = 0.15$ and $\lambda = 1.05$, a value $(\Delta M/M_0)_1 = 6.2$. Values close to this were indeed obtained experimentally for plate specimens immersed for just over 1 year. A similar estimate of $\Delta M/M_0$ for which cork sinks leads to the value 6; indeed a number of specimens were found to sink.

The penetration of liquid water into the cells probably occurs by a mechanism of evaporation-condensation, with the water evaporating into the cells where it condenses. Condensation reduces the water vapor pressure in the cells, which induces further evaporation from the cell walls into the cells. The gas inside the cells must diffuse out, but this does not seem to be the rate determining process. In fact, experiments carried out with plate specimens that were placed in a vacuum for one month, before immersion in water, showed an absorption kinetics similar to that of normal specimens.

CONCLUSIONS

The diffusion of water in cork is a slow process (compared for example with that in wood), but large amounts of water, enough to make a specimen sink, can be absorbed. Initially absorption causes a swelling of cork, which apparently ceases when the cell walls are saturated with water. The concentration at saturation was experimentally determined, the values $\Delta M/M_0$ at saturation being $\sim 60\%$ at 20 C and ~ 200–240% at 100 C. Swelling (volume changes of 5–10%) is anisotropic, with smaller expansion in the radial direction (note that the cork had been previously boiled). The initial dimensions are recovered upon drying when water is absorbed at 20 C, but a large contraction in drying is observed for 100 C absorption.

Diffusion coefficients were estimated using two different methods. Diffusion is faster in the radial direction, although the difference is slight. A strong effect of temperature on the diffusion rates was observed, the diffusion coefficient at 90–100 C being two orders of magnitude larger than at 20 C (see Table 4). In addition to diffusing along the cell walls, water also penetrates into the (initially empty) closed cells, probably by a mechanism of evaporation-condensation. The gas inside the cells does not seem to obstruct water penetration, which only ceases when the cells are filled with water. At this stage the density of cork exceeds by $\sim 3\%$ that of water. The kinetics of water penetration is rather slow, and it may take over one year for a 1-mm-thick cork plate to sink in water.

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