Predicting the service life of concrete exposed to frost action through a modelling of the water absorption process in the air-pore system

Fagerlund, Göran

1994

Citation for published version (APA):
Fagerlund, G. (1994). *Predicting the service life of concrete exposed to frost action through a modelling of the water absorption process in the air-pore system*. (Report TVBM (Intern 7000-rapport); Vol. 7085). Division of Building Materials, LTH, Lund University.

Total number of authors:
1

ISRN: LUTVDG/TVBM- -94/7085- -SE(1-32)

ISSN 0358-7911 TVBM

PREDICTING THE SERVICE LIFE OF CONCRETE EXPOSED TO FROST ACTION THROUGH A MODELLING OF THE WATER ABSORPTION PROCESS IN THE AIR-PORE SYSTEM

Göran Fagerlund

Report TVBM-7085

Lund, July 1994

Contribution to:

RILEM/NATO Workshop
THE MODELLING OF MICROSTRUCTURE AND ITS POTENTIAL FOR STUDYING TRANSPORT PROPERTIES AND DURABILITY

St. Rémy-les-Chevreuse, July 10-13, 1994

PREDICTING THE SERVICE LIFE OF CONCRETE EXPOSED TO FROST ACTION THROUGH A MODELLING OF THE WATER ABSORPTION PROCESS IN THE AIR-PORE SYSTEM

G. FAGERLUND
Division of Building Materials, Lund Institute of Technology
Box 118, S-221 00 Lund, Sweden

1. Frost destruction. The critical water absorption. The service life

1.1 THE CRITICAL SIZE

A completely water saturated cement paste volume is severely damaged by frost if its size exceeds a certain critical volume [1]. The critical size depends on the lowest temperature used in the test and it depends on the salt concentrations outside and inside the volume [2]. It also is, to a certain extent, dependent of the freezing rate [3]. One can use the concept *critical thickness* of a thin slice of the paste or one can use the *critical diameter* of a spherical piece of the paste. Normally however, one uses the concept *critical spacing factor* L_{CR} which is the thickest water-saturated cement paste shell surrounding an air-pore. The spacing factor is a geometrical entity that is calculated on basis of the geometrical model shown in *Figure 1*. Thus, all air-filled airpores are supposed to have the same diameter ϕ defined by:

$$\phi = 6/\alpha \qquad (1)$$

Where α is the specific surface of *the air-filled portion* of the air-pore system. This is defined by the total surface/volume ratio of all pores that are large enough not to stay air-filled.Then, the spacing factor L is; [4]:

$$L = \{3/\alpha\}\cdot\{1,4[V_p/a+1]^{1/3}-1\} \qquad (2)$$

Where V_p is the volume fraction of cement paste (no air-pores included) and a is the volume of air-filled air-pores. The geometrical model behind Eq (1.2) is too simplified. A more general, statistical, spacing factor L´ in which consideration can also be taken to the size distribution is derived in [5]. The following general equation is valid:

$$a\cdot\{1+L'\cdot\alpha+L'^{2}\cdot\alpha([u]_1/[u]_2) +1,33\cdot L'^{3}\cdot\alpha([u]_0/[u]_2\} = C \qquad (3)$$

Where $[u]_i$ is the i:th statistical moment of the size distribution of air-filled air-pores. This spacing factor implies that all points in the cement paste are with a certain probability located within the distance L´ from the periphery of the nearest air-filled air-pore. The probability that the whole cement paste volume is protected increases with increasing value of the factor C. When C=1 the probability is 63 %. When C=2,3 the probability is 90 %. Thus, the spacing factor depends both on the pore size distribution, as does the Powers spacing factor according to Eq (2), but also on the probability that all parts of the cement paste shall be protected. The critical spacing factor defined by Eq (2) is of the order of size 0,35 mm for freezing in pure water; [6]. The value for freezing in presence of de-icing salts is not well-known. Probably it is a bit lower than for freezing in water[1] .

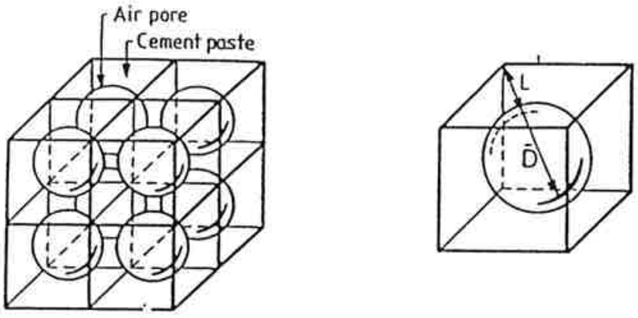

Figure 1: The geometrical air-pore/cement paste model on which the Powers´spacing factor is based; [4]

1.2 THE CRITICAL WATER ABSORPTION

The air-pores will not stay air-filled but will take up water by a slow air dissolution-diffusion process that is described below. This means that the residual spacing factor between pores that are still air-filled will increase with increasing time of water storage of the concrete. The relation between the residual spacing factor L_r and the degree of water-filling of the air-pore system can be calculated by Eq (2) when the residual specific surface α_r and the residual air volume a_r of pores that are not water-filled to such large extent that they cannot accomodate all water that is expelled from the surrounding cement paste shell, are known. a_r is calculated by:

$$a_r = \int_{r_{a,min}}^{r_{max}} f(r)\cdot(4\pi/3)r^3\cdot dr \qquad (4)$$

Where f(r) is the frequency function of pore radii. $r_{a,min}$ is the radius of the smallest air-filled pore that cannot accomodate any expelled water. Such a pore might be a completely water-filled pore or a pore that is water-filled to such an extent that the residual

---

[1] In the original derivation made by Powers [4] all air-pores were included in the values a and α in Eq(2). Thus, Powers did not consider that that some air-pores actually become water-filled due to the dissolution process described below. The critical Powers spacing factor assuming all air-pores being air-filled is about 0,25 mm for freezing in pure water and about 0,18 mm for freezing in the presence of salts; [6].

air volume is smaller than 9% of the freezable water contained in the water-filled cement paste shell surrounding the pore. In these cases water has to move to another, coarser pore. r_{max} is the radius of the largest air-pore. Eq (4) implies that a smaller pore is always water-filled before a larger pore.

The residual pore surface A_r is:

$$A_r = \int_{r_{a,min}}^{r_{max}} f(r) \cdot 4\pi \cdot r^2 \cdot dr \qquad (5)$$

Then, the residual specific surface of the portion of the air-pore system that is still air-filled, α_r is:

$$\alpha_r = A_r / a_r \qquad (6)$$

As a consequence of the gradual reduction in the residual air-pore volume and specific surface the residual spacing L_r between the air-pores increases; see Eq (2) and (3).

$$L_r = \{3/\alpha_r\} \cdot \{1{,}4 \cdot [V_p/a_r+1]^{1/3}-1\} \qquad (2.a)$$

Hypothetical examples of the changes in a_r, α_r and L_r are shown in *Figure 2* for two types of the air-pore system; a fine-porous and a coarse-porous.

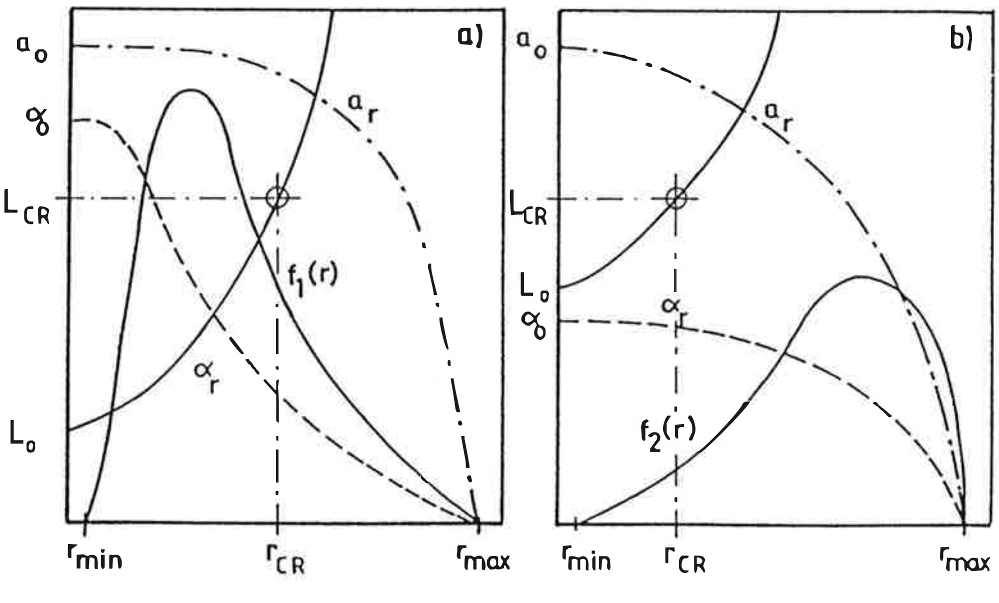

Figure 2: Hypothetical air-pore distributions and the influence of a gradual water-filling on; (i) the residual volume, a_r, of pores that can still act as recipients for expelled water; (ii) the specific surface of such pores, a $_r$; (iii) the spacing factor for air-filled pores. (a) Fine-porous system. (b) Coarse-porous system.

Frost destruction occurs when the degree of water-filling is so high that the critical spacing is exceeded ($L_r > L_{CR}$). Then, the residual air-pore volume is smaller than $a_{r,CR}$. This means that there exists a critical degree of saturation $S_{a,CR}$ of the air-pore system:

$$S_{a,CR} = 1 - a_{r,CR}/a_o \quad (0<S_{a,CR}<1) \tag{7}$$

There also exists a critical degree of saturation S_{CR} of the entire material, capillary pores and gel pores included in the definition of S. They are always water-filled before the air-pores start to take up water; see paragraph 2. Therefore, S_{CR} is defined:

$$S_{CR} = 1 - a_{r,CR}/P_{tot} \quad (0<S_{CR}<1) \tag{8}$$

Where P_{tot} is the total pore volume in the concrete. Thus, by knowing the total air-pore volume and by measuring the weight gain of a concrete stored in water for a long time the gradual water absorption in the air-pores can be followed. By also investigating the pore size distribution one can find relations between the pore size and the rate of water absorption. The relation between the two degrees of saturation is:

$$S_{a,CR} = 1 - P_{tot}(1-S_{CR})/a_o \tag{9}$$

Where a_o is the air-pore volume when all air-pores are actually air-filled. Two examples of the determination of the critical degree of saturation by freeze/thaw experiments are shown in *Figure 3*; [7].

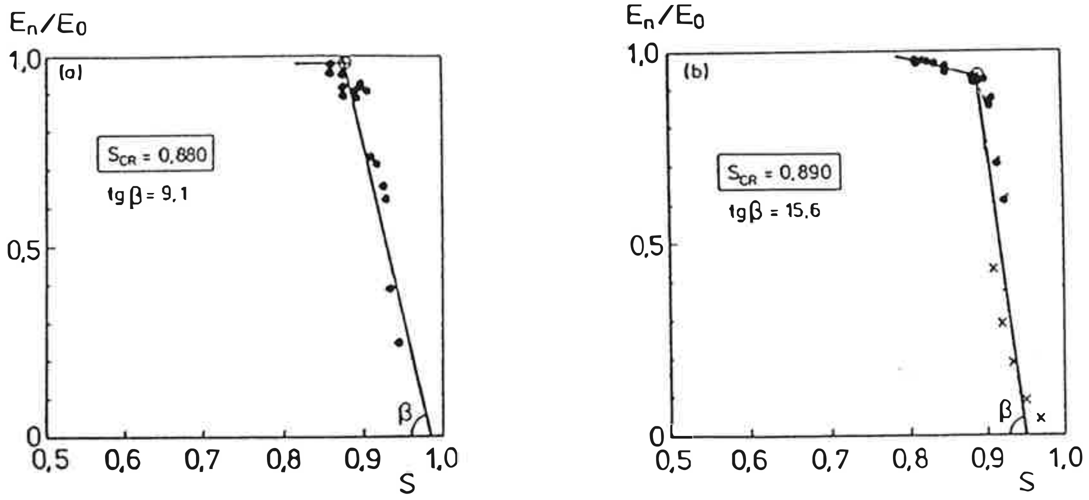

Figure 3: Example of determinations of the critical degree of saturation S_{CR}. Slag cement concretes with slag content 40 % and w/c-ratio 0,45; [7].
(a) Air content 4,2 %. (b) Air content 5,4 %.

1.3 THE SERVICE LIFE

The water absorption process is time-dependent:

$$S_a = S_a(t) \tag{10}$$

The service life of a representative unit volume inside the concrete is ended when $S_a(t)$ exceeds the critical degree of saturation of the air-pore system $S_{a,CR}$ which is supposed to be independent of time; at least for mature concrete.

The value of $S_{a,CR}$ can be calculated theoretically according to the principles described above, provided the value L_{CR} of the critical spacing factor is known. Another possibility is to determine the value of S_{CR} and $S_{a,CR}$ experimentally. Suitable methods are described in [8].

The time function $S_a(t)$ is calculated theoretically according to the principles described below, or it is measured experimentally by successive weighings of specimens that are stored for a long time in water. The most rational method is to make an experimental water absorption test for a limited space of time (e.g. 2 weeks) and then extrapolate the water absorption function until the extrapolated value of $S_a(t)$ reaches the value of $S_{a,CR}$. The time when this happens is a sort of *potential service life*, t_p which is defined:

$$S_a(t_p)=S_{a,CR} \quad \text{or} \quad S(t_p)=S_{CR} \tag{11}$$

As will be shown below the long term absorption can be described by an equation of the following type:

$$S_a(t_p)=B\cdot t^C \quad \text{or} \quad S(t_p)= A+B\cdot t^C \tag{12}$$

Where the coefficient B, and also to a certain extent the exponent C, is a function of the air-pore size distribution. The coefficient A is the degree of saturation of the entire pore system when all pores exept the air-pores are water-filled. Thus:

$$A=1-a_o/P_{tot} \tag{13}$$

Then, the potential service life, assuming eq (12) is valid for the absorption, is estimated by one of the following expressions:

$$t_p=[S_{a,CR}/B]^{1/C} \tag{14.a}$$

$$t_p=[(S_{CR}-A)/B]^{1/C} =[(S_{CR}-1+a_o/P_{tot})/B]^{1/C} \tag{14.b}$$

Principally, all coefficients in Eq (14) can be calculated theoretically on basis of information of the critical true spacing factor and the size distribution of the air-pores. In practise it is better, however, to determine the critical degree of saturation ($S_{a,CR}$ or S_{CR}) by freeze/thaw experiments and the coefficients A,B and C by a short-term water absorption experiment.

2. The capillary absorption process

When a piece of pre-dried concrete is placed in contact with a free water surface it immediately starts to take up water. A more or less sharp water front penetrates the concrete; below the front, the gel and capillary pores are saturated, above the front, the water content is almost the same as it was initially. In reality, when the water front has advanced a bit, there will be a diffusion of water from the front which makes this more blunt. As long as only the first few centimeters for ordinary concrete, or millimeters for dense concretes, are regarded the idea of a moving front is however acceptable. The water absorption rate q_c [kg/(m^2·s)] during this period is given by the following formula:

$$q_c = k/(2 \cdot t^{1/2}) \qquad (15)$$

Isolated coarser pores that are connected to finer continuous pores cannot become water-filled during a capillary process if they are coarser than about 0,1 µm. This can be shown easily by the geometrical model in *Figure 4*. The coarse spherical pore is connected to finer pores by a narrow bifurcation pore. The model is a good representation of an isolated air-pore in a web of fine capillary pores in a cement paste.

When the water front in pore 1 reaches the coarse pore, the capillary pressure, which is inversely proportional to the radius of the water meniscus, must be reduced if water should enter the coarse pore. The capillary pressure in the bifurcation pore 2 is however maintained on the high level. Therefore, the bifurcation pore immediately sucks water from the coarse pore. The meniscus will therefore not be able to enter the coarse pore. It will remain at its entrance. When the bifurcation pore is full, the fine pore 3 starts to fill by sucking water both downwards and upwards. The coarse pore will continue to be air-filled as long as the capillary pressure is higher in the surrounding fine pore system. An air bubble will therefore be enclosed in the coarse pore.

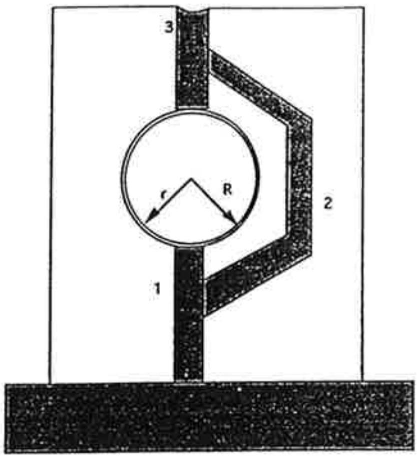

Figure 4: Geometrical pore model illustrating the enclosure of air-bubbles in coarser pores during a capillary water uptake process.

The air bubble is under pressure; see the next section. Therefore, it will be compressed. The relation between the compressed volume V_1 and the initial volume V_0 is calculated by Boyle´s law:

$V_o \cdot P_o = V_1 \cdot P_1$ (16)

P_o is 10^5 Pa (the ordinary atmospheric pressure). P_1 is given by the Laplace law:

$P_1 = P_o + 2 \cdot \sigma / r$ (17)

Where σ is the surface tension between water and air (0,074 N/m) and r is the bubble radius.

The volumes V_o and V_1 are:

$V_o = (4\pi/3)R^3$ (18)

$V_1 = (4\pi/3)r^3$ (19)

Where R is the radius of the coarse pore. Then, the pressure P_1 is:

$P_1 = [10^5 + (2\sigma/R) \cdot (V_o/V_1)^{1/3}]$ (20)

Inserting this equation in Eq (16), gives the following relation between the volume of the compressed bubble and the volume of the spherical pore:

$[V_1/V_o]^{1/3} \cdot [V_o/V_1 - 1] = 2\sigma/(10^5 \cdot R)$ (21)

This means that bubbles in smaller pores will immediately become almost totally compressed which is shown by the following calculation:

R= 0,05 μm: $V_1/V_o = 0{,}006 = <1\ \%$

R= 0,10 μm: $V_1/V_o = 0{,}018 = 2\ \%$

R= 1,00 μm: $V_1/V_o = 0{,}32 = 32\ \%$

R= 10 μm: $V_1/V_o = 0{,}87 = 87\ \%$

This means that all pores with diameters smaller than about 0,1 μm (gel pores and capillary pores) are completely compressed and water-filled already during the water absorption process. Larger isolated pores remain air-filled and stay so for shorter or longer times.

3. The gradual water absorption in the air-pore system

3.1 THE BASIC MECHANISM

An air bubble, which becomes enclosed in a coarse pore during the capillary water absorption process, is exposed to an internal over-pressure ΔP that is inversely proportional to its radius:

$\Delta P = 2 \cdot \sigma / r$ (22)

Where σ is the surface tension air-water and r is the radius of the spherical bubble. The total pressure is:

$$P = P_0+2\cdot\sigma/r \tag{17.a}$$

Where P_0 is the ordinary atmospheric pressure. The solubility of air in water is proportional to the air pressure. Hence, the bubble will gradually dissolve. Bubbles that are small enough will be dissolved in the pore water surrounding them already a short time after the capillary process ended. The size of these bubbles can be estimated by comparing the amount of air inside the bubble with the water volume needed to dissolve all that air. The total air mass inside a bubble of size r is:

$$m = \rho_1\cdot(4\pi/3)\cdot r^3 \tag{23}$$

Where ρ_1 is the density of the compressed air. This is directly proportional to the pressure of the air. Hence:

$$\rho_1 = \rho_0(P_0+2\cdot\sigma/r)/P_0 \tag{24}$$

Where ρ_0 is the density of air at 1 atm. $\rho_0 = 1{,}25$ kg/m^3 at +10°C. The "extra" solubility Δs of air in water which has become pre-saturated with air at the normal atmospheric pressure is:

$$\Delta s = 3\cdot 10^{-2}\cdot\Delta P/P_0 \text{ kg/m}^3 \tag{25}$$

Where $3\cdot 10^{-2}/P_0$ is the solubility of air at pressure 1 Pa and 10°C. This extra solubility due to the increased pressure can be used for dissolving air in the bubble. By inserting Eq (22), (17.a) and (25) in eq (23) it is possible to calculate the water volume V_w needed to dissolve all air in the bubble of size r:

$$V_w = (4\cdot\pi/3)\cdot 42\cdot[1 + P_0/\Delta P]\cdot r^3 \tag{26}$$

The porosity of the cement paste shell surrounding the bubble is of the order of size 40 to 60 %. The cement paste volume needed in order to take care of the dissolved air is therefore about twice as large as the volume given by eq (26). Thus, the thickness t (m) of the cement paste shell needed in order to rapidly dissolve an air bubble at +10°C is:

$$t=\{[1+2\cdot 42\cdot(1+P_0/\Delta P)]^{1/3}-1\}\cdot r =\{[1+84(1+6{,}8\cdot 10^5\cdot r)]^{1/3}-1\}r \tag{27}$$

The average spacing between airpores is probably shorter the smaller the bubble. An average spacing of 100 μm is assumed. This means that t≈50 μm. Then, according to eq (27) bubbles with a radius of about 7 μm will dissolve rapidly at +10 °C. At other temperatures the air solubility is different. For the temperatures 0 °C and +20 °C the coefficient 42 in eq (26) and (27) is changed to 33 and 52 respectively. This does, however, not very much change the size of the rapidly dissolved bubble.

Coarser bubbles will not dissolve directly but will stay air-filled for a long time. Air will disappear only gradually due to diffusion through the pore water to larger pores or to the surface. Due to this diffusion the bubble becomes smaller and smaller making the internal pressure higher. The dissolution rate will therefore increase with time. However, since the cross section of diffusion decreases with the reduction of the bubble size, the increase in dissolution rate is not directly proportional to the over-pressure. It might even be constant during the whole process; see paragraph 3.3.2. The dissolved air migrates through the pore water to larger air bubbles having a lower internal pressure and, finally, to the surface of the material. The dissolution rate depends on the diffusivity of air in the pore water and is therefore a function of the water/binder ratio and, since different binders create different pore structures, it is also a function of the type of binder.

Many diffusion processes in concrete can be described by a diffusion coefficient δ (m^2/s) which is a simple function of the w/c-ratio:

$$\delta=k_1\cdot(w/c)^n \approx k_1\cdot(w/c)^2 \qquad (28)$$

Alternatively, it is a function of the capillary porosity, P_c:

$$\delta= k_2+k_3\cdot P_c{}^n \approx k_3\cdot P_c{}^2 \qquad (29)$$

k_1, k_2, k_3 and n are empirical coefficients determined by the diffusivity of air in pore water.

The rate of dissolution will also be a function of the length of the diffusion path. Hence, an air bubble that is very close to the surface of the concrete ought to be water-filled before a similar bubble in the interior of the concrete. The dissolution will, however, not occur as a moving boundary process. Since all bubbles are over-saturated with air, a local dissolution will occur simultanously in the pore water surrounding each bubble. The dissolved air will move to a neighbouring pore with a lower pressure and from there to the next pore and so on. Finally, it reaches the surface. Therefore, due to this inter-bubble diffusion and due to the extremely large number of bubbles, the dissolution will probably occur rather homogeneously within a zone of a certain thickness. This zone is probably considerably thicker than the so called critical thickness which is a measure of the largest material volume which is not harmed by frost even when frozen in a completely water saturated condition. The critical thickness is only about 0,3 to 0,5 mm for concrete [6].

Seen over a larger material volume, there will of course be a certain gradient in air concentration in the pore water from the surface of the concrete inwards, due to the fact that diffusion to the surface must occur. This requires a gradient. In the normal, practical case, however, it is the outmost millimeters or centimeters of the concrete that is most interesting and this zone can be approximately treated as a "non-gradient" zone; at least when it comes to an analysis of the inter-bubble diffusion.

3.2 THE GLOBAL DIFFUSION

The global diffusion rate in the material as a whole will, due to the inter-bubble diffusion, be a function of the air or bubble content. The larger the air content, the lower the inter-bubble spacing and the larger the rate of air-diffusion and water-filling of the bubbles. The inter-bubble spacing L can be described by the Powers´ equation:

$$L= \{3/\alpha\}\cdot\{1{,}4[V_p/a+1]^{1/3}-1\} \qquad (30)$$

Where, α is the specific surface of the air-pore system, V_p is the volume fraction of cement paste (air pores excluded) and a is the air volume as a fraction of the concrete volume.

As a first approximation, the global diffusivity of dissolved air is therefore described by a function of the following type:

$$\delta = \delta_0 \cdot (w/c)^2/\{[3/\alpha_r]\cdot[1,4(V_p/a+1)^{1/3}-1]\} \qquad (31)$$

The constant δ_0 depends on the fineness of the pore structure. It might be a function of the type of cement and the type of mineral admixture used.

Eq (31) is plotted in *Figure 5*. The rate of air diffusion from the air bubbles will increase with increasing air content and increasing w/c-ratio. In the real case, a higher air volume will, however, be favourable since it will take a longer time before the critical distance is exceeded. Hence, the service life is increased.

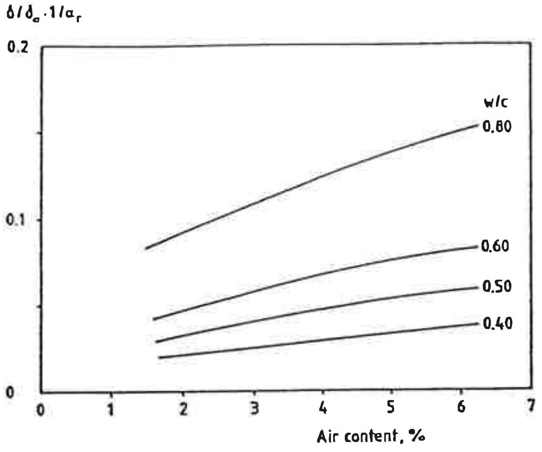

Figure 5: Theoretical effect of the w/c-ratio and air content on the diffusion coefficient of dissolved air through the pore water; eq (30) and (31). The amount of mixing water is supposed to be 180 kg/m^3 in all mixes.

In *Figure 6*, the observed values of the coefficient η describing the slow rate of water absorption during the long term storage of slag cement concretes in water is plotted versus the air content. η is defined by $\Delta S = \eta \cdot \log(\text{time})$ where ΔS is the increase in the total degree of saturation of the concrete. The general shape of the curves are similar to those predicted by eq (31) and shown in *Figure 5*; viz. the water absorption rate increases with increasing air content.

The total amount of air Q (kg) transferred over the distance Δx (m) during the time interval Δt (s) is described by:

$$Q = \delta \cdot A \cdot \Delta t \cdot \Delta c/\Delta x \qquad (32)$$

Where A is the cross section of flow (m^2) and Δc is the difference in concentration of dissolved air (kg/m^3) over the distance Δx (m). The concentration gradient Δc is proportional to the gradient in air pressure and therefore, according to eq (22) and seen over a larger material volume and cross section, approximately inversely proportional to the gradient in the "average size" r_m of the remaining air bubbles over the distance Δx.

$\Delta c = \text{constant} \cdot \sigma [1/r_{m,1} - r_{m,2}]$ (33)

Where $r_{m,2}$ and $r_{m,1}$ are the "average bubble radii" at distance x and and $x+\Delta x$ from the surface. The "average bubble radius" is the radius of a fictive bubble staying in equilibrium with the air concentration of the surrounding pore water. The constant in eq (33) describes the relation at equilibrium between air pressure and amount of dissolved air. For the concentration difference of dissolved air between the free concrete surface and the pore water inside the concrete on the distance Δx from the surface the following expression is valid:

$\Delta c = \text{constant} \cdot \sigma / r_{m,1}$ (34)

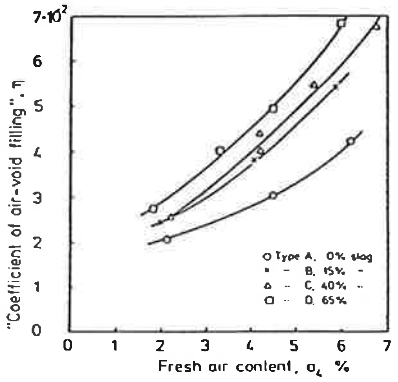

Figure 6: Experimentally determined rates of the water absorption during 30 days in concretes made with slag cements and varying air content; [7]. The "coefficient of air-void filling", η. It is defined by the relation $\Delta S = \eta \cdot \log(\text{time})$.

The cross section A for the global diffusion is, as a first approximation, considered to be directly proportional to the volume fraction of the sum of capillary pores and air bubbles in relation to the total cement paste volume, air bubbles included. Thus, the fine gel pores are not supposed to take part in the diffusion of air. Then, A is:

$A = [w/c - 0{,}39 \cdot \beta + a \cdot 1000/c] / [w/c + 0{,}32 + a \cdot 1000/c]$ (35)

Where β is the degree of hydration and a is the volume in m^3 of air bubbles in 1 m^3 of the concrete. No consideration is taken to the interfaces between aggregate grains and cement paste.

With this equation and eq (33) or eq (34) inserted in eq (32) the total air transport over the distance Δx in 1 m^2 of the concrete cross section can be estimated. A general equation for this global diffusion is:

$q = -\delta d^2c/dx^2$ (36)

Where q is the flux of dissolved air ($kg/m^2 \cdot s$). The main problem in using this general equation or the numerical eq (32) is that is difficult to estimate the concentration gradient dc/dx. Probably, however, as said above in 3.1, it is not always necessary to deal with the global diffusion since most of the water absorption in the bubbles occur due to local inter-bubble diffusion between neighbouring bubbles. This diffusion goes from smaller to larger bubbles as shown in the next paragraph.

3.3 THE LOCAL DIFFUSION BETWEEN NEIGHBOURING AIR-PORES

3.3.1 *Pressures and volume changes*

Let us consider two neighbouring bubbles with the radii r_1 and r_2 ($r_1<r_2$). Directly after the capillary uptake has ceased the radii of the bubble mensci in the pores are $r_{1,o}$ and $r_{2,o}$. According to Boyle´s law those radii are:

$$r_i=\{r_{i,o}{}^2[r_{i,o}+2\cdot\sigma/P_o]\}^{1/3} \tag{37}$$

Where i stands for either 1 or 2. $r_{i,o} \rightarrow r_i$ for large values of r_i. Diffusion starts from pore 1 to pore 2. The air volume in pore 1 diminishes and the air volume in pore 2 increases. After a certain time the new radii are $r_{1,t}$ and $r_{2,t}$. The initial air masses in pore 1 and 2 are m_1 and m_2 where $m_1/m_2=[r_1/r_2]^3$. After a certain time of diffusion $\gamma\cdot m_1$ is lost from pore 1 and transferred to pore 2. Then Boyle´s law gives:

Pore 1:

$$P_o+2\sigma/r_{1,o}=\{P_o+2\sigma/r_{1,t}\}\cdot\{r_{1,t}/r_{1,o}\}^3\cdot 1/(1-\gamma) \tag{38}$$

Pore 2:

$$P_o+2\sigma/r_{2,o}=\{P_o+2\sigma/r_{2,t}\}\cdot\{r_{2,1}/r_{2,0}\}^3\cdot 1/[1+(r_1/r_2)^3\cdot\gamma] \tag{39.a}$$

Air continues to flow to pore 2 even after all water that was initially contained in pore 2 has been displaced. The increased pressure in pore 2 is taken care of by curved menisci in the entrance to capillaries leading into pore 2. After this has happened the following relation is valid for pore 2:

Pore 2: $P_o+2\sigma/r_{2,o}=P_{2,t}\cdot\{r_2/r_{2,0}\}^3\cdot 1/[1+(r_1/r_2)^3\cdot\gamma]$ (39.b)

The pressures in the bubbles are:

Pore 1: $P_1= P_o+2\sigma/r_{1,t}$ (40)

Pore 2: $P_2= P_o+2s/r_{2,t}$ for $r_{2,t}<r_2$ (41.a)

$P_2= P_{2,t}$ for $r_{2,t}=r_2$ (41.b)

Air will flow from pore 1 until the pressure in pore 2 equals the pressure in pore 1. This condition is only valid when all water in pore 2 has been displaced. Before that, a transfer of air from pore 1 to pore 2 will always lead to a higher pressure increase in pore 1 than in pore 2 leading to a continued flow. By equaling eq (38) and (39.b) one obtains the following equation for the maximum fraction of air that can flow from pore 1 to pore 2:

$$\gamma < \{[P_o+2\sigma/r_{1,t}]/[(P_o+2\sigma)/r_{2,o})\cdot(r_{2,o}/r_2)^3] - 1\}\{r_2/r_1\}^3 \qquad (42)$$

Where $r_{1,t}$ is a function of γ. From eq (38) the following relation between $r_{1,t}$ and γ is obtained:

$$P_o\cdot r_{1,t}^3+2\sigma\cdot r_{1,t}^2=r_{1,o}^3\{P_o+2\sigma/r_{1,o}\}\{1-\gamma\} \qquad (43)$$

This equation must be solved numerically. The initial bubble radii $r_{1,o}$ and $r_{2,o}$ in eq (42) and (43) are functions of the pore sizes r_1 and r_2. The relation is given in eq (37).

Eq (42) shows that there is a maximum amount of air that can flow from pore 1 to pore 2. This amount is a function of the relative pore size (r_1/r_2) and a function of the absolute pore sizes (r_1 and r_2). It is clear from eq (42) that the amount of air that can flow from a smaller to a larger bubble increases with increased size ratio between the two bubbles.

The volume changes of the bubbles and the net volume changes $\Delta V$are:

Pore 1: $\Delta V_1= -\{r_{1,o}^3-r_{1,t}^3\}\cdot 4\cdot\pi/3$ (44)

Pore 2: $\Delta V_2= +\{r_{1,t}^3-r_{1,o}^3\}4\cdot\pi/3$ for $r_{2,t}<r_2$ (45.a)

$\Delta V_2= +\{r_2^3-r_{1,o}^3\}4\pi/3$ for $r_{2,t}=r_2$ (45.b)

$$\Delta V=\Delta V_1+\Delta V_2 \qquad (46)$$

The pressure in pore 1 will, at the start, always be higher than in pore 2. When the pores are small the pressure in pore 1 maintains a higher value even after all water in pore 2 has been displaced by the air arriving. Small bubbles will therefore vanish completely. Air from small pores can move to pores of almost all sizes without being stopped by too large a pressure increase in the larger pores. Air in larger pores, on the other hand, cannot be transferred to pores that are not very much larger; the pressure in the latter will soon reach the driving pressure in the smaller pore. Large pores can, however, be completely emptied to pores that are very much larger.

The volume changes and the pressures are best shown by a numerical example:

Example: $r_1=100$ µm, $r_2=400$ µm

Eq (37) gives:

$r_{1,o}=99{,}51$ µm. $r_{2,o}=399{,}50$ µm

Pore 1: Eq (38), (40) and (44) give:

$\gamma=0{,}25$: $r_{1,t}=90{,}3$ µm. $P_{1,t}=1{,}016\cdot 10^5$ Pa. $\Delta V_1=-1{,}043\cdot 10^{-12}$ m^3

$\gamma=0{,}50$: $r_{1,t}=78{,}9$ µm. $P_{1,t}=1{,}019\cdot 10^5$ Pa. $\Delta V_1=-2{,}069\cdot 10^{-12}$ m^3

$\gamma=0{,}75$: $r_{1,t}=62{,}5$ µm. $P_{1,t}=1{,}024\cdot 10^5$ Pa. $\Delta V_1=-3{,}103\cdot 10^{-12}$ m^3

$\gamma=1{,}00$: $r_{1,t}=0$. $P_{1,t}$=trivial. $\Delta V_1=-4{,}125\cdot 10^{-12}$ m^3

Pore 2: Eq (39), (41) and (45) give:

γ=0,25:	$r_{2,o}$=400 µm.	$P_{2,t}=1{,}004\cdot10^5$ Pa.	$\Delta V_2=+1{,}004\cdot10^{-12}$ m^3
γ=0,50:	-"-	$P_{2,t}=1{,}008\cdot10^5$ Pa.	-"-
γ=0,75:	-"-	$P_{2,t}=1{,}012\cdot10^5$ Pa.	-"-
γ=1:	-"-	$P_{2,t}=1{,}015\cdot10^5$ Pa.	-"-

In this case, the pressure is always higher in pore 1. The bubble in pore 1 will vanish completely. The total volume reduction due to the air transfer is:

γ=0,25: $\Delta V=-0{,}04\cdot10^{-12}$ m^3
γ=0,50: $\Delta V=-1{,}07\cdot10^{-12}$
γ=0,75: $\Delta V=-2{,}10\cdot10^{-12}$
γ=1: $\Delta V=-3{,}12\cdot10^{-12}$

Thus, there is a gradual decrease in volume. The total volume reduction when bubble 1 has disappeared is $3{,}12\cdot10^{-12}/4{,}12\cdot10^{-12}$=75 % of the initial volume of the dissolved bubble in pore 1.

The analysis performed above shows that there is a complicated network of local exchanges of air from smaller to adjacent larger bubbles. Besides, air that is displaced from one pore to a neighbouring larger pore will soon leave this for a still larger pore and so on. This process can hardly be described by other than statistical methods or computer simulations assuming a random distribution in space of the spherical air pores. It is quite clear, however, that there is a gradual coarsening of the remaining air-filled pore system; the smallest air-bubbles being lost at first. The biggest bubbles are lost only after a very long time.

It is also quite clear that there would be a gradual water-filling of bubbles even if there was no diffusion at all of air from those dissolved bubbles to the surface of the concrete. On the contrary, there must be a diffusion of water *from* the surface to the interior of the concrete. This depends on the fact that there is a net volume reduction when air is dissolved and transferred to larger bubbles. This water uptake due to numerous local air transfers occuring simultaneously over the entire concrete body explains the observation that the long term absorption rate in concrete stored in water seems to be independent of the thickness of the specimen as long as this is not too large, [9]. This also means that the gradient in air concentration of the pore water from the interior to the surface might be rather small even in cases where a large amount of the smallest air bubbles are lost due to dissolution and water absorption. In the long run, however, when also the largest bubbles are lost, there must be a global gradient in concentration of dissolved air towards the surface.

The driving potential for diffusion of dissolved air from pore to pore is rather small, especially for the largest bubbles. For a pore system, as that treated in the example above, the air-pressure gradient is only about 1000 Pa leading to a gradient in dissolved air of about $2{,}5\cdot10^{-4}$ kg/m^3 which is only 1 % of the the amount of dissolved air at normal pressure. Of course, the gradient is larger for smaller bubbles.

3.3.2 *Rate of local diffusion*

The rate of the local diffusion between neighbouring pores can be determined by eq (32) if reasonable values of the concentration difference Δc, the cross section of flow

A and the inter-pore spacing Δx are inserted. For the inter-pore diffusion between a small bubble with radius $r_{1,o}$ and an adjacent larger bubble with radius $r_{2,o}$ the concentration difference is according to eq(25):

$$\Delta c = s \cdot 2\sigma[1/r_{1,o} - 1/r_{2,o}] \cdot \kappa \quad \mathrm{kg/m^3} \tag{47}$$

Where s is the solubility of air in water. It is $2{,}4 \cdot 10^{-7}$ $\mathrm{kg/m^3}$ at +20°C and 1 Pa. κ is a correction factor that takes care of the changes in the air pressure in the pores caused by the air transfer, viz. the initial pressures $2\sigma/r$ will not be maintained. κ is a function of the pore sizes. For large pores $\kappa=1$. For small pores it is about 2.

The effective cross section of flow A is

$$A = \pi \cdot r_1 \cdot r_2 \tag{48}$$

The reason why the pore radii r_1 and r_2 have been inserted and not the bubble radii $r_{1,o}$ and $r_{2,o}$ is that the diffusion of air through the water phase inside the relatively coarse air-pore is supposed to be much more rapid than the diffusion through the dense capillary pore system.

The inter-bubble spacing is L. Then, the total air flow is:

$$Q=\delta \cdot \Delta t \cdot \pi \cdot r_1 \cdot r_2 \cdot s \cdot 2\sigma[1/r_{1,o} - 1/r_{2,o}] \cdot \kappa / L \quad [\mathrm{kg}] \tag{49}$$

The diffusion coefficient δ $[\mathrm{m^2/s}]$ of air in hardened cement paste is not very well known. For air in bulk water at +25 °C it is $2 \cdot 10^{-9}$ $\mathrm{m^2/s}$. In cement paste it is probably decreased by a factor 100 or even more. A value of 10^{-11} $\mathrm{m^2/s}$ is selected. The distance L between pores varies from pore to pore. An average value of 300 μm is selected. This is probably a bit too high for small bubbles but a bit too small for large bubbles. The surface tension σ is 0,074 N/m.

When those values and the solubility of air are inserted the following expression is obtained:

$$Q=3{,}9 \cdot 10^{-15} \cdot r_1 \cdot r_2 \cdot [1/r_{1,o} - 1/r_{2,o}] \cdot \kappa \cdot \Delta t \quad [\mathrm{kg}] \tag{50}$$

This equation can be used for a rough estimate of the time needed to empty a pore. The same example as above is used.

Example: $r_1=100$ μm, $r_2=400$ μm

The total amount of air in pore 1 is:

$Q=1{,}25 \cdot 4 \cdot \pi(100 \cdot 10^{-6}\}^3/3 = 5{,}23 \cdot 10^{-12}$ [kg]

The coefficient κ is about 1.

Insertion in eq (50) gives:

$5{,}23 \cdot 10^{-12}=3{,}9 \cdot 10^{-15} \cdot 100 \cdot 10^{-6} \cdot 400 \cdot 10^{-6}[1/100 \cdot 10^{-6} - 1/400 \cdot 10^{-6}] \cdot \Delta t$

The time needed to empty pore 1 is: *Δt = 1240 hours = 52 days.*

If the diffusivity was only 10^{-12} m^2/s, which is quite possible, the times needed should be increased by a factor 10 to 520 days. However, according to eq (50) there is an inverse proportionality between the size of the recipient bubble and the time needed to empty the smaller bubble. Therefore, the times should have been somewhat shorter had the recipent bubbles been larger than the value 400 μm assumed in the example.

The calculation indicates that the time to fill the air-pore system is quite long, especially for dense concretes and/or concretes with coarse air-bubble systems. Air-pore systems that are very fine will, however, rapidly become inactivated by water. It takes about 70 times as long to empty a bubble contained in a pore with radius 100 μm as a bubble in a pore with radius 10 μm. Their volume ratio is however 1000. The time needed is evidently not proportional to the volumes. This mainly depends on the fact that the cross section of diffusion increases with the bubble size at the same time as the length of the diffusion path has been supposed to be constant.

A complication with eq (49) is that the bubble size in pore 1 decreases as air is leaving ; it changes from $r_{1,0}$ to $r_{1,t}$. Therefore, the over-pressure in pore 1 increases with time. This is, however, approximately taken care of by the coefficient κ. Besides, the effective cross section of air flow becomes a bit lower than the value $\pi \cdot r_1 \cdot r_2$ assumed in eq (49). The net effect probably is that the flow from pore 1 is relatively constant during the whole process and fairly well described by eq (49). The complication is avoided in the model which will now be described.

In the real material, diffusion does not take place between individual pores as calculated above. There will be a sort of average local diffusion governed by a diffusion coefficient that is a function of the w/c-ratio and the air content. A diffusion coefficient of the type shown in eq (31) could perhaps be used. The value δ_0 is not known. It might be estmated from measurements of saturated gas flow through water-saturated concrete. It is supposed to be the same for diffusion from all pores.

Further on, the radius r_2 is supposed to be infinite corresponding to a free water surface or to the meniscus in a pore that is very much larger than r_1. Diffusion is supposed to be symmetrical within a material sphere surrounding the bubble. The radius of this sphere, or the length of the flow path, is L.

Then, the general equation for the flux of air q´ [kg/s] from a bubble with radius r_1 is:

$$q' = \delta \cdot \{(L+r_1)r_{1,t} \cdot 4\pi/L\} \cdot \Delta c = \delta \cdot \{(L+r_1)r_1 \cdot 4\pi/L\} \cdot s \cdot 2\sigma/r_{1,t} \qquad (51.a)$$

Or:

$$q' = \delta \cdot \{(L+r_1) \cdot 4\pi/L\} \cdot s \cdot 2\sigma \qquad (51.b)$$

Where δ is the bulk diffusion coefficient of air in pore water; s is the solubilty of air. It is $2{,}4 \cdot 10^{-7}$ [kg/(m^3·Pa)] at a pressure of 1 Pa and +20°C. In eq (51) it is assumed that the resistance to diffusion is just as high in the absorbed water phase inside pore 1 as it is in the cement paste.

It is reasonable to assume that the diffusion path increases with increasing size of the bubble being emptied; c.f. eq (30), which shows that there is an inverse proportionality between the specific surface of the pore and the average spacing provided the total bubble volume under consideration is constant. The following assumtion is made:

$$L = \varepsilon \cdot r_1 \quad \text{where } \varepsilon > 1 \qquad (52)$$

Thus, the diffusion path increases linearily with the bubble size. Then, eq (51) can be written:

$$q'=\delta\cdot[1+1/\varepsilon]\cdot 4\pi\cdot s\cdot 2\sigma \qquad [kg/s] \qquad (53)$$

The rate of flow of air from a certain bubble is therefore approximately independent of its size and is only dependent of the ratio ε between the length of the diffusion path and the pore size. The application of eq (53) is shown by two examples. The diffusivity is supposed to be 10^{-11} m^2/s. The coefficient $\varepsilon = 5$. Thus:

$q'= 5,6\cdot 10^{-18}$ [kg/s]

Example 1: Pore radius 10 µm
$L=5\cdot 10=50$ µm. The total amount of air (see above) = $5,23\cdot 10^{-15}$ [kg].
The time required is *0,25 hours.*

Example 2: Pore radius 100 µm
$L=500$ µm. The total amount of air = $5,23\cdot 10^{-12}$ [kg]
The time required is *259 hours or 11 days*

The time required is directly proportional to the bubble volume; viz. Eq (53) implies that the rate of air flow from a bubble in kg per second is independent of the bubble size. It is a constant which is a function of the diffusion coefficient δ, the ratio of diffusion path to the bubble radius, ε, the solubility of air in water, s, and the surface tension, σ:

$$q'= \text{constant}_1 \quad [kg/s] \qquad (54)$$

It might be that the diffusion coefficient in the water phase inside pore 1 is much higher than the diffusion coefficient in the cement paste. In such a case eq (53) is modified to:

$$q'=\delta[1+1/\varepsilon]\cdot r_1\cdot 4\pi\cdot s\cdot 2\sigma/r_{1,t} \qquad (55)$$

This equation is much more difficult to handle since it implies that the rate of water-filling of the air-pore is not a constant but a function of the actual degree of saturation of the pore. It must be solved numerically. For the smallest air-pores, at least, eq (53) and (54) can be used without too much error. For those pores, which are also the most important for frost resistance, the diffusion path outside the pore is much larger than the diffusion path inside the pore. Besides, most of the air-pore volume is filled before the difference between the pore radius r_1 and the bubble radius $r_{1,t}$ becomes very large.

4. The water absorption in model air-pore systems

4.1 INTRODUCTION

In a real air-pore system there are air-bubbles of all sizes varying from about 5 µm to 500 µm or more. Therefore, the simple solution performed above in which only a two-bubble system is regarded is too simplified. Such an analysis does however show that air will be transferred from every pore irrespectively of its size to larger pores in the neighbourhood. Certainly, the pore will also recieve air from smaller adjacent pores. This is the case especially for the larger pores. Therefore, it might be a certain delay before the pore will be "a net exporter" of air migrating to still larger pores, or to the surface. Two different models for a description of this water-filling process is treated below. Only Model 1 is treated in this paper:

Model 1: It is assumed that every pore starts to absorb water already when the capillary process is ended in its surroundings. The rate of air diffusion from a pore expressed in terms of kg per second and the rate of water-filling of a pore is supposed to be the same for all pores; c.f. eq (54). Thus, a smaller pore is always completely filled before a larger one, but the water absorption is going on simultaneously in all pores. This model implies that the total water content in the air-pore system is not only distributed among the smallest pores but that all air-pores contain more or less water. Model 1 is a non-equilibrium model; the total free energy of the air-water system is higher than in Model 2.

Model 2: The net diffusion process between all air-pores in the system is such that a coarser pore will not start to take up water until the next smaller pore is completely water-filled. This model implies that the total water content in the air-pore system is only distributed among the smallest pores while the coarser part of the pore system is completely air-filled (apart from a thin water meniscus along the periphery). Model 2 is the most plausible model from a thermodynamical point of view since it corresponds to the lowest free energy level of the system.

4.2 MODEL 1: ABSORPTION IN ALL BUBBLES SIMULTANEOUSLY

4.2.1 *Theory*

Let us consider an air-pore distribution curve f(r); see *Figure 2.* This distribution could be just a mathematical expression describing the shape of the real distribution curve but not the absolute level of this. A fictitious air-pore volume V_a' calculated by this distribution is:

$$V_a' = \int_{\approx 10\ \mu m}^{\infty} (4\pi/3)\cdot r^3\cdot f(r)\cdot dr \quad [m^3] \tag{56}$$

The lower limit 10 μm is supposed to be the smallest pore that is not water-filled already during the capillary process.

The real distribution F(r) is found by utilizing the real air-pore volume V_a:

$$V_a = \int_{\approx 10\ \mu m}^{\infty} (4\pi/3)\cdot r^3\cdot F(r)\, dr \quad [m^3] \tag{57}$$

The relation between the two distributions is:

$$F(r) = f(r)\cdot V_a/V_a' \tag{58}$$

In the following f(r) is used. The average pore radius $r_{m,i}$ in the interval Δr is defined:

$$r_{m,i} = (r_i + r_{i+1})/2 \qquad [m] \tag{59}$$

The initial volume of air in one bubble of this size is:

$$V_1(r_{m,i}) = (4\pi/3)\cdot(r_{m,i})^3 \qquad [m^3] \tag{60}$$

The initial weight of this air is:

$$Q_1(r_{m,i}) = V_1(r_{m,i})\cdot\rho_o \qquad [kg] \tag{61}$$

Where ρ_o is the density of air at normal pressure and at the actual temperature.

The number of pores with radius $r_{m,i}$ in the interval Δr is:

$$\Phi(r_{m,i}) = f(r_{m,i})\cdot\Delta r \tag{62}$$

The initial volume of air in all those bubbles is:

$$V'(r_{m,i}) = \Phi(r_{m,i})\cdot(4\cdot\pi/3)\cdot r_{m,i}^3 \qquad [kg] \tag{63}$$

The time needed to completely empty each one of these bubbles is:

$$t(r_{m,i}) = Q_1(r_{m,i})/q' = (\rho_o/\, q')\cdot(4\pi/3)\cdot(r_{m,i})^3 \quad [s] \tag{64}$$

Where q'is the rate of air diffusion from the bubble in kg/s. q'is a function of the diffusion coefficient of the cement paste but not of the bubble size; see eq (51). Therefore, it depends on the total airpore volume, the w/c-ratio the type of binder etc; see eq (31). The time needed to empty an air bubble is directly proportional to the bubble volume.

The time process of air diffusion is schematically shown in *Figure 7.* The total air volume that has diffused in the concrete during the time 0 to $t(r_{m,1})$ corresponding to the time it takes to completely fill the smallest bubbles ($r_{m,1}$) is:

$$\begin{aligned} V'_1 = t(r_{m,1})\cdot\{\, & V'(r_{m,1})/t(r_{m,1}) + V'(r_{m,2})/t(r_{m,2}) + \cdots\cdots + \\ & + V'(r_{m,n})/t(r_{m,n}) \qquad [m^3] \end{aligned} \tag{65}$$

The total amount of air that has diffused after time $t(r_{m,i})$ is:

$$\begin{aligned} V'_i = V'(r_{m,1}) + V'(r_{m,2}) + \ldots + V'(r_{m,i-1}) + t(r_{m,i})\cdot\{\, & V'(r_{m,i})/t(r_{m,i}) + \ldots\ldots + \\ & + V'(r_{m,n})/\, t(r_{m,n})\} \quad [m^3] \end{aligned} \tag{66}$$

The total volume of air transported from the air bubbles, V'_i is evidently a time function; $V'_i=V'[t(r_{m,i})]=V'(t)$.

After a very long time the total airpore system is water-filled. Then, the volume of air that has diffused equals the total initial air content in the air-pore system V_a':

$$V'_n = V'(r_{m,1}) + V'(r_{m,2}) + \ldots\ldots + V'(r_{m,n}) = V'_a \qquad [m^3] \qquad (67)$$

The real volume of air transferred in the real air-pore system is obtained by multiplying eq (65), (66) and (67) by the factor V_a/V'_a where V_a is the real air-pore volume; see eq (58). The water volume $V_w'(t)$ that has been taken up by the material at time t of diffusion is supposed to be equal to the volume at normal pressure of diffused air $V'(t)$:

$$V_w'(t) = V'(t) \qquad [m^3] \qquad (68)$$

The mass of water taken up at time t is:

$$W_w'(t) = V_w'(t)\cdot 1000 \qquad [kg] \qquad (69)$$

The degree of water-filling at time t, or the "real" degree of saturation $S_a(t)$, of the entire airpore system is:

$$S_a(t) = V_w'(t)/V_a' \qquad [m^3/m^3] \qquad (70)$$

The *"effective" degree of saturation"* $S_a(t_j)_{eff}$ after time $t_j=t(r_{m,j})$ is defined as the degree of saturation when only water in completely water-filled air-pores, i.e. pores with radii smaller than $r_{m,j}$, are considered. The effective degree of saturation is

$$S_a(t_j)_{eff} = \{\sum_1^j V'_i\}/ V_a' = \{\sum_1^j V'_i\}\cdot S_a(t_j)/V_w'(t_j) \qquad (71)$$

The effective degree of saturation can also be obtained analytically from the air-pore distribution. The volume $V_{w,i}'$ of totally water-filled pores with radii smaller than r_i (μm) is:

$$V_{w,i}' = \int_{\approx 10}^{r_i} (4\pi/3)\cdot r_i^3\cdot f(r)\cdot dr \qquad (72)$$

The radius can be substituted by the corresponding time t_i required to fill completely the pore with radius r_i. Eq (64) gives the relation between the radius and the time. The final result is:

$$V_{w,i}'=\Psi\cdot\int_{\approx 10}^{t_i^{1/3}} f(t)\cdot t^{1/3}\cdot dt \qquad (73)$$

Where the constant Ψ is:

$$\Psi = [(1/3^{1/3})\cdot(4\pi)^{2/3}]\cdot[q'/\rho_o]^{5/3} = 0{,}128\cdot[q'/\rho_o]^{5/3} \qquad (74)$$

The function f(t) is the radius distribution function in which r has been substituted by t using the relation Eq (64).

Principally, it is the effective degree of saturation and not the real degree of saturation that should be used for calculating the residual airpore spacing; see Eq (2a).

By utilizing eq (65) to (67) one can calculate the process of air transport from the air-pore system and consequently the time process of water-filling of the air-pore system.

A simplification made in the derivation is that the the density of air is supposed to be constant. In reality, the density increases as the bubble decreases in size; see eq (24). This means that the calculated water absorption is a bit too high. On the other hand, the cross section of diffusion is assumed to decrease in proportion to the decrease in bubble size; see eq (51). In reality, the cross section is almost constant and determined by the radius of the pore itself. This leads to a too high clculated rate of air diffusion. The two effects probably compensate each other fairly well.

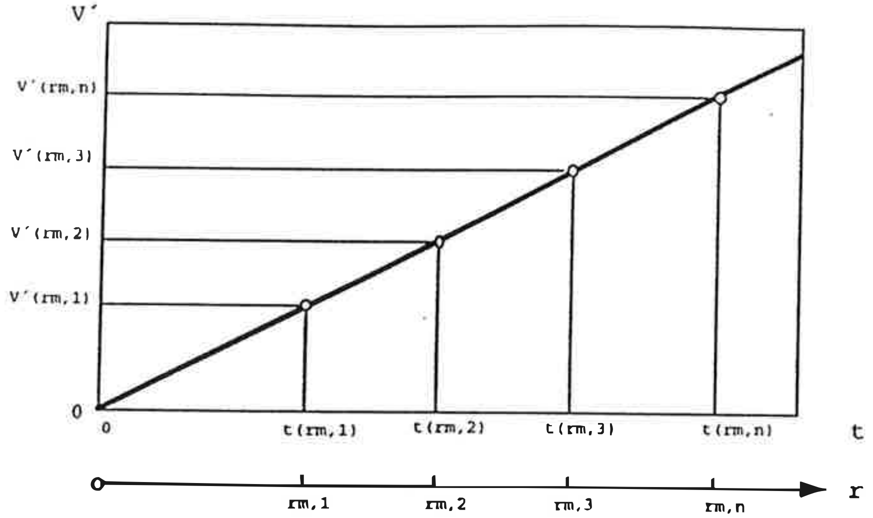

Figure 7: Graphical representation of Model 1 of water absorption in the air-pore system.

4.2.2 *Exponential function of pore radius*

The pore size distribution can be determined by means of microscopical examinations (e.g. ASTM C457) or by automatic image analyses of thin sections or polished impregnated surfaces. The observed one- or two-dimensional pore data are transformed into a three-dimensional pore radius distribution using conventional stereomeric laws. From them the specific surface and the pore volume can be calculated.

A mathematical frequency function that sometimes fit an airpore distribution in a fair manner is:

$$f(r) = a_1\cdot\ln b/b^r \qquad (75)$$

high value 0,587 of the exponent. It might also depend, to some extent, on the values chosen for the diffusion coefficient. The values suggested might be too large.

The effective degree of saturation defined by eq (71) can be calculated analytically utilizing Eq(73) and (74). The following relation for the volume of completely water-filled pores is valid for the actual type of distribution:

$$V_{w,i}' = \Psi \cdot \int_{\approx 10}^{t_i^{1/3}} \{\ln b/b^{[3\cdot q'/(4\pi\cdot\rho o)]}\}^{1/3} \cdot \{ t^{1/3}/(b^{t})^{1/3} \} \cdot dt \qquad (82)$$

Where the constant Ψ is given by Eq (74). This equation can be solved analytically giving the relation between suction time and the effective degree of saturation of the air-pore system.

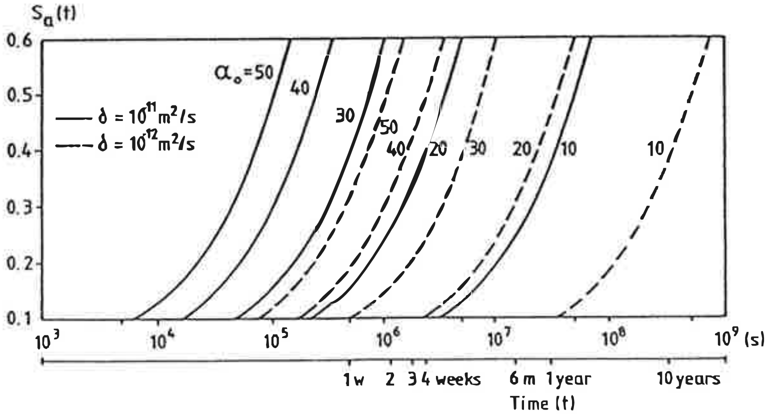

Figure 9: The real degree of saturation of the air-pore system versus the water storage time for two different diffusivities of air transport through pore water. Exponential frequency function. Absorption according to Model 1; [Eq (81)].

The effective degree of saturation is obtained by dividing the values $V_{w,i}'$ by the total air-pore volume V_a'. The relation between the real and the effective degrees of saturation are plotted in *Figure 10*. The relation is almost linear in a log-log scale and independent of the specific surface of the pore system. The following relation is valid:

$$S_{a,eff} = 0{,}918 \cdot S_a^{1{,}45} \qquad (83)$$

This means that a considerable fraction of the absorbed water is contained in pores that are coarser than the colmpletely water-filled finer pores which is shown by the following example:

> ***Example***: The effective degree of saturation is only 0,34 when the real degree of saturation is 0,50. This means that only 68 % of the water is contained in completely water-filled pores and the rest in coarse, partly air-filled pores.

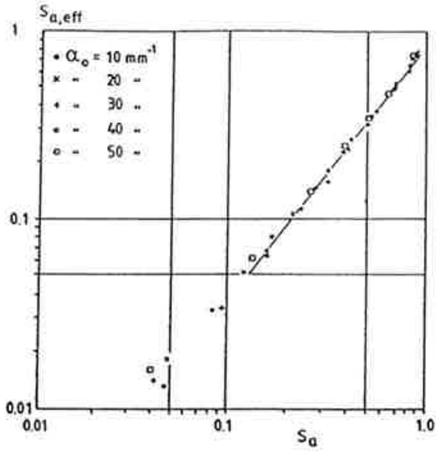

Figure 10: Relation between the real and the effective degrees of saturation of the air-pore system. Exponential frequency function. Absorption according to Model 1.

4.2.3 Power function of pore radii

An alternative frequency function of pore radii is:

$$f(r) = a_2 \cdot \{ 1/r^b - 1/r_{max}^b \} \qquad (84)$$

Where a_2 is a constant which is determined by the total air-pore volume. b is a constant that gives the shape of the distribution. r_{max} is the radius of the largest pore. The power function gives a much more wide distribution than does the exponential function.

The total airpore volume is (for a_2=1):

$$V_a' = [\pi/3] \cdot [b/(4-b)] \cdot \{ r_{max}^{4-b} - r_{min}^{4-b} \} \qquad (85)$$

The total surface area is:

$$A_a' = [4\pi/3]\, [b/(3-b)] \cdot \{ r_{max}^{3-b} - r_{min}^{3-b} \} \qquad (86)$$

The specific surface is A_a'/V_a'.

In *Figure 11* the real degree of saturation is plotted versus the parameter $t \cdot q'/\rho_o$ for some air-pore systems with different specific area.. The relation is fairly linear in a log-log scale. Therefore, the same type of relation as Eq (79) can be used:

$$S_a(t) = B' \cdot [t \cdot q'/\rho_o]^{C'} \quad \text{for} \quad 0{,}1 < S_a(t) < 0{,}6 \qquad (87)$$

The coefficients B´ and C´ are listed in TABLE 2. Note: ρ_o in Eq (87) must be expressed in kg/μm^3.

TABLE 2: The coefficients B′and C′in Eq (87).

Specific surface (mm^{-1})	B′	C′
50	$1,47\cdot10^{-2}$	0,208
30	$2,89\cdot10^{-3}$	0,280
10	$4,84\cdot10^{-5}$	0,465

A general equation is:

$$S_a(t) = 1,33\cdot10^{-8}\cdot\alpha_0^{3,58}\cdot[t\cdot q'/\rho_0]^{1,46\cdot(\alpha_0)^{-0,49}} \tag{88}$$

Where α_0 is expressed in mm^{-1}.

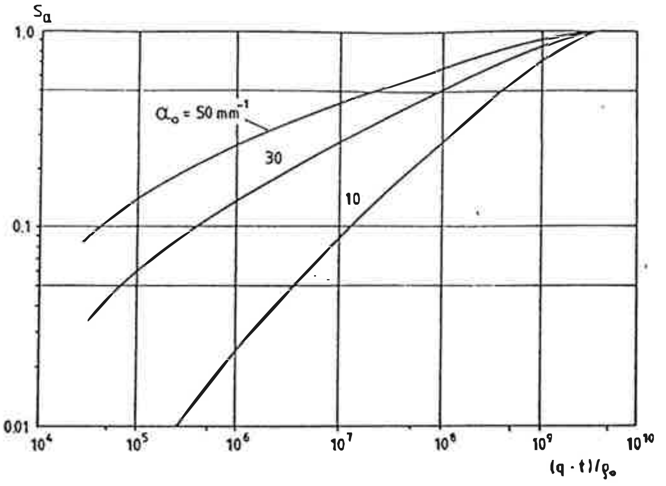

Figure 11: The real degree of saturation of the air-pore system versus the water storage time expressed in terms of the parameter $t\cdot q'/\rho_0$. Power function of pore radius. Absorption according to Model 1; [Eq(88)].

In *Figure 12* the real degree of saturation is plotted versus the suction time for two diffusivities; $\delta=10^{-11}\ m^2/s$ and $\delta=10^{-12}\ m^2/s$. The power function distribution evidently gives a considerably slower water absorption than does the exponential distribution which is shown by the following two examples. The examples also show that the shape of the air-pore system has a very large effect on the rate by which it becomes water-filled.

Example 1: Two concretes with different types of the air-pore system are compared. The specific surface of the pore system is the same, 30 mm^{-1}. This means that the mean value of the pore radius is the same (100 μm) but the median pore radius and the shape of the volume size distribution is different; see above. The diffusivity of air diffusion is $\delta=10^{-11}\ m^2/s$. The time needed to reach a real degree of saturation of 0,5 is calculated.

* *Exponential function*: Eq (81.a) gives: $t = 7{,}5 \cdot 10^5$ sec ≡ *9 days* for $S_a = 0{,}5$.

* *Power function*: Eq (88) gives: $t = 2{,}2 \cdot 10^7$ sec ≡ *260 days* for $S_a = 0{,}5$

Example: The same as above but the specific surface is only 10 mm^{-1}.

* *Exponential function:* Eq (81.a) gives: $t = 5{,}2 \cdot 10^7$ sec ≡ *600 days* for $S_a = 0{,}5$.

**Power function:* Eq (88) gives: $t = 10^8$ sec ≡ *1160 days* for $S_a=0{,}5$.

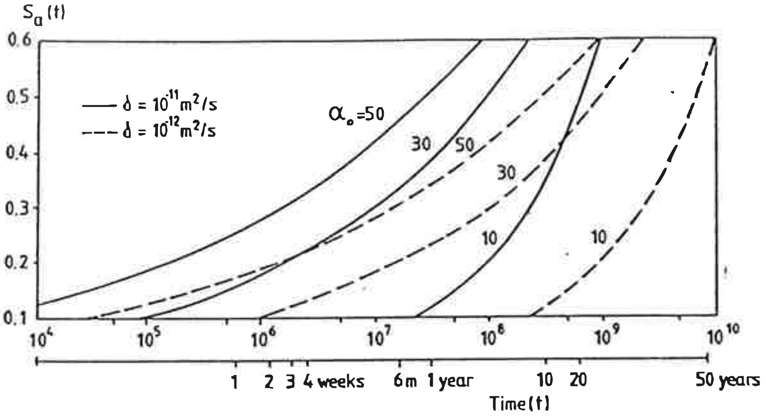

Figure 12: The real degree of saturation of the air-pore system versus the water storage time for two different diffusivities of air transport through pore water. Power frequency function. Absorption according to Model 1.

5. Experimental results

In [7] a series of capillary absorption tests of concretes made with slag cements are presented. Four different cements made of a blend of the same clinker and the same ground granulated blast furnace slag were tested. The slag content was 0 %, 15 % ,40 % and 65 %. The w/c-ratio was 0,45 in all concretes. The nominal air contents of the concretes were 2 % (non-air entrained), 4,5 % and 6 %. The real air content differed a bit from the nominal values.

The air-pore structure of some of the concretes was determined by automatic image analysis. The water absorption was followed up to 30 days. The degree of saturation of the air-pore system versus the time was analyzed according to Eq (12). The results are listed in Table 3. A measure of the absorption rate is obtained by calculating the time needed for a certain fraction of the airpore system to become water-filled. For $S_a=0{,}50$ this time is $t_{0,5}$. It is calculated by:

$$t_{0,5} = [0{,}5/B]^{1/C} \qquad (89)$$

All results of the calculations for the individual concretes are listed in TABLE 4. In Table 3 the mean values and the spread in the coefficients B and C are listed for each cement type separately but including all concretes with the same cement but with different air contents. The spread in the results is not so large. It is a general trend that the exponent C increases with the slag content. The coefficient B is more constant. Therefore, the time needed for a certain degree of water-filling of the airpore system decreases con-

TABLE 4: Results of capillary absorption tests of slag cement concretes. The total test time is 30 days.

slag content (%)	air (%)	α_0 mm^{-1}	B [Eq (12)] (sec.)	C [Eq (12)]	$t_{0,5}$
	2,1	16	$6,55\cdot 10^{-3}$	0,253	$2,8\cdot 10^{7}$
0	4,5	36	$6,22\cdot 10^{-3}$	0,238	$1,0\cdot 10^{8}$
	6,2	45	$6,31\cdot 10^{-3}$	0,244	$6,1\cdot 10^{7}$
	2,0	23	$9,94\cdot 10^{-3}$	0,238	$1,4\cdot 10^{7}$
15	4,1	54	$7,16\cdot 10^{-3}$	0,247	$2,9\cdot 10^{7}$
	5,9	44	$7,47\cdot 10^{-3}$	0,248	$2,3\cdot 10^{7}$
	2,2	52	$6,24\cdot 10^{-3}$	0,277	$7,5\cdot 10^{6}$
	4,2	40	$5,85\cdot 10^{-3}$	0,268	$1,6\cdot 10^{7}$
40	5,4	55	$4,71\cdot 10^{-3}$	0,286	$1,2\cdot 10^{7}$
	4,2	52	$5,59\cdot 10^{-3}$	0,274	$1,3\cdot 10^{7}$
	6,8		$6,32\cdot 10^{-3}$	0,272	$9,5\cdot 10^{6}$
	1,8	26	$6,28\cdot 10^{-3}$	0,281	$5,8\cdot 10^{6}$
65	3,3	43	$6,85\cdot 10^{-3}$	0,277	$5,3\cdot 10^{6}$
	4,5	50	$7,55\cdot 10^{-3}$	0,268	$6,2\cdot 10^{6}$
	6,0	49	$5,50\cdot 10^{-3}$	0,289	$6,0\cdot 10^{6}$
Average		32	$6,67\cdot 10^{-3}$	0,264	$1,3\cdot 10^{7}$ 1)

1) Based on the average values of all values of B and C

TABLE 5: The time needed to water-fill 30, 50 and 70 % of the airpore system. The calculation is based on the mean coefficients of B and C from TABLE 4.

Slag content (%)	time (days)		
	$t_{0,3}$	$t_{0,5}$	$t_{0,7}$
0	80	640	2550
15	30	240	960
40	20	130	450
65	10	70	220

6. Summary

Frost damage occurs when a certain critical water content in the pore system of the concrete is transgressed. Below the critical water content no harm is caused when the concrete freezes; above the critical value severe damage occurs. Therefore, the residual service life of concrete that is exposed to frost action is coupled to the future moisture conditions inside the concrete. The critical absorption is individual for each concrete and depends on its water-cement ratio, its air content, its air-pore structure etc. It is almost independent of the number of freeze/thaw cycles and the freezing rate but it is to a certain extent dependent of the minimum freezing temperature.

The critical water content is a "fracture value" that is individual for every concrete. It does always correspond to a certain absorption in the so called air-pores by which is meant pores that are coarse enough not to take part in the capillary absorption process. Therefore, in order to make a prediction of the future service life possible one has to be able to predict the long term absorption in the air-pore system.

In this report a theoretical and quantitative analysis is made of the absorption process in air-pores within a concrete that is permanently stored in water. The absorption depends on the dissolution of air from air-bubbles that became enclosed in the air-pores already during the first rapid capillary absorption process. The dissolved air moves by diffusion to larger air-bubbles and, finally, to the surface of the specimen. This process is very slow, especially for coarse air-bubbles .

Two main models for the absorption process are imaginable. Only model 1 is treated in the paper:

Model 1: According to which water absorption takes place simultanously in bubbles of all sizes. It leads to a rather rapid water absorption process, the smallest bubbles being lost at first but the coarser bubbles also absorbing water from the onset of water storage.

Model 2: According to which a coarser bubble does not start to absorb water until the next smaller bubble is completely filled. This model is the most plausible one from a thermodynamical point of view. It leads to a considerably slower absorption rate than Model 1 and, thus, to a longer service life.

Equations for calculation of the water absorption in an arbitrary air-pore system are provided. Two types of frequency curves of the pore radius are investigated in detail; (a) exponential functions; (b) power functions. Diagrams for the prediction of the absorption-time curves in such pore systems are provided.

The absorption rate is found to be very much depending on the shape of the pore size distribution; the exponential function giving much more rapid absorption at a given average specific surface of the air-pore system.

Experimental long term water absorptions for 15 concretes are presented. The agreement between the theoretical absorption curves and the observed is fairly good.

7. References

1. Fagerlund G. (1986) The critical size in connection with freezing of porous materials. *Cementa Report* CMT 86039, Stockholm.
2. Fagerlund G. (1980) Influence of slag cement on the frost resistance of concrete - a theoretical analysis. *Swedish Cement and Concrete Research Institute.* Research Fo 1:80, Stockholm.
3. Fagerlund G. (1992) Effect of the freezing rate on the frost resistance of concrete. *Nordic Concrete Research*, Publication Nr 11, Oslo.
4. Powers T.C. (1949) The air requirement of frost resistant concrete. *Highway Research Board*, Proceedings, Vol 29.
5. Fagerlund G. (1977) Equations for calculating the mean free distance between aggregate particles or air-pores in concrete. *Swedish Cement and Concrete Research Institute.* Research Fo 8:77, Stockholm.
6. Fagerlund G. (1993) The critical spacing factor. *Division of Building Materials, Lund Institute of Technology*, Report TVBM-7058, Lund.
7. Fagerlund G. (1992) The influence of slag cement on the frost resistance of the hardened concrete. *Swedish Cement and Concrete Research Institute.* Research Fo 1:82, Stockholm.
8. Fagerlund G. (1977) The critical degree of saturation method of assessing the freeze/thaw resistance of concrete. *Materials and Structures*, Vol 10, No 58.
9. Fagerlund G. (1979) Prediction of the service life of concrete exposed o frost action. *Studies on Concrete Technology.* Swedish Cement and Concrete Research Institute. Stockholm.