AIR-PORE INSTABILITY AND ITS EFFECT ON THE CONCRETE PROPERTIES

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ABSTRACT

Three different mechanisms for the air-pore instability of the fresh concrete are described quantitatively, together with their effects on the concrete properties - especially the freeze/thaw resistance.

Mechanism 1: Loss of coarse air-bubbles due to handling and compaction; It gives small effects on the freeze/thaw resistance, but increases the strength and E-modulus.

Mechanism 2: Dissolution of small bubbles in the water. It might lead to large reductions in the freeze/thaw resistance.

Mechanism 3: Transfer of air from small bubbles to coarser bubbles; It might lead to a considerable increase in the air-content and to reductions in the freeze/thaw resistance, strength and E-modulus.

Keywords: Air-pore stability, Freeze/thaw resistance, Strength, E-modulus.

1. DIFFERENT TYPES OF AIR PORE INSTABILITY

The "primitive" air pore system of an air-entrained concrete is established during the mixing process. If the air-pore system is completely stable, the primitive system will be identical with the "hardened" system. Due to different mechanisms, the air-pore system will, however, normally undergo changes between mixing and hardening. There are three possible mechanisms behind this instability of the air-bubble system:

1. Fig 1 (a). Migration of air bubbles to the surface of the concrete due to density difference between air bubbles and cement paste. The driving force is proportional to the square of the bubble diameter. Therefore, the largest air bubbles are lost at first. The mechanism leads to substantial air losses, but to rather small changes in the specific surface.

2. Fig 1 (b). Complete and rapid collapse of individual bubbles due to the internal over-pressure in the bubble leading to dissolution of air in the surrounding water. Since the over-pressure is highest in the smallest bubbles the mechanism leads to an increase in the spacing factor but to small or no air losses.

3. Fig. 1 (c). A gradual migration of air from smaller to larger air-bubbles due to different gas pressure inside air-bubbles of different size. This mechanism leads to a gradual increase in the spacing factor at the same time as the air volume increases.

Mechanism 1 has been widely studied, e.g. in tests where the air loss during prolonged vibration was investigated. The presence of mechanisms 2 and 3 were pointed out by Mielenz et al /1/ but were not expressed quantitatively. Mechanism 2 is a special case of mechanism 3. The three mechanisms and their effects, especially on the frost resistance, will be discussed below.

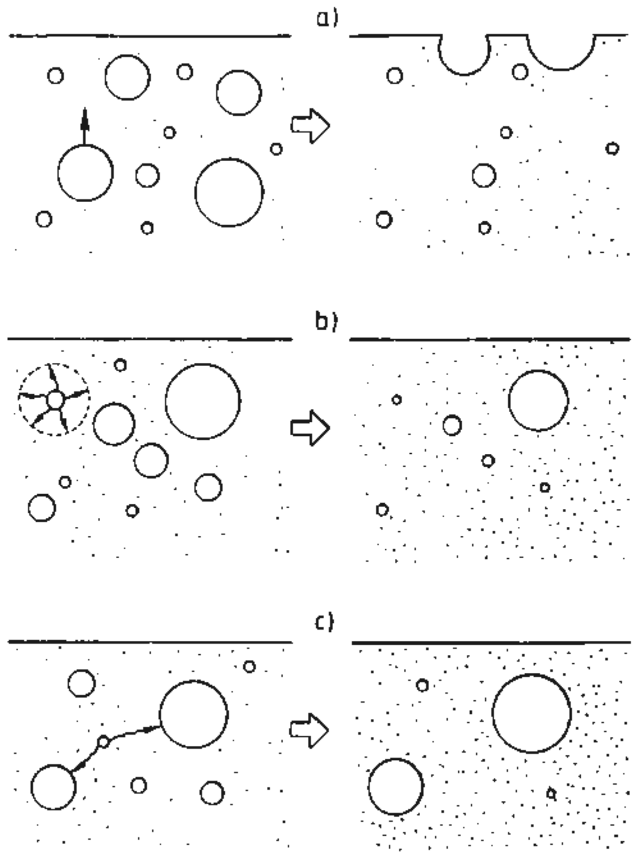

Fig. 1. Three mechanisms for air bubble instability.
(a) Loss of coarse air bubbles due to handling and compaction.

(b) Dissolution - collapse - of small air bubbles.

(c) Migration of air from small to coarse air bubbles.

2. MECHANISM 1: LOSS OF COARSE AIR-BUBBLES

During transport, handling, placing and compaction of concrete a migration of air-bubbles upwards - or to the form wall - takes place. Many smaller pores coalesce into bigger ones which increases their rate of upward migration. As a result of this process a substantial fraction of the total air might be lost.

The net upward force - the buoyancy - is higher the larger the bubbles. Therefore, the largest bubbles are lost at first. The process is described theoretically in /2/.

The air-loss is often considerable but the effect on the air-pore spacing is, despite this, often small. This can be shown by a rather simple analysis.

Let us assume that the relative air-pore radius frequency curve of the "primitive" air-pore system, i.e. before any air loss has taken place, can be described by the following equation, which is a fair approximation for many air-void systems /3/

$$f(r) = \frac{\ln b}{b^r} \qquad (1)$$

where r is the pore-radius and b is a constant that expresses the shape of the frequency curve; the larger the value of b the smaller the average pore size and the more narrow the frequency curve.

By solving eq (4)-(6) below for $0 \le r \le \infty$ the following equation is found for the relation between the constant b and the specific surface α_o of the air-bubble system before any air loss has taken place

$$b = e^{\alpha_o} \qquad (2)$$

The value of b will depend on the unit used for radius and specific surface; (Example; the specific surface of a pore system with the average pore size 0.2 mm is 30 mm^{-1} corresponding to b = $1.069 \cdot 10^{13}$ or 0.030μm^{-1} corresponding to b = 1.03; In the following the units μm is used.)

The total relative air-pore volume before air loss is

$$V_o = \int_0^\infty f(r) \, \frac{4}{3} \pi r^3 dr = \frac{8\pi}{(\ln b)^3} \qquad (3)$$

Let us assume that all air-pores larger than r have been lost. Then, the residual air-content is

$$V_r = \int_0^r f(r)\,\frac{4}{3}\pi r^3 dr \qquad (4)$$

The residual internal pore surface is

$$S_r = \int_0^r f(r)\,4\pi r^2 dr \qquad (5)$$

And the residual specific surface is

$$\alpha_r = \frac{S_r}{V_r} \qquad (6)$$

Let us consider an air-void system defined by b=1.03 (i.e. $\alpha_o=0.030\mu m^{-1}=30\ mm^{-1}$). Eqs (4)-(6) are solved for different values of the upper integration limit r. The result of such calculations is shown in Fig 2. We see that the larger the air-loss the higher the residual specific surface.

We can now calculate the residual spacing L_r between air-voids using the Powers equation.

$$\bar{L}_r = \frac{3}{\alpha_r}\left(1.4\left(\frac{P}{V_r}+1\right)^{1/3}-1\right) \qquad (7)$$

where P is the cement paste volume excluding air-pores and α_r and V_r are calculated by eq (6) and (4).

Let us consider a concrete with P=30 %, an initial air-content of 6 % and an initial specific surface of 30 mm^{-1} (i.e. b=1.03). Then, the curves in Fig 2 together with eq (7) can be used for a calculation of the relation between the air-loss (in unit-%), the specific surface and the spacing factor. See Fig 3.

We find that the spacing factor is almost uninfluenced by the air-loss until this becomes very large. To begin with, there is even a slight decrease which is of course theoretically impossible since the total number of air-voids have been reduced. The reason behind this error is the way by which the Powers spacing factor is defined; viz. in eq. (7) it is assumed that all pores are equal to the average pore, the size of which is determined by the specific surface of the total air-pore system, and that all pores are placed in a symmetrical "lattice". A method for calculating a more true spacing factor based on the real size distribution is presented in /4/.

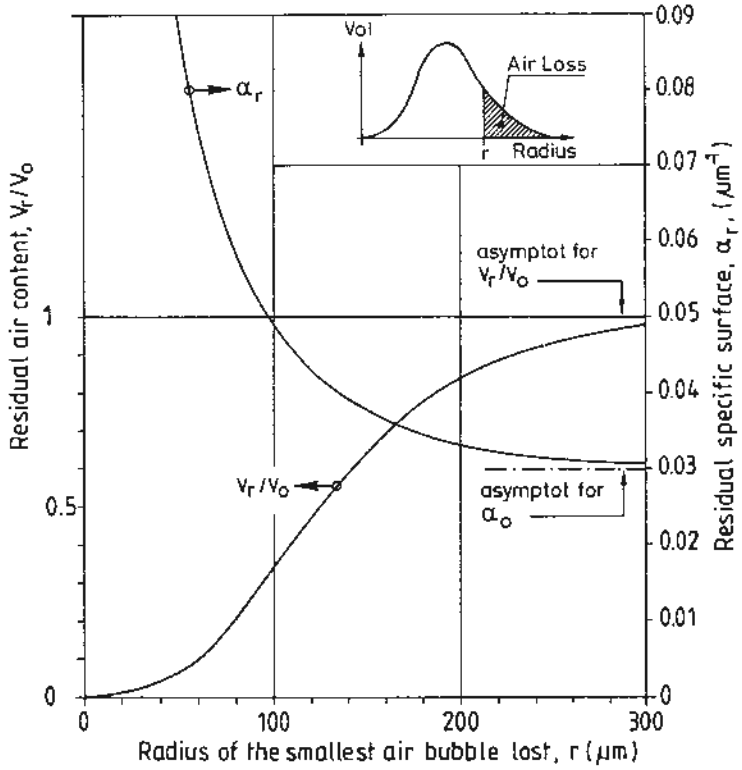

Fig. 2. Example of changes in the air-volume and the specific surface due to loss of the coarsest air bubbles; Mechanism 1.

Results very similar to those found in the theoretical analysis above have also been obtained during practical tests; e.g. see Fig. 4 where the air-content, the specific surface and the spacing factor for three concretes are plotted versus the vibration time /7/. Even in these tests, the calculated spacing factor increases only slightly.

Air loss due to mechanism 1 could evidently, from a theoretical point of view, not lead to any dramatic decrease in the frost-resistance provided the smallest bubbles stay in their place and that only the largest bubbles are lost. This statement is verified by practical freeze/thaw tests; see Fig 4. according to which there is even a slight increase in the frost resistance after the first air-loss has taken place. On the other hand, if the air-pore system is so unstable that the smaller bubbles do also migrate and eventually coalesce into larger bubbles, the freeze/thaw resistance could be very much impaired.

Since mechanism 1 leads to a reduction of air-content it will also lead to an increase in strength and E-modulus.

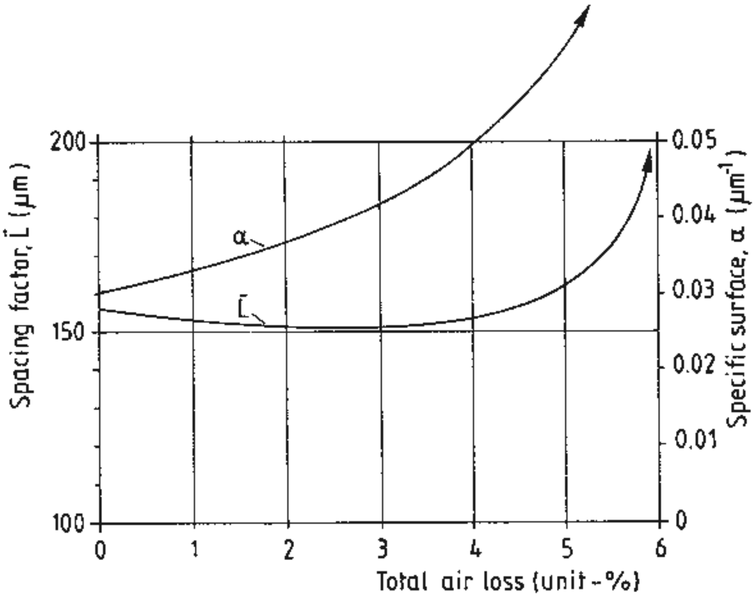

Fig. 3. Changes in the specific surface and the spacing factor as function of the amount of air lost; Data from Fig. 2.

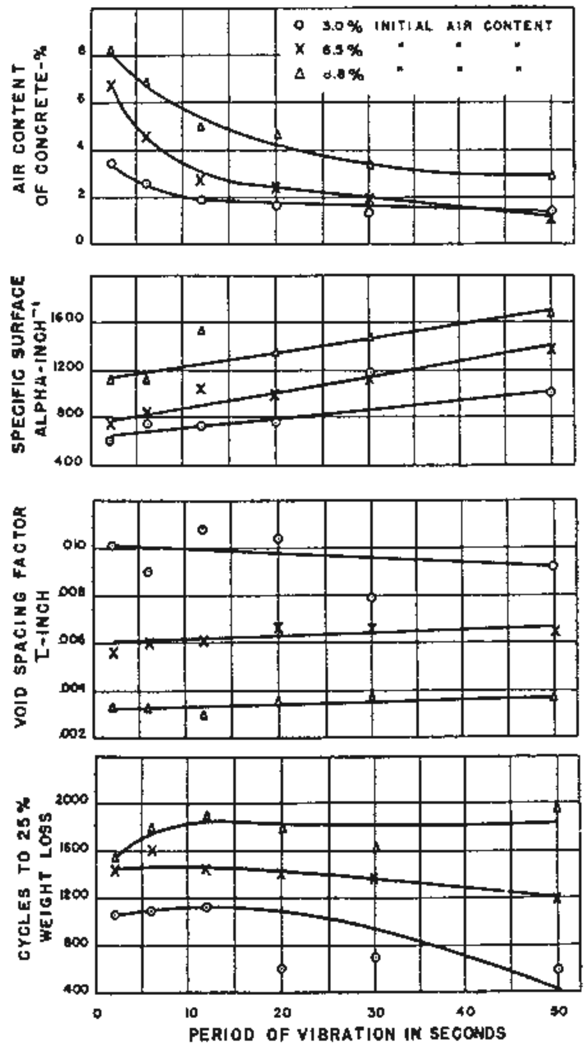

Fig. 4. Effects of the vibration time on the air void characteristics and the freeze/thaw resistance /7/.

3. MECHANISM 2. TOTAL COLLAPSE OF SMALL AIR-BUBBLES DUE TO DISSOLUTION

The pressure in an air-bubble is

$$P = P_o + \frac{2\sigma}{r} \qquad (8)$$

where σ is the surface tension between the air and the liquid meniscus. σ will be depend on the air-entraining agent used, but will always be lower than the surface tension water-air. The reduction in surface tension could be as high as 25 % (from 0.073N/m to 0.053N/m) or even more /1/.

The pressure P_o is the pressure in the liquid surrounding the bubble. This is composed of the atmospheric pressure, 10^5 Pa, and the hydrostatic pressure of the concrete. Thus, P_o will depend on the extent by which the weight of solid particles above the actual bubble could be carried by other solid particles below the bubble. The minimum value of P_o is

$$(P_o)_{min} = 10^5 + \gamma_w \cdot g \cdot h \qquad (9)$$

where γ_w is the density of water (1000 kg/m^3), g the gravitation constant and h the depth below the upper concrete surface.

The maximum value is

$$(P_o)_{max} = 10^5 + \gamma_c \cdot g \cdot h \qquad (10)$$

where γ_c is the density of concrete (a normal value is 2300 kg/m^3).

Thus, compared with the liquid phase, the air in the bubble is exposed to an over-pressure $\Delta P = 2\sigma/r$. The solubility of air in water is almost directly proportional to the pressure. At P_o=1 atm (10^5 Pa) the solubility is $2.5 \cdot 10^{-2}$ kg/m^3. At the actual over-pressure the "extra" solubility is

$$s = 2.5 \cdot 10^{-2} \cdot \frac{2\sigma/r}{P_o} \qquad (11)$$

Due to this over-pressure the bubbles will gradually dissolve; the smaller the bubble the larger the tendency of dissolution. Very small bubbles will disappear completely. The total air mass m_r in an air-bubble of size r is

$$m_r = \rho_1 \cdot \frac{4}{3} \pi r^3 \qquad (12)$$

where ρ_1, is the density of the compressed air. But, the density is directly proportional to the pressure. Hence, according to eq (8) (neglecting the hydrostatic pressure component of eq (9) and (10)).

$$\rho_1 = \rho_o \frac{P_o + 2\sigma/r}{P_o} \qquad (13)$$

where ρ_o is the air density at 1 atm (1.25 kg/m^3). By inserting eq (13) in (12) and utilizing the solubility according to (11) we can calculate the water volume V_w that is required in order to dissolve all air in a bubble of size r assuming the water is saturated by air of normal atmospheric pressure. This water volume will be

$$V_w = 210 \cdot \left(\frac{P_o}{2\sigma/r} + 1\right) \cdot r^3 \qquad (14)$$

This volume can easily be transformed to a required thickness of a water shell surrounding the bubble. The result of such a calculation is shown in Fig. 5. It is assumed that the cement paste has a W/C-ratio of 0.5, i.e. the volume fraction of water is 60 %.

The required shell thickness grows very rapidly with increasing bubble size; for a bubble diameter of 10 μm it is only 32 μm; for a bubble diameter 100 μm it is as large as 672 μm.

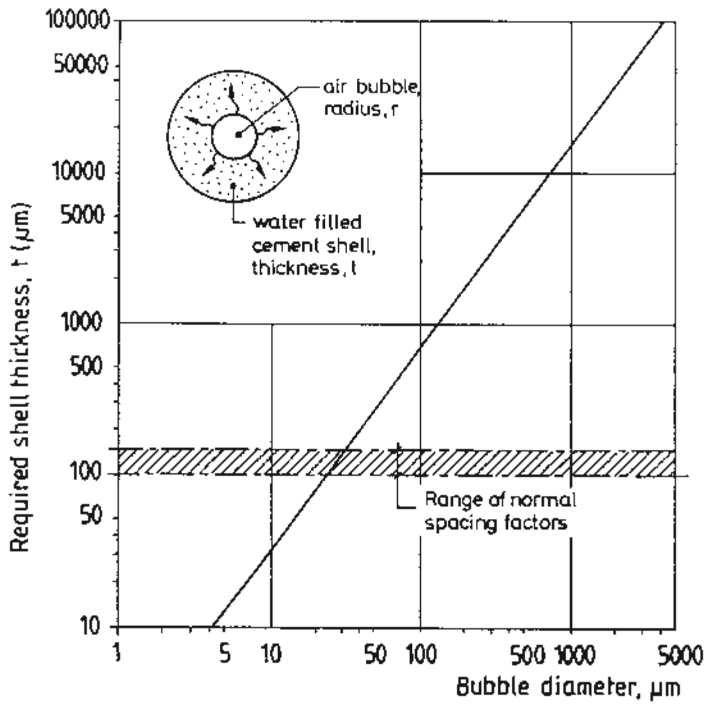

Fig. 5. Thickness of the cement paste shell surrounding an air bubble required for total dissolution of the bubble (W/C=0.50).

For normal air-pore systems the spacing factor (half the average spacing between air-pores) is only 100 à 150 μm. This means, in theory at least, that bubbles with diameters below 23 à 42 μm can be completely dissolved in the water "belonging" to them provided the rate of dissolution is rapid enough to be completed while the concrete is fresh (2-4 hours). Bubbles that are larger cannot be completely dissolved.

This dissolution of small bubbles is the most plausible reason why very small air-voids (≤10μm) are missing in concrete.

The rate of dissolution is unclear. It must depend on the characteristics of the air-liquid interface, which depends on the type and amount of the air-entraining agent; the thicker and more impermeable the interface, the slower the dissolution. The dissolution rate must also be a function of the permeability of the fresh cement paste; Hence, the lower the W/C-ratio the lower the dissolution. A low W/C ratio will therefore promote a high specific surface of the air-pore system. This is also found in practice; see Fig. 14. An estimate of the dissolution rate is made in the next paragraph.

The proposed dissolution mechanism has been studied experimentally /1/; see Fig. 6 showing the gradual reduction of the size of air-bubbles in mixtures of different air-entraining agents and pure water. In these tests the dissolution rate is high even for rather big bubbles. There is, however, a clear diffference between different air-entraining agents.

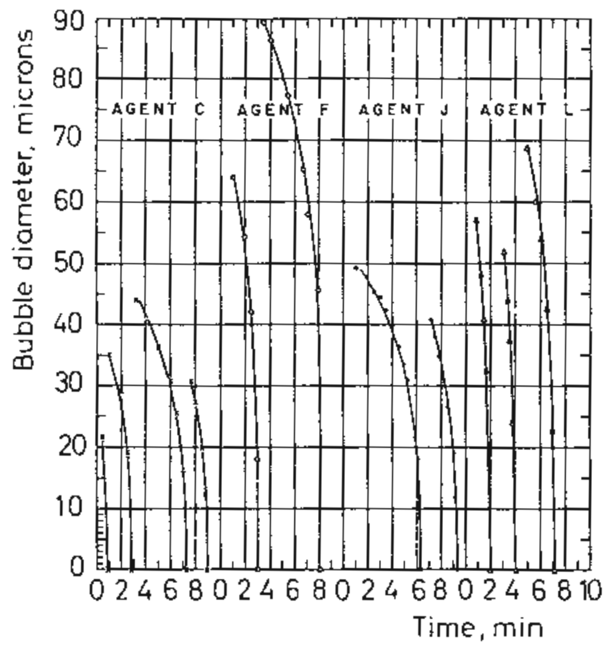

Fig. 6. Experimental studies of the dissolution of air bubbles in solutions of air entraining agents and water /1/.

We can calculate the effect of the dissolution process by analyzing a concrete with the same bubble size distribution and air content as that used for Fig. 2 and 3; i.e. eq. (1) is used with b=1.03 (size in μm), 6 % initial air content and 30 % cement paste content.

The dissolution process leads to loss of the smallest air bubbles. Therefore eq. (3) and (4) are now integrated between the limits r and ∞, where r is the radius of the smallest undissolved bubble (all bubbles larger than r are supposed to be uninfluenced by dissolution).

The result of the calculations is shown in Fig. 7 and 8. Even a small air-volume loss leads to substantial and detrimental changes in the specific surface and the spacing factor; e.g. an air loss of 0.5 % caused by dissolution of all pores smaller than 55 μm (radius) leads to 22 % increase in the spacing factor.

Thus, air-entraining agents creating highly permeable air liquid interfaces and cement pastes with a high degree of permeability (diffusivity) will stimulate the dissolution and decrease the freeze/thaw resistance.

The effects of mechanism 2 on other concrete properties, such as strength and E-modulus are negligble due to the small changes in air-content.

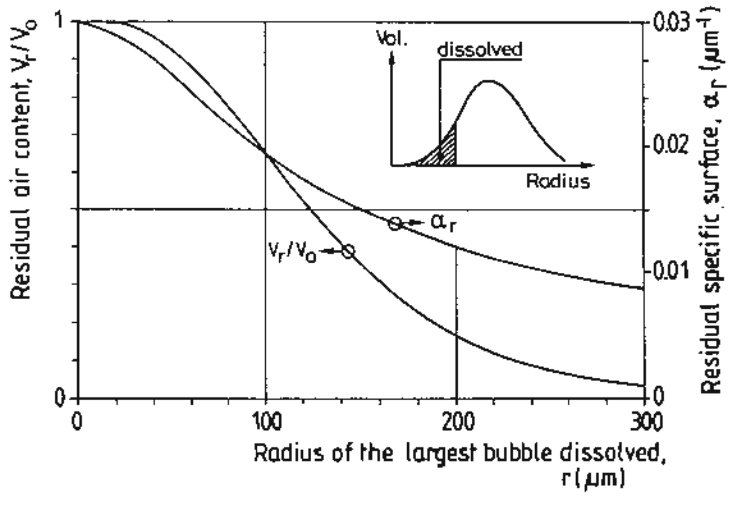

Fig. 7. Example of changes in the air volume and the specific surface due to dissolution; Mechanism 2.

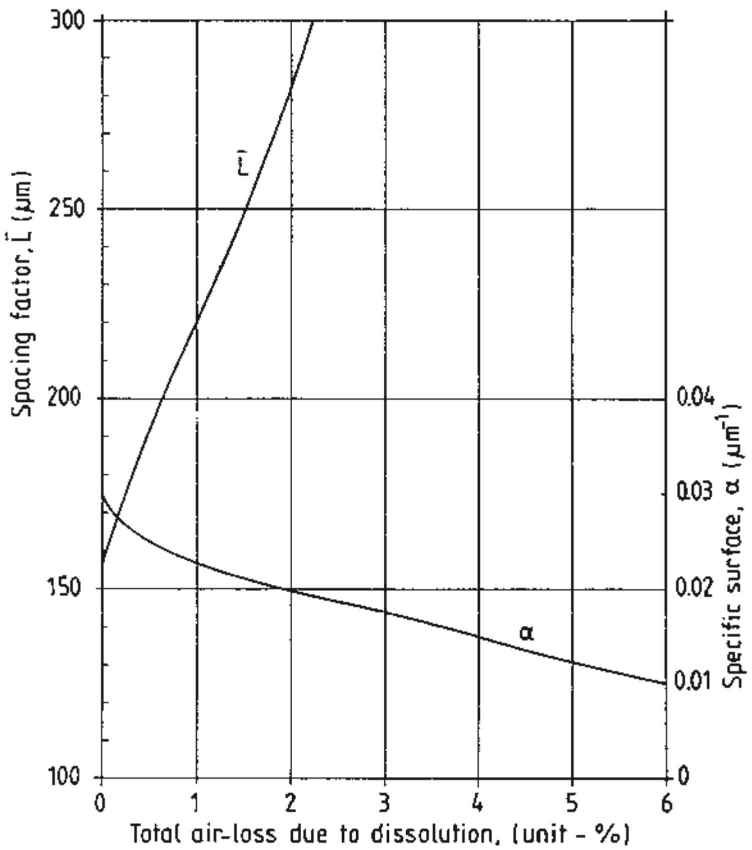

Fig. 8. Changes in the specific surface and the spacing factor as function of the amount of dissolved air; Data from Fig. 7.

4. MECHANISM 3. MIGRATION OF AIR FROM SMALLER TO LARGER AIR BUBBLES

The concentration of dissolved air is inversely proportional to the pore radius, eq. (11). Therefore, there will be a migration of air from a smaller bubble to a larger. This process was found to occur in the experiments presented in Fig. 6 /1/. See Fig. 9 showing the size change of an individual bubble in a foam created by Neutralized Vinsol Resin in pure water. During the first 35 minutes the bubble grows due to inflow of air that is transferred from smaller bubbles through the liquid phase. Thereafter, when all neighbouring small bubbles are lost, it starts to decrease due to dissolution.

When the compressed air in a small bubble reaches a larger bubble it expands due to the pressure reduction. Therefore, the total air-content of the air pore system will increase.

The rigorous theoretical derivation leads to complicated equations, and is not shown here. Under certain assumptions the equations can, however, be simplified.

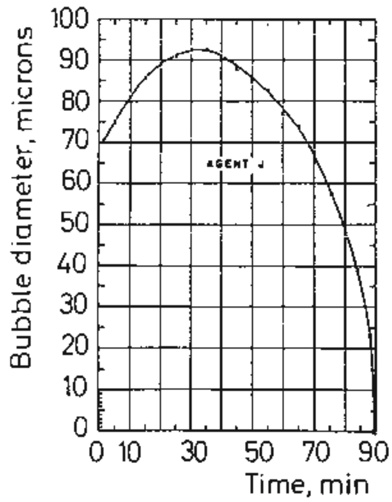

Fig. 9. Changes in the air bubble size as function of time. Mixture of air entraining agent in water /1/.

<u>Case 1:</u> The initial air bubbles are so small that the capillary pressure in all bubbles is considerably larger than the atmospheric pressure. This means that the bubble diameter must be below 1 à 2 µm. Then, for a pore system containing pores of two different size classes - 1 and 2, class 1 having a smaller diameter than class 2 - the following expression is valid for the ratio V/V_o of the total air pore volume after and before transfer of all air in pores of class 1 to pores of class 2 /5/

$$\frac{V}{V_o} = \frac{1}{1 + \frac{V_1}{V_2}} \left[\sqrt{1+ \frac{1}{\alpha}\frac{V_1}{V_2}}\right]^3 \qquad (15)$$

where V_1 and V_2 are the initial total bubble volumes of pores of class 1 and 2 and α is the ratio of air-pore sizes in the two classes.

This expression is shown in Fig. 10.

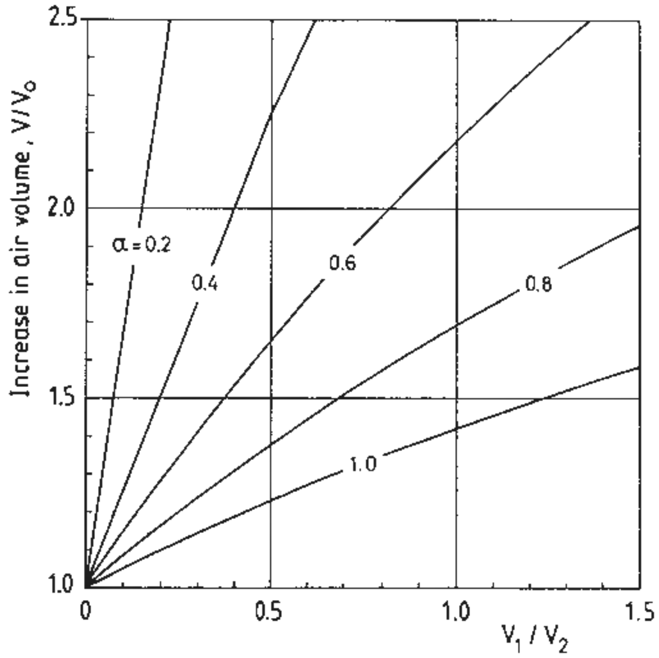

Fig. 10. Air-volume increase due to transfer of air from very small bubbles (index 1) to somewhat larger bubbles (index 2); c.f. eq. (15).

Mechanism 3 could evidently lead to considerable increases in the total air-pore volume provided the initial air bubbles are very small and the size ratio is large. If the initial bubbles are so large that the atmospheric pressure is dominating the increase in air-volume is much more limited.

Case 2: The pores serving as recipients for the transferred air are so coarse that the capillary pressure in them is negligible. Then, the relative air-volume after and before collapse of the smaller bubbles is

$$\frac{V}{V_o} = \frac{\frac{V_1}{V_2}\left(1 + \frac{2\sigma}{r \cdot p_o}\right) + 1}{\frac{V_1}{V_2} + 1} \qquad (16)$$

where r is the radius of the small bubbles.

This expression is shown in Fig. 11. Case 2 leads to a considerably smaller increase in the air-content. However, an increase of 50 % or more is theoretically possible provided there is a large fraction of small air-bubbles created initially during the mixing.

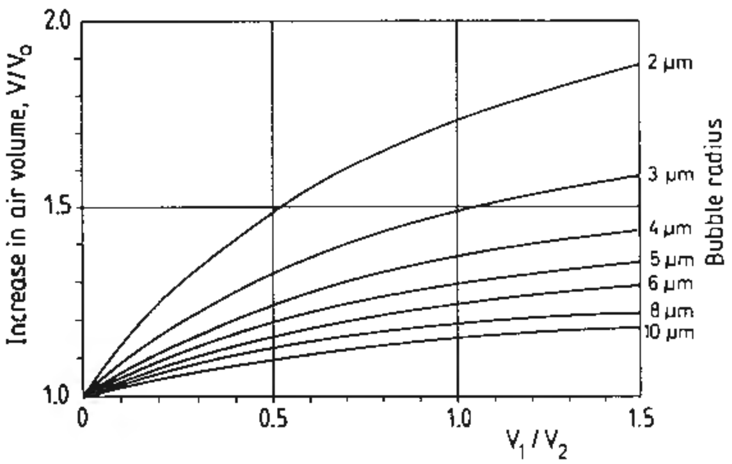

Fig. 11. Air-volume increase due to transfer of air from very small bubbles with radius r to coarse bubbles; c.f. eq. (16).

The time process of air migration could be estimated. The diffusion rate is described by

$$q = \delta \cdot \frac{A}{L} \cdot \Delta C \qquad (17)$$

where q is the flux (kg/s), δ is the diffusivity of air in cement paste (m^2/s) A is the effective cross-section of the flow, (m^2), L is the diffusion path (m) and ΔC is the concentration difference of solved air (kg/m^3).

The cross-section of flow is supposed to be equal to the cross-section of the smaller bubble; $\pi \cdot D^2/4$ where D is the bubble diameter, L is the average spacing between bubbles (≈300µm), $\delta \approx \beta \cdot 2 \cdot 10^{-9}$ m^2/s, where $2 \cdot 10^{-9}$ m^2/s is the diffusivity of air in water, β is a reduction factor for cement paste, ΔC depends on the bubble sizes - se eq. (11). The bubble recieving air is supposed to be very large. Then

$$\Delta C = 2.5 \cdot 10^{-2} \frac{4\sigma}{DP_o} \qquad (18)$$

Insertion in eq. (17) gives

$$q = 3.83 \cdot 10^{-13} \cdot \beta D \text{ (kg/s)} \qquad (19)$$

The total air-mass in a pore of size D is (see eq (12) and (13):

$$m = 0,65(1+ \frac{2.92 \cdot 10^{-6}}{D})D^3 \text{ (kg)} \qquad (20)$$

Thus, the time needed for emptying a pore with diameter D is

$$t=1.7\cdot 10^{12} \left[1+ \frac{2.92\cdot 10^{-6}}{D}\right]\cdot \frac{D^2}{\beta} \text{ (s)} \qquad (21)$$

This equation gives a maximum value; viz. in reality the concentration gradient increases with time due to the gradually increased pressure occurring when the bubble conctracts. Besides the effective cross section for the flow is larger than that assumed.

The reduction factor β is crucial. Its value is unknown but it must depend on the w/c-ratio. The maximum possible value is equal to the volume fraction of water in cement paste; i.e.

$$\beta_{max} = \frac{W}{C} / (\frac{W}{C} + 0.32) \qquad (22)$$

The real value is probably much smaller. In Fig. 12 eq. (21) has been plotted for two values of β; 0.1 and 0.6 (the value 0.6 corresponds to β_{max} for w/c=0.48).

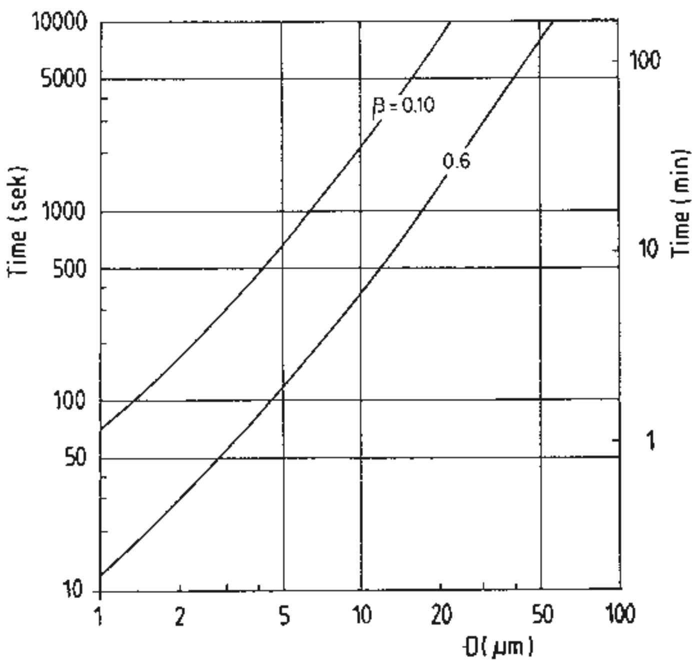

Fig. 12. The time required to completely transfer all air from a smaller bubble to a larger. The inter-bubble spacing is 300 µm; C.f. eq. (21).

Evidently, it takes a very long time to empty larger pores (>20 à 50 μm) whilst it seems as if smaller pores have time to vanish completely during the hours the concrete is fluid. Therefore mechanism 3 is likely to occur in practice. It leads to increased air-content, decreased specific surface and increased spacing factor. The effect on the spacing factor can be calculated in exactly the same way as shown above; see Fig. 7 and 8; the fact that the larger bubbles grow could be neglected since it will have little effect on the specific surface, and therefore little effect, on the spacing factor.

There are numerous observations that the air-content of the hardened concrete could be higher than for the fresh concrete /6, 7, 8/. One example is shown in Fig. 13. The only plausible explanation is this interchange of air between small and coarse air-bubbles.

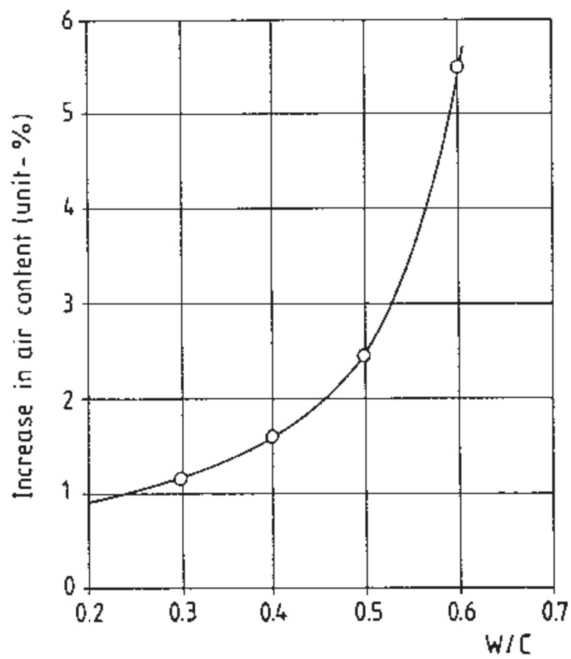

Fig. 13. Examples of the increase in the air-content of neat cement pastes from the fresh to the hardened state /1/.

The magnitude of this effect must be a function of the air-entraining agent used (possibly in combination with a plasticizing agent) and the w/c ratio. Air entraining agents creating "primitive" air pore systems that contain exceptionally fine bubbles should cause geater effects - see Fig. 10, 11 - and so should concretes with higher w/c-ratios. Therefore, one could expect that concretes with higher w/c-ratios will have a larger increase in air-content and end up with lower specific surfaces and larger spacing factors. This is also experimentally confirmed, see Fig. 13 and 14.

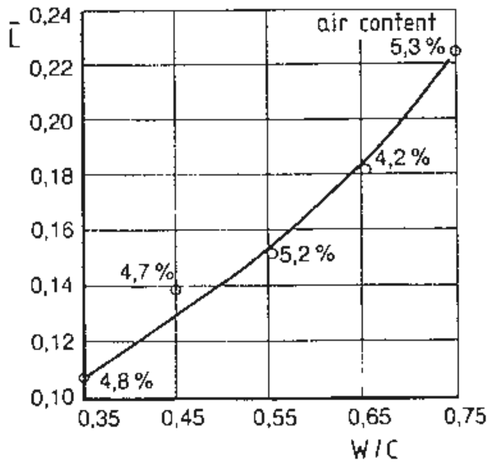

Fig. 14. Relation between the w/c-ratio and the spacing factor of concretes with almost the same air content /7/.

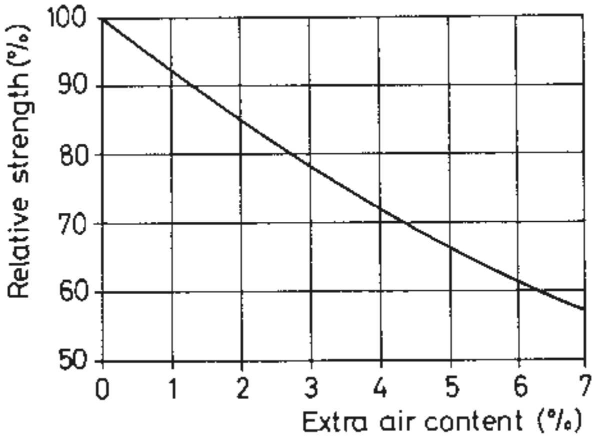

Fig. 15. Decrease in strength due to an air-content that is higher than intended /6/.

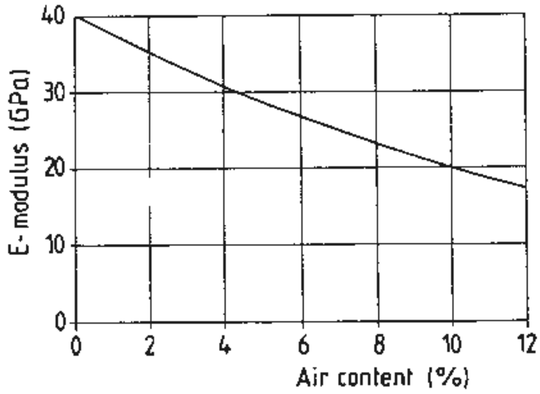

Fig. 16. Relation between the air-content and the E-modulus of concrete /6/.

Mechanism 3 has two negative effects:

1. It leads to increased spacing factor and therefore to reduced freeze/thaw resistance.

2. It leads to increased porosity and therefore to reduced strength and E-modulus. In Fig. 15 a theoretical relation between strength and air-content is shown /6/. If the air-content grows by 3 unit-% the reduction in strength is 22 %.

   In Fig. 16 similar relation between E-modulus and air-content is shown. If the air-content grows from expected 5 % to 8 % the E-modulus changes from 29 GPa to 23GPa.

5. CONCLUSIONS

The air-bubble system of the fresh concrete might undergo many changes before the concrete is set; the coarsest bubbles might escape during handling and vibration; the smallest bubbles might be lost due to complete dissolution or transfer to larger bubbles. A theoretical analysis made in the report shows that the loss of coarse bubbles has little effect on the freeze/thaw resistance. This is also experimentally confirmed (Fig. 4).

In another analysis it is shown that the dissolution and the transfer mechanisms are rapid enough to permit a complete loss of all air-bubbles smaller than about 20μm provided the cement paste is not too viscous (Fig. 5 and 12). It is theoretically shown that the dissolution and transfer mechanisms lead to increased spacing factor and therefore to reduced freeze/thaw resistance (Fig. 8). The transfer mechanism might, theoretically, lead to increased air-content. This could explain the frequent experimental observation that the air-content increases between mixing and hardening (Fig. 13).

The increase in air-content seems to be higher the higher the W/C-ratio (Fig. 13). This could be explained by the transfer mechanism; i.e. the rate of transfer of air must increase with a more fluid cement paste (eq. (21)). Thus, the higher the W/C-ratio the larger the air transfer.

6. REFERENCES

/1/ Mielenz, R. C. et al., "Origin, Evolution and Effects of the Air-Void System in Concrete. Part I", Journal of ACI, July 1958, p. 95 f.f.

/2/ Johansson, R., "Characterisation of the air-void system in concrete by a vibration test". Int. Symp. on Admixtures for Mortar and Concrete,Brussels, Aug. 30-Sept. 1, 1967.

/3/ Larson, T. D. et al., "The protected paste volume concept using new air void measurement and distribution techniques". J. of Materials, Vol.2, No 1, March 1967, p. 202 f.f.

/4/ Fagerlund, G., "Equations for calculating the mean free distance between aggregate particles or air-pores in concrete". CBI Research 8:77, 1977.

/5/ Fagerlund, G., "Air-volume changes caused by the gradual collapse of the air-pore system", (in Swedish). Cementa CM Report T 88047, 1988.

/6/ Fagerlund, G., Div. of Build. Materials, Lund Inst. of Techn. Internal Report U90.05, 1990.

/7/ Mielenz, R.C. et al, "Origin, Evolution, and Effects of the Air-Void System in Concrete, Part 3". J. of ACI, Sept. 1958, p. 359 f.f.

/8/ Malmström, K., "Influence of the cement type on the freeze/thaw resistance of the concrete", (in Swedish). Statens Provningsanstalt, Byggnadsteknik, SP Report, 1990:07, Borås, 1990.