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Water-entrained cement-based materials
I. Principles and theoretical background☆

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Abstract

This paper describes a new concept for the prevention of self-desiccation in hardening cement-based materials. The concept consists of using fine, superabsorbent polymer (SAP) particles as a concrete admixture. This leads to water entrainment, i.e. the formation of water-filled macropore inclusions in the fresh concrete. Consequently, the pore structure is actively designed to control self-desiccation. In the paper, self-desiccation and water entrainment are described and discussed. The description is based on a reinterpretation of Powers' model for the phase distribution of a hydrating cement paste. The paper forms the first part of a series. In the second part, experimental observations will be presented. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During the last decade, it has become clear that self-desiccation is an important phenomenon in high-performance concrete. A low water/cement (*w*/*c*) ratio, 0.20–0.35, and addition of silica fume change the chemistry of the hydration reactions and the internal pore structure of such concretes. This causes the internal relative humidity (RH) in the concrete to drop during the hardening; self-desiccation occurs in the absence of an external source of water. Closely connected with self-desiccation, the concrete also undergoes bulk shrinkage. This shrinkage, self-desiccation shrinkage, may lead to cracking of the concrete if its deformation is restrained [1].

Several different means to avoid crack formation due to self-desiccation are known. One example is based on addition of lightweight aggregate (LWA) particles to the concrete [2,3]. LWA saturated with water can mitigate self-desiccation by providing so-called internal curing. However, major problems are connected to this technique including difficulties in controlling consistency and a significant reduction in strength and elastic modulus.

This paper describes a new means for the prevention of self-desiccation: incorporation of superabsorbent polymer (SAP) particles in the cement-based material. During mixing of the concrete, the SAP will absorb water and form macroinclusions, which essentially consist of nothing but free water. Conceptually, this has strong similarities with air entrainment, which is used for frost protection of concrete. For this reason, the described technique will be referred to as water entrainment.

Water entrainment has similarities to LWA addition, but the technique is more straightforward and free of significant drawbacks. The SAP can be used as a dry concrete admixture, and, contrary to LWA, the use of SAP permits free design of the pore shape and the pore size distribution of the hardening concrete. Furthermore, with a SAP, the undesirable addition of a large amount of mechanically poor aggregate particles is avoided.

A brief introduction to SAPs is given below. More comprehensive information can be found in the literature [4].

2. Superabsorbent polymers

SAPs are a group of polymeric materials that have the ability to absorb a significant amount of liquid from the surroundings and to retain the liquid within their structure

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☆ A patent application on *water-entrained cement-based materials* has been filed by the company Densit, Aalborg, Denmark. However, the opinions expressed in this paper are entirely the responsibility of the authors.

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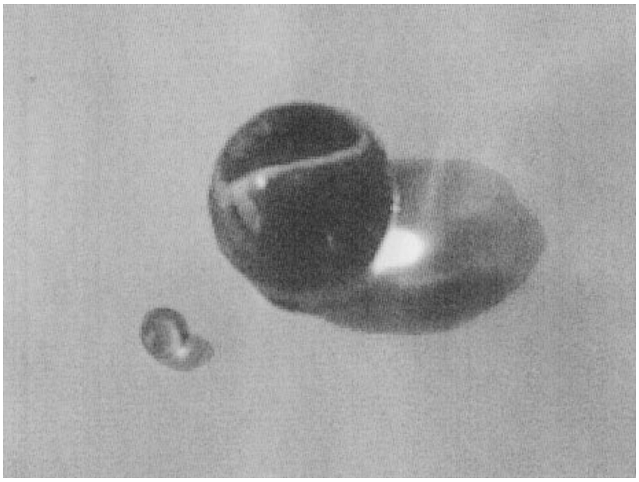

Fig. 1. Superabsorbent polymers are swellable substances, which can absorb many times their own weight of liquids by forming a gel. The absorbed liquid is not released even under pressure. The picture shows a dry, collapsed and a swollen suspension polymerized SAP particle.

without dissolving. SAPs are principally used for absorbing water and aqueous solutions; about 95% of the SAP world production is used as a urine absorber in disposable diapers. SAPs can be produced with a water absorption of up to 5000 times their own weight. However, in dilute salt solutions such as urine, the absorbency of commercially produced SAPs is around 50 g/g.

Many different types of SAPs are known. They can be produced by either solution or suspension polymerization, and the particles may be prepared in a variety of different sizes and shapes including spherical particles. The commercially important SAPs are covalently cross-linked polyacrylates and copolymerized polyacrylamides/polyacrylates. Because of their ionic nature and interconnected structure, they can absorb large quantities of water without dissolving. From a chemical point of view, all the water inside a SAP can, essentially, be considered as bulk water (see Fig. 1).

SAPs exist in two distinct phase states, collapsed and swollen. The phase transition is a result of a competitive balance between repulsive forces that act to expand the polymer network and attractive forces that act to shrink the network. Several mechanisms are involved in this. The macromolecular matrix of a SAP is a polyelectrolyte, i.e., a polymer with ionizable groups that can dissociate in solution, leaving ions of one sign bound to the chain and counterions in solution. For this reason, a high concentration of ions exists inside the SAP leading to a water flow into the SAP due to osmosis. Another factor contributing to increase the swelling is water solvation of hydrophilic groups present along the polymer chain. Elastic free energy opposes swelling of the SAP by a retractive force.

The salinity of the aqueous solution is of special importance for the swelling of SAPs. The ions in the solution change the inter- and intramolecular interactions of the polyelectrolytes due to shielding of charges on the polymer chain. Furthermore, as the concentration of ions outside the SAP increases, the osmotic pressure inside the gel decreases, leading to a reduced swelling of the SAP.

Important properties of SAPs include swelling capacity, strength and elastic modulus of the swollen gel. All these properties depend on the cross-link density of the network: the elastic modulus increases and the swelling capacity decreases with increasing cross-link density. Generally, the higher the water content of the gel, the poorer the mechanical properties of the gel.

3. Powers' model of the phase distribution of cement paste

Knowledge of the phase distribution of a hardening cement paste is necessary to explain the chemical and physical properties of a cement-based material. The phase distribution is important to very different properties such as permeability, strength and frost resistance.

Based on 12 years of extensive research, Powers and Brownyard [5] presented an empirical model for the phase distribution of a hardening cement paste in 1948. This model is a benchmark in cement research since it enables quantitative calculations of the volumetric composition of cement-based materials to be carried out. In the following years, Powers [6,7] (Fig. 2) modified the model slightly for which reason the model is today referred to as Powers' model. In the following, self-desiccation and water entrainment are described based on a reinterpretation of Powers' model. A

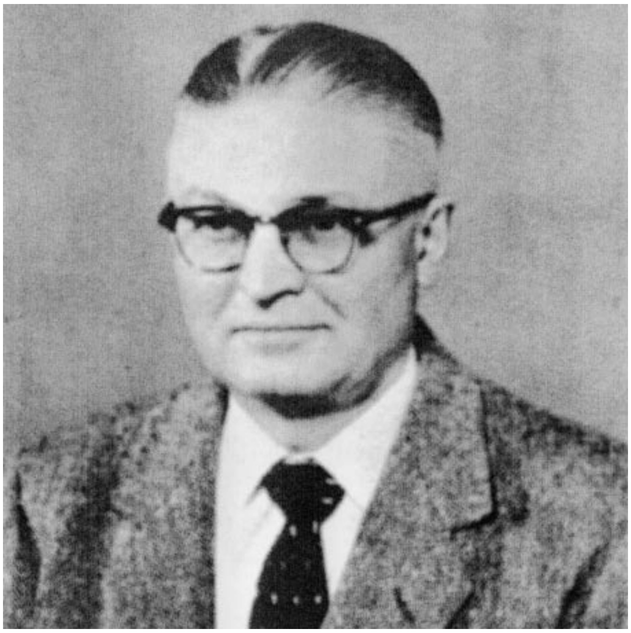

Fig. 2. T.C. Powers (1900–1997) was for many years Research Manager at the Portland Cement Association Research Laboratory in Chicago, IL. He contributed very significantly to the development of concrete technology. One of his most important publications is the so-called PCA Bulletin 22 [5].

thorough, general description of Powers' model can be found in the literature [5,7–9].

Powers' model is largely based on a comprehensive study of water vapour sorption isotherms and chemically bound water in hardening cement pastes. Based on these studies, it seemed reasonable to classify water held in cement pastes into three phases: *capillary water* (free water), *gel water* (physically bound water) and *chemically bound water* (nonevaporable water).

Powers' measurements showed that, chemically, approximately 0.23 g water is bound per gram of cement reacted during hydration. This water is called *chemically bound water* or *nonevaporable water*, since it is an integral part of the structure of the gel solid, and is only driven off at temperatures above 105°C. On the surface of the gel solid, an amount of water is adsorbed equivalent to approximately 0.19 g water per gram of cement reacted. This *physically bound water* or *gel water* has a range of binding energies corresponding to the RH interval 0–100%. Unbound water in the cement paste is called *free water* or *capillary water*, indicating that it is the water present in the coarse capillary pores. Only capillary water is unimpededly accessible for cement hydration. Here, and in the following, the small RH depression due to dissolved salts in the pore fluid is neglected. Capillary water is, therefore, considered to be in equilibrium with 100% RH. The reaction products formed during cement hydration have a lower volume than the cement and water reacted. This volume reduction is called chemical shrinkage and amounts to approximately 6.4 ml/100 g cement reacted.

The above three key figures for chemically bound water, gel water and chemical shrinkage depend on the cement composition. In this paper, Powers' figures have been used as representative values within the composition limits of Portland cement. Based on the above three key figures, the following approximate volume relations for a hydrating, air free cement paste can be set up:

$$V_{\mathrm{cs}} = \rho_{\mathrm{c}} 6.410^{-5}(1-p)\alpha = 0.20(1-p)\alpha \quad \text{(chemical shrinkage)} \tag{1}$$

$$V_{\mathrm{cw}} = p - (\rho_{\mathrm{c}}/\rho_{\mathrm{w}})(0.19 + 0.23)(1-p)\alpha = p - 1.32(1-p)\alpha \quad \text{(capillary water)} \tag{2}$$

$$V_{\mathrm{gw}} = (\rho_{\mathrm{c}}/\rho_{\mathrm{w}})0.19(1-p)\alpha = 0.60(1-p)\alpha \quad \text{(gel water)} \tag{3}$$

$$V_{\mathrm{gs}} = (1 - \rho_{\mathrm{c}} 6.410^{-5} + (\rho_{\mathrm{c}}/\rho_{\mathrm{w}})0.23)(1-p)\alpha = 1.52(1-p)\alpha \quad \text{(gel solid)} \tag{4}$$

$$V_{\mathrm{uc}} = (1-p)(1-\alpha) \quad \text{(unhydrated cement)} \tag{5}$$

where V_i is the relative volume fraction (m^3/m^3 cement paste), α is the degree of hydration (kg cement reacted/kg initial cement), $\rho_{\mathrm{c}} = 3150$ kg/m^3 the cement density, $\rho_{\mathrm{w}} = 1000$ kg/m^3 the water density, p is the initial porosity, $p = V_{\mathrm{cw},0} = (w/c)/(w/c + \rho_{\mathrm{w}}/\rho_{\mathrm{c}})$ and w/c is the water/cement ratio (kg/kg).

As mentioned previously, it is only the capillary water that is freely accessible for cement hydration. The hydration is significantly retarded when the capillary water is used up. At complete hydration, 1 g of cement binds approximately 0.23 g water chemically and 0.19 g gel water. Complete and unimpeded hydration is, therefore, only possible at *w/c* ratios above 0.42 (= 0.23 + 0.19). If a small cement paste sample hydrates under water the volume reduction due to chemical shrinkage will be replaced by imbibed water from the surroundings. This water will, thereafter, be freely available for cement hydration. At a *w/c* lower than 0.42, free access to water, therefore, will increase the maximum degree of hydration.

In the literature, observations conflicting with Powers' model can be found, as well as other interpretations and definitions of the concepts of gel water and capillary water [10]. Surely, Powers' classification of water phases is somewhat arbitrary, since there must be an overlap in binding energies between the different water phases. However, this simple classification has proven to be a very useful quantitative description of water binding in cement paste since many, very different cement paste properties can be explained by Powers' model. A further illustration of the potential of Powers' model is the flexibility, whereby the model can be extended. As an example, measurements indicate that the pozzolanic reaction of silica fume can be roughly described by the following approximate key figures [11,12]:

Chemical shrinkage	22 ml/100 g reacted silica fume
Gel water	0.50 g/g reacted silica fume
Chemically bound water	0 g/g reacted silica fume

Note that water originally present in the calcium hydroxide is bound in the pozzolanic C–S–H as implied by the value for the chemically bound water.

Based on these key figures, Eqs. (1)–(5) for the volumetric phase distribution can be extended to include paste systems with silica fume [12].

4. Development of phase distribution and sorption isotherms

Fig. 3 shows the volumetric relations calculated with Powers' model for a hydrating cement paste at a high *w/c* ratio. The diagram applies to a closed system, i.e., a system without transport of moisture to or from the cement paste. Due to the high *w/c* ratio (*w/c* > 0.42), the fully hydrated cement paste contains an excess of

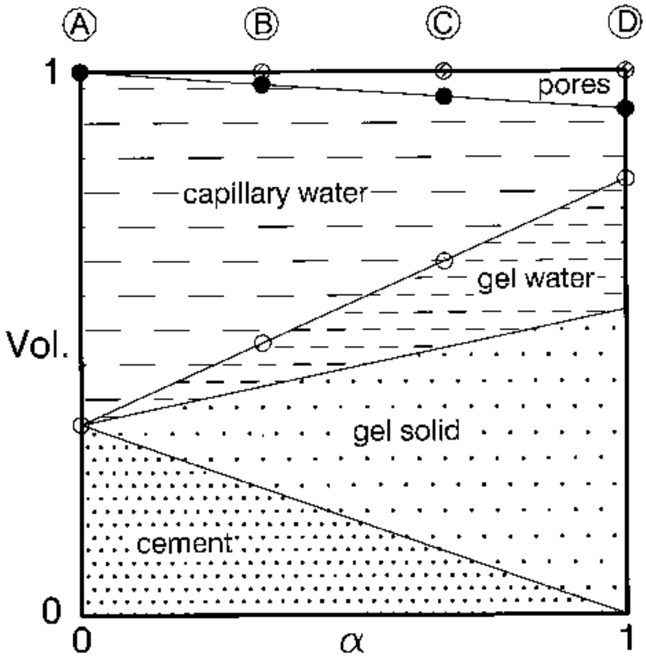

Fig. 3. Volumetric phase distribution of cement paste as a function of the degree of hydration, α, at $w/c=0.6$. The diagram applies to sealed hydration (= closed system), i.e., without exchange of water with the surroundings. Due to the high w/c ratio, full hydration ($\alpha=1$) of the cement can theoretically be obtained.

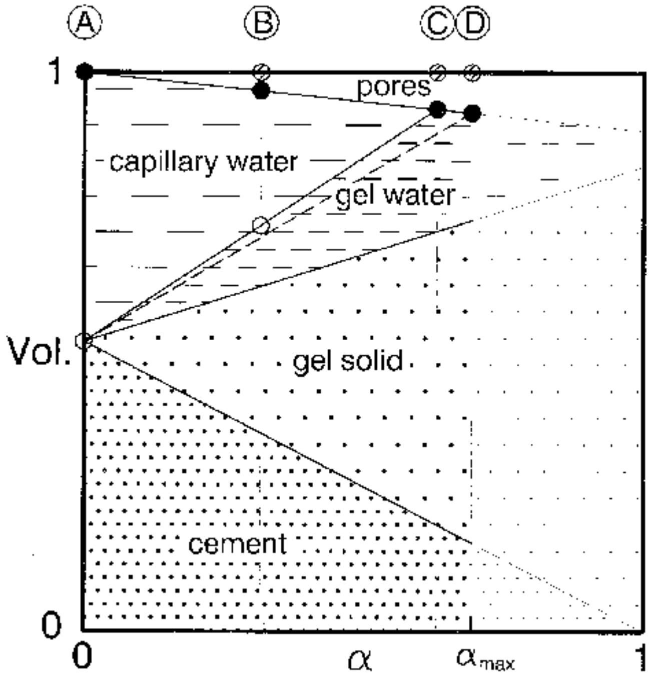

Fig. 5. Volumetric phase distribution of cement paste as a function of the degree of hydration, α, at $w/c=0.3$. The diagram applies to sealed hydration, i.e., a closed system. Due to the low w/c ratio, full hydration of the cement cannot be obtained.

unbound water in the large capillaries. The cement, therefore, can hydrate completely. As hydration proceeds, the cement reacts with water and forms gel solid. On the surface of the gel solid, a specific amount of water, the so-called gel water, is bound by adsorptive forces. Because the gel solid occupies less space than the cement and water from which it is formed, gas-filled pores are formed within a closed cement paste system.

Fig. 4 shows schematically how the sorption isotherm develops during hydration at a high w/c ratio. The capillary water is in equilibrium with a RH of 100%. The gel water has a range of binding energies corresponding to the RH interval from 0% to 100%. With a rising degree of hydration, the capillary water is partly used, and the amount of gel water increases. Due to the large amount of unbound capillary water, the RH in the pores of the cement paste

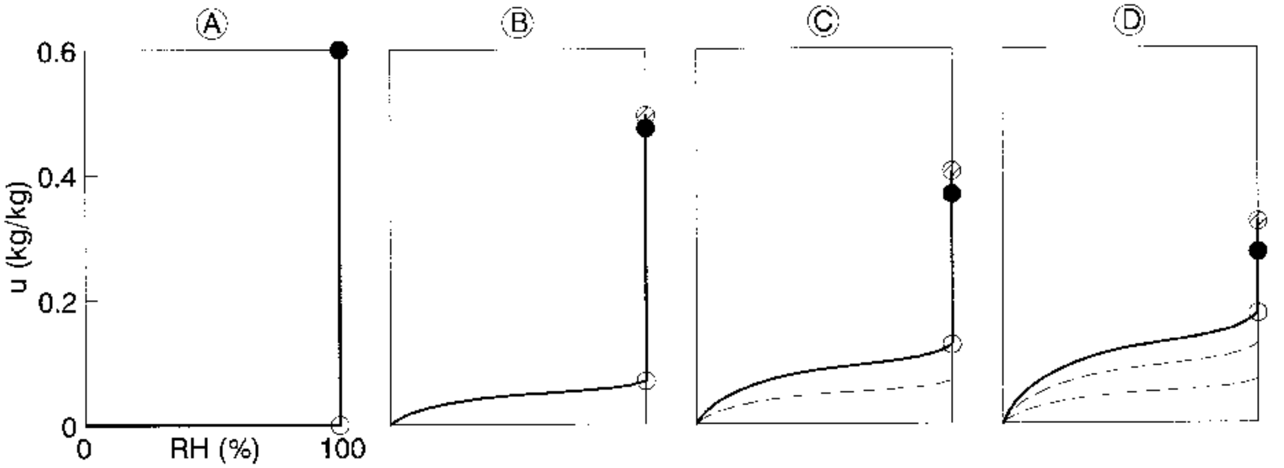

Fig. 4. Schematic development of the sorption isotherm during sealed hydration at $w/c=0.6$ according to Powers' model. The four isotherms (A–D) refer to the different degrees of hydration shown in Fig. 3. The content of evaporable water, u, is shown as kilogram of water per kilogram of solid (cement and gel solid). Symbols: (⊘) content of evaporable water at water saturation; (●) content of evaporable water after hydration in a closed system; (○) content of gel water at 100% RH.

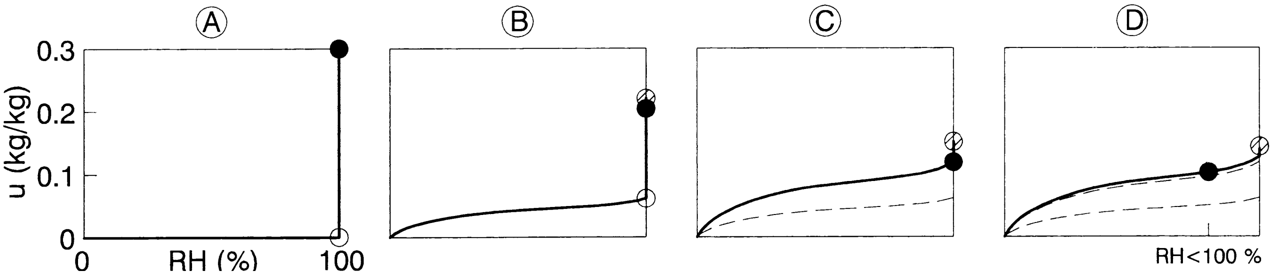

Fig. 6. Schematic development of the sorption isotherm during sealed hydration at $w/c = 0.3$ according to Powers' model. The four isotherms (A–D) refer to the different degrees of hydration shown in Fig. 5. Due to a deficit of capillary water, the cement paste self-desiccates during the last phase of hydration.

will, neglecting the RH-depression from dissolved salts, be 100% after full hydration of the cement.

At a *w/c* ratio below about 0.42, there is not enough capillary water for unrestricted hydration of the cement (see Fig. 5). According to Powers' measurements [5,7], cement hydration cannot proceed when a certain minimum porosity of the cement gel (gel solid and gel water) is reached. Powers explained the minimum gel porosity as a consequence of restricted growth of existing gel particles and inability of new particles to form in surface adsorbed water (gel water). The minimum gel porosity, about 26–28%, is reached in state D in Fig. 5 where hydration stops.

Fig. 6 shows schematically how the sorption isotherm will develop during hydration at a low *w/c* ratio. At a certain degree of hydration, state C, the capillary water is consumed, and the hydration is significantly retarded as the cement attempts to react with the harder bound gel water. This results in an RH decrease, i.e., the hydrating cement paste self-desiccates (states C–D).

5. Application of Powers' model to water-entrained cement paste

A water-entrained cement paste is a cement paste that in the freshly mixed state has predesigned, water-filled cavities. Such water entrainment may be used to avoid self-desiccation during hydration. Fig. 7 shows the phase distribution of a cement paste at a low *w/c* ratio that is freely supplied with water during hydration. This water supply permits the cement to reach a higher degree of hydration. In addition, no gas-filled micropores are formed within the cement paste phase. The "external water" in Fig. 7 may be entrained in the cement paste, which means that the external water may be disposed in the cement paste as a discontinuous phase of predesigned, water-filled macropores. During hydration, these inclusions with the entrained water phase are emptied and end up as gas-filled macropores.

The schematic sorption isotherms in Fig. 8 show that self-desiccation of the cement paste is prohibited as a consequence of this water entrainment. When cement hydration stops due to the minimum porosity requirement of the precipitated cement gel, state D, the RH is still 100%. Self-desiccation, therefore, is prevented.

Since pores generally have a negative influence on the properties of a cement paste, only the amount of water that just suffices to prohibit self-desiccation should be entrained. Based on Powers' model, Eqs. (1)–(5), it is possible to estimate how much entrained water is needed to prevent self-desiccation.

In the above description, Powers' original model was slightly modified and reinterpreted in order to describe self-desiccation with the simplified concepts of capillary and gel water, cf. Figs. 3–8. From a calculative point of view, Powers defined gel water as unavailable for the cement hydration. So, if we assume in accordance with Powers that hydration at a low *w/c* ratio stops when all the available

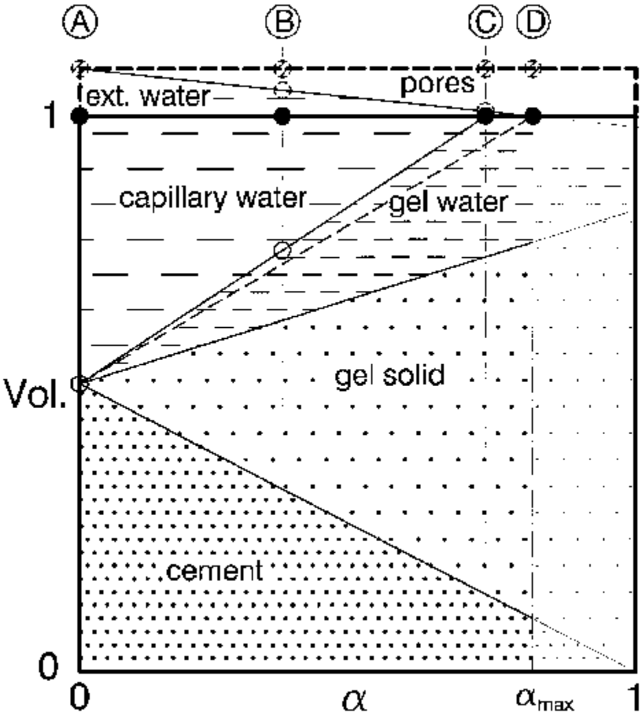

Fig. 7. Volumetric phase distribution of cement paste as a function of the degree of hydration, α, at $w/c = 0.30 + 0.05$. The diagram applies to hydration with an external water supply, i.e., an open system, or a water supply from entrained water. Due to the low *w/c* ratio, full hydration of the cement cannot be obtained.

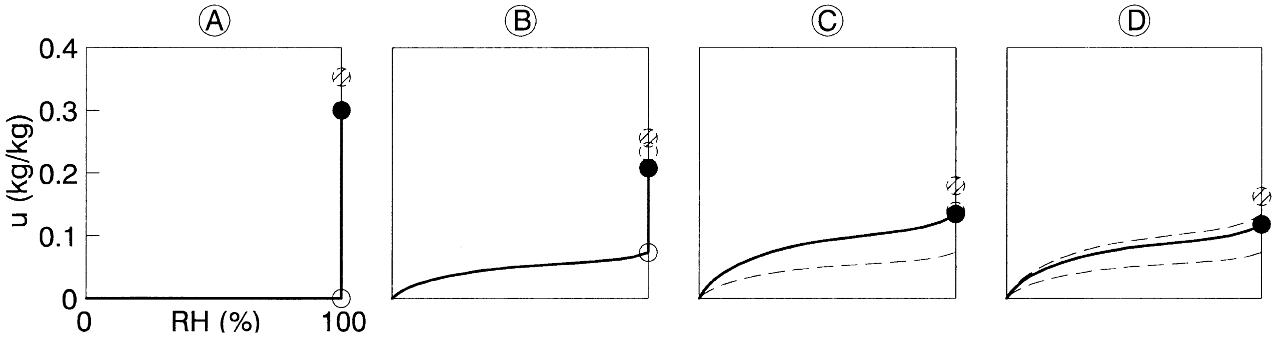

Fig. 8. Schematic development of the sorption isotherm during hydration at $w/c = 0.3$ when external or entrained water is supplied to the cement paste. The four isotherms (A–D) refer to the different degrees of hydration shown in Fig. 7. Due to an external or entrained water supply, the relative humidity will stay at 100%, even though the capillary water is consumed.

space is taken up by gel water, gel solid and unhydrated cement, we have from Eqs. (3)–(5):

$$\begin{aligned}
&\alpha = \alpha_{\max} \quad \text{for} \quad V_{\mathrm{gw}} + V_{\mathrm{gs}} + V_{\mathrm{uc}} = 1 \\
&\Rightarrow \\
&0.60(1-p)\alpha_{\max} + 1.52(1-p)\alpha_{\max} \\
&+(1-p)(1-\alpha_{\max}) = 1
\end{aligned}$$

Hence, in an open system with a low *w/c* ratio:

$$\alpha_{\max} = \frac{p}{1.1(1-p)} \tag{6}$$

The relative volume of initially entrained water, $V_{\mathrm{ew},0}$, cf. Fig. 7, should equal the chemical shrinkage developed at the maximum degree of hydration given by Eq. (6). Since $p = V_{\mathrm{cw},0}$, insertion of Eq. (6) into Eq. (1) gives:

$$V_{\mathrm{ew},0} = 0.20(1-p)\alpha_{\max} = 0.18p = 0.18V_{\mathrm{cw},0} \tag{7}$$

On a *w/c* ratio basis (kg water/kg cement), entrained water and initial capillary water can be expressed through:

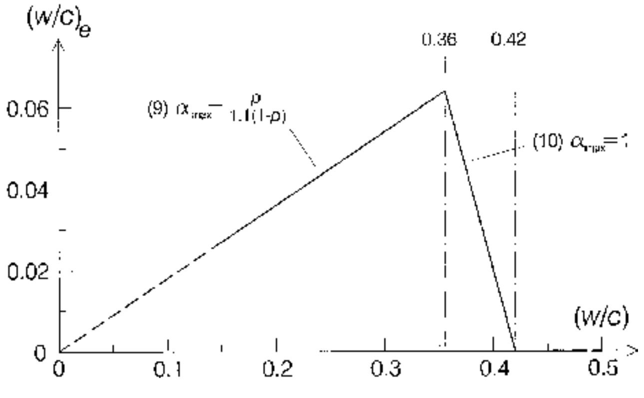

Fig. 9. Minimum amount of entrained water needed to obtain $\alpha_{\max}$ and, thereby, prevent self-desiccation during hydration according to Eqs. (9) and (10).

$$(w/c)_{\mathrm{e}} = \frac{V_{\mathrm{ew},0}\,\rho_{\mathrm{w}}}{V_{\mathrm{c},0}\,\rho_{\mathrm{c}}}; \quad (w/c) = \frac{V_{\mathrm{cw},0}\,\rho_{\mathrm{w}}}{V_{\mathrm{c},0}\,\rho_{\mathrm{c}}} \tag{8}$$

Hence from Eqs. (7) and (8), the necessary water entrainment to obtain $\alpha_{\max} = p/(1.1(1-p))$ is:

$$(w/c)_{\mathrm{e}} = 0.18(w/c) \qquad \text{for } w/c \le 0.36 \tag{9}$$

Eq. (9) is only relevant for $w/c < 0.36$. Above this *w/c* ratio, complete hydration can be achieved with less entrained water than stated in Eq. (9). According to Powers' model, complete hydration, $\alpha_{\max} = 1$, is possible in the range $0.36 \le w/c \le 0.42$ if:

$$(w/c) + (w/c)_{\mathrm{e}} = 0.42$$

Hence, the necessary condition to obtain $\alpha_{\max} = 1$ in this *w/c* range is:

$$(w/c)_{\mathrm{e}} = 0.42 - (w/c) \qquad \text{for } 0.36 \le w/c \le 0.42 \tag{10}$$

As an example, Eq. (9) shows that a cement paste at $w/c = 0.30$ (Fig. 7) requires $0.18 \cdot 0.30 = 0.05$ g entrained water/g cement. Fig. 9 shows the minimum amount of entrained water needed to obtain $\alpha_{\max}$ according to Eqs. (9) and (10).

6. Consequences of water entrainment

Water entrainment in its purest form, macroinclusions with SAP particles, will effectively prevent self-desiccation of the hardening cement paste. However, it will also influence other properties both in the fresh, hardening and hardened material. Strength and durability are two very important issues in connection with high-performance concrete. For this reason, the influence on these two properties will be briefly addressed here. The entrained water should exist, preferably, as spherical inclusions to affect strength and diffusivity/permeability of the concrete as little as possible.

A water-entrained cement paste at $w/c = 0.30 + 0.05$ is identical to a nonwater-entrained cement paste at $w/c = 0.35$ from a point of view of maximum degree of hydration or total porosity. However, the pore size distribution of the two hydrated cement pastes differs significantly. The water-entrained cement paste contains geometrically predesigned macropore inclusions at the expense of finer, irregular, partly connected capillary pores; the cement paste in between the macropore inclusions is a cement paste with a w/c ratio of 0.3 with optimum curing conditions since it hydrates locally under free access to water.

This modification of the pore structure is most likely beneficial with respect to both strength and durability. Both experimentally and theoretically, it has been shown that spherical macropores reduce strength less than the same volume of fine pores of uncontrolled shape [13]. A water-entrained cement paste at $w/c = 0.30 + 0.05$ should, therefore, be stronger than a nonwater-entrained cement paste at $w/c = 0.35$.

To estimate the influence on strength, it is convenient to compare a water-entrained cement paste at $w/c = 0.30 + 0.05$ to a nonwater-entrained cement paste at $w/c = 0.30$. With this starting point, the water entrainment has two opposite effects on strength: the water-entrained cement paste has spherical macropores added that reduce the strength, but at the same time improve curing conditions, which increases the strength. These contributions can be estimated separately. After hydration, the entrained water inclusions end up as gas-filled inclusions comparable to entrained air. From concrete practice, it is known that a 1% increase of the air content of a concrete results in a 5% decrease of the compressive strength [13]. Based on this, the strength reduction due to the spherical macropores can be calculated as 16% using Powers' model and assuming an aggregate volume fraction of 60% for the corresponding concrete. However, the maximum degree of hydration is increased from 0.72 to 0.85 due to the water entrainment, cf. Figs. 5 and 7. This leads to a strength increase of 18% if strength on the safe side is assumed to be proportional to the degree of hydration [13]. The potential maximum strength of a water-entrained cement paste at $w/c = 0.30 + 0.05$ should, therefore, be comparable to the strength of a nonwater-entrained cement paste at $w/c = 0.30$.

Durability of concrete is a complex property, since a variety of chemical and physical processes may be involved in the deterioration process. However, the permeability or diffusivity of a concrete is very important because, in general, the speed of the deterioration depends on the ease with which the attacking agent is transported into the concrete. The above reasoning used for the influence of water entrainment on strength can also be applied to permeability and diffusivity. Mathematically, it is possible to show that inclusion of a discontinuous phase has an inferior influence on the diffusion properties of a material [14]. Therefore, durability should generally be improved by replacing finer, irregular, partly connected capillary pores by discrete, spherical inclusions from entrained water, since the connectivity of the pore structure may be of major importance in relation to durability.

As noted by Bentz and Snyder [3], frost resistance is a special case of durability where water entrainment may be beneficial. This is due to the gas-filled voids produced when the inclusions from entrained water are emptied due to chemical shrinkage. These voids are similar to voids created by air entrainment. Based on computer simulations, Bentz and Snyder calculated the maximum distance from a water-filled inclusion to any point in the hardening cement paste, which would ensure internal curing throughout the cement paste. The value, approximately 200 μm, is similar to the protected paste volume for air-entrained concrete. This figure corresponds to a size of the entrained water inclusions around 100 μm. This may be close to the optimum size, since other factors may limit the minimum size such as growth of reaction productions into the inclusions.

7. Final remarks

By means of water entrainment, it seems possible to avoid self-desiccation in hardening high-performance concrete, without impairing strength and durability. In this connection, it should be emphasized that ultimately concrete has to equilibrate with the surroundings, and, normally, this implies a desiccation of the concrete. During this desiccation, the concrete will be subjected to drying shrinkage and may subsequently crack. However, self-desiccation shrinkage is more problematic than normal drying shrinkage because self-desiccation shrinkage takes place at early ages where also thermal deformations take place and where the strain capacity of the concrete passes through a minimum. In addition, self-desiccation shrinkage develops very fast relative to normal drying shrinkage. Cracking due to drying shrinkage can be avoided if the rate of deformation is kept lower than the rate of relaxation.

The discussion in this paper has focused on the use of SAP as a water-entraining admixture to mitigate self-desiccation shrinkage of hardening cement-based materials. In concrete, SAP may potentially be used for many other purposes. Examples of these include use of SAP as a donor of substances to the concrete or dry addition of SAP in the nozzle during spray casting to create a rapid viscosity change after placing.

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