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Chloride migration in concrete with superabsorbent polymers

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ABSTRACT

Superabsorbent polymers (SAP) can be used as a means for internal curing of concrete. In the present study, the development of transport properties of concrete with SAP is investigated. The chloride migration coefficient according to NT BUILD 492 is used as a measure of this. Twenty concrete mixtures are tested 7, 14, and 28 days after casting. The development of degree of hydration is followed for 20 corresponding paste mixtures.

Both when SAP is added with extra water to compensate the SAP water absorption in fresh concrete and without extra water, the internal curing water held by SAP may contribute to increase the degree of hydration. No matter if SAP is added with or without extra water, it appears that the so-called gel space ratio can be used as a key parameter to link age and mixture proportions (water-to-cement ratio and SAP dosage) to the resulting chloride migration coefficient; the higher the volume of gel solid relative to the space available for it, the lower the chloride migration coefficient, because the pore system becomes more tortuous and the porosity becomes less.

1. Introduction

Superabsorbent polymer (SAP) has been introduced in concrete mix design as a means for internal water curing of cementitious materials with low water-to-cement (*w*/*c*) ratios to mitigate autogenous shrinkage [1,2]. However, before SAP can be used in concrete production on a larger scale, it is important to clarify not only how SAP influences autogenous shrinkage, but also how it influences other concrete properties.

Concrete is a material with open porosity, and for this reason there is a possibility of transport through the pore system. Transport of matter is often involved in the deterioration of concrete. For example, the diffusion of chloride ions has implications for reinforcement corrosion, and the change of moisture content can lead to frost damage, if the concrete is exposed to sub-zero temperatures. Despite the importance of transport, the influence of SAP on transport properties in general and chloride transport in particular has only been superficially examined. In a recent state-of-the-art report [3], the presented results regarding chloride migration comprises only 4 concrete mixtures with SAP. The 4 concrete mixtures represent 2 different *w*/*c* ratios, 2 different types of SAP, and different SAP sizes, and according to the authors, it is not possible to deduce a final conclusion on how SAP influences chloride migration. The authors of the present paper are not aware of other data published.

SAP addition can influence cement hydration, as the cement paste can imbibe water from a swelled SAP particle, if water within the paste itself becomes in short supply. The objective of the present study is to link development of transport properties and cement hydration through a systematic study of both parameters. Chloride migration is used as a measure of transport. In real concrete structures, e.g. structures in marine environment, chloride transport often takes place as a diffusion process. Measurements of chloride transport can be seen as an indication of how the concrete will sustain ingress of other substances, where the transport is driven by a concentration gradient. The methodology, where a specific property is assumed to be the result of cement hydration and therefore can be modelled as a function of degree of hydration has been successfully applied for other concrete properties [4,5].

2. Theory

2.1. Powers' model

In 1948, Powers and Brownyard published results showing that when 100 g of cement hydrates, then 23 g of water is bound chemically in the gel solid, and 19 g of water is bound by physical adsorption on the gel solid surfaces [6]. The adsorbed water phase is called gel water. Powers and Brownyard also showed that cement hydration is followed by chemical shrinkage: when 100 g

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of cement fully hydrates, the volume of the resulting gel solid and gel water is 6.4 ml smaller than the volume of cement and water before hydration. In this way, the distribution of phases in the hardening cement paste depends linearly on the degree of hydration, see Eqs. (1a)–(1e):

$$V_{cs} = 64 \cdot 10^{-6} \cdot \rho_c(1-p)\alpha \tag{1a}$$

$$V_{cw} = p - (0.19 + 0.23)\left(\frac{\rho_c}{\rho_w}\right)(1-p)\alpha \tag{1b}$$

$$V_{gw} = 0.19 \cdot \left(\frac{\rho_c}{\rho_w}\right)(1-p)\alpha \tag{1c}$$

$$V_{gs} = \left(1 - 64 \cdot 10^{-6} \cdot \rho_c + 0.23 \cdot \left(\frac{\rho_c}{\rho_w}\right)\right)(1-p)\alpha \tag{1d}$$

$$V_{uc} = (1-p)(1-\alpha) \tag{1e}$$

where

- V is the relative volume fraction specified by the subscript: cs = chemical shrinkage; cw = capillary water; gw = gel water; gs = gel solid; uc = unhydrated cement (m^3/m^3 cement paste).
- ρ_c and ρ_w are densities of cement and water, respectively (kg/m^3).
- α is the degree of hydration (–).
- p is the initial porosity, i.e. the volume fraction of capillary water at $\alpha = 0$, $p = (w/c)/((w/c) + (\rho_w/\rho_c))$ (–).

The essence of Eqs. (1a)–(1e) can be presented graphically, see Fig. 1 (left). The model is known as Powers' model. This model predicts that if cement paste with w/c ratio lower than 0.42 hydrates in sealed conditions, complete hydration is not possible, i.e. the maximum degree of hydration $\alpha_{max} < 1$.

Fig. 1 (right) illustrates how Powers' model can be extended to account for entrained water [1], e.g. water which in the fresh cement paste is present in swollen SAPs. For cement paste in sealed conditions with w/c ratio lower than 0.42, access to an entrained water source increases α_{max}.

2.2. SAP influence on transport properties

It is difficult prior to experiments to forecast if SAP addition will increase or reduce chloride transport in concrete. On one hand, if SAP addition increases the maximum degree of hydration, the paste phase will be more dense due to a higher amount of gel solids; the capillary pore network will be more tortuous and there will be more cut-offs of connections between capillary pores. This suggests that ion transport is reduced. On the other hand, if as assumed in Fig. 1 (right), water from SAP will fill up pore space created by chemical shrinkage that would otherwise be empty, then SAP addition leads to a higher amount of capillary water. Moreover, without the empty spaces, the capillary water will form a more or less continuous phase. As ion transport mainly takes place in capillary water and only to a limited extent in gel water, this may suggest that SAP addition will increase ion transport.

There may also be an effect of the voids created by SAP, and again there are 2 possibilities: If the SAP voids are empty, ions have to travel a slightly longer route to pass the void. This is similar to the effect of dense aggregates in mortar and concrete, as ion transport does not go through the stone materials. As regards aggregates, this effect has been shown to be small [7]. But if SAP voids are filled with liquid, they may provide an expressway without obstacles for ion transport. However, the liquid in the void may be wholly or partly held within a swelled SAP particle and the transport properties in a swelled SAP particle are not known. It is likely that transport will be slower than in liquid not held by SAP, just as transport has been shown to be slower, if a viscosity modifying agent has been added to the liquid [8].

3. Materials and methods

3.1. Test specimens

The test program is based on 3 reference concrete mixtures without SAP, see Table 1. The mixtures are laboratory mixtures suitable for research purposes, where it is the intention to have as few variables as possible. This is for example the reason why high range water reducing agents (HRWRA) have not been used in some of the stiffer mixes: HRWRAs may have a retarding effect and thereby introduce a new variable that has to be taken into account.

The reference mixtures are chosen so they all have the same paste content (37% of concrete volume), and at the same time workability is acceptable for all mixtures, though the concrete becomes stiffer as the w/c ratio decreases. For each w/c ratio, 4 mixtures are prepared with different amounts of SAP (0.05%, 0.1%, 0.2% and 0.3% relative to cement mass) without adding extra water, see example 1 in Table 1. Moreover, 2 mixtures are prepared for each w/c ratio with 0.2% and 0.6% SAP, where extra water is added to account for the amount of water absorbed by SAP (only 0.6% is tested for the w/c ratio of 0.40), see example 2 in Table 1. In both cases, the volume of dry SAP and possible extra water

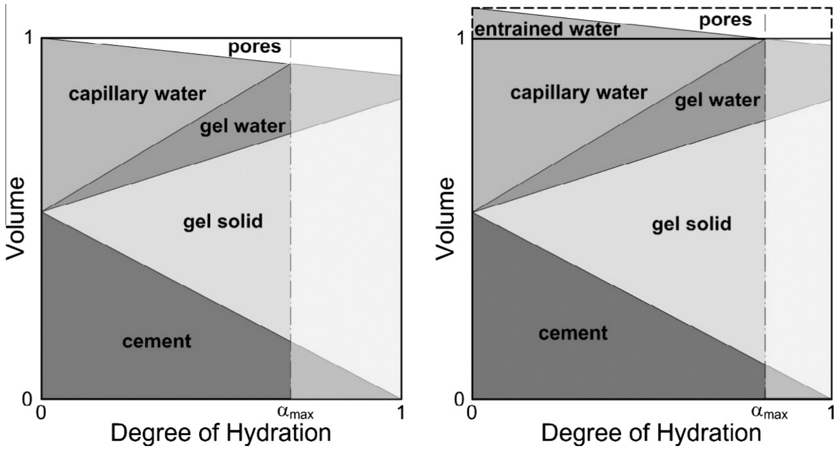

Fig. 1. Powers' model for cement hydration in sealed conditions. Left: w/c ratio = 0.30. Right: w/c ratio = 0.30, entrained water w_e/c = 0.05. Illustrations are taken from [1].