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Effect of alkalinity and calcium concentration of pore solution on the swelling and ionic exchange of superabsorbent polymers in cement paste

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ABSTRACT

Swelling kinetics of superabsorbent polymers (SAP) in fresh concrete is complex, but its understanding is crucial for optimisation in practical applications. In this study, the effect of concentration of ions common in pore solution (Na^+, K^+, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}) and cyclic wetting/drying on the swelling and ionic exchange of poly(AA) and poly(AA-co-AM) were investigated. Results show that swelling is not a simple function of concentration or ionic strength. In cement paste, SAP absorbs Ca^{2+} and releases its counterion (Na^+, K^+) into pore solution. Ca^{2+} binds with SAP and decreases initial swelling, but the bound Ca^{2+} can be displaced and swelling gradually recovers. Swelling increases with increase in alkalinity, but decreases with increase in calcium concentration. The higher the degree of ion exchange, the lower the swelling of SAP. Poly(AA) is more susceptible to Ca^{2+} complexation and therefore achieves a lower swelling ratio and slower swelling recovery compared to poly(AA-co-AM).

1. Introduction

There has been much interest in recent years on the potential use of superabsorbent polymers (SAP) in concrete. Superabsorbent polymers are cross-linked polymers that have the ability to absorb a disproportionately large amount of water relative to their own mass and expand to form an insoluble gel. SAPs are a subset of a large family of hydrogels and polyelectrolytes polymer gels [1]. The majority of commercially available SAP are anionic gels comprised of cross-linked acrylic acid that is partially neutralised with sodium hydroxide. These are referred to as polyacrylate (poly(AA)) and they contain partially neutralised carboxylate functional groups with the counterions typically being hydrogen, sodium and potassium. Other monomers are also used such as acrylamide to produce poly(acrylate-co-acrylamide) (poly(AA-co-AM)). The acrylamide group is non-ionic, while the carboxylate group is anionic in water due to partial dissociation of the counterions. Poly(AA) and poly (AA-co-AM) are also the most commonly used SAP in cement-based materials.

The key properties of SAP is their ability to absorb and retain water, during which the swollen gel forms a barrier to flow, and to release the absorbed water when the surrounding humidity drops. The main application of SAP is in personal hygiene products (diapers). Other uses include biomedical (bandages, tissue engineering, implants), pharmaceutical (drug delivery), agricultural (soil conditioning), waste treatment/separation, meat packaging and water blocking tapes for undersea cables [1,2]. Several potential applications of SAP in concrete have been suggested. These include its use as an internal curing agent to reduce self-desiccation and autogenous shrinkage in low water/cement mixtures [3–5], rheology control, frost protection [6,7] and crack sealing/healing [8–15]. A state-of-the-art report on the application of superabsorbent polymers in concrete was published by RILEM in 2012 [16].

A detailed description of the swelling mechanism of SAP is available elsewhere, e.g. Tanaka et al. [17], Ricka & Tanaka [18], Hooper et al. [19], Buchholz & Graham [1] and Gedde [20]. In essence, when SAP is exposed to an aqueous solution, a transition in chemical potential occurs between the gel and solution leading to swelling or shrinkage of the SAP. The main driving force for swelling is osmotic pressure arising from the difference in the concentration of ions between the gel and solution. This is balanced by the elastic forces arising from deformation of the polymer chains that restrain swelling. The amount of deformation depends on the

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elastic modulus of the gel, which in turn depends on its cross-link density. SAP also de-swells under compression by reverse osmosis. Equilibrium is achieved when these potentials are equalised and the net swelling pressure becomes zero. As such, the amount and kinetics of SAP swelling depends on the properties of the polymer such as ionic groups, degree of cross-linking and particle size as well as the properties of the solution such as type of ions present, concentration, ionic strength, pH, pressure and temperature [1,21–25]. For example, the mass of water absorbed per mass of SAP, known as the swelling ratio or absorption capacity, can be as high as 500 g/g in distilled water, but reduces to ~50 g/g in dilute salt solution and ~10 g/g in concrete pore solution.

Swelling of SAP in cement-based materials is a complex phenomenon. This is because the pore solution of cement-based materials consists of multi-species (mainly Na^+, K^+, Ca^{2+}, OH^- and SO_4^{2-}) and the concentration of each species varies with cement type, mixture composition. Furthermore, the composition of pore solution varies over time due to hydration (dissolution of cement, precipitation of hydration products) and interactions with the exposure environment (wetting/drying, ingress of external fluids, leaching etc). Understanding the factors influencing swelling and shrinkage of SAP in cement-based materials is essential in order to optimise its usage as well as to understand its long-term effects in concrete. For example, the swelling kinetics of SAP in fresh concrete is important because it influences mixture design, the amount of entrained water and SAP dosage required for a particular application, rheology and workability [26]. The ionic groups of the SAP affect when the absorbed water is released for internal curing application [23,27], how ingress of external fluids influence its re-swelling in crack sealing [13] and how repeated swelling/shrinkage influences long-term performance. The swelling of SAP changes the microstructure (void content) of hardened concrete; this in turn can have a great impact on strength and long-term durability.

This study aims to investigate the effects of alkalinity and calcium content in the pore solution on the swelling of poly(AA) and poly (AA-co-AM) SAP in cement paste. Furthermore, the study will investigate the effects of SAP type and dosage on the composition of pore solution extracted from cement paste, to establish the ion exchange that may occur between SAP and pore solution, and how this influences swelling. Swelling ratio of SAP was first measured in various simple aqueous solutions and synthetic pore solutions to investigate the effects of ion type (Na^+, K^+, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}, NO_3^-) and concentration, ionic strength and repeated wetting/drying. Then, a range of cement pastes with various levels of alkalinity, calcium content and SAP dosage were prepared and tested. Pore solution was extracted and analysed using ICP-OES and the swelling of SAP in hardened cement paste was measured using image analysis. Finally, energy dispersive X-ray microanalysis was used to map element distribution in the SAP and surrounding cement paste. It is hoped that the findings from this study will help in optimisation and enhancing the effectiveness of SAP in concrete applications.

2. Experimental

2.1. Materials

The cements used in this study were white Portland cement (WPC, 52.5 N) and ordinary grey Portland cement (CEM I, 52.5N) complying with BS EN 197-1 from Lafarge. White Portland cement was used in addition to grey Portland cement because of its low alkalinity. The oxide compositions and other properties of the cements are shown in Table 1. Two types of SAPs were investigated: crosslinked polyacrylic acid neutralised with sodium hydroxide and crosslinked copolymer of acrylic acid and acrylamide, neutralised with potassium hydroxide. These will be referred to as polyacrylate (poly AA) and polyacrylate-co-acrylamide (poly AA-co-AM), designated as S2 and S5 respectively so as to be consistent with our previous publications [10,13]. S2 has relatively higher degree of cross-linking and density of anionic groups compared to S5. Their particle sizes are in the range of 100–300 μm and 1–200 μm for S2 and S5 respectively. The SAPs are synthesised from bulk polymerisation and subsequently ground into small particles. When viewed using an optical microscope in transmitted light and scanning electron microscope, the SAPs appear as smooth, angular shaped granules with a small amount of convoluted sheets. This is a result of the grinding process after solution polymerization in their manufacture. Fig. 1 shows scanning electron micrographs highlighting the particle size, surface texture and particle shape of the SAPs.

The properties of the SAPs including their swelling ratios in deionised water, 0.12 wt% NaCl, synthetic shallow groundwater and synthetic pore solution are shown in Table 2. The composition of synthetic groundwater was based on a relatively concentrated groundwater with ionic strength of 21 mmoL/L [28], in mmol/L: $NaHCO_3$ (8.2), $CaSO_4$ (1.04), $MgSO_4$ (2.08) and $CaCl_2$ (0.14). The composition of synthetic pore solution (PS1) was based on pore solution extracted from a 0.5 w/c ratio cement paste (ordinary grey Portland cement) within 30 min of mixing [29], in mmol/L: $CaSO_4$ (20.6), K_2SO_4 (163.4), KOH (71.2) and NaOH (73.9). The SAP (S5) was sieved to remove a small fraction of particles smaller than 75 μm. This was done to ensure that the SAP voids in hardened cement paste can be imaged with a flatbed scanner so that the SAP swelling in cement paste can be accurately measured with image analysis (see Section 2.4).

2.2. Mixtures

Forty one cement paste mixtures were prepared at water-to-cement ratio of 0.6. These are divided into six series, and the details of the mixtures are summarised in Table 3. Cement paste rather than mortars or concretes were prepared in this study for the sake of convenience and simplicity. The presence of aggregates is not expected to have a significant influence on pore solution composition, therefore the findings from this study should also be applicable to mortars or concretes. A relatively high w/c ratio was used to facilitate expression of pore solution for the work described in Section 2.5. Series I and II were prepared with the aim of understanding the influence of alkali and calcium content on the absorption capacity of SAP in cement paste. Series III to VI were prepared to investigate the effect of SAP on the composition of pore solution. In Series I and V, a measured amount of sodium hydroxide was dissolved in the batch water to produce samples with total equivalent Na_2O content ranging from 0.09% to 0.9% wt. cement. In Series II and VI, calcium nitrate was added to the batch water to increase the calcium concentration of the pore solution. The amount of calcium nitrate added ranged from 0.5% to 4% wt. cement.

Dosage of SAP was either 0.6% or 2% by weight of cement. The relatively high SAP dosage of 2% wt. cement was used because these samples were prepared as part of a study on the feasibility of SAP as an admixture for self-sealing cracks in concrete [12]. Deionised water was used as batch water in all cases. Additional water was added to mixtures with SAP to account for the amount absorbed by the SAP so that the target free w/c ratio was achieved. This was determined by conducting many trial mixtures to measure the additional water required to obtain a mixture with similar consistency to the control mixture. Consistency was judged by comparing the spread of the freshly prepared mixture on a flow table. This