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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).

Keywords: Superabsorbent polymer; Swelling; Pore solution; Crack sealing; Internal curing, Durability

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.

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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 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 500g/g in distilled water, but reduces to ~50 g/g in dilute salt solution and ~ 10g/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 minutes 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 method assumes that the SAP itself does not significantly influence the rheology of the cement paste.

Batching was carried out by dry mixing cement with the required amount of SAP for 2 minutes. Batch water was then added and mixed for 15 minutes. An extended mixing time was used to ensure homogeneity and to allow the SAP swelling to stabilise before casting. Samples were cast in plastic cylindrical containers (50Ø × 60 mm) and compacted in three equal layers by gentle tapping to remove entrapped air. Each compacted sample was capped with a plastic lid, sealed with water-resistant tape, and continuously rotated for the first 48 hours to prevent segregation. Samples were then sealed cured by wrapping in a generous amount of cling film, then placed in sealed polythene bags and cured in a CO_2 free environment at 20°C for a further 7 days.

2.3 Swelling and repeated swelling of SAP in test solutions

Swelling ratio of SAP in aqueous solution was measured using suction filtration [30]. In this method, 100 mg of SAP pre-dried at 50°C (to constant mass) was added to a beaker containing 100 mL of the test solution, which was then sealed and left for 24-30 hours at 20°C. The swollen SAP was then filtered by suction at 0.17 bar over a pre-saturated filter paper (Waterman No.1) for 5 minutes. The filtered SAP and the wet filter paper were then immediately transferred into a polystyrene weighing boat and weighed. Swelling ratio (s) was calculated from the following equation:

$$s = \frac{(w_2 - w_3) - w_1}{w_1} \qquad \text{(Eq. 1)}$$

Where w_1 is the initial mass of the pre-dried SAP, w_2 is the mass of the swollen SAP and wet filter paper, and w_3 is the mass of the wet filter paper obtained from a control experiment with no SAP. Repeated measurements (5 replicates) were carried out for both SAPs and the standard deviation was less than 3% in all cases. The variability within replicates is small compared to the effect of the imposed experimental parameters on swelling ratio.

It should be noted that there exist a number of methods for measuring SAP swelling ratio. The most commonly used is the gravimetric “tea-bag” method, for example as described in [31]. In this study, vacuum filtration with a small negative pressure was adopted rather than the tea-bag method because it has the advantage of removing physically held capillary water between SAP particles. However, it is possible that the small negative pressure may not completely remove all inter-particle water. Nevertheless, this does not matter to the current study as long as the same consistent method is used throughout.

In the first set of experiments, the swelling of SAP was measured after exposure to two synthetic pore solutions, PS1 and PS2. PS1 is the same as the synthetic pore solution described in Section 2.1 and is relatively concentrated (‘strong’). PS2 is a relatively less concentrated (‘weak’) pore solution containing the following in mmol/L: $CaSO_4$ (15.7), KOH (20.4), NaOH (5.3) and $Ca(OH)_2$ (4) [29]. The swelling ratio was measured after various periods of exposure to study the absorption kinetics in synthetic pore solution. The exposure time steps were ~ 5, 10, 30, 60, 120, 240, 480 and 1000 minutes.

In the second set of experiments, the swelling of SAP was measured in various salt solutions to examine the influence of anion/cation type, concentration and ionic strength. The solutions were KCl, NaCl, $CaCl_2$, NaOH and Na_2SO_4 at the following concentrations: 1, 2, 5, 10, 20, 50, 100, 200 and 500 mmol/L. Swelling ratio was also measured in solutions containing 20 mmol/L $CaCl_2$ with increasing amount of NaCl at 10, 20, 50, 100, 200, 400, 600, 800, 1000 and 1200 mmol/L. In these measurements, the SAP was left in the beaker for 24-30 hours to allow swelling to reach equilibrium.

In the third set of experiments, the same SAP sample was tested repeatedly to examine the effect of wetting and drying cycles on swelling behaviour. After the first measurement, the swollen SAP was removed from the filter paper and oven-dried at 50°C until constant mass. The dried SAP was then weighed and added to a beaker containing fresh test solution to determine the amount of absorption in the second cycle. This was repeated following the regimes shown in Table 4. The solutions used in regimes A, B and C were either NaCl or $CaCl_2$ to simulate groundwater at different concentrations. Regime D was used to study the combined effects of monovalent and divalent cations (Na^+, Ca^{2+}) on repeated swelling. Regimes E, F and G were used to simulate re-swelling of SAP in groundwater following an initial swelling in a relatively concentrated calcium bearing solution. Around 10-20% of the SAP was 'lost' to the filter paper at each cycle. Therefore, the amount of solution used in the subsequent cycle was adjusted accordingly to maintain a constant mass ratio of test solution to SAP at 500:1. 400 mg of SAP was used at the start to ensure a sufficient amount remaining throughout the entire experiment.

2.4 Swelling of SAP in cement paste

The swelling ratio of SAP in cement paste was determined using image analysis by measuring the volume fraction of the SAP and its macro-inclusions, i.e. the voids that are produced when cast-in SAP dries and shrinks in the hardened cement paste [32]. According to stereology [33, 34], the volume fraction of particular phase in a multi-phase material equals its area fraction measured on a random plane through the material. This random plane was produced by sectioning each cement paste sample with a diamond abrasive cutter to produce three blocks of 50 × 25 × 15 mm along the length of the cylinder. The top and bottom surfaces of each block were flat ground with silicon carbide paper at 70 rpm and at gradually increasing fineness, starting from a coarse grit of 120 down to 220, 600 and 1000 grit, for 2 minutes at each step. At the end of each grinding step, the blocks were cleaned with paper towel followed by acetone in a sonication bath for 1 minute to dislodge and remove debris from the SAP voids. The grinding process removed approximately 1 mm from the top and the bottom surfaces of each block.

A significant amount of SAP particles remained on the surface and these must be removed to enable accurate measurement of swelling ratio with image analysis. Several means for achieving this were trialled including wetting and oven drying (105°C), and sonication in various solvents (acetone, toluene and sodium chloride) to agitate the SAP particles followed by oven drying. It was found that the most effective approach was by heating the blocks at 600°C for an hour, and then cooling gradually to room temperature followed by sonication in acetone to release the SAP particles. At such high heating rate, it is unlikely that the SAP would form a liquid substance that diffuses into the cement paste matrix. In any case, this does not influence the measured swelling ratio. Visual inspection found that cracking was avoided by heating and cooling gradually and by using thin blocks.

Subsequently, the blocks were surface treated to enhance the contrast between the hardened cement paste and SAP voids to facilitate image analysis. This was done by colouring the surface with a black permanent marker pen in two coatings, each coat applied perpendicular to the other. Then, white talcum powder (particle size < 10 μm) was spread on the dry coated surface and gently pressed into voids with a glass slide. Excess powder was swept off with the edge of a razor blade. The entire top and bottom surfaces of each block were then imaged with a flatbed scanner at 2,400 dpi, achieving a pixel size 10.6 μm, which is sufficient to resolve the SAP voids. Six scans were collected per mixture and the total surface area analysed was 125 cm^2. The total number of individual SAP particles measured per sample was more than 1000. Prior to imaging, trials were carried out to determine the optimum contrast and brightness settings of the scanner to achieve a broad image brightness histogram. This ensures that the entire dynamic range of available greyscale is utilised to achieve the best possible contrast. The same scanner settings were applied for all samples for consistency. Visual inspection of the scanned images found no significant amount of preparation damage (e.g. cracks) that would otherwise influence results.

Image analysis and processing were performed using AnalySIS (Soft Imaging System GmbH). Fig. 2a shows a magnified portion from a scanned image of surface-treated cement paste containing SAP. It can be seen that the voids are highly contrasted from the cement paste. The brightness histogram (Fig. 2c) shows a bi-modal distribution. The peak to the right of the histogram represents voids that have been filled with the white talcum powder and the peak to the left represents cement paste that has been coated with black ink. The grey value at midpoint between the two peaks was selected as the threshold value to segment the voids. It should be noted that this method produced very consistent threshold values (~ 120) for all images and this is attributable to the surface treatment to enhance void contrast and also to the care in imaging using consistent settings.

Fig. 2b shows an example of the resulting binary image of the segmented voids. The area fraction of the segmented voids represents the sum of the SAP voids (F_{SV}), SAP particles (F_{SAP}) and any entrapped air (F_{AV}). However, SAP voids may appear spherical and so distinguishing them from entrapped air in the binary image becomes problematic. To overcome this, a control cement paste (no SAP) at the same w/c ratio was prepared and surface treated in the same manner, and analysed. The measured void fraction in the control represents the volume fraction of entrapped air (F_{AV}) and this was assumed to be the same as that in samples containing SAP. Therefore, the swelling ratio of the SAP can be calculated using the following equation as derived in Lee et al. [32]:

$$s = \frac{F_{sv+SAP}\rho_{as}}{m_{SAP}\rho} - \frac{\rho_{as}}{\rho_{SAP}} \qquad \text{(Eq. 2)}$$

Where m_{SAP} is the mass fraction of SAP to the sample, and ρ, ρ_{as} and ρ_{SAP} are the densities of the sample (measured), absorbed solution (1 g/cm^3) and SAP (1.66 g/cm^3). This equation assumes that the volume of the measured SAP voids is equal to the volume of the absorbed solution.

2.5 Pore solution composition

The ion exchange, specifically the uptake of calcium and the release of sodium and potassium by the SAP, was studied by measuring the change in concentration of pore solution extracted from cement pastes with and without SAP. Pore solutions were extracted from freshly mixed cement pastes from Series III to VI

(Table 3) and immediately analysed using inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer, Optima 7300DV) to measure elemental composition. The pastes were prepared in plastic containers and sealed to avoid carbonation as described in Section 2.2. The pore solutions were extracted and analysed at various periods between 40 and 500 minutes from the start of mixing. To extract the pore solution, about 40-80 g of the cement paste was transferred to a test tube and centrifuged at 10,000 rpm for 5 minutes. Trials with only the swollen SAP found that this procedure did not remove significant amount of the absorbed solution. The extracted pore solution from cement paste was then injected through a PES syringe filter (0.22 μm millipore) to remove any residual solids. The syringe filter was tested using various standard solutions to confirm its compatibility with the pore solution. 1 ml of the extracted pore solution was diluted with 1M HCl at a dilution factor of 200, and 5 ml of the diluted solution was then used for elemental analysis.

The concentration of OH^- was determined by acid-base titration. About 0.5 to 2 ml of the extracted pore solution was first diluted with deionised water at a dilution factor of 20. Then, 5 ml of the diluted solution was titrated against 0.01M HCl using phenolphthalein as an indicator. The concentration of OH^- can also be calculated by assuming electrostatic balance between the cations and anions and that the concentration of total sulfur is the same as that of sulfate in the solution. Comparison between the two results provides an indication of error in the experimental measurements.

2.6 SEM-EDX analysis

Scanning electron microscopy (SEM) in the backscattered electron (BSE) mode and energy dispersive X-ray (EDX) analysis were carried out to examine the microstructure of selected samples. In the first sample, dry SAP (S2) was mixed with CEM I and low-viscosity epoxy. The mixture was then cast into 40 × 20 × 10 mm blocks, de-aired under vacuum and cured in air until the epoxy hardened. The second sample is a CEM I cement paste containing S2 that was cast into a similar block size and allowed to harden at room temperature. The paste was then oven-dried at 50°C and vacuum impregnated with a low viscosity fluorescent epoxy resin according to the procedure described in [35]. Both samples were then ground using silicon carbide papers of grit sizes 220, 500 and 1200, and diamond polished at 9, 6, 3, 1 and ¼ μm. The polished surface was then gold coated and examined in high vacuum with a field-emission scanning electron microscope (Camscan Apollo 300) at 10 keV beam energy.

EDX was carried out using Oxford Instruments INCA. An electron beam energy of 15 keV was chosen as a compromise to achieve good spatial resolution, low X-ray absorption of the lighter elements, and to provide a sufficient overvoltage for heavier elements such as Fe. The beam current, measured with a Faraday cup, was maintained at 1.5 nA. This provided an acquisition rate of about 3 kcps at 30% dead time, on all points measured. Beam dwell time was set at 100 μs and more than 250 frames were averaged to produce the element maps. Mapping was carried out at either 256 × 208 or 512 × 416 pixel resolution to approximately match the size of the X-ray sampling volume, which was determined via Monte-Carlo simulations [36].

3. Results and discussion

3.1 Swelling in synthetic pore solutions

Fig. 3 shows the changes in swelling ratio of SAP with time in synthetic pore solutions. Swelling of S5 (poly AA-co-AM) was consistently higher than S2 (poly AA) in all cases. Interestingly, both polymers achieved a higher swelling ratio in the 'strong' pore solution (PS1) compared to the 'weak' pore solution (PS2). This is surprising as one would expect the SAP to absorb less with increasing ionic concentration. We note that both pore solutions have similar concentration of Ca (~ 20 mmol/L), but PS1 has significantly higher amount of alkalis ([K + Na] ~ 470 mmol/L) compared to PS2 ([K + Na] ~ 26 mmol/L).

It can also be observed that most of the swelling for S5 (poly AA-co-AM) occurred within the first 10 minutes of mixing in both solutions. The liquid uptake increased only slightly beyond this and the swelling ratio achieved a relatively steady value after about 200 minutes in the pore solution. The swelling kinetics for S2 (poly AA) in the 'strong' pore solution (PS1) was similar to that for S5 and can be characterised by a fast absorption followed by a slight increase over time. However, its swelling kinetics in the weak pore solution (PS2) was very different. There was a fast absorption to 17g/g in the first 10 minutes, but this was followed by a gradual release of the absorbed water and the swelling ratio stabilised to approximately 3g/g beyond 120 minutes.

The observation above is consistent with Schroefl et al. [23, 27] who reported that polyacrylate SAP with high anionic functional group density swells very rapidly in pore solution, but releases most of the absorbed water over the first one to three hours. In contrast, polyacrylate-co-acrylamide SAP with lower anionic density is able to retain its absorbed water for much longer. However, our study also found that this behaviour is dependent on alkalinity. Essentially, a pore solution with higher alkalinity can decrease ion exchange and Ca^{2+} complexation, and so the SAP retains its swelling for a longer period. This explains why S2 behaved differently in PS1 compared to PS2. The higher swelling in the 'strong' pore solution (PS1) is because the higher concentration of monovalent cations in PS1 reduces the formation of swelling prohibiting bidentate complex by displacing the Ca^{2+} from the acrylate chain [37]. These effects will be shown and discussed in subsequent sections.

3.2 Swelling in simple test solutions

The effects of cation type, concentration and ionic strength on the swelling of poly(AA) and poly(AA-co-AM) are shown in Fig. 4 and Fig. 5. Ionic strength (I) was calculated from the equation: $I = 0.5 \sum c_i z_i^2$, where c_i and z_i are the molar concentration (mmol/L) and charge number of ion i in the solution respectively. The results demonstrate clearly that the swelling of SAP decreases with increase in concentration of the salt solution. It is interesting to note that for any particular concentration, the swelling of both SAPs in NaCl and KCl are of similar values, but significantly larger than that in $CaCl_2$. This is consistent throughout the entire range of concentration tested from 1 to 500 mmol/L and it suggests that swelling behaviour is influenced by the valency of the cations in the test solution. When swelling ratio is plotted against ionic strength in Fig. 5, the disparity between absorbency in monovalent and bivalent cation decreases, but remains substantial.

The effects of anion type and concentration are shown in Fig. 6. The results also show that the swelling ratio of both SAP decreases with increasing concentration and ionic strength. Both SAPs achieved the lowest swelling ratio in NaCl. However, the disparity between monovalent and bivalent anions is very small compared to the case for cations. This suggests that anion valency, at least for Cl^-, OH^- and SO_4^{2-}, has little influence on the swelling behaviour of SAP. Swelling ratio decreased by a factor of 10 in the range of concentration investigated for Na+, K+, Cl^-, OH^- and SO_4^{2-}. For Ca^{2+}, a 100 times decrease in swelling ratio was observed.

Swelling of SAP decreases with increase in solution concentration because of the reduction in osmotic pressure that comes from the difference in ionic concentration between SAP and test solution. Furthermore, the dissolved ions screen repulsive forces between charged groups within the polymer. This charge screening effect reduces the driving force for swelling and so decreases absorption. However, the results also show that valency of the cations in the test solution has significant influence. Presence of multivalent cations such as Ca^{2+} produce a greater reduction in absorption compared to monovalent cations such as Na^+ and K^+, and this observation is consistent with other studies, for example [23, 24, 38, 39]. The is caused by the ability of Ca^{2+} to interact and bind with carboxylate groups from different acrylate chains in the polymer, forming additional cross-links that restrain the movement between acrylate chains and drastically reduce the SAP swelling capacity [37, 40-43]. However, the effect of anion type and valency is relatively small. Both SAP swell slightly more in NaOH than that in NaCl, probably because NaOH neutralises the acrylic acid in the SAP and increases the osmotic swelling pressure.

Fig. 7 shows the effect of increasing saline concentration on SAP swelling by adding NaCl to a $CaCl_2$ solution. The $CaCl_2$ concentration was fixed at 20 mmol/L so that the initial Ca^{2+} concentration is similar to the synthetic pore solutions used in Section 3.1. The concentration of NaCl was gradually increased to simulate an increase in alkalinity. The results show that absorption was initially very low because of the Ca^{2+} complexation as described earlier. However, swelling gradually increases with increase in NaCl, despite an increase in total concentration of the test solution. This effect is stronger for S5, where the swelling ratio increased by about a factor of 3, from 6 g/g to 18 g/g, when the concentration of NaCl increased from 0 to 1200 mmol/L. The increase in swelling ratio despite an increase in total saline concentration is rather unexpected and this is also observed when swelling ratio was measured in synthetic pore solutions (Fig. 3). The results show that absorption capacity is not a simple function of saline concentration or ionic strength. It appears Ca^{2+} is much more effective in restraining the swelling of SAP compared to the other ions. However, addition of Na^+ produces a partial recovery in swelling. This effect will be further investigated in subsequent sections.

3.3 Effect of repeated wetting and drying on swelling ratio

Fig. 8 shows the effect of repeated wetting and drying on SAP swelling in NaCl and $CaCl_2$ solutions. Details of the test solutions and cyclic conditions used are described in Table 4 (Regimes A to D). The results show that when cyclic wetting and drying was carried out in NaCl, the swelling ratios of both polymers remained approximately constant at ~80g/g for each cycle. This shows that SAP can repeatedly collapse on drying and re-swell on wetting with no apparent loss in swelling capacity in NaCl. This swelling reversibility is obviously a desirable property for certain applications such as crack sealing.

However, when tested in $CaCl_2$, both polymers displayed a substantial loss in absorption capacity for each cycle. The swelling ratio of S2 drops to almost zero beyond the third cycle, while S5 achieves a stable value at ~ 25g/g beyond the fourth cycle. The rate of decrease in swelling is greater in the 3.2 mmol/l $CaCl_2$ solution compared to that of the 1.6 mmol/l $CaCl_2$ solution. However, the swelling ratios in both solutions converge to a similar value as the number of cycles increased. It is also noted that cyclic wetting in a solution containing equal amounts of NaCl and $CaCl_2$ did not significantly alter the swelling behaviour of the SAP.

Fig. 9 shows the effect of repeated exposure to NaCl after an initial cycle in either $CaCl_2$, $Ca(NO_3)_2$ or the synthetic ‘strong’ pore solution (PS1) (Regimes E to F, Table 4). It can be observed that exposure to $CaCl_2$, $Ca(NO_3)_2$ or synthetic pore solution in the first cycle produced very low swelling for both polymers. However, the swelling gradually recovers when the same polymer is exposed to NaCl in subsequent cycles. The results also show that S5 recovers much faster than S2. A complete recovery of the swelling ratio appears to be possible, particularly for S5 if the cyclic wetting/drying is extended.

The loss in absorption capacity with each wetting/drying cycle in calcium bearing solution suggests that there is gradual binding between Ca^{2+} and acrylate chains in the SAP. The binding is cumulative and occurs even in low Ca^{2+} concentrations. For crack sealing, this effect is undesirable since calcium is found in many exposure environments (groundwater for example) and calcium is leached when flow occurs through cracks. The Ca^{2+} complexation can lead to ineffective crack sealing. However, if the SAP is exposed to NaCl in subsequent cycles (Fig. 9), swelling gradually recovers because the complexes can be removed when monovalent cations are available to displace the Ca^{2+} from acrylate chains via ion exchange. This is consistent with the results shown in Figs. 3 and 7.

3.4 Effect of alkalinity and calcium content on SAP swelling in cement paste

Fig. 10 shows the swelling ratio of SAP in cement pastes that contain a range of alkalinity and calcium content in the pore solution. Note that alkalinity and calcium content were varied by adding dissolved sodium hydroxide and calcium nitrate to the batch water, and swelling ratio was measured using image analysis as described in Section 2.4. The cement paste samples are from Series I and II (Table 3) that were made with white Portland cement. The error bars represent the standard error of the measurements. The results show that pore solution alkalinity and calcium content have strong influences on SAP absorption capacity. The swelling ratios for both SAPs increase with increase in alkalinity, but decrease with increase in calcium concentration. Swelling ratio increased from ~2.5 g/g at 0.09% equivalent Na_2O to more than 16 g/g at 0.9% equivalent Na_2O content. When the calcium nitrate content was increased to 4% wt. cement, the swelling ratio of S5 in cement paste dropped to less than 1g/g, while the swelling ratio of S2 remained very low over the entire range of calcium nitrate. The results also show that S2 swells significantly less than S5, consistent with previous results in synthetic pore solutions.

It can be seen that the SAP swelling ratios measured in hardened cement paste are close, but slightly lower than the free swelling ratios measured in synthetic pore solutions (Fig. 3). This discrepancy may be due to the fact that the composition of real pore solution is much more complex and variable because of the dissolution and precipitation processes occurring during hydration. The SAP may lose part of the absorbed water before setting due to cumulative binding with Ca^{2+} and so the measured swelling ratio on hardened paste will be lower than that measured in fresh state. This was seen in our results (Fig. 3) for S2 and was also observed by Schroefl et al. [23, 27]. Furthermore, mixing and compaction during batching induce physical confinement that will reduce the absorption capacity of the SAP relative to its free swelling. It should also be noted that the absorption of SAP was measured in hardened cement pastes instead of mortars or concretes for the sake of simplicity and convenience. Presence of aggregate particles will not significantly change the pore solution composition, but it provides another physical restraint to the swelling of SAP. Further work is required to establish whether this has a significant effect on the absorption capacity of SAP.

A comment should be made regarding the image analysis method used for determining the swelling ratio of SAP in cement paste. The reliability of this method depends on the contrast between SAP voids and cement paste, which was enhanced via the surface treatment described in Section 2.4. There are other methods, for example BSE image analysis [32], X-ray computed tomography [44], NMR relaxation [45] and neutron tomography [46]. Each of these has advantages and limitations. We used a flatbed scanner because it is relatively straight forward and allows a large sample area to be measured rapidly. However, the method requires the dried SAP to be removed and this can be problematic if it bonds strongly to the cement paste. The method is also limited by the resolution of the scanner and so may be inappropriate for SAP with particle sizes much smaller than those used in this study. The method requires testing of a companion control sample with no SAP and assumes it has the same entrapped air to that of cement paste containing SAP. This may not be strictly valid in some cases since the swollen SAP affects the rheology of the fresh cement paste.

3.5 Pore solution composition and ion exchange

The compositions of the pore solutions extracted from white Portland cement pastes containing 2% S2 at various times after mixing are shown in Table 5. The analysis using ICP-OES and acid-base titration found that the pore solution contained mainly Na^+, K^+, Ca^{2+}, SO_4^{2-} and OH^-, while other elements were in trace quantities. The measured concentrations of OH^- are reasonably close to the calculated values, thus giving confidence in the measured values. The results show that the concentration of Na^+ was consistently very high, from the earliest measurement at 40 minutes (228 mmol/L) to the final measurement at 8.5h (253 mmol/L). In contrast, the concentration of Na^+ for the control WPC paste without SAP was only ~7 mmol/L

(Series IV, Table 6). This shows that the presence of SAP increases the concentration of alkali (Na^+ for S2) and this occurs very soon after mixing. The concentration of K^+ was also relatively constant (~3 to 4.5 mmol/L), but close to the value of the control paste (~3 mmol/L). The total alkalinity [Na + K] is stable after about 4 hours after mixing. However, the concentrations of Ca^{2+} and SO_4^{2-} decreased with increase in time. The reason for the decline is due to precipitation of hydration products (particularly ettringite), but it could also be partly due to ion exchange with the SAP (discussed later). The concentration of OH^- increased with time and this is attributable to the continuous dissolution of the cement phases.

Table 6 shows the composition of pore solutions extracted after ~ 4 hours of mixing (between 245 and 280 min) from a range of cement pastes from Series III to VI. The objective is to study the effect of SAP type and amount on the pore solution composition, to establish if ion exchange occurs between SAP and pore solution, and how this influences SAP swelling. Since the concentration of alkalis during the first few hours of hydration (dormant period) is relatively constant [47-49] and because the pore solutions were measured at the same time, the observed changes in alkali concentration must be indicative of the exchange process between the SAP and pore solution. Furthermore, the SAP itself should not influence hydration kinetics at such an early age.

The results show that the pore solutions from WPC pastes (Series IV) have lower alkali content compared to that of the CEM I pastes (Series III), as expected. The pore solution from WPC paste also show consistently higher Ca^{2+} content and lower SO_4^{2-} compared to that of the CEM I paste. The WPC pastes with added sodium hydroxide (Series V) gave the highest alkali content, as expected. It is also noted that the concentration of Na^+ for the WPC + NaOH control paste (no SAP) compares well with the known amount of sodium hydroxide added and this shows that the sodium hydroxide remains dissolved in the pore solution after 4 hrs of hydration. This is also the case for the pastes with added calcium nitrate (Series VI).

When the pore solutions of pastes containing SAP are compared against their respective reference control paste, it can be seen that the presence of SAP increases the concentration of alkalis significantly; S2 (poly AA) increases the concentration of Na^+, while the presence of S5 (poly AA-co-AM) increases the concentration of K^+. However, pastes containing SAP registered a drop in concentration of Ca^{2+}. To examine this further, data from Table 6 are used to plot the change in concentration of alkalis (ΔC_{Na+K}) and calcium (ΔC_{Ca}) in pastes containing SAP relative to the control in Figs. 11 to 13. Fig. 11 shows that all samples displayed positive ΔC_{Na+K} values, indicating the release of Na^+ and K^+ from the SAP into the pore solution. All samples bar one showed negative ΔC_{Ca} values, indicating that Ca^{2+} is absorbed by the SAP. However, the magnitudes of ΔC_{Na+K} are not strongly correlated to ΔC_{Ca} and this is probably due to the fact that the calcium content is also affected by dissolution of cement and precipitation of hydration products. Overall, the degree of ion exchange is higher in pastes containing S2. Furthermore, the degree of ion exchange decreases with increase in alkalinity, and this correlates well to the observed increase in swelling ratio of the SAP. S5 has the highest swelling ratio and it is also more resistant to ion exchange compared to S2.

Addition of dissolved calcium nitrate increases the concentration of Ca^{2+} in the pore solution substantially, as seen in Table 6 (Series VI). Fig. 12 and Fig. 13 show that increasing Ca^{2+} content in the pore solution increases the magnitude of ΔC_{Na+K} and ΔC_{Ca} . Therefore, the amount of ion exchange and Ca^{2+} complexation increases and this depresses the swelling of the SAP. WPC pastes without calcium nitrate display the lowest ΔC_{Ca} because their Ca^{2+} concentration (~50 mmol/L) is relatively small such that the lost of Ca^{2+} ions to SAP can be partially replenished by dissolution of the cement phases. In contrast, the pore solution of WPC pastes containing calcium nitrate is already supersaturated with Ca^{2+} (> 400 mmol/L), so this effect is less significant. It can also be seen that increasing the SAP content in the cement paste increases the magnitude of ΔC_{Na+K} and ΔC_{Ca} , which is again consistent with expectation. The results also show that S5 has the higher swelling ratio and exhibits lower ion exchange compared to S2.

The results consistently show that the presence of S2 increases [Na^+] in pastes while S5 increases [K^+] (Table 6) because these counter-ions are released from the SAP in exchange with Ca^{2+} ions from the pore solution that binds with the acrylate chains. Increasing the Ca^{2+} content in the pore solution by adding dissolved $Ca(NO_3)_2$ increases Ca^{2+} complexation and this depresses swelling further (Figs. 10b, 12 & 13). In contrast, increasing the alkalinity of the pore solution (Figs. 10a & 11) increases SAP swelling because it inhibits ion exchange and therefore Ca^{2+} complexation. These are significant factors controlling swelling of SAP in cement paste in addition to osmotic pressure. The higher the degree of ionic exchange, the lower the swelling ratio of the SAP, and vice versa. The results are consistent with the measurements made in weak/strong synthetic pore solution (Fig. 3), in NaCl + $CaCl_2$ solution (Fig. 7) and in the cyclic wetting/drying experiments (Fig. 9).

3.6 SEM-EDX analysis

Figs. 14 and 15 show backscattered electron (BSE) images and energy dispersive X-ray (EDX) element maps of samples containing SAP. The first sample contained dry SAP (S2) mixed with CEM I and cast in a low-viscosity epoxy. The second sample is a CEM I cement paste containing S2. EDX mapping shows that the dry SAP (Fig. 14) contains mainly sodium, carbon and oxygen, which is consistent with the type of polymer used. However, when the SAP is cast into cement paste (Fig. 15), the EDX mapping shows that the SAP has gained a substantial amount of calcium, which must have been absorbed from the pore solution. There is also a significant gain in potassium on the SAP. These observations support the measured changes in pore solution composition presented in the previous section and the described ion exchange process that occurs between the SAP and pore solution. There is also a slightly higher content of sulphur on the surface of the SAP. However, this is due to precipitation of hydration products on the surface of the SAP as can be seen in the BSE image. Other detectable elements were Al, Mg, Si and Fe, but these were only found in the cement paste and not in the SAP.

4. Implications

This study has shown that while the swelling of both polymers is similar in non-calcium bearing solutions, the swelling of poly(AA) in calcium bearing solution is reduced sharply. This can be seen from the measurements in test solutions and also in hardened cement paste. Furthermore, the swelling of S2 recovers at a much slower rate compared to S5 (Fig. 9). The difference in behaviour is because poly(AA) has a higher amount of acrylate chains than poly(AA-co-AM) and therefore is more susceptible to Ca^{2+} complexation. The amount of ion exchange deduced from the measured change in pore solution composition showing pastes with S2 consistently having greater magnitudes of ΔC_{Na+K} and ΔC_{Ca} supports this. Poly(AA-co-AM) has lower acrylate content and so forms less Ca^{2+} acrylate complex. Furthermore, non-ionic acrylamide groups act as spacers between the acrylate groups, thus weakening the short range bonding between absorbed Ca^{2+} and neighbouring acrylate groups, and reducing the stability of the Ca^{2+} complex. The absence of acrylamide in S2 means that Ca^{2+} complex can form between close neighbouring acrylate groups and restrain its swelling capacity.

In terms of practical implications, the findings from this study suggest that the swelling kinetics of SAP could be altered to optimise a particular application in concrete. For crack sealing for example, it would be desirable to depress the initial SAP swelling in fresh concrete so that its reswelling capacity and potential for crack sealing at later age is enhanced. This is also beneficial because it decreases the SAP void content, enabling a higher SAP dosage in the mixture and limiting its negative impact on strength. Initial swelling can be suppressed by using low alkalinity cement and by increasing the calcium concentration in the pore solution. Calcium nitrate or calcium nitrite are good candidates to achieve the latter because both have high solubility and are also good corrosion inhibitors for embedded steel reinforcement. The swelling of poly(AA) is easier to suppress than poly(AA-co-AM) due to its greater susceptibility to binding with Ca^{2+}.

In contrast, it would be desirable to increase the initial swelling of SAP in fresh concrete for the purpose of internal curing, mitigating autogeneous shrinkage and frost protection. This could be achieved by increasing alkalinity, but the risk of alkali-aggregate reaction needs to be considered. Limiting calcium concentration is also not feasible and the use of calcium based additives should be avoided. Therefore, the practical approach is probably to use SAP that is more resistant to the ion exchange process such as poly(AA-co-AM). Furthermore, a well-timed release of absorbed water is important because it can be detrimental to microstructure (e.g. by increasing w/c ratio) and efficiency of internal curing if desorption occurs too quickly. The release of absorbed water can be influenced by alkali content as shown in this study. Another factor that could influence sorption kinetics is the density of anionic groups in the SAP network as shown in previous studies [23, 24].

In addition to swelling of the SAP, this study also shows the effect of SAP as an ionic exchanger on the pore solution composition. The binding of Ca^{2+} ions in the solution leads to the increase in the solubility of OH^- ions, therefore increasing the pH of the pore solution. This is most prominent in the WPC+2%S2 sample. While this will increase the degree of protection of steel reinforcement, it may also increase the vulnerability to alkali-aggregate reaction. The change of pore solution composition also affects the hydration process. For example, the increase in pH increases the rate of hydration of cement containing supplementary cementitious materials and the decrease in calcium content in pore solution may affect the hydrates assemblage. Further study is required to investigate the significance of these effects.

This study demonstrates the swelling and ionic exchange behaviour of SAP with acrylates and acrylamide groups in pore solutions. Indeed, there are other factors that affect the swelling property of SAP such as cross-linker type and density, and functional group type and density. This provides a much wider possibility of optimisation.

5. Conclusions

The effect of alkalinity and calcium concentration of the pore solution on the swelling of polyacrylate (poly AA) and polyacrylate-co-acrylamide (poly AA-co-AM) superabsorbent polymers in cement paste was investigated. The study also looked at the effect of cation and anion type, concentration, ionic strength and repeated wetting/drying on the absorption capacity of SAP. Furthermore, the effect of SAP type and dosage on the pore solution composition and the ion exchange occurring between SAP and pore solution was studied. The following conclusions can be drawn:

a) In simple test solutions, absorbency of SAP decreases with increase in concentration and ionic strength of the test solution due to reduction in osmotic pressure. However, bivalent cations such as Ca^{2+} in the test solution produce a much greater decrease in swelling because they bind with carboxylate groups in the acrylate chains, forming additional cross-links that inhibits swelling further. The effect of anion type and valency on swelling behaviour of SAP is relatively small.

b) Cyclic wetting/drying experiments in NaCl show that SAP can repeatedly collapse and re-swell with no apparent loss in absorption capacity. However, cyclic wetting/drying experiments in calcium bearing solutions show that absorption decreases with every cycle because of gradual binding between Ca^{2+} and SAP. This effect is cumulative and occurs even at low calcium concentration. If the SAP is exposed to an alkaline solution in subsequent cycles, the Ca^{2+} complexes are gradually removed because monovalent cations (Na^+, K^+) displace the bound Ca^{2+} via ion exchange. This produces a gradual recovery in swelling.

c) Significant ion exchange takes place between SAP and pore solution in cement paste. This is characterised by adsorption of Ca^{2+} by the SAP and the release of Na^+ and K^+ into the pore solution.

d) The calcium content and alkalinity of the pore solution have strong influences on SAP absorption capacity. Increasing Ca^{2+} content in the pore solution increases the amount of Ca^{2+} complexation and this depresses swelling. In contrast, increasing the alkalinity of the pore solution increases SAP swelling because it inhibits ion exchange and therefore Ca^{2+} complexation. These are significant factors controlling the swelling of SAP in cement paste in addition to osmotic pressure. The higher the degree of ionic exchange, the lower the swelling ratio of the SAP, and vice versa.

e) Poly (AA) type SAP is more susceptible to Ca^{2+} complexation and therefore achieves a lower swelling ratio compared to poly(AA-co-AM) in calcium bearing solutions. Furthermore, the release of absorbed water is more rapid and recovery in swelling capacity of poly (AA) is much slower than that of poly(AA-co-AM). The findings from this study can be applied to alter the swelling kinetics of SAP to suit a particular application in concrete, such as crack sealing or internal curing.

f) SAP such as Poly(AA) are ionic exchangers that affect pore solution composition. They increase Na^+ and OH^- concentration while reducing Ca^{2+} concentration. This may affect hydration kinetics and the development of microstructure.

6. Acknowledgement

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Table 1 Composition of the Portland cements used.

Cement	Oxide composition (%)											
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	$EqNa_2O$	P_2O_5	Free CaO	Cl
CEM I	20.2	4.64	1.99	63.8	2.77	3.11	0.66	0.18	0.61	0.18	0.95	0.053
WPC	24.0	3.63	0.47	69.6	0.69	2.21	0.12	0.01	0.09	0.56	2.0	0.016

Cement	Specific gravity	Specific surface area (m^2/kg)	Bogue composition (%)			
			C_3S	C_2S	C_3A	C_4AF
CEM I	3.13	340	62.9	10.9	8.93	6.05
WPC	3.04	430	69.2	17.0	8.83	1.43

Table 2 Properties of the SAP used.

SAP	Source	Diameter (µm)	Bulk density (kg/m^3)	Polymer type	Swelling ratio, g/g			
					Deionised water	0.12 wt% NaCl	Synthetic groundwater	Synthetic pore solution (PS1)
S2	Evonik	100-300	n/a	Poly(AA)	222	79	89	21
S5	ETi	1-200	540	Poly(AA-co-AM)	208	73	71	23

Table 3 Cement paste mixture composition. The alkalinity and calcium content was varied by using white Portland cement (WPC) and adding either NaOH or $Ca(NO3)_2$ to the batch water.

Series	**Cement**	**Batch water***	**SAP dosage (% wt. cement)**
I	WPC	Deionised water + NaOH to produce Na_2O_{eq} of 0.09, 0.25, 0.4, 0.55, 0.7 or 0.9% wt. cement	0.6% S2 or 0.6% S5
II	WPC	Deionised water + 0.5, 1, 2, 3 or 4% $Ca(NO_3)_2$ wt. cement	2% S2 or 2% S5
III	CEM I	Deionised water	0% SAP, 0.6% S2 or 0.6% S5
IV	WPC	Deionised water	0% SAP, 0.6% S2, 0.6% S5, 2% S2 or 2% S5
V	WPC	Deionised water + NaOH to produce Na_2O_{eq} of 0.6 or 0.9% wt. cement	0% SAP, 0.6% S2 or 0.6% S5
VI	WPC	Deionised water + 4% $Ca(NO_3)_2$ wt. cement	0% SAP, 0.6% S2, 0.6% S5, 2% S2 or 2% S5

* Note: Free water/cement ratio was 0.6 for all mixtures.

Table 4 Test solutions used to study the effect of repeated wetting and drying on swelling capacity.

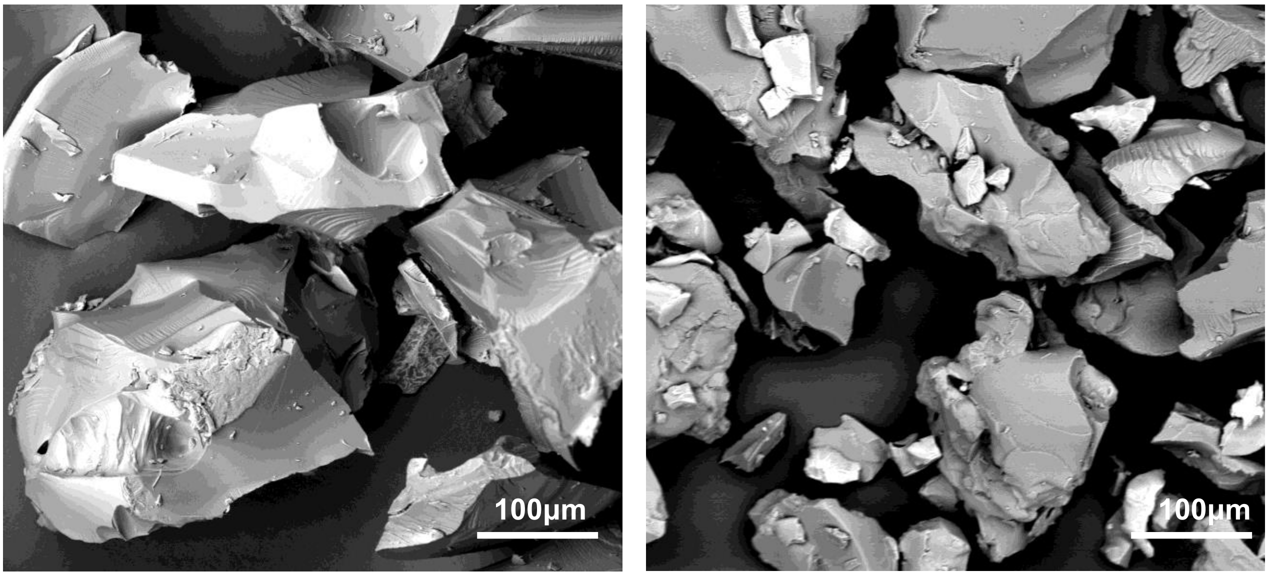
Regime	Designation	Test condition
A	*20mM NaCl*	7 cycles in 20mmol/l NaCl
B	*3.2mM* $CaCl_2$	7 cycle in 3.2mmol/l $CaCl_2$
C	*1.6mM* $CaCl_2$	7 cycles in 1.6mmol/l $CaCl_2$
D	*1.6mM* $CaCl_2$ *+1.6mM NaCl*	7 cycles in 1.6 mmol/l $CaCl_2$ and 1.6mmol/l NaCl
E	*20mM* $CaCl_2$*+6@20mM NaCl*	1 cycle in 20mmol/l $CaCl_2$, followed by 6 cycles in 20mmol/l NaCl
F	*500mM* $Ca(NO_3)_2$*+6@20mM NaCl*	1 cycle in 500mmol/l $Ca(NO_3)_2$, followed by 6 cycles in 20mmol/l NaCl
G	*PS1+6@20mM NaCl*	1 cycle in PS1, followed by 6 cycles in 20mmol/l NaCl

Table 5 Composition of pore solution extracted from white Portland cement paste containing 2% S2 at various times after mixing.

Time (min)	Concentration (mmol/L)					
	Na^+	K^+	Ca^{2+}	SO_4^{2-}	OH^-	OH^- (Calculated)
40	227.7	3.1	49.7	121.8	93.8	86.6
89	236.5	4.1	31.8	95.1	117.4	114.0
157	246.2	3.8	31.1	77.2	133.1	157.8
274	249.3	3.6	30.3	68.3	184.4	176.9
509	253.1	4.5	19.6	54.5	226.8	187.7

Table 6 Composition of pore solution extracted from cement pastes at ~4 hours after mixing.

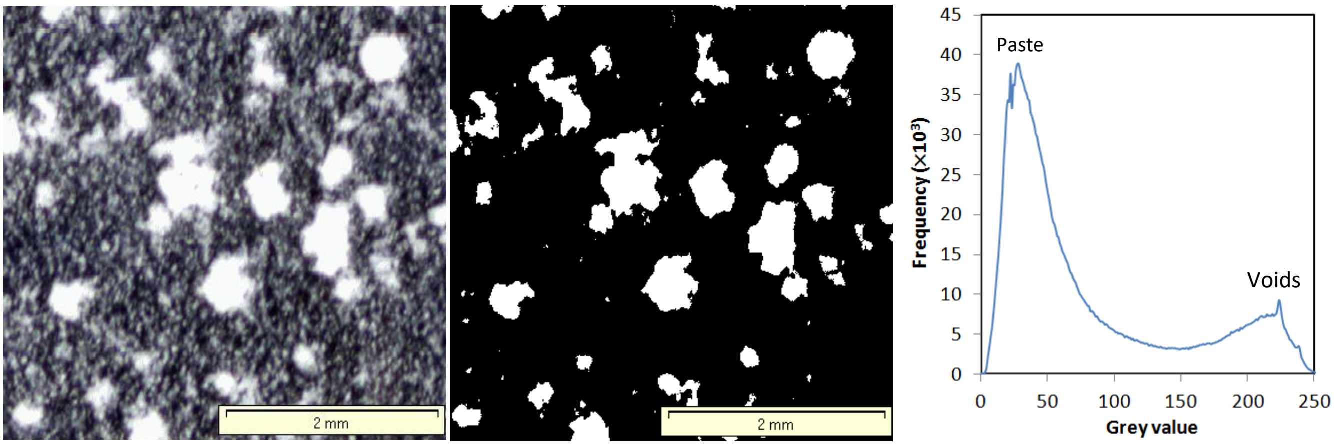
Sample	Time (min)	Concentration (mmol/L)				
		Na^+	K^+	Ca^{2+}	SO_4^{2-}	OH^-
a) Series III: CEM I						
CEM I *(control)*	256	47.1	180.9	26.2	41.5	211.6
CEM I + 0.6% S2	254	114.5	172.9	24.8	55.4	257.9
CEM I + 0.6% S5	265	44.4	194.2	24.5	49.4	223.9
b) Series IV: WPC						
WPC *(control)*	249	6.8	3.0	48.7	14.7	93.1
WPC + 0.6% S2	252	82.6	6.9	32.7	23.3	127.2
WPC + 0.6% S5	249	7.9	33.4	47.2	17.2	98.9
WPC + 2% S2	274	249.3	3.6	30.3	68.3	184.4
WPC + 2% S5	265	7.7	99.7	47.7	36.6	135.0
c) Series V: WPC + NaOH						
WPC + 0.9% Na_2O_e *(control)*	253	424.6	5.1	16.4	60.3	376.7
WPC + 0.9% Na_2O_e + 0.6% S2	253	478.8	4.1	9.5	77.6	431.5
WPC + 0.6% Na_2O_e *(control)*	278	290.8	4.6	24.6	67.5	253.8
WPC + 0.6% Na_2O_e + 0.6% S5	265	271.3	32.2	27.7	77.5	245.1
d) Series VI: WPC + $Ca(NO_3)_2$						
WPC + 4% $Ca(NO_3)_2$ *(control)*	250	7.8	4.2	428.0	6.0	80.2
WPC + 4% $Ca(NO_3)_2$ + 0.6% S2	248	89.4	4.4	406.9	7.2	77.9
WPC + 4% $Ca(NO_3)_2$ + 0.6% S5	254	8.3	36.6	419.9	11.3	86.9
WPC + 4% $Ca(NO_3)_2$ + 2% S2	270	289.5	3.7	309.4	7.2	68.1
WPC + 4% $Ca(NO_3)_2$ + 2% S5	255	8.4	108.4	395.8	18.7	103.0



(a) S2 (poly AA)

(b) S5 (poly AA-co-AM)

Fig 1 Scanning electron micrographs of the SAPs used in this study.



(a)

(b)

(c)

Fig. 2 a) Magnified portion from a scanned image of surface-treated cement paste showing the dark coloured paste region and voids filled with white talcum powder, b) binary image of the voids segmented by greyscale thresholding, and c) brightness histogram of the original scanned image showing peaks representing the cement paste and voids.

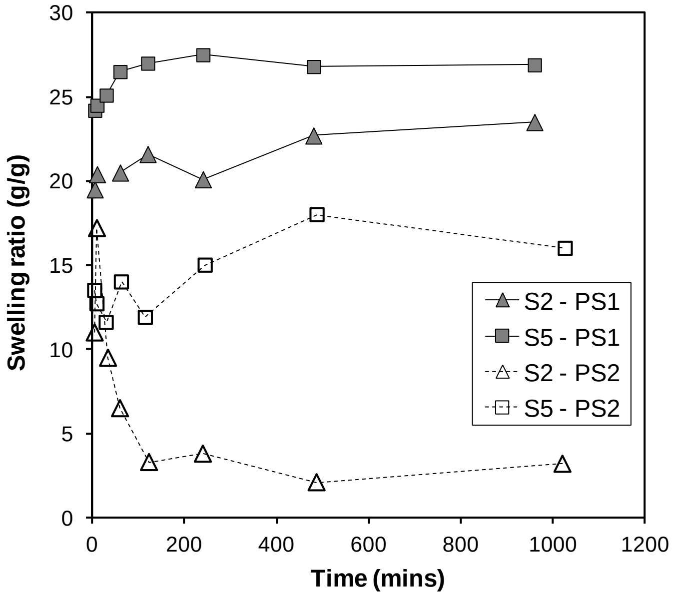
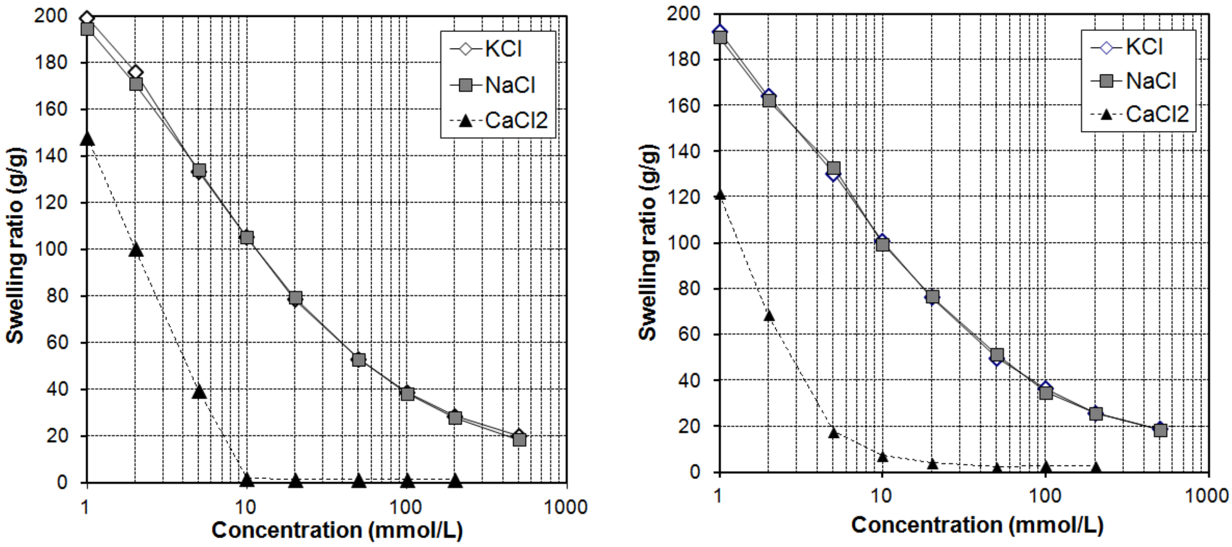


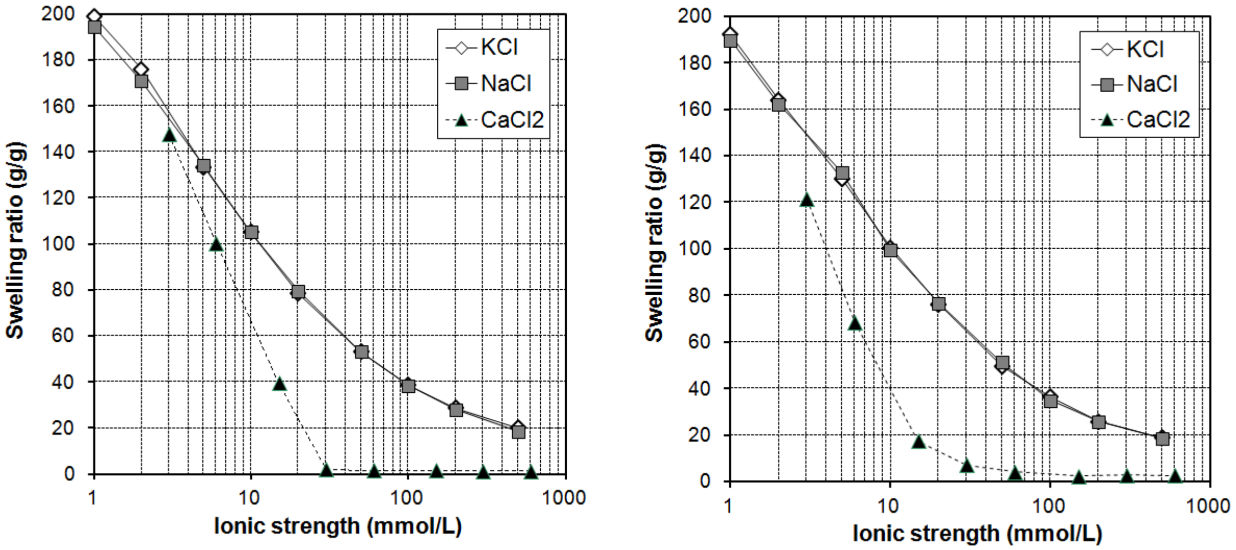
Fig. 3 Effect of exposure time on the swelling of S2 (poly AA) and S5 (poly AA-co-AM) in two synthetic pore solutions of different concentrations (PS1: 'strong', PS2: 'weak'). Swelling is highest in the 'strong' pore solution.



(a) S2 (poly AA)

(b) S5 (poly AA-co-AM)

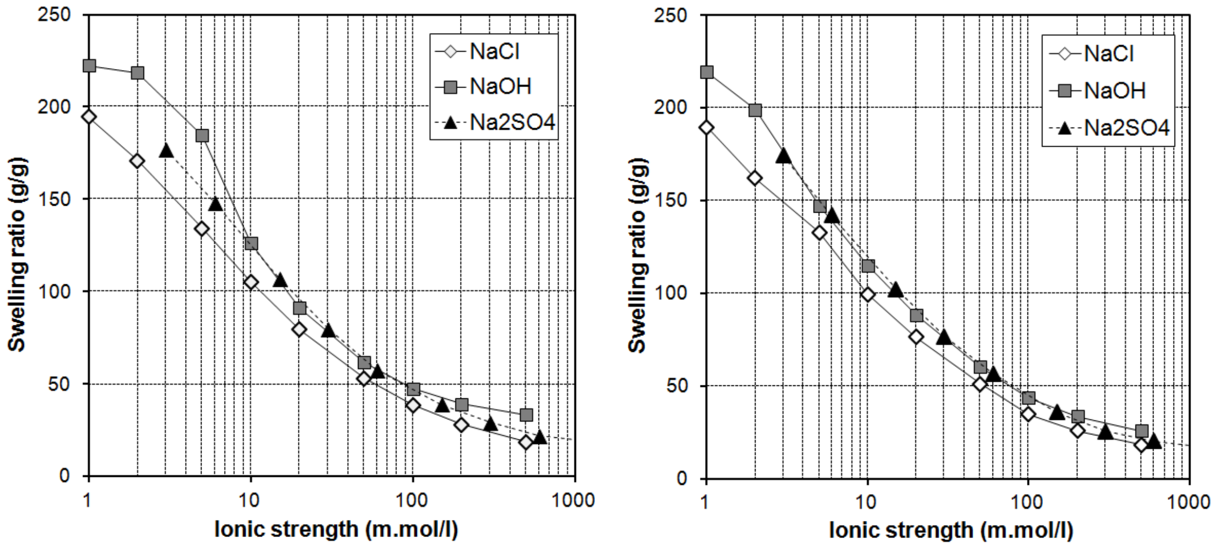
Fig. 4 Effect of cation type and concentration on the swelling of a) S2 (poly AA) and b) S5 (poly AA-co-AM) in various chloride salt solutions. Measurements were made after 24-30 hours in solution (see Section 2.3 for details).



(a) S2 (poly AA)

(b) S5 (poly AA-co-AM)

Fig. 5 Effect of cation type and ionic strength on the swelling ratio of a) S2 (poly AA) and b) S5 (poly AA-co-AM) in various chloride salt solutions. Measurements were made after 24-30 hours in solution (see Section 2.3 for details).



(a) S2 (poly AA)

(b) S5 (poly AA-co-AM)

Fig. 6 Effect of anion type and ionic strength on the swelling of a) S2 (poly AA) and b) S5 (poly AA-co-AM) in various sodium salt solutions. Measurements were made after 24-30 hours in solution (see Section 2.3 for details).

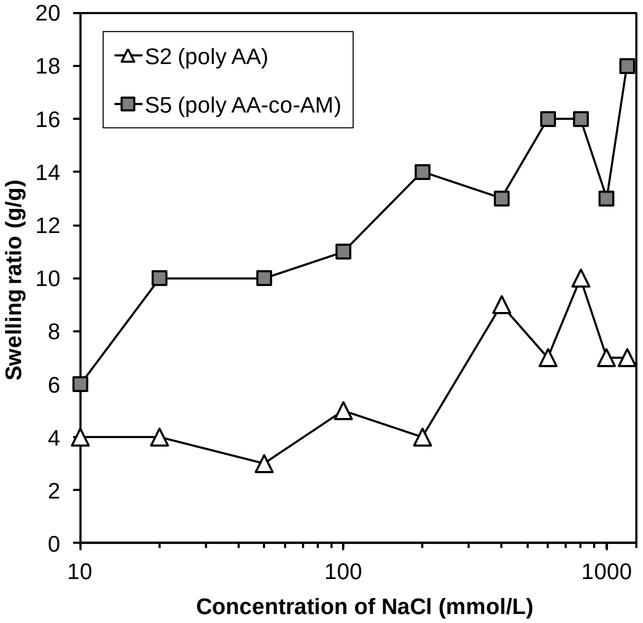


Fig. 7 Swelling ratio of S2 (poly AA) and S5 (poly AA-co-AM) in solutions containing 20 mmol/L $CaCl_2$ and increasing amount of NaCl. The swelling of SAP increases despite an increase in total saline concentration. Measurements were made after 24-30 hours in solution (see Section 2.3 for details).

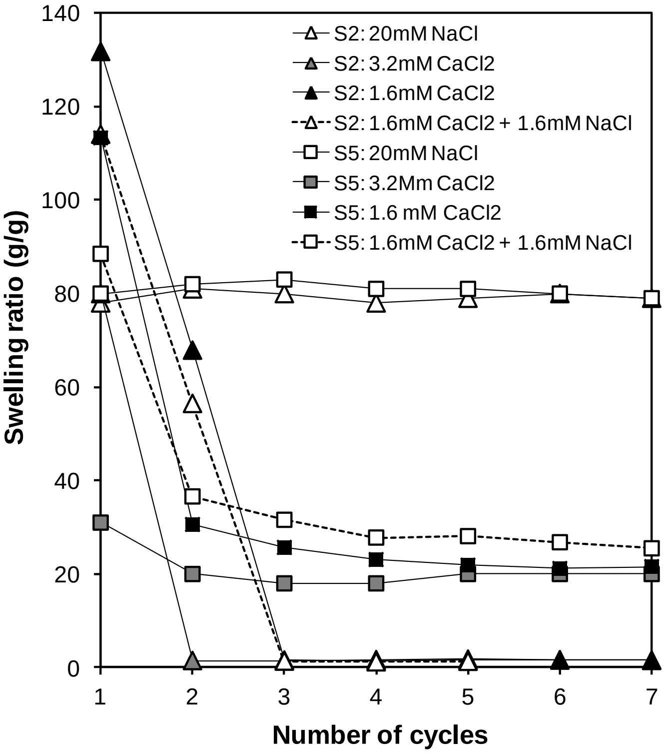


Fig. 8 Effect of repeated wetting and drying in NaCl and $CaCl_2$ on the swelling ratio of S2 (poly AA) and S5 (poly AA-co-AM). Both polymers show substantial reduction in absorption capacity in solutions containing Ca^{2+}, but not Na^+.

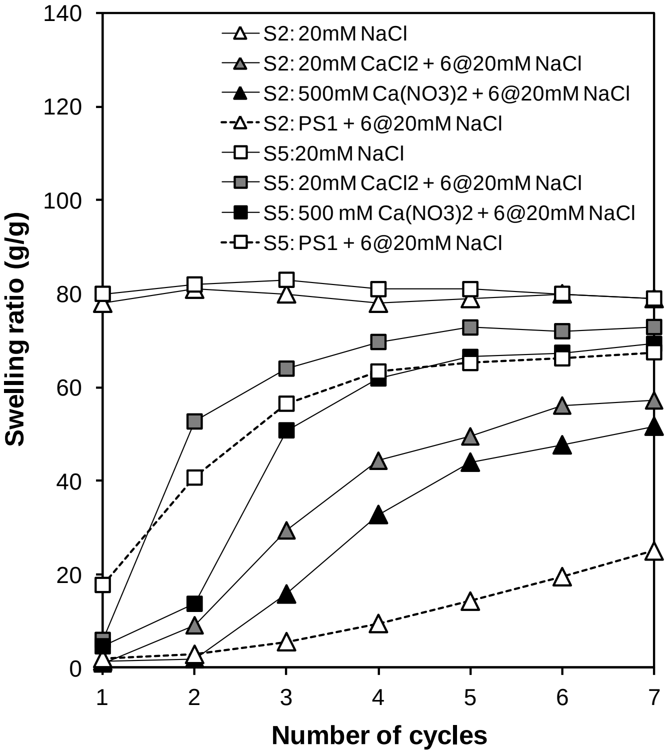
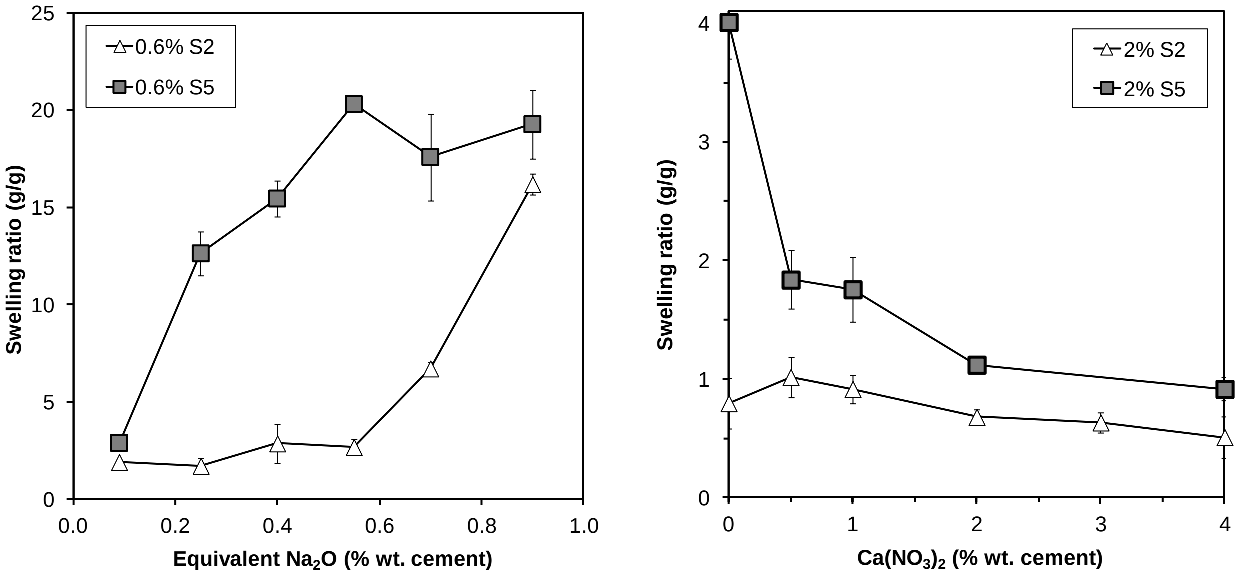


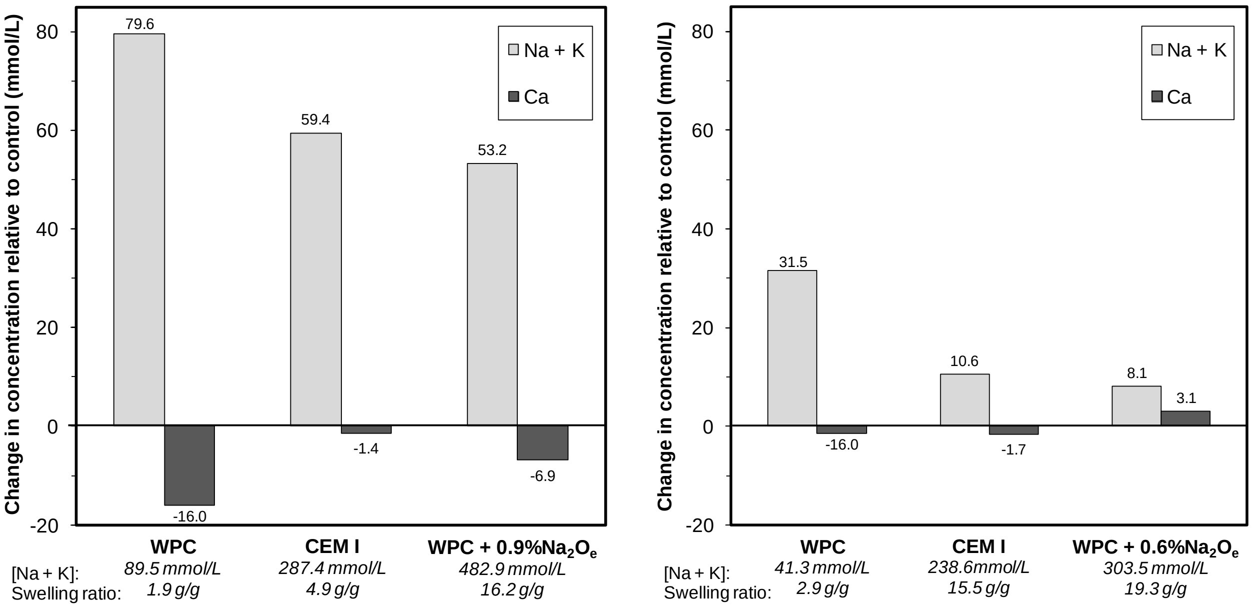
Fig. 9 Effect of repeated wetting and drying in NaCl after an initial cycle in either $CaCl_2$, $Ca(NO_3)_2$ or synthetic pore solution (PS1) on the swelling ratio of S2 (poly AA) and S5 (poly AA-co-AM). Swelling of both polymers gradually recovers due to ion exchange (Ca^{2+}, Na^+) between pore solution and SAP.



(a) Series I

(b) Series II

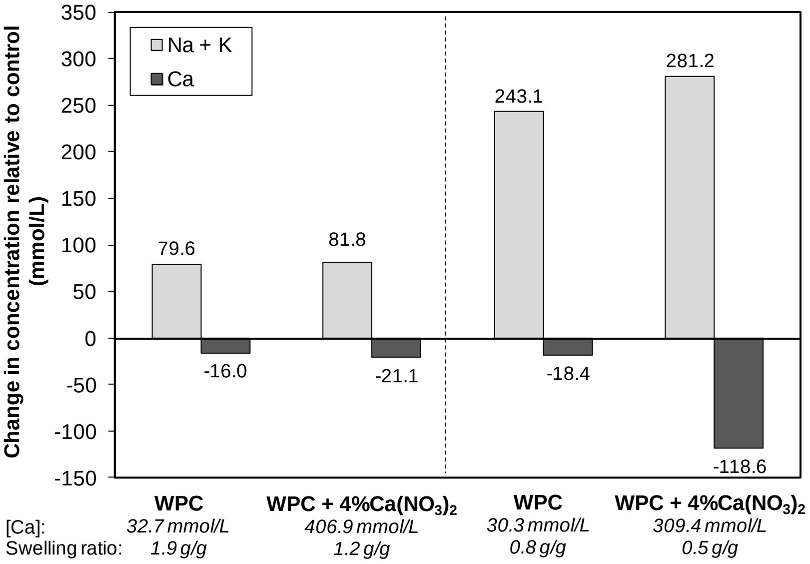
Fig. 10 Effect of alkalinity (a) and calcium content (b) on the swelling of S2 (poly AA) and S5 (poly AA-co-AM) in hardened cement paste measured with image analysis. Samples are from WPC pastes from Series I and II shown in Table 3.



(a) 0.6% S2

(b) 0.6% S5

Fig. 11 Effect of alkalinity and SAP on the change in pore solution composition of cement paste containing 0.6% S2 (poly AA) and 0.6% S5 (poly AA-co-AM) at ~4 hours after mixing. Ion exchange between pore solution and SAP decreases with increase in alkalinity. S5 (poly AA-co-AM) has higher swelling and resistance against ion exchange.



(a) 0.6% S2

(b) 2% S2

Fig. 12 Effect of calcium content and SAP on the change in pore solution composition of cement paste containing S2 (poly AA) at dosage of 0.6% and 2% at ~4 hours after mixing. Ion exchange between pore solution and SAP increases with increase in calcium content and SAP dosage.

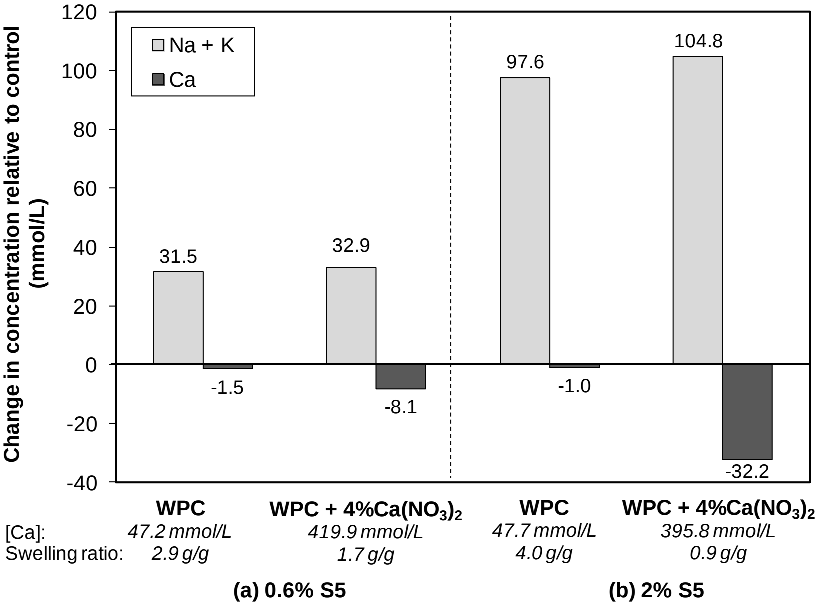


Fig. 13 Effect of calcium content and SAP on the change in pore solution composition of cement paste containing S5 (poly AA-co-AM) at dosage of 0.6% and 2% at ~4 hours after mixing. Ion exchange between pore solution and SAP increases with increase in calcium content and SAP dosage.

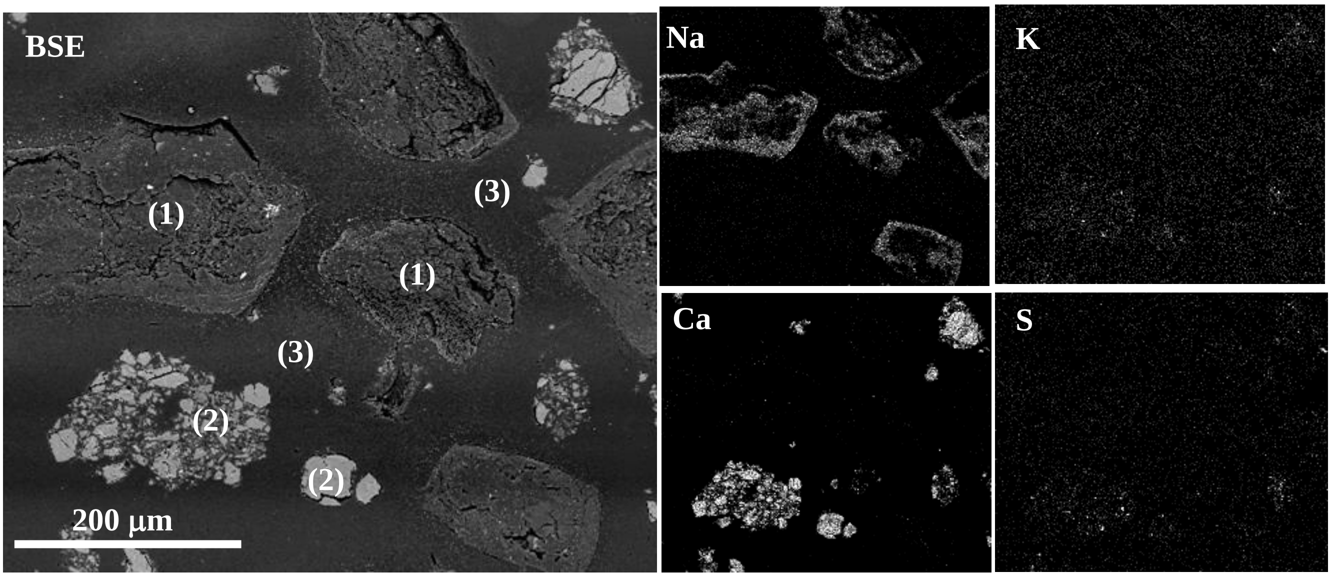


Fig. 14 Backscattered electron image (BSE) and energy dispersive X-ray (EDX) mapping showing the distribution of Na, K, Ca and S in a mixture containing dry SAP (1) and unreacted cement (2) encased in epoxy (3).

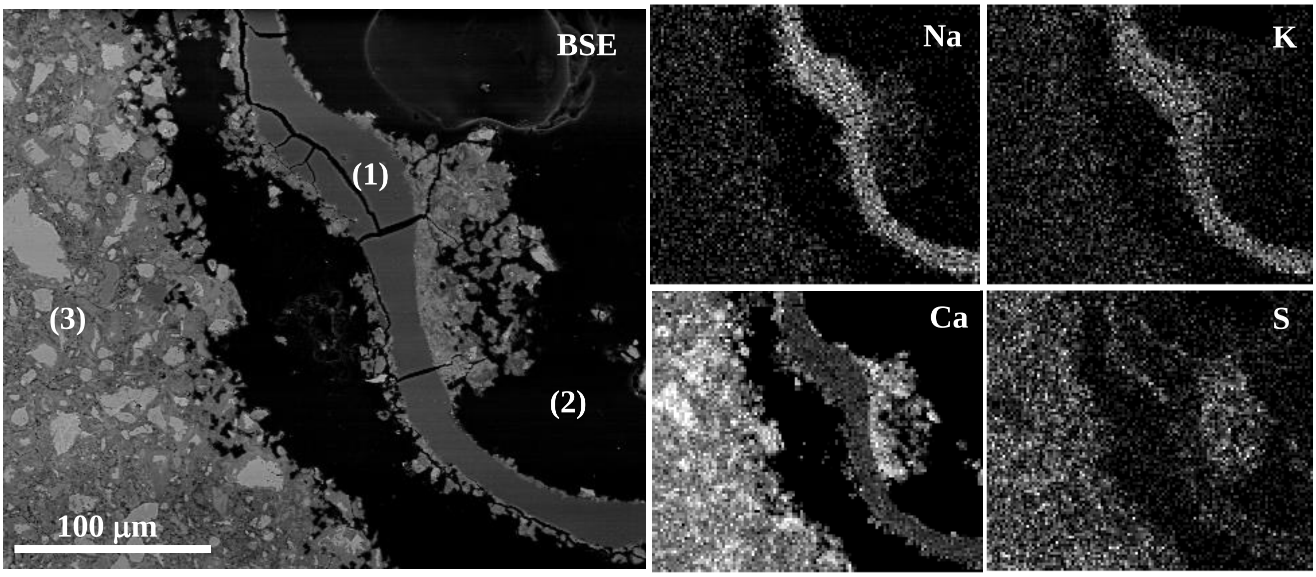


Fig. 15 Backscattered electron image (BSE) and energy dispersive X-ray (EDX) mapping showing the distribution of Na, K, Ca and S in cement paste containing SAP (S2-poly AA). The BSE image highlights the collapsed SAP (1), SAP void (2) and cement paste (3). Results show accumulation of Ca in the SAP due to ion exchange.

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