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Interactions between shrinkage reducing admixtures (SRA) and cement paste's pore solution

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Abstract

Shrinkage reducing admixtures (SRA) have been developed to combat shrinkage cracking in concrete elements. While SRA has been shown to have significant benefits in reducing the magnitude of drying and autogenous shrinkage, it has been reported that SRA may cause a negative side effect as it reduces the rate of cement hydration and strength development in concrete. To examine the influence of SRA on cement hydration, this study explores the interactions between SRA and cement paste's pore solution. It is described that SRA is mainly composed of amphiphilic (i.e., surfactant) molecules that when added to an aqueous solution, accumulate at the solution–air interface and can significantly reduce the interfacial tension. However, these surfactants can also self-aggregate in the bulk solution (i.e., micellation) and this may limit the surface tension reduction capacity of SRA. In synthetic pore solutions, SRA is observed to form an oil–water–surfactant emulsion that may or may not be stable. Specifically, at concentrations above a critical threshold, the mixture of SRA and pore fluid is unstable and can separate into two distinct phases (an SRA-rich phase and an SRA-dilute phase). Further, chemical analysis of extracted pore solutions shows that addition of SRA to the mixing water depresses the dissolution of alkalis in the pore fluid. This results in a pore fluid with lower alkalinity which causes a reduction in the rate of cement hydration. This may explain why concrete containing SRA shows a delayed setting and a slower strength development.

Keywords: Hydration (A); Retardation (A); Pore solution (B); Shrinkage (C); Admixture (D); Alkalis (D)

1. Introduction

Shrinkage cracking is a common source of distress in concrete structures. In addition to being unsightly, these cracks serve to accelerate other forms of damage in concrete (e.g., corrosion and freezing and thawing), thereby shortening the service life of structures. One solution to reduce the potential for shrinkage cracking is to incorporate a shrinkage reducing admixture (SRA) in concrete mixtures. SRAs belong to a special type of organic chemicals (i.e., surfactants) that when mixed in water, reduce the surface tension of the liquid. It is commonly understood that by reducing the surface tension of concrete's pore fluid, SRA significantly reduces the magnitude of capillary stresses and shrinkage strains that occur when concrete is losing moisture (i.e., through drying or self-desiccation) [1–8].

Research on shrinkage reducing admixtures was first initiated during the 1980's in Japan and led to the development of the first generation of SRA [1]. Today, several different SRAs are commercially available, and although they do not exactly have the same chemical composition, they are similar in nature and all serve to reduce the surface tension of concrete's pore fluid. During the past 25 years, various research studies [3–20] have been performed to evaluate the performance of SRAs and to quantify their shrinkage reduction capacity in concrete mixtures (for a comprehensive review of the available literature, see [17,21]). It has been shown that by lowering the surface tension of pore fluid, SRA can reduce drying shrinkage of concrete by up to 50% [5,6,8–10,12]. In addition, SRA was shown to reduce the capillary stresses that are generated by

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autogenous shrinkage in high performance low *w*/*c* concretes [7,14,15,18]. These attributes are extremely beneficial in reducing the risk of shrinkage cracking in concrete elements [22]. The addition of SRA was also shown to improve the resistance of concrete against plastic shrinkage cracking [23,24].

In contrast to the significant benefits of SRA in improving the shrinkage performance of concrete, some negative side effects have also been reported. Namely, it has been observed that SRA reduces the rate of cement hydration and strength development in concrete [17,25–29]. Comparing to control specimens with similar mixture proportions, concrete containing SRA exhibits a delay in setting [8,9,12,14,30] and a reduction in the early-age compressive and tensile strength for well-cured specimens [6,8,14,31] (for specimens with similar (water+SRA) to cement ratio, strength reduction can be as high as 25% at 1 day [6,9] but improves to less than 10% at 28 days [9,14]). In addition, it has been reported that inclusion of SRA may cause loss of entrained air which can negatively affect the resistance of concrete against freezing damage [32,33].

Although extensive research has been performed on measuring the shrinkage and mechanical properties of concrete containing SRA, very few studies have looked at the effect of SRA on hydration of cement and examining the sources of retardation in strength development [26,34]. The influence of SRA has been assumed to be limited to the reduction in pore fluid's surface tension. In addition, it has been commonly assumed that the ionic concentration of pore fluid has negligible effect on the performance of SRA (i.e., miscibility in pore fluid and surface tension reduction) and in fact, SRA has similar performance in pore fluid as it does in pure water [5,8,11,35,36].

The present study is aimed at evaluating three main hypotheses:

1. *Performance in pore fluid:* Shrinkage reducing admixtures are surfactants. Except at low concentrations, surfactants are known to aggregate (e.g., to form micelles) when dissolved in a liquid medium (this is discussed in details in Section 3). The formation of such aggregates is dependent on the properties and composition of the host liquid. As such, the performance of SRA in pore fluid could be different that the performance in pure water.
2. *Influence on pore solution composition:* Pore fluid contains various types of ions (mainly Na^+, K^+, Ca^{2+}, OH^-, and SO_4^{2-}). These ions have gradually dissolved from cement particles into the pore fluid. If the mixing water contains SRA, the surfactant nature of SRA can affect the dissolution affinity of ions. This could cause a reduction in the ion concentrations of pore fluid which can contribute to the retardation effect observed in concretes with SRA.
3. *SRA concentration versus degree of hydration:* As the water in pore fluid is consumed in hydration reactions, the concentration of SRA should increase with specimen age. Since the electrical conductivity of SRA is negligible comparing to the conductivity of pore fluid, conductivity measurement of extracted pore solutions could enable determination of the SRA concentration in pore solution as a function of age or degree of hydration.

2. Research significance

Shrinkage reducing admixtures are sufficiently soluble in water and can effectively reduce the surface tension of the liquid [5,8,11,12,36]. While it is readily assumed that SRAs have similar behavior in water and in concrete's pore fluid (an ionic aqueous solution), there is very limited experimental evidence on how SRA would interact with pore fluid. To ensure a desirable performance, in this study, the solubility and self-aggregation of SRA in synthetic pore solutions are investigated. Changes in the surface tension of the solution are monitored as a function of the SRA concentration. Also, the effect of SRA on the ions concentration of pore solution is investigated. The findings shed light on why SRA causes a retardation of hydration and strength development in concrete. In addition, the results can help in optimizing the dosage of SRA in concrete mixtures.

3. Background on the action of surfactants in aqueous solutions

Shrinkage reducing admixtures belong to a class of organic chemicals known as surfactants. At a molecular level, surfactants are amphiphilic; i.e., each surfactant molecule is composed of a hydrophilic (i.e., polar) head that is covalently bonded to a hydrophobic (i.e., non-polar) tail [37,38] (Fig. 1). The hydrophilic head can be ionic or non-ionic and is attracted by polar and hydrogen bonding solvents (such as water), and oppositely charged surfaces [39]. The hydrophobic tail is a non-polar hydrocarbon chain (e.g., alkyl chain) and is attracted by non-polar solvents (such as oil) but is repelled from polar molecules such as water [38].

In general, amphiphilic molecules are soluble in both polar and non-polar solvents. When dissolved in water, amphiphiles are attracted to non-polar interfaces (such as water–air or water–oil interfaces) as shown in Fig. 1 [38]. Adsorption of surfactant at interfaces causes a reduction in the interfacial energy; as such, addition of SRA leads to reduction in the surface tension of the water–air (i.e., liquid–vapor) interface. There is naturally a saturation limit for the number of surfactant molecules that can be adsorbed on an interface. This stems from the electrostatic repulsion between the polar heads of adjacent surfactant molecules [37]. Correspondingly, reduction in the surface tension of the water–air interface is limited and plateaus for high surfactant concentrations [11,36]. Excess surfactant molecules that cannot be adsorbed remain in the bulk water. At low concentrations, these molecules can be present as monomers dissolved in water (Fig. 1). However, at higher concentrations, amphiphiles tend to aggregate and form micelles in order to reduce the unfavorable contact between the hydrophobic tails and water molecules [38].

Spherical micelles (as shown in Fig. 1) are the common form of surfactant aggregation. Each micelle is few nanometers in diameter and is formed by aggregation of approximately 20 to 100 surfactant molecules [38,39]. In addition to spherical micelles, other forms of surfactant aggregation (such as elliptical and cylindrical micelles, bi-layers, and vesicles) are also

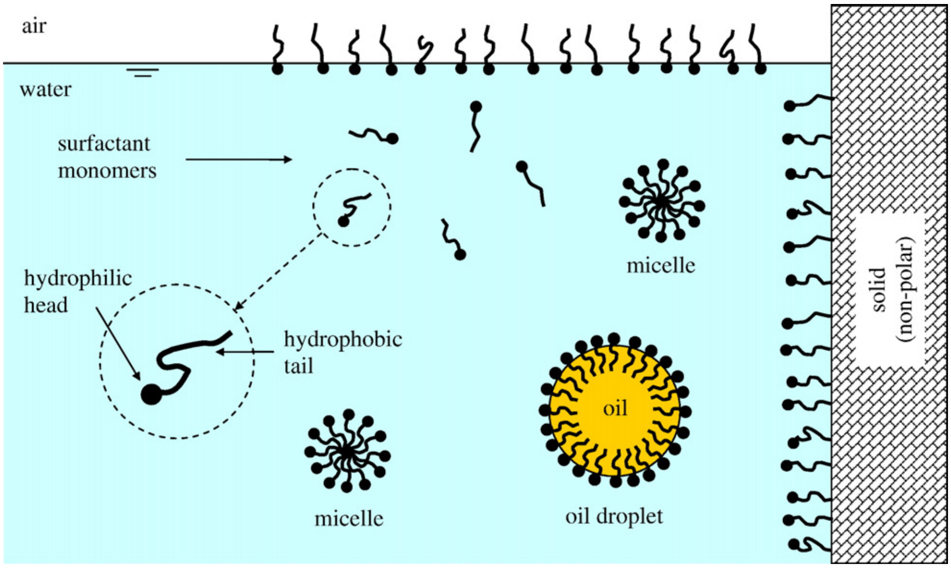

Fig. 1. Interactions of surfactant (amphiphilic) molecules with a polar solvent (e.g., water); adapted from [38].

possible [37,38] depending on the properties of surfactant molecules and the host liquid. The aggregation phenomenon is associated with a threshold surfactant concentration known as the critical micelle concentration (CMC) [40]. Below the CMC, surfactant molecules are mainly adsorbed on interfaces and as such, the surface tension is continuously reduced with increasing surfactant concentration [37]. Above the CMC, excess surfactant molecules form micelles in the bulk water and cannot serve to further reduce the surface tension [37].

In addition to surfactant molecules, the commercially available shrinkage reducing admixtures often contain oil impurities. Generally, oil is immiscible in water and a mixture of oil in water separates when kept at rest. In the presence of a surfactant, however, amphiphiles are adsorbed on the surface of oil droplets (Fig. 1). As two oil droplets approach one another, the electrostatic repulsion between the hydrophilic heads of the amphiphiles opposes the attractive van der Waals forces that otherwise would cause flocculation and coalescence of the droplets [37,39,40]. As such, an emulsion of oil in water forms which may or may not be stable.

If the repulsive force between amphiphiles is stronger than the attractive force between oil droplets, the emulsion would be stable; i.e., it would not separate into two distinct phases. Such emulsion contains millions of microscopic (10–40 nm diameter) oil droplets that are covered by surfactant molecules [37]. These "micro-emulsions" are transparent or translucent and macroscopically homogenous [38]. On the other hand, if the attractive force between oil droplets exceeds the repulsive force of surfactants, the droplets start to merge and form larger and larger particles. In other words, there are not sufficient surfactant molecules or electrostatic repulsion between the hydrophilic heads to secure the oil droplets and prevent their coalescence. Such "macro-emulsions" are unstable and eventually lead to complete separation of the emulsion into two distinct phases. As the oil droplets become large enough to scatter light (i.e., several μm in diameter), macro-emulsions appear cloudy (or milky) and are heterogeneous [37].

In addition to particulate (i.e., oil droplets) micro- and macro-emulsions discussed above, other forms of oil–water–surfactant mixtures are also possible. For examples, several types of bi-continuous structures could occur depending on the volume fractions and properties of the constituent phases [37–39]. Bi-continuous emulsions are stable and homogenous and form a molecular structure in which both the water and oil phases are percolated across the emulsion. The interface between oil and water is protected by the adsorbed surfactant molecules [38].

4. Materials and experiments

The shrinkage reducing admixture used in this study is Tetraguard® AS20 which is a commercially available product mainly composed of poly-oxyalkylene alkyl ether [12]. The results provided in this paper are based on the measurements performed on this product only; however, similar results were obtained from preliminary measurements on other commercial brands of SRA. The cement used in this study is a type I ordinary portland cement with Blaine fineness of 360 m^2/kg and a Bogue phase composition of 60% C_3S, 12% C_2S, 12% C_3A, 7% C_4AF and a Na_2O equivalent of 0.72%. As described in the following paragraphs, three groups of experiments were performed in this work corresponding to the three-fold research hypothesis discussed earlier. All experiments were performed at the laboratory temperature of 23 ± 1 °C.

First, the miscibility of SRA in deionized (DI) water and in a synthetic pore solution (0.35 M KOH + 0.05 M NaOH in DI water) was monitored. Several solutions were prepared containing different concentrations of SRA. Miscibility was monitored through observing the transparency and stability of each solution, as discussed in Section 5.1. Also, the surface tension

Table 1
Vicat time of setting for the four cement paste mixtures

Mixture number	(1)	(2)	(3)	(4)
Paste proportions	$w/c=0.30$	$w/c=0.30$	$w/c=0.30$	$w/c=0.30$
	Plain	5% SRA	Plain	5% SRA
Remixed after 18 min?	No	No	Yes	Yes
Initial set (h)	6.0	7.5	8.2	8.8
Final set (h)	7.0	9.0	10.6	10.8

of these solutions was measured using a du-Nouy tensiometer according to the procedure of ASTM D1331-89.

Second, to monitor the influence of SRA on cement hydration and composition of pore solution, four different cement paste mixtures were prepared (Table 1). Mixtures (1) and (3) are plain cement paste with $w/c=0.30$ while mixtures (2) and (4) are cement paste with $w/c=0.30+5\%$ SRA replacement of water. A high range water reducer (Glenium® 3000NS) was added to the mixing water for all mixtures at a rate of 0.5% by weight of cement. Mixing was performed according to ASTM C305-06. For mixtures (1) and (2), mixing was performed in one step with the SRA added directly to the mixing water. Mixtures (3) and (4) were mixed in two steps to simulate a delayed addition of SRA. Mixture (4) was initially mixed with all the mixing water (not containing SRA) following ASTM C305. The plastic paste was then kept at rest for 18 min inside the mixing bowl while the bowl was covered with nylon sheets to minimize water evaporation. After 18 min, the SRA (5%) was added to the paste and mixed for an additional 3 min at the medium speed. For mixture (3), a similar procedure was performed with 95% of water mixed initially, followed by 18 min rest, and then the remaining 5% of water was added and mixed for 3 min.

For each mixture, the time of setting was determined using Vicat needle according to ASTM C191-04b. Further, a series of cylindrical cement paste specimens (22 mm diameter and 50 mm height) were casted and seal cured inside cylindrical plastic vials. These specimens were demolded at specific ages and used for extraction of their pore solution. Pore fluid extraction was performed using pressure filtration [41] for plastic paste specimens (at 1, 3, and 6 h after water addition) or using a high pressure extraction die [42] for hardened specimens (at 10, 14, 19, 24, 33, and 48 h after water addition). The ionic composition of extracted pore solutions was measured using atomic absorption (for Na^+, K^+, Ca^{2+}), ion chromatography (for SO_4^{2-}), and acid titration (for OH^-). Details of such measurements are provided in [42].

Third, the concentration of SRA in extracted pore solutions was determined indirectly using electrical conductivity measurements. Conductivity of extracted pore solutions was measured using a conductivity meter connected to an impedance analyzer (Solartron 1260™). The measured conductivity was compared with the values predicted analytically based on the composition of pore fluid [43]. The SRA concentration in the pore fluid was back calculated from the ratio of the experimental to analytical values. This is discussed in Section 5.3.

5. Results and discussion

5.1. Miscibility of SRA and surface tension reduction

When SRA (which contains a mixture of surfactant and oil) is mixed in an aqueous liquid, an oil–water–surfactant emulsion is formed which may or may not be stable. Fig. 2 shows examples of such emulsions prepared by mixing 5%, 10%, and 20% SRA in deionized (DI) water or the synthetic pore solution (0.35 M KOH + 0.05 M NaOH in DI water). When mixed in DI water (Fig. 2(a)), at all three concentrations, SRA formed clear emulsions which were stable and macroscopically homogenous (at 10% SRA concentration, the emulsion was slightly less transparent). Stability was examined by monitoring the emulsions for a period of 60 days while they were kept at rest.

When SRA was mixed in the synthetic pore solution (Fig. 2(b)), at 5% and 20% concentrations, the resulting emulsions were stable, clear, and macroscopically homogenous. At 10% concentration, however, the solution was cloudy and when kept at rest, a complete phase separation occurred within 12 h in which an SRA-rich phase formed on the top of an SRA-dilute phase (Fig. 3). Electrical conductivity measurements described in Section 5.3 indicated that SRA concentration in the top phase is close to 50% while the bottom phase contained approximately 7.5% SRA.

Similar experiments on mixtures containing different concentrations of SRA reveal three types of miscibility of SRA in the synthetic pore solution. At low concentrations (<7.5%),

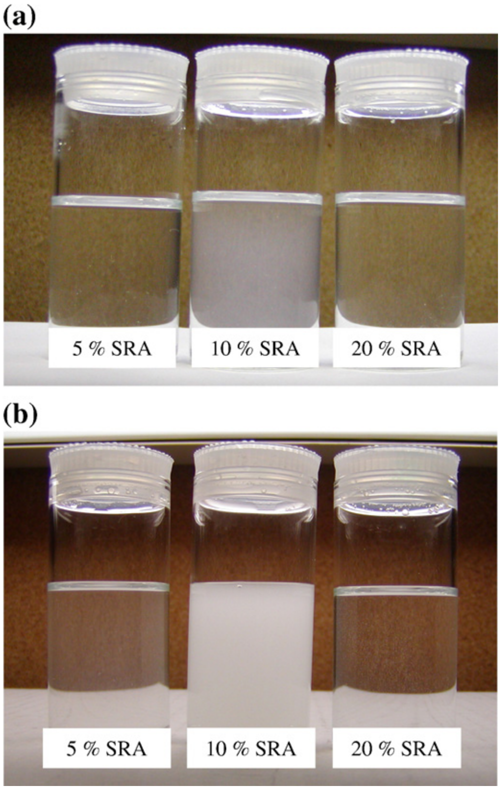

Fig. 2. Dissolution of SRA in (a) deionized water and (b) synthetic pore solution immediately after mixing.

Fig. 3. Separation of emulsion made by mixing 10% SRA in the synthetic pore solution; (left) immediately after mixing, (right) kept at rest for 12 h.

SRA forms a stable, transparent, and macroscopically homogenous micro-emulsion. Due to the low concentration of SRA, it is estimated that this micro-emulsion has a particulate structure in which microscopic oil droplets are dispersed in a continuous medium of aqueous phase and are protected by the adsorbed surfactant molecules. At medium SRA concentrations (~7.5% to 15%), an unstable macro-emulsion is formed. This instability may be caused by a reduced mean distance between individual oil droplets which increases the potential for flocculation and coalescence of the droplets. It is interesting to notice that this macro-emulsion separates into a stable micro-emulsion (formed at the bottom) with SRA concentration close to 7.5% and an SRA-rich phase (formed at the top) which contains excess SRA that was not miscible in the synthetic pore solution; Fig. 3. At higher concentrations of SRA (>15%), the resulting emulsion, again, becomes stable, transparent, and macroscopically homogenous. This may be caused by a shift in the microscopic structure of the emulsion from a particulate system to a bi-continuous structure.

Measurements of the surface tension of the emulsions of SRA in DI water and SRA in pore solution lead to the following observations. As shown in Fig. 4, the surface tension of the emulsions exhibits a bilinear trend as a function of SRA concentration (in log scale). At lower concentrations, a steep reduction in the surface tension is observed with addition of SRA. Beyond a critical threshold, however, further addition of SRA does not significantly reduce the surface tension. This critical threshold is conceptually similar to the critical micelle concentration (CMC) discussed earlier in Section 3 which corresponds to the saturation of the liquid–air interface. In addition, formation of oil droplets in the bulk liquid causes adsorption of surfactant molecules at the oil–water interface. Further addition of SRA causes formation of more oil droplets which compete with the air interface to adsorb surfactant molecules. Ultimately, beyond the critical concentration, addition of SRA does not result in a considerable increase in the concentration of adsorbed surfactants at the emulsion–air interface. This is possibly due to a combination of interface saturation and competition from the oil interfaces. As a result, further addition of SRA beyond the critical concentration cannot cause a further reduction in the surface tension.

Based on Fig. 4, the critical SRA concentration is approximately 11% when SRA is mixed in deionized water, and is approximately 7.5% when SRA is mixed in the synthetic pore solution. This means that the critical SRA concentration is reduced when ions are present in the solution. Obviously, the value 7.5% obtained here depends on the composition of the pore fluid and lower values of critical SRA concentration would be expected for pore solutions with higher ionic strengths. Meanwhile, it is interesting to note that the critical SRA concentration also corresponds to the borderline concentration between a stable micro-emulsion (SRA <7.5%) and an unstable macro-emulsion (SRA ~7.5% to 15%), as discussed earlier.

The experimental results discussed in this section have an important practical implication. It can be concluded that while addition of SRA to concrete at low dosages can have significant shrinkage reduction benefits, high SRA dosages (>7.5%) could be ineffective since beyond the critical SRA concentration, further reduction in the surface tension is marginal. Also, SRA concentrations beyond the critical threshold are not miscible in concrete's pore fluid and would separate soon after the mixing is completed. It should be noted that even for concrete that contains SRA in dosages smaller than the critical concentration (e.g., for concrete containing 5% SRA), the concentration of SRA in pore fluid can increase as a result of cement hydration or concrete exposure to drying. This is discussed in Section 5.3.

5.2. Hydration retardation and influence on pore solution composition

The results of Vicat time of setting for the four cement paste mixtures are reported in Table 1. By comparing the results for mixtures (1) and (2), it is observed that adding SRA to the mixing water resulted in a 2-hour delay in the time of final set. However, a delayed addition of SRA (mixture (4)) resulted in a much smaller delay in the final setting when compared to the plain mixture (3). An explanation is offered at the end of this section as to why a delayed SRA addition may remedy the retardation in cement hydration. Table 1 also shows that the remixed cement pastes (mixtures (3) and (4)) set later than the other two mixtures. This is potentially caused by the breaking of early hydration products during remixing which delays the

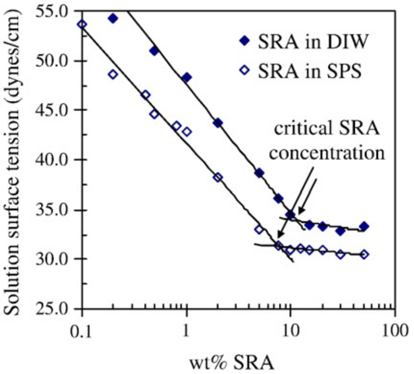

Fig. 4. Surface tension of emulsions of SRA in deionized water (DIW) and the synthetic pore solution (SPS).

setting. Nevertheless, the results presented in Table 1 could show the practical benefits of a delayed SRA addition. In practice, SRA is typically added at concrete plant during the initial mixing. The concrete is further mixed in truck mixers while being transported. Alternatively, SRA can be added to concrete only after the truck arrives at the job site and this could considerably reduce the retardation in setting and strength development.

Pore solutions were extracted from paste mixtures (1) and (2) to examine their chemical composition. Fig. 5 shows the molar concentrations of five major ions (Na^+, K^+, Ca^{2+}, OH^-, and SO_4^{2-}) as a function of specimen age. Previous research [41,44,45] provides a good understanding of the time-dependent concentration of different ions in cement paste's pore solution. The goal of the present work is not to study the time-dependent nature of ion concentrations; but to compare the composition of pore solutions for cement pastes with and without SRA. Meanwhile, a brief description of the sources of individual ions is provided.

Calcium (Ca^{2+}) ions originate from the dissolution of gypsum ($CaSO_4$) and free lime (CaO) and by the hydration of cement compounds (e.g., C_3S and C_3A) [44,46]. Due to the continuous release of Ca^{2+} from cement compounds and the availability of solid portlandite ($Ca(OH)_2$), calcium concentration always remains near (and in fact slightly above) the portlandite saturation point [45,46]. Potassium (K^+) and sodium (Na^+) ions originate mainly from dissolution of alkali sulfates (K_2SO_4 and Na_2SO_4) into pore solution [45,46]. Taylor [47] showed that the concentration of K^+ and Na^+ ions can be calculated with a reasonable accuracy from the alkali content (K_2O and Na_2O) of the cement powder. A significant portion of alkali sulfates dissolve in the pore fluid by the mixing action (i.e., during mixing of concrete) [44]. However, further dissolution can occur as concrete ages [41] and results in an increase in the concentration of K^+ and/or Na^+ ions as a function of age (as shown in Fig. 5(a)). In general, the concentrations of K^+ and Na^+ ions are governed by the amount of alkalis available in the cement and the kinetics (i.e., rate) of their dissolution in pore fluid. A very high solubility limit (≈ 1.4 mol/l for K^+ from K_2SO_4) [48] ensures that pore solution almost always remains under-saturated with respect to potassium (K^+) and sodium (Na^+) ions.

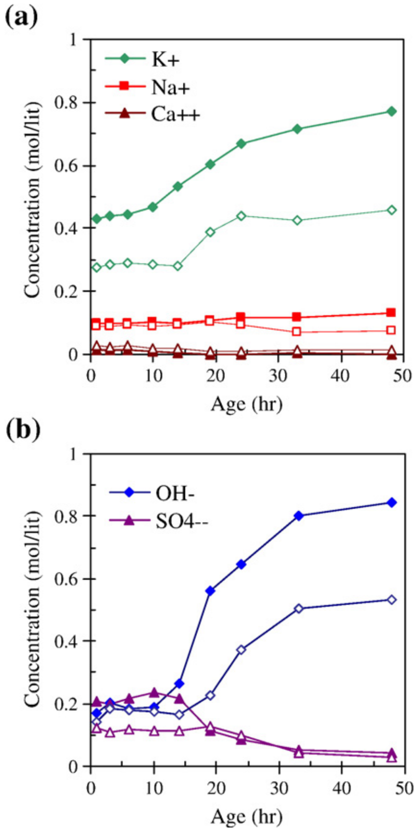

Fig. 5. Ion concentrations obtained from chemical analysis of extracted pore solutions: (a) cations, (b) anions. (solid points = plain paste (1); hollow points = paste with SRA (2)).

Sulfate (SO_4^{2-}) ions originate from the dissolution of gypsum and alkali sulfates. A considerable amount of sulfate ions dissolve in the pore fluid by the mixing action. As cement hydrates, sulfates in the solution are consumed by the hydration of aluminate phases (e.g., to form ettringite and monosulfate) [45]. As long as solid gypsum is available, the consumed sulfates are replaced by further dissolution of gypsum into pore fluid. As a result, the sulfate concentration remains relatively constant [41] (see the constant SO_4^{2-} concentration up to 14 h in Fig. 5(b)). Depletion of solid gypsum coincides with a gradual reduction in the SO_4^{2-} concentration. To remain electrically neutral, sulfates in the pore solution are replaced by hydroxyl (OH^-) ions released from solid phases (e.g., from C_3S or CH) [41,45,46]. As a result, the reduction in sulfate (SO_4^{2-}) concentration is simultaneous with an increase in the concentration of hydroxyl (OH^-) ions (Fig. 5(b)). Beyond 24 h, the pore fluid is essentially a solution of alkali hydroxide (i.e., KOH and NaOH) in water [41,45].

By comparing the ionic composition of pore solutions obtained from mixtures (1) and (2) an interesting observation can be made. It is noticeable in Fig. (5) that initially, the concentrations of K^+ and SO_4^{2-} ions are considerably higher in the pore solutions obtained from the plain cement paste (mixture (1)). Later during the hydration process, as the sulfates are replaced by hydroxyl ions, the plain cement paste shows a significantly higher OH^- concentration. To explain this observation, one hypothesis can be that addition of SRA (which is a mixture of surfactant and non-polar oil) reduces the polarity of mixing water. As such, the affinity of salts (e.g., K_2SO_4) to dissolve and ionize into this "less polar" solvent is reduced. To test this hypothesis, a series of experiments were performed to study the dissolution of potassium sulfate (K_2SO_4) in a solution containing SRA.

First, the solubility limit of K_2SO_4 in deionized (DI) water and a solution of [95% DI water + 5% SRA] was measured at 23 °C. The procedure was to add K_2SO_4 powder in 0.1 g steps to 10 g of solvent. The solubility limits were found as 120 g of K_2SO_4 per liter of DI water (i.e., 0.66 mol/l of solution) and 100 g of K_2SO_4 per liter of [95% DI + 5% SRA] (i.e., 0.55 mol/l of solution). As a result, the presence of SRA was observed to depress the solubility limit of potassium sulfate. Nevertheless,

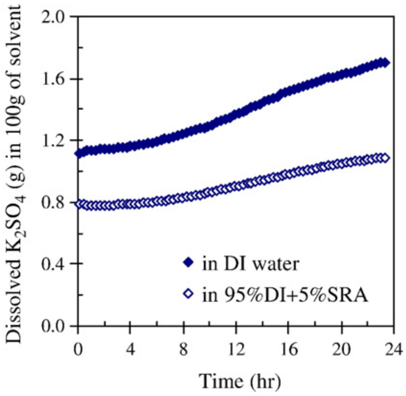

Fig. 6. Dissolution of K_2SO_4 powder in solvents with and without SRA.

the concentrations of K^+ and SO_4^{2-} ions in the cement pore solutions were considerably lower than the solubility limit of potassium sulfate (Fig. 5). As such, depression in the solubility limit of K_2SO_4 in the presence of SRA cannot by itself explain why the concentrations of ions are lower in the pore solution containing SRA.

To examine the rate of dissolution, 100 g of solvent (i.e., DI water or 95% DI+5% SRA) was added slowly to 4.57 g of K_2SO_4 powder in a plastic container. The number 4.57 g is equivalent to the total K_2SO_4 available per 100 g of water in the cement paste with $w/c=0.30$ (considering the K_2O content of the cement used here). The plastic container was equipped with stainless steel electrodes that facilitate the measurement of the electrical conductivity of the contained solution. These electrical conductivity measurements enabled determining the concentration of the dissolved K_2SO_4. The solvent was added slowly in order to dissolve only a portion of the K_2SO_4 powder while the remaining powder could dissolve gradually into the static solution as time passes.

Fig. 6 shows the results of this experiment. It is observed that inclusion of SRA reduces the amount of K_2SO_4 that dissolves initially into the solvent (1.12 g in DI water versus 0.79 g in 95% DI+5% SRA). Also, the rate of further dissolution as a function of time is lower for the solution containing SRA. This confirms the hypothesis that the presence of SRA reduces the affinity of K_2SO_4 to dissolve into the mixing water. Similar results were obtained regarding the solubility of Na_2SO_4 in the presence of SRA.

These observations can further shed light on the origins of the retardation effect exhibited by the concrete mixtures containing SRA. It has been reported by several researchers [41,45,46] that alkali sulfates are effective accelerators and a high concentration of alkali ions in the pore fluid leads to a considerable acceleration of cement hydration and strength development at early ages. Consequently, when SRA depresses the dissolution of alkalis, it results in a slower rate of hydration and strength gain and a delay in setting (Table 1). This also explains why a delayed addition of SRA can be beneficial in alleviating the retardation effect. When SRA is not present in the original mixing water, alkali sulfates can freely dissolve during the mixing action. As a result, a higher concentration of alkali ions is anticipated when SRA is added after the initial mixing rather than when it is added directly to the mixing water.

The findings of this study suggest that by reducing the dissolution of alkali ions, SRA can cause a reduction in the rate of hydration. This may not be the only cause of the observed retardation and other mechanisms such as admixture adsorption on cement particles or delaying bond formation among hydration products [49] may also contribute to the delayed setting. Further research is needed to evaluate the plausibility and contribution of different mechanisms.

5.3. Age dependent concentration of SRA in pore solution

The concentration of SRA in the extracted pore solutions can be approximated using electrical conductivity measurements. Fig. 7 shows the electrical conductivity of the pore solutions extracted from mixtures (1) and (2). In addition, solution conductivities were estimated based on the ion concentrations obtained from the chemical analysis of pore solutions (Fig. 5). For this purpose, a model developed by Snyder [43] was used that relates the electrical conductivity of an electrolyte to its ionic concentrations.

The estimated conductivities are shown as dash lines in Fig. 7. For the plain paste (mixture (1)), the estimated pore fluid conductivity is in good agreement with the experimental measurements. For the paste containing SRA (mixture (2)), however, the difference between the measured and estimated conductivities is notable. This difference stems from the fact that the model [43] estimates the conductivity solely based on the ion concentrations and does not account for the effect of non-conductive SRA present in the solution. The SRA used in this study has the electrical conductivity 5×10^{-4} S/m that is approximately four orders of magnitude lower than the conductivity of a typical pore solution. As a result, the ratio of the measured pore solution conductivity (σ_{meas}) to the estimated solution conductivity ($\sigma_{\text{est}-0\%\text{SRA}}$) can be used to approximate the concentration of SRA present in the pore solution.

For this purpose, a calibration graph was developed that shows the effect of SRA addition on the electrical conductivity of an aqueous electrolyte. A synthetic pore solution (0.35 KOH+0.05 NaOH molar concentrations) was used for

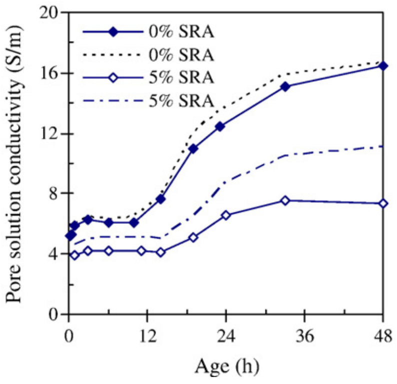

Fig. 7. The measured (solid lines with points) and estimated (dash lines) pore solution conductivity for mixture (1) (0% SRA) and mixture (2) (5% SRA).

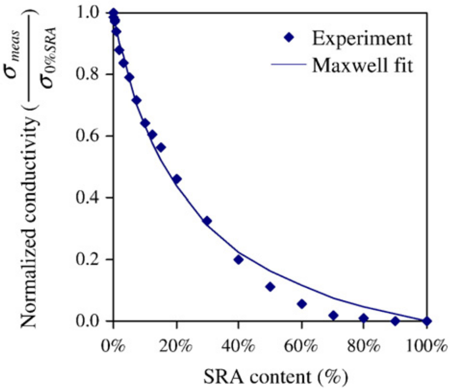

Fig. 8. Calibration curve for the measurement of SRA concentration in pore solution.

this experiment. The electrical conductivity of this solution was measured when specific amounts of SRA were added to the solution. Fig. 8 shows the results in terms of the measured electrical conductivity (σ_{meas}) normalized by the conductivity of the solution with 0% SRA ($\sigma_{0\%\text{SRA}}=6.72$ S/m). Further, a Maxwell expression (Eq. (1)) was fit to these data points:

$$\frac{\sigma_{\text{meas}}}{\sigma_{0\%\text{SRA}}}=\frac{(d-1)(100-\text{SRA\%})}{100(d-1)+\text{SRA\%}}. \tag{1}$$

This expression represents a composite model in which non-conducting particles are dispersed in a conducting medium [50]. In Eq. (1), SRA% is the weight percentage of SRA in the solution, and d (−) is intended to be the system's dimension (here, however, d was used as a fitting parameter). A value of $d=1.24$ was obtained for the best fit to the experimental data points.

Using the obtained calibration curve (Fig. 8 and Eq. (1)), the concentration of SRA in the extracted pore solutions can be approximated. SRA concentration was back calculated from Eq. (1) by knowing the experimentally measured pore solution conductivity (σ_{meas}) and the conductivity estimated from the model by neglecting the effect of SRA ($\sigma_{\text{est}-0\%\text{SRA}}$). The results are presented in Fig. 9 (solid data points). It is observed that SRA concentration increases with specimen age. As the water in pore fluid is consumed by hydration reactions, the concentration of SRA increases in the remaining pore solution. A similar phenomenon can occur in concrete exposed to drying. Since water is removed from pore fluid by evaporation, the concentration of SRA in the remaining pore fluid increases.

It is also shown in Fig. 9 that the estimated concentration of SRA at 1 h is 3.1% which is lower than the SRA concentration in the mixing water (5%). This disagreement could be initiated from the fact that some SRA is adsorbed to solid surfaces (e.g., cement particles or hydration products) and as such, the SRA concentration in the extracted pore fluid is smaller than the amount of SRA initially added.

In addition to the conductivity-based method described above, the concentration of SRA in the pore fluid can be estimated from the initial concentration in the mixing water (5%) and by knowing the volume of pore fluid at a particular age. Assuming that SRA is not taken up by hydration products and remains entirely in the pore fluid while the water is consumed in hydration reactions (this is not a totally valid assumption as some SRA are adsorbed to solid surfaces), the concentration of SRA can be approximated from the volume of evaporable water as a function of age. The volume of evaporable water can be measured directly or estimated using the Power's model [51] based on the degree of cement hydration. In this study, the degree of cement hydration was determined from the measurement of the chemical shrinkage of the cement pastes (details of these measurements are provided in [27]). Further, the degree of hydration was used to estimate the volume of evaporable water according to [52]:

$$\phi_{\text{evaporable}}=p-0.72(1-p)\alpha. \tag{2}$$

In Eq. (2), $\phi_{\text{evaporable}}$ (−) represents the volume fraction of evaporable water, α (−) is the degree of hydration, and $p=0.486$ is the initial porosity of the cement paste ($w/c=0.30$). The SRA concentration at each age can be approximated as:

$$\text{SRA\%}=5\%\left(p/\phi_{\text{evaporable}}\right). \tag{3}$$

These results are also shown in Fig. 9 (as hollow data points). It is not surprising that the two methods for estimating the SRA concentration in pore fluid do not yield identical results. This stems from the difference in the essential assumptions that were made in each method. The conductivity-based method assumes that the extracted pore fluid is identical to the pore fluid inside the cement paste. During extraction, pore fluid is exposed to new surfaces such as the extraction die and tubes as well as the conductivity meter. As such, during the extraction process, some SRA in the pore fluid may get adsorbed to these new surfaces. This indicates that the conductivity-based method may under-estimate the SRA concentration in the pore fluid by neglecting the SRA that is adsorbed during extraction (and as such removed from the pore fluid). Meanwhile, the method based on the evaporable water assumes that SRA in the cement paste is not adsorbed to the solid surfaces and remains entirely in the pore fluid. As such, this method can potentially over-estimate the amount of SRA present in the pore fluid.

Based on this discussion, it seems reasonable to assume that the actual concentration of SRA in the pore fluid lies between

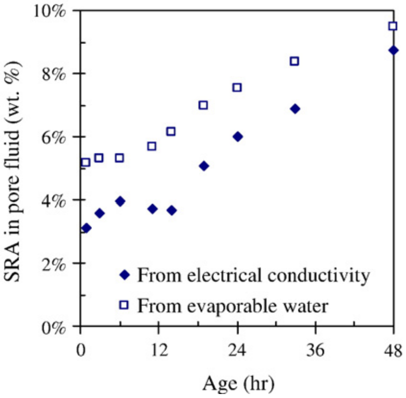

Fig. 9. Approximated concentration of SRA in the pore fluid as a function of age.

the upper and lower limits obtained from the two methods discussed above. Meanwhile, it is valuable to note that both methods indicate an increasing trend of SRA concentration as the cement paste ages and continues to hydrate.

6. Conclusions

Based on the information provided in this paper, the following conclusions can be drawn:

- The mixture of SRA and pore fluid forms an oil–water–surfactant emulsion which may or may not be stable depending on the concentration of SRA. At some intermediate concentrations (7.5% to 15% for the synthetic pore solution used in this study), the emulsion becomes unstable and separates into two distinct phases; an SRA-dilute phase which contains approximately 7.5% SRA and an SRA-rich phase which contains the excess SRA (i.e., in excess of 7.5%). Below 7.5% and above 15%, the emulsion is stable, clear, and macroscopically homogeneous.
- SRA reduces the surface tension of pore fluid when added up to a threshold concentration (e.g., 7.5% for the synthetic pore solution used herein). Beyond this critical threshold, further addition of SRA results in accumulation of surfactant molecules within the bulk solution rather than the solution–air interface. As such, beyond the critical threshold, further reduction in pore fluid's surface tension becomes marginal.
- The addition of SRA reduces the polarity of mixing water. This results in lowering the affinity of alkalis (e.g., K_2SO_4) to dissolve and ionize in the mixing water. Consequently, the resulting pore fluid contains a smaller concentration of alkali ions compared to the pore fluid of a plain cement paste. The reduced alkalinity of the pore fluid has a direct impact on the rate of cement hydration and can contribute to retardation in hydration and strength development of concrete containing SRA.
- A delayed addition of SRA (e.g., addition of SRA to concrete at job site instead of addition during the initial mixing at concrete plant) can be beneficial in alleviating the hydration retardation. The absence of SRA in the original mixing water promotes the dissolution of alkalis. As a result, a higher alkali concentration may be achieved when SRA is added after the initial mixing.
- SRA concentration in the pore fluid increases as hydration progresses. This stems from the fact that water is consumed in the hydration process while SRA is not taken up by the hydration products (at least not at the same rate as water). As such, the concentration of SRA increases in the remained pore fluid. A similar phenomenon can occur when concrete is exposed to drying as water is removed by evaporation while SRA remains in the pore fluid.

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