Scientific paper

Effects of Retarding Admixture, Superplasticizer and Supplementary Cementitious Material on the Rheology and Mechanical Properties of High Strength Calcium Sulfoaluminate Cement Paste

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Abstract

In this paper, the effects of retarding admixture, polycarboxylate (PCE) superplasticizer and supplementary cementitious material (SCM) on the rheology of high strength calcium sulfoaluminate (CSA) cement paste are investigated. At the water to binder ratio of 0.3, one PCE, two retarding admixtures, and three SCMs were used in the test. The test results show that much more PCE is needed for paste with citric acid than that with sodium borate to achieve a similar initial flowability. The reference paste and pastes mixed with sodium borate or fly ash exhibit shear thickening; pastes mixed with citric acid or silica fume exhibit shear thinning. The addition of citric acid increases the maximum shear stress of pastes, while the maximum shear stress can be significantly reduced by silica fume. Both the retarding admixtures and SCMs will strongly reduce the early-age compressive strength of the cement paste. At 28 days of age, CSA cement paste incorporating retarding admixtures has comparable strength to the reference paste. Silica fume has less negative effect on the compressive strength of the CSA cement paste due to the significant filling effect.

1. Introduction

The brittle nature of concrete upon tensile loading is one of the adverse properties of concrete represented by tensile-softening. Therefore, in concrete structures, when the stress exceeds the cracking strength of concrete, a single crack forms and the crack width quickly achieves a macro visible level to dissipate the large deformation from both mechanical and environmental loads. Cracks in concrete structures allow water and other chemical agents, such as deicing salt, to penetrate the cover layer and contact steel reinforcement, leading to corrosion of the reinforcement. Shrinkage and thermal deformation of concrete under service environments should be the major mechanisms leading to the initial cracking of concrete structures. Concrete shrinks as moisture is lost to the environment or by self-desiccation. As concrete shrinks, a certain amount of tensile stress will develop in its structure due to restraints from adjacent materials or connected members. Therefore, concrete shrinkage reduction has been a hot topic in either the research and in industrial communities.

Several studies have revealed that concrete made with calcium sulfoaluminate (CSA) cement displays relatively low shrinkage, especially drying shrinkage, compared to ordinary Portland cement (OPC) concrete (Luosun et al. 2012; Zhang et al. 2009, 2015, 2017). This interesting result encourages us to attempt to design a crack-free concrete structure with CSA cement. In addition, CSA cement with calcium sulfoaluminate as the main mineral has low CO\textsubscript{2} emission and low firing temperature during production compared to Portland cement (Winnefeld and Lothenbach 2010). Therefore, CSA cement may be selected as one of the most promising low CO\textsubscript{2} alternatives to OPC in view of sustainable development for modern concrete (Fu et al. 2003; Gartner 2004; Glasser and Zhang 2001; Péra and Ambroise 2004; Quillin 2001). However, CSA cement sets rapidly, so the CSA cement concrete is currently used only for relatively small-scale repairs. Relatively little is known about the mixture design that links the selection of material proportioning with the desired fresh and hardened properties, such as the retarder dosage and development of strength and elastic modulus of the concrete. Currently, citric acid and sodium borate are both primary set retarding agents recommended for use in CSA cement concrete (Burris et al. 2018; Champenois et al. 2015).

For relatively large placements of CSA cement concrete, the efficiency of retarding the CSA cement reaction with water for different retarding admixtures should be the first issue to be studied. Second, for modern concrete, superplasticizer has already become the main constituent of concrete to allow sufficient flow ability making the concrete self-consolidating or self-compacting during construction. The effect of retarding agent on the amount of polycarboxylate (PCE) superplasticizer required should be investigated to optimize the mixture proportion of CSA cement concrete considering cost. Third, in modern concrete, supplementary cementing materials (SCMs), such as silica fume (SF), fly ash (FA) and steel slag (SG), have become necessary constituents to make...
the concrete green and sustainable. The effects of SCMs on fresh and hardened CSA cement concrete also lack detailed studies. Furthermore, retarding admixture, superplasticizer and SCMs are normally used together in concrete. Currently, little is known regarding the combination effects of retarding admixture, superplasticizer and SCMs on the rheology and mechanical properties of CSA cement concrete.

The purpose of this paper is to investigate the effects of retarding admixture, superplasticizer and SCM on the rheology and mechanical properties of high-strength CSA cement paste, which in turn improves the mixture design method for high-strength CSA cement concrete for large amount applications. High strength cement matrix was investigated is because the shrinkage-induced cracking may be more pronounced for high-strength concrete than that for low or medium strength concrete (Zhang et al. 2015). High strength concrete refers to concrete with a compressive strength of more than 60 MPa at 28 days curing, and its water to binder ratio is generally approximately 0.3. Therefore, water to binder ratio of 0.3 was used for all mixtures in this study. Two retarding admixtures and three SCMs were used in the test. PCE superplasticizer was used to give all the mixtures similar flow ability after mixing. The rheological properties of fresh cement paste, including shear stress and viscosity, and initial and final setting time, as well as compressive strength at different ages after casting were measured. The results may contribute to the design of CSA cement concrete that may satisfy casting and setting requirements during construction.

### 2. Experimental program

#### 2.1 Materials

The main mineral composition of 4CaO·3Al₂O₃·SO₃ (38.34%), 2CaO·SiO₂ (31.33%), CaSO₄ (13.25%), and 12CaO·7Al₂O₃ (0.86%) of commercial CSA cement was used. All cement pastes were prepared with water to cementitious binder ratio by mass of 0.3. Two kinds of retarding admixtures normally used for CSA cement, sodium borate (SB) and citric acid (CA), were used to investigate their effect on cement paste setting performance. Three kinds of SCMs were employed in the experiments: Tangshan I grade fly ash, Tangshan ground granulated blast furnace slag, S95 grade and silica fume with 95% silicon content (Beijing Bond Printing Co., Ltd.). The chemical compositions and physical properties of the CSA cement and the three SCMs (SF, FA, and SG) used in the tests are listed in Table 1. A polycarboxylate (PCE) based water reducer (powder agent) with 35% water reduction rate was used in the mixtures to guarantee that all fresh cement paste has similar initial flow-spreading after mixing.

#### 2.2 Mix proportions

In the test programs, three series of tests were conducted. The purpose of the first series of tests (Series I) was to study the effect of sodium borate on the rheological properties of fresh cement paste. In this series, seven mixtures were prepared by adding sodium borate at 0, 0.1%, 0.2%, 0.3%, 0.4%, 0.5% and 0.6% of the cementitious binder weight (Nos. 0 to 6).

In the second test series (Series II), the effect of citric acid on the rheological properties of fresh cement paste was investigated. A total of eight mixtures with citric acid additions of 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, and two additional mixtures with mixed use of 0.3% sodium borate and 0.3% citric acid, and 0.3% sodium borate and 0.6% citric acid, were conducted (Nos. 7 to 14).

In the third series (Series III), the effects of SCMs, silica fume, fly ash and grounded granulated blast furnace slag on the rheological properties of fresh cement paste were investigated. In this series of tests, six mixtures were designed with 10% silica fume addition to the weight of cement, 10% fly ash addition, and two mixtures with mixed silica fume and fly ash, each at 10% of the cement weight, and mixed use of silica fume, fly ash and grounded granulated blast furnace slag, 10% of the cement weight of each (Nos. 15 to 18). In the above mixtures, no retarding admixture was used. To study the mixed effect of SCM and retarding admixture, two additional mixtures were designed with 10% fly ash and 0.6% citric acid addition, and 10% silica fume, 10% fly ash, 10% furnace slag and 0.6% citric acid (Nos. 19 and 20). Detailed mix proportions of each test series are listed in Table 2.

#### 2.3 Test measurements

The fluidity of the cement paste was measured by a small slump cone with a top diameter of 36 mm, bottom diameter of 60 mm and height of 60 mm. Preparation of fresh paste can be described as following. First, water and superplasticizer were added into the mixer, and then cementitious materials and other admixtures were

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**Table 1 Chemical composition and physical properties of the cementitious materials used in the tests.**

| No. | Chemical composition (wt%) | Apparent density, (g/cm³) | Specific surface area, (m²/kg) |
|-----|---------------------------|---------------------------|------------------------------|
| CSA | SiO₂ | CaO | Al₂O₃ | Fe₂O₃ | MgO | K₂O | Na₂O | SO₃ | LOI |          |          |
|     | 6.19 | 42.9 | 24.16 | 1.04 | 1.96 | 0.48 | 0.08 | 12.91 | 8.91 | 2.82 | 423      |
| Silica fume (SF) | 90.56 | 0.81 | 0.41 | 0.52 | 0.95 | 1.59 | 0.63 | -     | 3.72 | 2.11 | 20000     |
| Fly ash (FA) | 47.02 | 5.08 | 35.06 | 3.88 | 1.36 | 1.30 | 1.18 | 0.89 | 1.85 | 2.30 | 540      |
| Slag (SG) | 38.83 | 38.70 | 12.92 | 1.46 | 4.63 | 0.37 | 0.28 | 0.60 | 0.06 | 2.78 | 550      |

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gradually introduced over a time span of 90 seconds into the mixer at 62 rpm. After 15 seconds interval, mixing was resumed for an additional 75 seconds at 125 rpm. Subsequently, freshly mixed paste was subject to the initial fluidity test. The paste was poured into the cone right away and then the cone was quickly lifted up. As the flowing of the paste was stopped, the average value of the two spread diameters perpendicularly crossing the flowed cement paste was recorded as the fluidity of the paste. For the fluidity over time, the paste was added into the mixer and mix for 30 seconds at 125 rpm at the time required, and then the fluidity test was performed again.

The initial and final setting times of the cement paste were measured according to the Chinese standard on the method of testing cements for strength (China GB/T 17671-1999), and the compressive strength test specimens of the cement paste were prepared and cured according to the same standard. The compressive strengths at 1, 3 and 28 days after casting were measured.

A viscometer (Brookfield RV-III, USA) was utilized to evaluate the rheological properties of fresh cement paste. First, water, cementitious materials and admixtures were mixed under fast shear speed for 120 seconds. Then, the shear rate was increased from 1 s\(^{-1}\) to 300 s\(^{-1}\) within 60 seconds. After that, measurements were continued under constant shear rate of 300 s\(^{-1}\). All above tests were conducted in a room with constant temperature of 25°C. A flow chart showing the tests and measurements is displayed in Fig. 1.

### 3. Experimental results and discussion

#### 3.1 Effect of retarding admixture

The test results, including the initial spread diameter measured with the small cone test, and the spread diameter after mixing 1, 2 and 3 hours, as well as the initial and final setting time of each mixture are listed in Table 2. Figure 2 displays the diagram of initial and final setting time and the retarding admixture dosage used in pure cement paste. Figure 3 presents a diagram between the dosage of superplasticizer and dosage of retarding admixtures used in the paste in which superplasticizer was used to maintain a similar initial paste spread diameter.

From Fig. 2, it can be seen that the setting time of cement paste increases with increasing dosage of retarding admixture. As sodium borate is used, the setting time gradually increases with the increase in the dosage. For example, the initial setting time is 30, 45, 60 and 120 minutes for 0, 0.2%, 0.4% and 0.6% of the retarding admixture dosage, respectively. Meanwhile, from Fig. 3,
it can be seen the required amount of superplasticizer to achieve a spread diameter of 200 to 250 mm is gradually reduced with increasing sodium borate. The amount of superplasticizer used in the paste is 0.20%, 0.15%, 0.11% and 0.07% of the weight of cement for sodium borate dosages of 0, 0.2%, 0.4% and 0.6%, respectively. Again from Fig. 2, when citric acid is used as the retarding agent, setting time first increases gradually with an increase in retarding admixture as the dosage is less than 0.2%. After that, the setting time increases significantly with an increase in retarding admixture. For instance, the initial cement paste setting time is 30, 110, 460 and 810 minutes for retarding admixture dosages of 0, 0.2%, 0.4% and 0.6%, respectively. It seems that the retarding efficiency of citric acid is much higher than that of sodium borate, especially as the dosage exceeds 0.2%. However, from Fig. 3 again, it can clearly be observed that as citric acid is used, much more superplasticizer is needed to achieve the required flowability of the fresh cement paste compared to that of sodium borate used. The amount of superplasticizer is 0.20%, 0.30%, 0.65% and 1.60% of the weight of cement used in the paste for citric acid dosages of 0, 0.2%, 0.4% and 0.6%, respectively. This interesting finding indicates that the use of citric acid in CSA cement concrete may lead to needing a high amount of superplasticizer to reach high flowability. By contrast, if the retarding time is sufficient using sodium borate as the retarding admixture, the amount of superplasticizer to reach high flowability of concrete should be greatly reduced. With mixed use of sodium borate and citric acid in the paste, such as 0.3% sodium borate and 0.3% citric acid (No. 17), or 0.3% sodium borate and 0.6% citric acid (No. 18), the initial setting time becomes 180 and 690 minutes, respectively, which is shorter than when citric acid is used alone with the same amount (260 and 810 minutes for 0.3% and 0.6%, respectively). However, the amount of superplasticizer becomes 0.35% and 0.9%, respectively, which is approximately 87% and 56% of the amount if citric acid is used alone.

Figures 4 and 5 display the rheological properties of cement paste with different dosages of retarding admixture, including shear stress versus mixing time and viscosity versus mixing time diagrams, with Figs. 4(a) and 5(a) showing the overall results while Figs. 4(b) and 5(b) present the results during the initial short mixing period. From Fig. 4, first, the variation of shear resistant stress with mixing time is shown in Fig. 4(a) and Fig. 4(b) presents the results during the initial short mixing period.
mixing time of fresh cement paste can be seen experiencing the following three stages. At the beginning of mixing, shear stress increases with mixing time. Roughly at 60 seconds after mixing, peak shear stress is achieved. After that, shear stress starts to decrease with increasing mixing time, which may be called progressing stage (Stage II). After passing the lowest shear stress, it starts to increase again with mixing time until the paste sets (Stage III).

Second, the above variation of shear resistance versus mixing time is greatly influenced by the addition of retarding agent and by the type of retarding admixture. The addition of citric acid increases the initial peak shear stress (the maximum shear stress), whereas the peak shear stress is almost not affected by the addition of sodium borate. The length of the second stage significantly increases when using retarding admixture in the paste, although even more time is needed to achieve the lowest shear stress if citric acid is used than for mixtures with sodium borate. This result is well coincident with the test results of the initial and final setting time.

Here, it may be valuable to note that as citric acid is used, the cement paste viscosity at the beginning of mixing is much higher than the reference mixture and mixtures with sodium borate, exceeding 5 Pa·s. This means that the use of citric acid may increase the mixing load in the initial period. Stronger mixer may be needed for mixtures with citric acid.

With mixed use of sodium borate and citric acid in the paste, such as 0.3% sodium borate and 0.3% citric acid (No. 17), or 0.3% sodium borate and 0.6% citric acid (No. 18), the relationship between shear stress or viscosity versus paste mixing time is likely controlled by adding citric acid. A similar variation trend in the progress of shear stress and viscosity is observed between the use of citric acid and the mixed use of citric acid and sodium borate. By contrast, paste with sodium borate only shows similar rheological properties to the reference mixture without any retarding admixture, as shown in Figs. 4 and 5. In general, an increase in viscosity with increasing shear rate is called shear-thickening, and a decrease in viscosity with increasing shear rate is called shear-thinning. It can be seen from Figs. 4 to 7 that as long as the CSA cement pastes incorporating citric acid exhibit shear-thinning, the reference paste and pastes incorporating borax exhibit shear-thickening. The shear-thickening behavior, especially in the case of a low water to cement ratio, may greatly influence the casting quality of concrete structures (Yahia 2011).

The spread diameters after mixing 1, 2 and 3 hours shown in Table 2 indicate that if citric acid is used as a retarding agent, the flowability of the fresh paste can last for 3 hours after mixing with little lost workability when the dosage is higher than 0.3%. However, when sodium

Fig. 5 Viscosity versus mixing time diagram of fresh cement paste with different type and dosage of retarding agent.

Fig. 6 Shear stress versus mixing time diagram of fresh cement paste with mixed use of retarding agent.
Sodium borate is used, the spread diameter becomes 140 mm after 1 hour from the initial value of 250 mm even with a dosage of 0.6% of the weight of cement. In addition, it also is noted that as the amount of citric acid used in the paste reaches 0.3% or more, spread diameter of the paste at 1 and 2 hours becomes greater than that of the initial value. It should be due to competitive adsorption between citric acid and polycarboxylate water reducer. The compressive strengths at 1, 3 and 28 days of cement paste with different retarding admixture dosages in Series I and II are listed in Table 3. As expected, the longer the setting time is, the lower the early-age strength of the paste. For example, paste strength at 1 day is decreased with increase in the dosage of the retarding admixture. As sodium borate is used alone, the compressive strength at 1 day after casting is 68.2, 63.5, 60.7 and 58.4 MPa for 0, 0.2%, 0.4% and 0.6% of the retarding admixture dosage, respectively. As citric acid is used, the compressive strength at 1 day after casting is 68.2, 63.5, 60.7 and 58.4 MPa for 0, 0.2%, 0.4% (460) and 0.6% (810) of the retarding admixture dosage, respectively. At 28 days, all the mixtures using only sodium borate or citric acid and mixed use of them have comparable strength to the reference paste. For instance, as sodium borate is used alone, paste strengths at 28 days become 86.4, 89.6, 93.4 and 91.7 MPa for 0, 0.2%, 0.4% and 0.6% of the retarding admixture dosage, respectively. As citric acid is used, the compressive strengths at 28 day after casting are 86.4, 88.2, 87.0 and 90.2 MPa for 0, 0.2%, 0.4% and 0.6% of the retarding admixture dosage, respectively. For mixed use of retarding admixture, such as mixture Nos.13 and 14, the compressive strengths at 1 and 28 days are 53.9 and 88.7 MPa, 5.7 and 86.4 MPa respectively, with the corresponding initial setting time being 180 and 690 minutes. The above results are consistent with previous research results (Burris and Kurtis 2018), where CSA cement pastes,

| Series | No. | 1 day (MPa) | 3 days (MPa) | 28 days (MPa) |
|--------|-----|-------------|--------------|--------------|
| I      | 0   | 68.2        | 74.3         | 86.4         |
|        | 1   | 67.4        | 73.4         | 87.3         |
|        | 2   | 63.5        | 77.5         | 89.6         |
|        | 3   | 60.7        | 82.8         | 90.1         |
|        | 4   | 63.5        | 69.8         | 93.4         |
|        | 5   | 58.4        | 67.5         | 95.1         |
|        | 6   | 52.0        | 71.2         | 91.7         |
|        | 7   | 59.6        | 77.0         | 87.0         |
|        | 8   | 54.7        | 69.1         | 88.2         |
|        | 9   | 50.7        | 61.3         | 87.8         |
|        | 10  | 47.2        | 56.1         | 87.0         |
|        | 11  | 49.7        | 62.3         | 87.2         |
|        | 12  | 5.7         | 43.6         | 90.2         |
|        | 13  | 5.9         | 63.7         | 88.7         |
|        | 14  | 6.5         | 55.8         | 88.8         |
|        | 15  | 52.4        | 68.6         | 83.4         |
|        | 16  | 45          | 57.3         | 72.5         |
|        | 17  | 39.9        | 48.5         | 72.0         |
|        | 18  | 35.1        | 42.5         | 70.5         |
|        | 19  | 4.5         | 40.1         | 85.0         |
|        | 20  | 1.2         | 25.9         | 72.8         |
| II     | 6   | 52.0        | 71.2         | 91.7         |
|        | 7   | 59.6        | 77.0         | 87.0         |
|        | 8   | 54.7        | 69.1         | 88.2         |
|        | 9   | 50.7        | 61.3         | 87.8         |
|        | 10  | 47.2        | 56.1         | 87.0         |
|        | 11  | 49.7        | 62.3         | 87.2         |
|        | 12  | 5.7         | 43.6         | 90.2         |
|        | 13  | 5.9         | 63.7         | 88.7         |
|        | 14  | 6.5         | 55.8         | 88.8         |
|        | 15  | 52.4        | 68.6         | 83.4         |
|        | 16  | 45          | 57.3         | 72.5         |
|        | 17  | 39.9        | 48.5         | 72.0         |
|        | 18  | 35.1        | 42.5         | 70.5         |
|        | 19  | 4.5         | 40.1         | 85.0         |
|        | 20  | 1.2         | 25.9         | 72.8         |
| III    | 13  | 53.9        | 63.7         | 88.7         |
|        | 14  | 5.7         | 43.6         | 90.2         |
|        | 15  | 5.9         | 63.7         | 88.7         |
|        | 16  | 6.5         | 55.8         | 88.8         |
|        | 17  | 52.4        | 68.6         | 83.4         |
|        | 18  | 45          | 57.3         | 72.5         |
|        | 19  | 39.9        | 48.5         | 72.0         |
|        | 20  | 35.1        | 42.5         | 70.5         |
|        | 21  | 4.5         | 40.1         | 85.0         |
|        | 22  | 1.2         | 25.9         | 72.8         |

![Fig. 7 Viscosity versus mixing time diagram of fresh cement paste with mixed use of retarding agent.](image-url)
especially those with greater retarder dosages, appear to show a regression in strength over time.

3.2 Effect of supplementary cementitious materials

Figures 8 and 9 display the variation of shear stress and viscosity for cement paste vs. paste mixing time with the addition of different supplementary cementitious materials, including fly ash (FA), silica fume (SF) and furnace slag (SG), with Figs. 8(a) and 9(a) displaying the overall results while Figs. 8(b) and 9(b) presenting the results of the initial short mixing period. From Fig. 8, first, a similar variation trend can be observed for shear stress between pure cement paste and the paste with 10% addition of fly ash. The shear stress first increases with mixing time, and then it starts to decrease after achieving a peak shear stress of 650 to 700 Pa. After reaching a minimum shear stress of approximately 300 to 400 Pa, it begins to increase again with mixing time. By adding silica fume in the paste (also 10% by weight of cement), the mode of shear stress with mixing time is obviously changed compared to the reference mixture. The maximum shear stress is reduced to 300 Pa.

Meanwhile, a similar trend is observed in the pastes with combined use of silica fume and fly ash, and silica fume and fly ash and slag. This reduction of the initial shear resistant stress of fresh cement paste may help improve concrete mixing quality. From Fig. 9, it can be seen that the addition of silica fume can increase the initial viscosity of cement paste and make the fresh paste exhibit shear-thinning, which is similar to the action of citric acid. The addition of silica fume in the paste is also responsible for the results of the two-component (SF+FA) and three-component additions (SF+FA+SA) in the paste. Regarding the effect of SCM on the cement paste strength, as expected, compressive strength, especially in early age, decreases after using SCM in the mixture under water to binder ratio of 0.3 (see Table 3).

3.3 Mechanism analyses

Regarding the retarding mechanism of sodium borate on the hydration of CSA cement, most researchers conclude that borate can be precipitated with calcium ion and adsorbed onto cement grains to form a calcium borate layer on the surface of cement particles (Péra and Ambroise 2004; Tan et al. 2017). This adsorption reduces the concentration of calcium ions in pore water and then reduces ettringite formation and the cement hydration rate. On the other hand, the formation of a calcium borate layer also helps separate cement particles from each other. Therefore, borate may also play the role of superplasticizer in the paste, which is the reason why the amount of

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![Fig. 8 Shear stress versus mixing time diagram of fresh cement paste with different supplementary cementitious material.](image1.png)

![Fig. 9 Viscosity versus mixing time diagram of fresh cement paste with different supplementary cementitious material.](image2.png)
superplasticizer required to achieve a certain flowability is slightly reduced when borate is used. In addition, competitive adsorption between calcium-based borate and PCE superplasticizer may take place, and that may be the reason as well that the amount of superplasticizer is reduced when borate is used in the paste.

Existing research reveals that citric acid retards cement hydration not by complex formation but by slowing down the dissolution of clinker grains, which are actually similar to the action of sodium borate (Burris and Kurtis 2018). However, compared with sodium borate, citric acid more effectively retards the hydration of CSA cement. Meanwhile, the reaction between citric acid and PCE superplasticizer is likely different from that between sodium borate and PCE superplasticizer. Much more superplasticizer is needed to obtain cement paste of comparable initial flowability with citric acid used than that with sodium borate used. In addition, studies have shown that increasing the amount of superplasticizer retards CSA cement, and especially when the amount of gypsum is insufficient, the retardation is more obvious (Winnefeld 2012). Under the combined action of PCE, the paste setting time can be extended up to three times longer by adding citric than by adding sodium borate.

The initial shear stress and viscosity are obviously higher for the paste with citric acid than for the one with sodium borate. This difference may be fairly explained by the molecular structure of sodium borate and citric acid, presented in Fig. 10. There are three strong polar carboxyls in citric acid that may be attracted to single or multiple cement grains. The case of a three polar carboxyl attracted to a single cement particle is similar to adsorption of sodium borate on cement: it reduces the concentration of calcium ions in pore water and then reduces ettringite formation and the cement hydration rate. In the case of three polar carboxyl attracted to multiple cement particles, the moving ability of the cement particles should be restrained by the above attraction, which significantly increases the initial peak shear stress of the fresh cement paste compared with the referencing mixture, as shown in Figs. 4(b) and 6(b). More likely, more molecules of citric acid should be attracted to multiple cement particles initially than a single grain attraction. As long as the above attractive connections between different cement particles are broken down by continuous mixing, the shear resistance of the fresh paste can gradually be reduced and it finally steps into a steady reduced stage with increasing mixing time. This changing from multiple to single particle adsorption should be the principal mechanism of the shear stress and viscosity variation with mixing time for the cement paste with citric acid addition.

By contrast, the sodium borate polar link is relatively weaker than that of citric acid. Meanwhile, the space-like structure of sodium borate may generate certain steric hindrance action that may help release more water and improve the flowability of the cement paste. However, the chain structure of citric acid provides little assistance to the flowability of the cement paste. Therefore, more superplasticizer is needed to reach a given initial paste flowability with citric acid addition. In addition, stronger adsorption of citric acid to cement grains than that of sodium borate may also lead to more superplasticizer needed in the paste with citric acid.

Studies have shown that silica fume in cement paste can act as a stabilizer like a viscosity modifying agent to prevent segregation (Vikan and Justnes 2007; Mouhcine et al. 2015). It is possible that the very fine silica fume forms a gel-like state with a dynamic flocculated spatial weak network structure under high-speed shearing, which can not only uniformly distribute and stabilize the cement particles but also functions as a distraction and dispersion, reducing the probability of overlap between the cement particles, thereby reducing the maximum shear stress (Fig. 8). This can also explain that the paste with silica fume has a lower shear viscosity than the reference (Fig. 9). The initial mixing is because the thixotropy effect makes the viscosity of the system larger. During the shearing process, the cement particles are uniformly distributed and stabilized, and the system viscosity is greatly reduced. Meanwhile, the silica fume is much finer than the cement (Table 1), and with the content increasing, the specific surface area increases, the paste spread diameter decreases accordingly (Zhu et al. 2013), and the setting time is shortened, as shown in Table 2. The substitution of CSA cement with SCM has two main effects on the mechanical properties of the paste: i) filler and ii) dilution effects (García-Maté et al. 2013). The former slightly increases the compressive strength of the corresponding paste. In contrast, the latter has a negative impact on the mechanical strength. At 28 days of age, silica fume has less effect on the compressive strength of the CSA cement paste due to the significant filling effect.

![Fig. 10 Molecular structure of sodium borate (a) and citric acid (b).](image-url)
4. Conclusions

The effects of the retarding admixture, superplasticizer and SCM on the rheology of CSA cement paste are investigated. Water to binder ratio of 0.3, one PCE, two retarding admixtures, and three SCMs were used in the test. The rheological properties of fresh cement paste, including the shear stress and viscosity, and initial and final setting time, and compressive strength at different ages after casting were measured. The following conclusions may be drawn from the present work:

(1) Setting time of CSA cement paste can be extended by using retarding admixtures either of sodium borate or citric acid, and a mixed use of them. With the same amount of sodium borate or citric acid, approximately 2 to 5 times PCE is needed for paste with citric acid than that with sodium borate to achieve similar paste initial flowability. Under the combined action of PCE, more than three times the paste setting time can be obtained with citric acid addition than that with sodium borate.

(2) The rheological properties of fresh cement paste, such as the progress of shear stress and viscosity with mixing time, are also significantly influenced by the addition of retarding admixture. The addition of citric acid increases the initial peak shear stress, whereas the peak shear stress is nearly unaffected by the addition of sodium borate. The addition of SCMs in CSA cement paste reduces the peak shear stress of fresh cement paste, and the effect of silica fume is most significant. The reference paste and pastes mixed with sodium borate or fly ash exhibit shear thickening; pastes mixed with citric acid or silica fume exhibit shear thinning. Among them, the initial viscosity of the pastes with citric acid exceeds 5 Pa·s, and the thixotropy is more obvious. The rheological properties of pastes mixed with citric acid or silica fume are closely related to the corresponding three strong polar carboxyl and the gel-like state weak network structure, respectively.

(3) The longer the setting time is, the lower the early-age strength of the paste. At 28 days, using only sodium borate or citric acid and their combined use produced comparable strength to the reference paste. The addition of SCMs in CSA cement paste can strongly reduce the early-age compressive strength under water to binder ratio of 0.3. At 28 days, silica fume has less negative effect on compressive strength of the CSA cement paste due to the significant filling effect.

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