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**Effect of different retarders and their combination with superplasticizer on the properties of CSA**

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**Synopsis:** The aim of this work was to investigate the effect of polycarboxylate type superplasticizers (PCE), and three different retarders (citric acid, tartaric acid, potassium gluconate) and their combination on hydration process and rheological properties of CSA at early age. The hydration process was described through isothermal calorimetry, while the rheological properties were characterized through yield stress of cement pastes determined by rheometry. The results show that gluconate is the most powerful retarder, followed by tartaric acid, then citric acid. PCE strongly improves the fluidity of the pastes but a rapid loss of workability is noticed. On the contrary, retarders slightly decrease the yield stress of the pastes but slowdown the loss of fluidity. The combination of the both admixtures allows to maintain high fluidity for longer time. However, for citric acid, and even more for tartaric acid, a rheological instability, characterized by a decrease followed by an increase in the yield stress over time, is noticed. Potassium gluconate seems to be the best retarder to combine with PCE since no instability and longer maintenance of workability were observed. An optimum dosage, leading to the best initial fluidity to the pastes, was also determined for the three retarders. The rheological results are related to the delay induced by the retarder on the hydration products formation for the first hours of hydration and to competitive adsorption between retarder and PCE.

**Keywords:** CSA, Hydration, Rheology, Admixtures

## INTRODUCTION

It is well known that the concrete industry, and more specially Portland cement production, contributes to 5-7% of global CO<sub>2</sub> emissions [1]. Among the many potential solutions, Calcium sulfoaluminate (CSA) cements are one of low-CO<sub>2</sub>-alternatives to Portland cement. Indeed, CSA contains less amount of limestone to be decarbonated compared to OPC and the maximum kiln temperature for CSA clinker production is around 200 °C less than for OPC clinker production. Additionally, CSA clinkers require less energy for grinding than OPC clinkers [2,3]. CSA are mainly composed of ye'elimite (C<sub>4</sub>A<sub>3</sub>S) as the major phase, sulfate source such as gypsum (C<sub>2</sub>S) and/or anhydrite (C<sub>3</sub>S), belite (C<sub>2</sub>S), bredigite (Ca<sub>7</sub>Mg(SiO<sub>4</sub>)<sub>4</sub>), and other minor phases (C<sub>3</sub>A, CA, C<sub>12</sub>A<sub>7</sub>, CA<sub>2</sub>, C<sub>4</sub>AF) [4]. Pure ye'elimite reacts with water to form monosulfate (C<sub>4</sub>A<sub>3</sub>H<sub>12</sub>) and aluminum hydroxide (AH<sub>3</sub>) as described in equation (1). However, the hydration kinetics of CSA is mainly controlled by the type and the amount of calcium sulfate it contains [5]. If the molar ratio of calcium sulfate/ye'elimite = 2, ye'elimite reacts to form crystalline ettringite (C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>) and amorphous aluminum hydroxide (AH<sub>3</sub>) according to equations (2) or (3). For molar ratio lower than 2, monosulfate will be formed after sulfate depletion according to Eq. (1).



CSAs are often considered to be fast setting cements with poor workability [6]. In order to extend their use in large-scale applications, admixtures are required. Polycarboxylate ether (PCE), the most used superplasticizers in modern concrete, can be used to improve the workability. By adsorbing on the surface of the cement particles, PCEs create steric hindrance, which prevents contact between particles, and thus disperse them, by compensating the van der Waals attractive forces [7]. However, fast loss of workability is generally observed when PCEs are introduced alone in CSAs. In order to improve the maintenance of the dispersion, retarders such as citrate, tartrate, gluconate, borax..., can be combined with PCE. Retarders delay the precipitation of hydration products and thus reduce the consumption of free water and PCE. However, the combination of two admixtures may lead to adverse effects on the properties of concrete. Indeed, competitive adsorption may occur between the PCE and the retarder, which limits the adsorption of PCE and thus affects its dispersing efficiency. Several authors mention that retarders tend to form complexes with calcium ions. These complexes, being small and highly charged, adsorb first onto the surface of cement particles and partially hinder the adsorption of the PCE [6,8,9]. The aim of this study is to investigate the effect of the combination of three different retarders (citric acid, tartaric acid and potassium gluconate) with PCE on hydration and rheology of CSA. These results could help to choose the best retarder for this kind of cementitious system.

## RESEARCH SIGNIFICANCE

Several studies have already been devoted to understanding the effect of retarders and PCE on the rheological and hydration properties of sulfoaluminate cements. However, less work are dedicated to the combined effects of admixtures. Most of them focus on only one combination PCE-retarder. The authors believe that comparing different retarders and their combination with a PCE could be useful to better understand interactions between admixtures and could help to select the most adapted retarder to CSA plasticized with PCE.

## EXPERIMENTAL INVESTIGATION

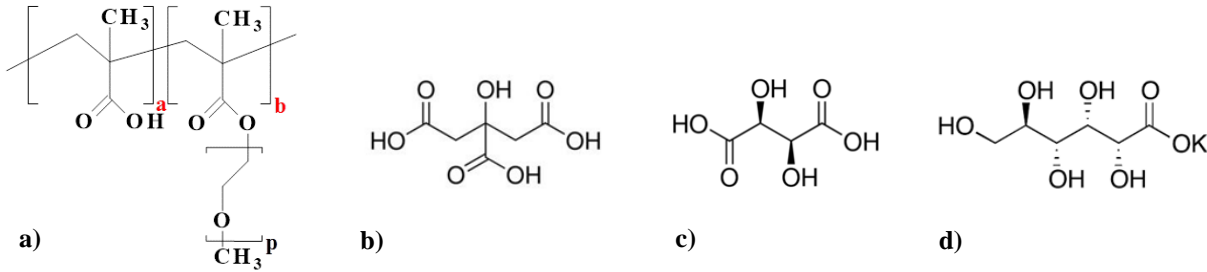
### Materials

The present study was carried out with a commercial sulfoaluminate cement (CSA) (i.tech ALICEM from Ciment Calcia / Heidelberg Cement). The mineral and phase compositions were determined by X-Ray fluorescence (XRF) and X-Ray diffraction combined with Rietveld algorithm. The results are given in Table 1.

**Table 1 –Mineral composition (% weight) of the investigated cement determined by XRF and XRD-Rietveld refinement**

Chemical composition (% wt)				Phase composition (% wt)			
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)	Phases	XRD (Rietveld)
CaO	38.9	SO <sub>3</sub>	22.9	C <sub>4</sub> A <sub>3</sub> \$	48.8	CaF <sub>2</sub>	0.8
SiO <sub>2</sub>	6.7	Na <sub>2</sub> O	0.9	C\$	22.2	Amorphous	14.0
Al <sub>2</sub> O <sub>3</sub>	20.2	K <sub>2</sub> O	0.5	C <sub>7</sub> MS <sub>4</sub>	11.0		
MgO	2.0	TiO <sub>2</sub>	0.3	C <sub>12</sub> A <sub>7</sub>	1.1		
Fe <sub>2</sub> O <sub>3</sub>	1.1	LOI	1.1				

A comb-type polycarboxylate superplasticizer, called PCE1, was used in this study. Its molecular structure is illustrated in Fig. 1a. This superplasticizer was chosen because it was identified as a good admixture for sulfoaluminate cement. Indeed, it exhibited a good compatibility with this cement and brought good rheological properties to the cement pastes [9,10]. It was composed of a polymethacrylic acid backbone and grafted side chains of polyethylene oxide (Fig. 1a). The main characteristics of the PCE, given by the manufacturer (Chryso), are detailed in Table 2. The carboxylate to ether ratio (C/E) corresponds to the number of nongrafted carboxylate functions per side chain. The charge density of PCE was measured experimentally by conductimetric titration with NaOH solution.



**Fig. 1–Chemical structure of the PCE used (a), citric acid (b), tartaric acid (c) and potassium gluconate (d)**

**Table 2 –Main characteristics of the different admixtures (PCE and retarders) and charge density of PCE and the main Ca<sup>2+</sup>-retarder complexes existing in a highly alkaline solution**

	Solid content (%)	Mw [g/mol]	Charge density [mmol of Charge/g]	P	N (=a+b)	n	C/E	Backbone conformation
PCE1	20	48300	0.79	45	5	12	4	FBW
		Mw [g/mol]	Charge density [mmol of Charge/g]			pKa		
Citric acid		192.1				3.13, 4.76, 6.40		
[CaCitrate <sub>2</sub> ] <sup>4-</sup> [8]			9.5					
Tartaric acid		150.1				3.04, 4.37		
[CaTartrate <sub>2</sub> ] <sup>2-</sup> [8]			5.9					
Potassium gluconate		234.2				3.86		
[Ca <sub>2</sub> Gluc <sub>2</sub> H <sub>-4</sub> ] <sup>2-</sup> [11]			4.2					
[Ca <sub>3</sub> Gluc <sub>2</sub> H <sub>-4</sub> ] <sup>0</sup> [11]			0					

FBW = Flexible Backbone Warm; SBW = Stretch Backbone Warm according to Gay & Raphael [12]

Three different retarders, citric acid (99.5%, Honeywell), tartaric acid (99.5%, Merck) and potassium gluconate (99%, Acros Organics), were used in this study and noticed AC, AT and GK, respectively. Their chemical structure is shown in Fig. 1 (b, c, d). Due to the pH of the cement interstitial solution (>12) and the different values of the pKa, all the retarders exist in their ionized form, i.e. citrate, tartrate and gluconate (Table 2). The three retarders differ in their molecular weight: potassium gluconate > citric acid > tartaric acid. They are also distinguished by the main complexes

they form in alkaline solution and by their associated charge density [8,11]. Here, the charge density shown in Table 2 is a theoretical value; it was calculated by dividing the charge of the complex by its molar mass. Ca-Citrate complex ( $[\text{CaCitrate}_2]^{4-}$ ) has the highest charge density, followed by Ca-tartrate complex ( $[\text{CaTartrate}_2]^{2-}$ ) and finally by Ca-gluconate complexes ( $[\text{Ca}_2\text{Gluc}_2\text{H}_{-4}]^{2-}$  or  $[\text{Ca}_3\text{Gluc}_2\text{H}_{-4}]^0$ ).

### **Cement paste preparation**

All the experimental investigation was carried out on cement pastes with deionized water, with a water-to-cement ratio (W/C) of 0.4. The mixing was carried out according to the NF EN 196-1 standard except for calorimetry investigation (detail given in section: Hydration process) [13]. The admixtures (PCE and retarders) were added into the dry mix at the same time as the water with the chosen dosage. As the PCE was in suspension, the amount of water contained in the PCE's solution was taken into account to maintain a constant W/C ratio between all formulations.

## **ANALYTICAL INVESTIGATION**

### **Hydration process**

The hydration process was followed by isothermal calorimetry (Calvet calorimeter C80, Setaram) on cement pastes. The temperature was set at 25°C. To reduce thermal unbalances induced by the introduction of the sample, the device was modified so that the sample was the only moving part introduced with a rod into the calorimeter. The pastes were prepared by manually premixing cement, admixtures and deionized water for 30 s, followed by mixing with a small stirrer for 1 min at 500 rpm. Paste samples of approximately 1.2g were placed in the calorimeter and the heat flow was recorded from 4 min after the first contact between cement and water to 72 h. The heat release during the hydration process was obtained by integrating the heat flow. However, due to the external mixing adopted here, the heat released during the initial period may be misinterpreted, therefore the first 20 min were not taken into account in this paper [14]. When retarders were used alone, dosages of 0.1, 0.2, 0.3 and 0.4 by weight of cement were tested. When 0.1 wt.% of PCE was introduced in the formulation, only 0.1 wt.% of retarder was used.

### **Rheological measurements**

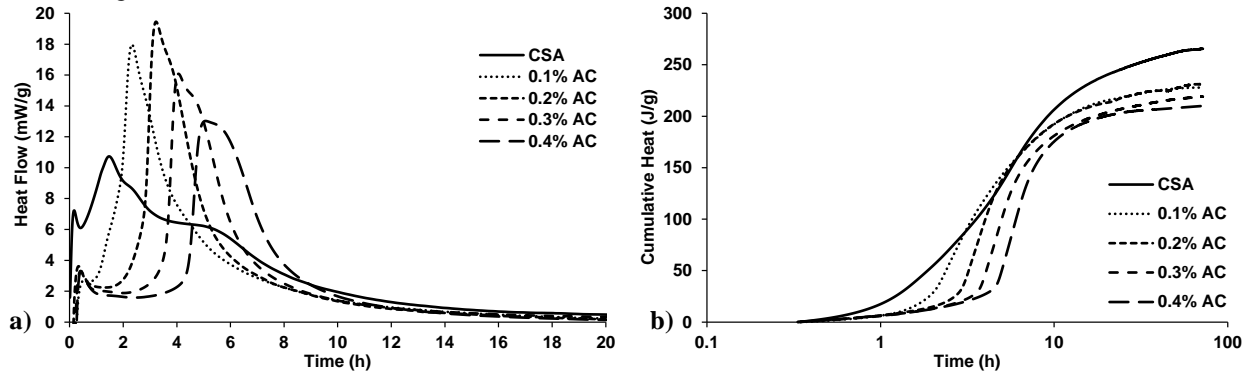
Rheological measurements were performed on cement pastes with a MCR 302 Rheometer (Anton-Paar), thermostated at 20 °C. The rheological properties of the fresh cement pastes were investigated through a vane-cylinder geometry with a gap thickness of 2 mm. Shear stress and shear rate were calculated from torque and rotational velocity, respectively, using the Couette analogy and a calibration with glycerol [15]. The cement paste was introduced into the cell at the end of the mixing cycle. At 8 min, the cement paste was first pre-sheared for 30 s at 200 s<sup>-1</sup> to re-homogenize the sample and erase its shear history [16,17], and then measurements were performed by imposing shear stress. The range of imposed shear stresses was tailored to achieved a shear rate ranging from 150 s<sup>-1</sup> to extremely low values (<10<sup>-5</sup> s<sup>-1</sup>). This latter is reached abruptly when the system blocks, i.e. when the paste no longer flows. The corresponding shear stress was defined as the yield stress of the paste. The pre-shear and measurement steps were repeated every 10 min to monitor the yield stress as a function of time. The method was applied to pure CSA and cement pastes containing admixtures. When admixtures (PCE or retarders) were introduced alone, the dosage was set at 0.1 % by weight of cement and was used as a reference. For combinations of admixture, the dosage of PCE was set at 0.1 wt.% and the dosage of retarder varied from 0.0125 to 0.15 wt.%. These dosages were chosen because we showed in a previous paper that using 0.1 wt.% of PCE alone, PCE adsorption leads to a coverage (expressed as the ratio of adsorbed amount to maximum adsorbed amounts) of more than 60% of the cement particle surface [10]. In this case, by adding increasing dosages in retarder, we assume that competitive adsorption between the two admixtures can be highlighted.

## **EXPERIMENTAL RESULTS AND DISCUSSION**

### **Hydration of CSA in presence of retarders**

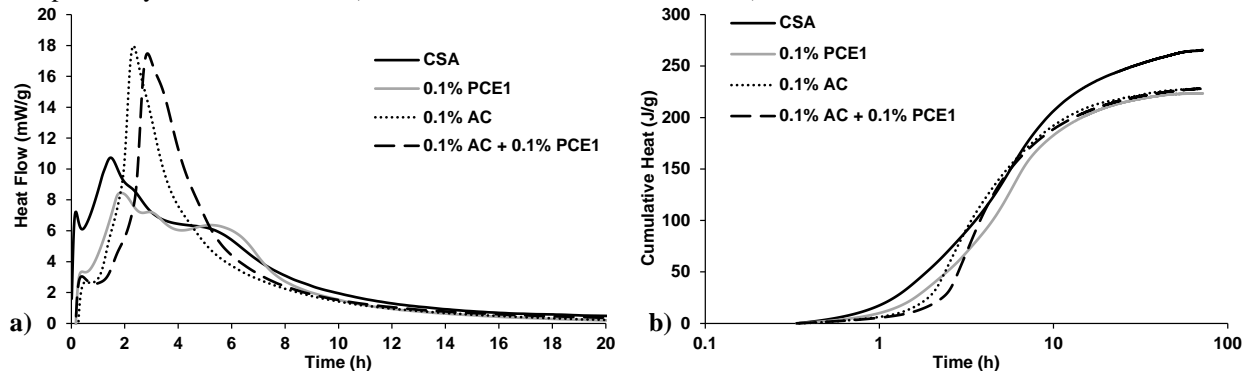
Figure 2a shows the effect of citric acid on the heat flow resulting from the hydration of CSA cement paste. The hydration process of CSA begins with an instantaneous increase in heat release due to the rapid initial dissolution of the anhydrous CSA phases [18]. The first peak is followed by a short induction period that ends after only 0.4h (25 min) of hydration, showing the high reactivity of the CSA studied in this work. Afterwards, the main hydration period starts with a rapid heat release, resulting in a main hydration peak with a maximum at 1.4h (85 min). The increase in

heat release is ascribed to the rapid dissolution of ye'elinite and anhydrite, and to the strong precipitation of hydration products (ettringite,  $AH_3$  and/or amorphous phases) [9,14]. Finally, the heat flow starts to decrease, showing two shoulders, before reaching a steady state with low heat release. The addition of citric acid to the CSA paste modifies the hydration process. Citric acid extends the induction period by 2.3 to 9.7 times and shifts the maximum of the hydration peak by 0.9 to 3.6h, compared to the reference for increasing dosages of 0.1 to 0.4 wt.%. The delay may result from the chelation of calcium ions by citrate, preventing the hydrate precipitation and ye'elinite dissolution [9,19,20]. The maximum intensity of the main hydration peak increases sharply up to citric acid dosage of 0.2 wt.%, and then decreases for higher dosages. However, it still remains higher than that of CSA alone. This indicates that when the effect of citric acid disappears, the hydration process seems to accelerate. However, since the cumulative heat of the plain cement paste is never reached, the degree of hydration remains lower (Fig. 2b). The cumulative heat at 72 h of hydration seems to be slightly affected by the citric acid dosage since it converges to values between 210 and 230 J/g.



**Fig. 2– Heat flow (a) and cumulative heat (b) of CSA cement pastes admixed with increasing dosage in citric acid**

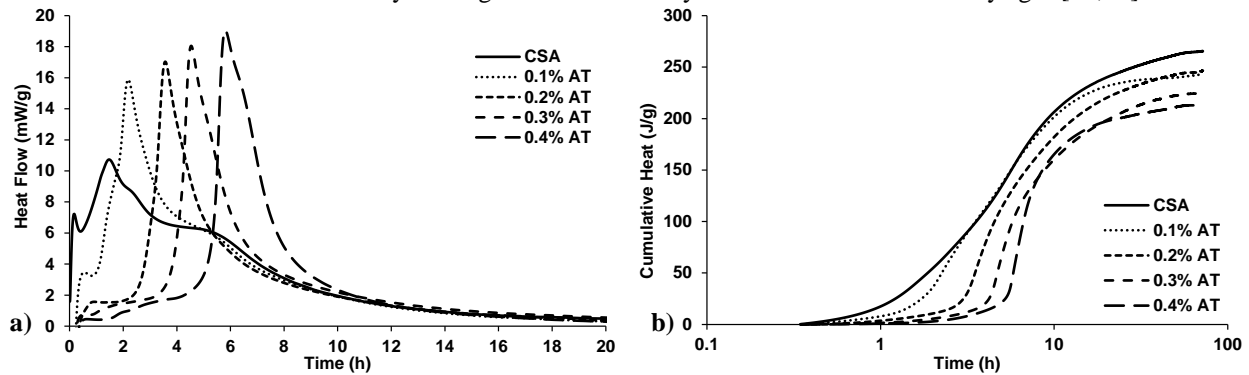
Figure 3 shows the effect of 0.1 wt.% of PCE combined with 0.1 wt.% of citric acid on the hydration of the CSA pastes. The combination of the two admixtures results in a short additional delay in the hydration process, mainly due to the extension of the induction period by about 0.5 h. After 72 h of hydration, the cumulative heat converges to a common value for all the admixed pastes. This could mean that a similar degree of hydration may be achieved independently on the admixture (citric acid, PCE and the combination).



**Fig. 3–Heat flow (a) and cumulative heat (b) of CSA cement pastes admixed with 0.1 wt.% of citric acid and its combination with 0.1 wt.% of PCE**

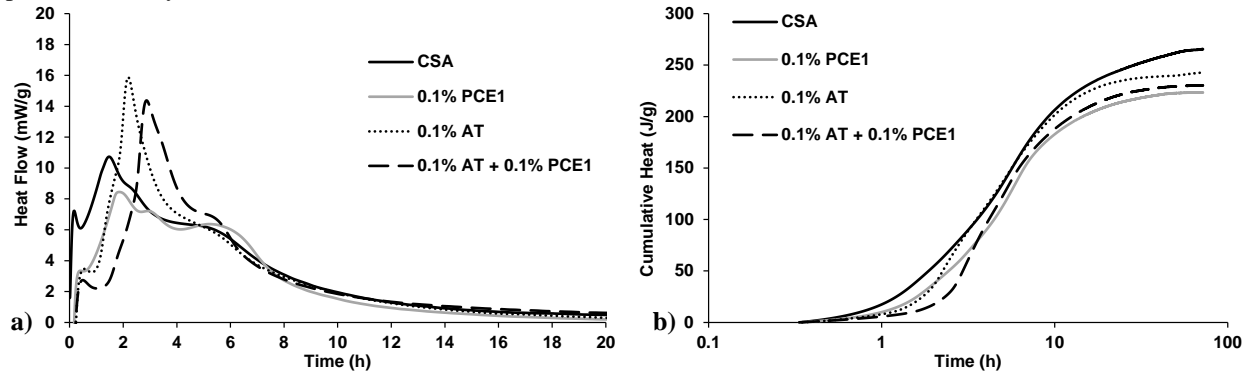
The effect of tartaric acid on the hydration of CSA is depicted in Fig. 4. Tartaric acid also retards the hydration by extending the induction period by around 2.9 to 11.5 times compared to CSA alone, when 0.1 to 0.4 wt.% of retarder is added. This suggests that tartaric acid is a slightly more powerful retarder than citric acid. Afterwards, the main hydration step begins with a rapid release of a large amount of heat, resulting in a higher hydration peak than for pure CSA. The maximum of the hydration peak is also delayed by 0.8 to 4.4 h depending on the dosage. Increasing the dosage of tartaric acid results in a fast increase in heat flow, an increase in the maximum intensity of the heat peak and a narrowing of the peak. This suggests that when the induction period is over, hydration accelerates sharply, leading to an increase in the rate of hydrate precipitation. This is justified by the slope of the cumulative heat curves in Fig. 4b. However, the cumulative heat release during the first 72 h of hydration remains lower than that of CSA

alone and evolves inversely with the dosage of tartaric acid (from 250 to 210 J/g). According to several authors, the addition of tartaric acid to CSA delays ettringite formation and ye'elimite dissolution at early ages [21,22].



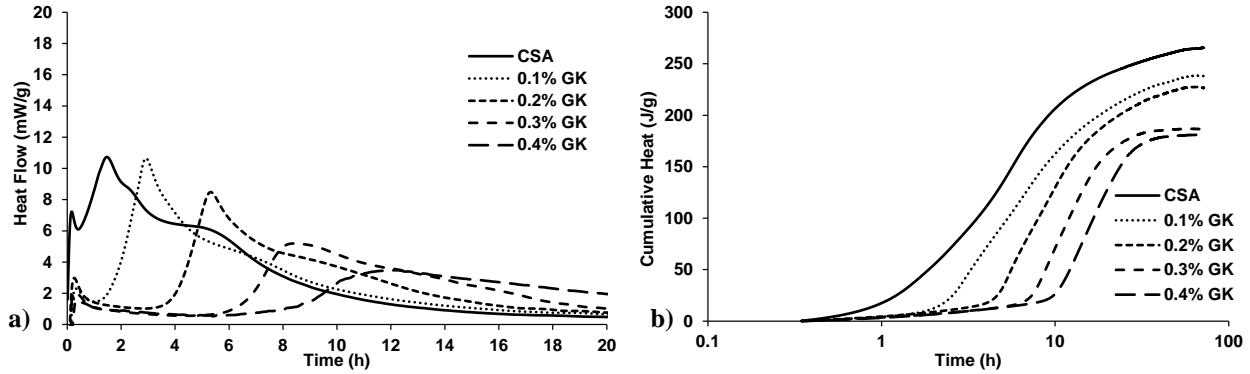
**Fig. 4– Heat flow (a) and cumulative heat (b) of CSA cement pastes admixed with increasing dosage in tartaric acid**

The effect of adding 0.1 wt.% of PCE and 0.1 wt.% of tartaric acid is shown in Fig. 5. This results in an additional delay compared to tartaric acid alone. The shape of the curves is broadly similar and a lengthening of the induction period is mainly observed.



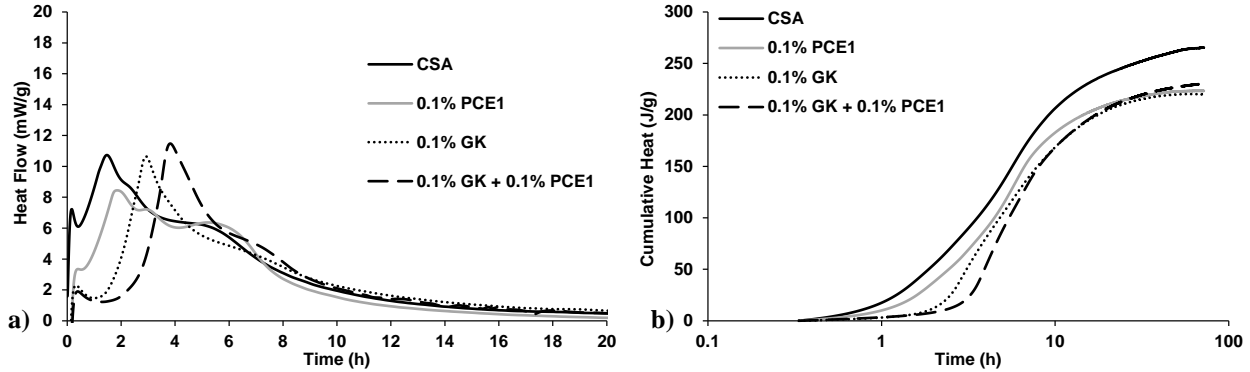
**Fig. 5– Heat flow (a) and cumulative heat (b) of CSA cement pastes admixed with 0.1 wt.% of tartaric acid and its combination with 0.1 wt.% of PCE**

The effect of increasing gluconate dosage on CSA hydration is shown in Fig. 6. Potassium gluconate appears to be the most powerful retarders among the three tested here. Indeed, the induction period is extended by 1.2 h compared to pure CSA by adding only 0.1 wt.% of gluconate, i.e. a duration 3.5 times longer. When the dosage is equal to 0.4 wt.%, the induction period is prolonged by 8 h compared to CSA alone (i.e. 19 times longer). For the same dosage, the induction period was extended by only 3.6 h and 4.4 h for citric acid and tartaric acid, respectively. The maximum heat flow is also strongly affected by the presence of gluconate since it is reached much later than with the two other retarders and its value is strongly lowered. This suggests that potassium gluconate delays and slows down the hydration of the CSA. This is easily observed in Fig. 7b, where the cumulative heat at 72 h decreases sharply to 180 J/g, with increasing gluconate dosage. Gluconate is known to be good set retarder for sulfoaluminate cement, retarding the formation of the main hydration product (ettringite) [22,23]. However, the greater retarding effect of gluconate than citric acid or tartaric acid is not in agreement with the findings of other authors [22,23]. Indeed, these authors observed a higher delay in the hydration process of CSA pastes induced by citric acid or tartaric acid compared with sodium gluconate. However, the mineralogical composition of their cement was different than that of the CSA studied here, i.e. more concentrated in  $C_2S$  but poorer in ye'elimite and sulfate source.



**Fig. 6– Heat flow (a) and cumulative heat (b) of CSA cement pastes admixed with increasing dosage in potassium gluconate**

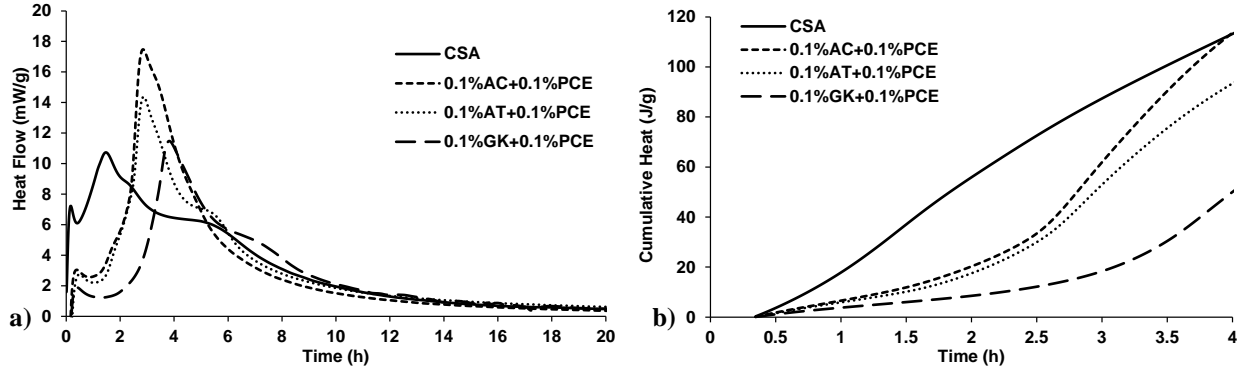
The addition of 0.1 wt.% of PCE in the cement paste containing 0.1 wt.% of gluconate results in an additional delay in the hydration process. This delay is characterized by an extension of the induction period by 1 h compared to gluconate alone and results in a lower cumulative energy during the first hours of hydration. At the end of the 72 h of hydration, the cumulative heat reaches similar values ( $\approx 230$  J/g) regardless of the admixtures.



**Fig. 7– Heat flow (a) and cumulative heat (b) of CSA cement pastes admixed with 0.1 wt.% of potassium gluconate and its combination with 0.1 wt.% of PCE**

The effect of the three retarders (0.1 wt.%) combined with 0.1 wt.% of PCE on the hydration process is shown in Fig. 8. The comparison between the three formulations highlights that, even with the addition of PCE, the most powerful retarder is again potassium gluconate, followed by tartaric acid and then citric acid. In order to provide useful information for the rheological results detailed in the following section, a focus on the first 4 hours of cumulative heat release is presented in Fig. 8b. Indeed, most rheological measurements were performed in less than 4 h because of the sharp increase in yield stress induced by cement hydration and paste stiffening. For combinations of 0.1 wt.% PCE with 0.1 wt.% citric acid or tartaric acid, the cumulative heat first increases gradually to about 2.5 h, while remaining much lower than that of cement without admixture. Then the heat release accelerates to reach, after 4 h, values close to that of cement alone. However, the heat release by the paste plasticized with PCE and containing tartaric acid remains always slightly lower than that with citric acid. This means that tartaric acid leads to a slightly lower degree of hydration than citric acid when combined with PCE. The addition of 0.1 wt.% potassium gluconate to 0.1 wt.% PCE results to the greatest delay in the hydration of the paste since the cumulative heat increases very slightly for the first 3 h before slowly increasing. Nevertheless, the cumulative heat remains always much lower than those obtained with the two other retarders. It is about 2 to 3 times lower during the first 3 hours, confirming the lowest degree of hydration and the strongest retarding effect of potassium gluconate.

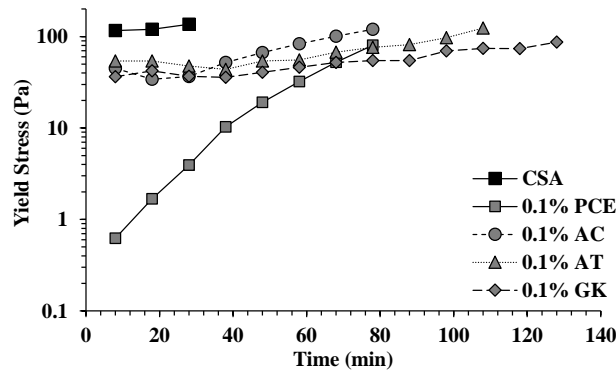




**Fig. 8–Effect of the combination of 0.1 wt.% of PCE and 0.1 wt.% of the different retarder on the heat flow (a) and cumulative heat (b)**

### Rheological investigation

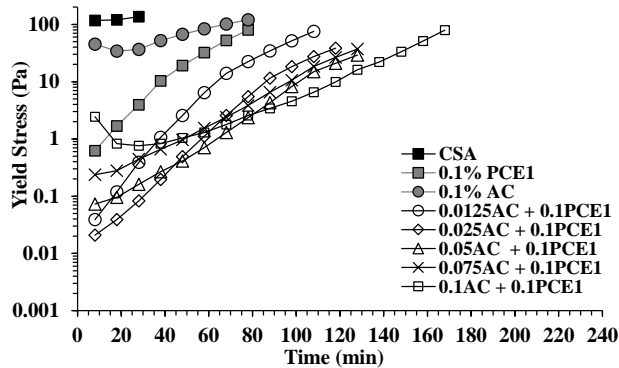
Figure 9 shows the evolution of the yield stress for the plain CSA cement pastes and for the cement pastes with 0.1 wt.% admixture (PCE and the three retarders). The yield stress of CSA paste without admixture reaches values above 100 Pa after only 8 min of hydration, which confirms the poor workability of the CSA and justifies the need to use superplasticizers with this type of cement. The addition of 0.1 wt.% PCE to the cement paste results in a dramatic drop of the initial (8 min) yield stress to 0.6 Pa. However, a rapid loss of workability, characterized by a rapid increase in the yield stress, is observed. Indeed, the yield stress of the paste reaches a value of about 80 Pa after 78 min of hydration. The loss of workability of the paste admixed with PCE is ascribed to the fast hydration of the CSA and the massive precipitation of hydrates that leads to the consumption and entrapment of PCE molecules in the hydrates [9,14]. On the contrary, the introduction of retarder slightly decreases the initial yield stress but maintains it over time. The initial yield stress of the CSA pastes admixed with 0.1 wt.% citric acid, tartaric acid and potassium gluconate reaches values of 45 Pa, 55 Pa and 36 Pa, respectively. However, although the yield stress remains relatively constant over time, fluctuations and differences between formulations appear. The addition of 0.1% wt.% citric acid initially results in a slight decrease in the yield stress of the paste, from 45 Pa to 35 Pa, between 8 min and 18 min, followed by a gradual increase to 120 Pa after 78 min of hydration. The paste admixed with 0.1 wt.% tartaric acid has a minimum yield stress of 45 Pa after 38 min of hydration. The yield stress then increases more slowly than that of citric acid since a value above 120 Pa is reached after 108 min. Finally, the CSA admixed with 0.1 wt% gluconate shows the best rheological stability since the yield stress seems to be constant until 48 min of hydration and a value of only 85 Pa is reached after more than 2 hours of hydration (128 min).



**Fig. 9– Evolution of the yield stress as a function of time for the non-admixed CSA cement paste and CSA cement pastes admixed with 0.1 wt.% of each admixture**

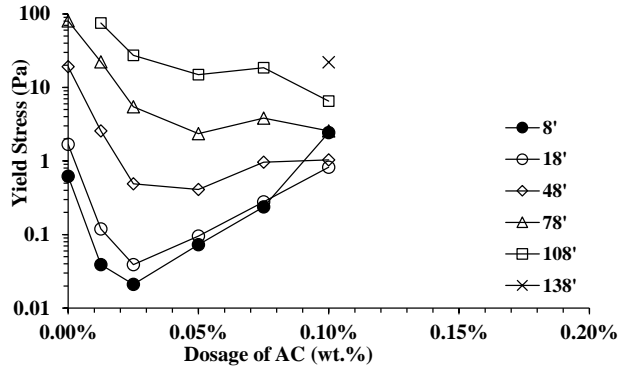
The change in the yield stress as a function of time for cement pastes plasticized with 0.1 wt.% PCE and increasing dosage of citric acid is shown in Fig. 10. The results show that it is possible to improve the initial fluidity and extend the workability of the CSA cement pastes by combining PCE and citric acid. Indeed, from a general point of view, the combination of citric acid (AC) with PCE1 (0.1 wt.%) leads to a decrease in the initial yield stress (8 min), and thus to an improvement of the initial fluidity, compared to CSA without admixture. After the initial yield stress decrease, the yield stress slowly increases over time. It appears that the kinetics of the yield stress increase over time,

characterized by the slope of the curve, depends on the dosage of citric acid. Indeed, a yield stress of 80 Pa is reached after 78 min of hydration for cement paste admixed with only 0.1 wt.% PCE1 (without citric acid). Combining 0.1 wt.% PCE with increasing dosages of citric acid, from 0.0125 to 0.1 wt.%, similar values of yield stress are obtained after 108 to 168 min of hydration respectively. This improvement in workability, i.e. reduction in workability loss, is explained by the slowdown of the cement hydration induced by the retarder. We have shown in a previous paper that the carboxylate groups ( $\text{-COO}^-$ ) of citric acid bind to  $\text{Ca}^{2+}$  to form highly charged complexes that adsorb on the surface of cement grains and prevent the dissolution of ye'elinite and anhydrite, as well as the precipitation of ettringite, inducing a delay in hydration of CSA. When citric acid and PCE are combined, the amount of hydrates formed is lowered by the presence of citric acid, which limits the coverage of PCE side chains by hydrates and maintains the effectiveness of PCE dispersion over time [8]. However, when combining 0.1 wt.% PCE with 0.1 wt.% citric acid, the paste exhibits a peculiar evolution of the yield stress over time (Fig. 10). First, the initial yield stress (at 8 min) is about 2.5 Pa, which is higher than that obtained for PCE alone (0.6 Pa). The same results were described in our previous paper and were ascribed to competitive adsorption between the both admixtures. Indeed, due to the higher charge density, smaller molecule size and thus to higher mobility of citrate complexes compared to PCE, citric acid adsorbs first on the surface of cement particles, partly hindering the adsorption of PCE. Since fewer PCE molecules are adsorbed, the fluidity of the paste is lower than for PCE alone [9]. Second, after 8 min, the yield stress decreases to a minimum ( $\tau_0 \approx 0.7$  Pa) at approximately 28 min. The drop in yield stress was explained by the gradual adsorption of unadsorbed PCE molecules onto the new adsorption sites created as hydration progresses [9]. Finally, the yield stress slowly increases to 80 Pa after 168 min of hydration due to the continuous precipitation of hydrates, which gradually cover the PCE side chains.



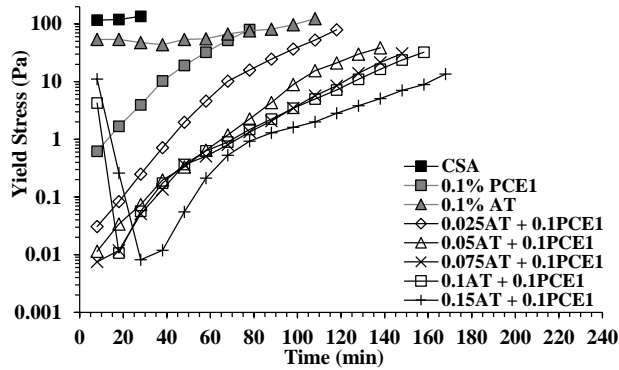
**Fig. 10 – Evolution as a function of time of the yield stress of the cement paste plasticized by 0.1 wt.% PCE and increasing dosage in citric acid**

Figure 11 shows the effect of citric acid dosage on the yield stress determined at several hydration times. It is clear that the dosage of citric acid has a strong influence on the initial fluidity, characterized by the values of yield stress at 8 min, of the cement pastes plasticized with 0.1wt.% PCE. Indeed, the increase of citric acid dosage leads first to a drop of the initial yield stress, meaning a better fluidity of the paste, then to an increase, indicating a loss of fluidity. In fact., the cement paste admixed with PCE alone has a yield stress of 0.6 Pa, whereas this decreases to 0.02 Pa with the addition of 0.025 wt.% citric acid. For citric acid dosage higher than 0.025 wt.%, the yield stress increases to 2.5 Pa (for 0.1 wt.% citric acid). This result indicates that an optimum of fluidity is obtained for a specific dosage of citric acid (0.025 wt.% here). For increasing dosages, but less than or equal to 0.025 wt.%, citric acid reduces the amount of precipitated hydrates, which is favorable for dispersion since fewer molecules and their side chains are trapped in the hydrates. However, as the dosage increases, competitive adsorption, in favor of citric acid, may occur limiting the dispersion of the cement paste. Similar results were obtained by Tan et al. when studying the effect of borax on the dispersion efficiency of PCE in CSA paste [6].



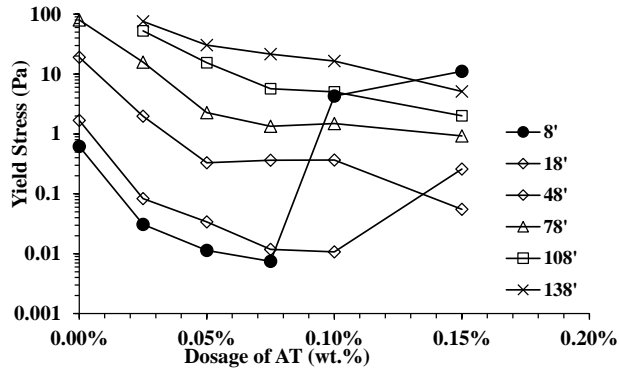
**Fig. 11 – Effect of citric acid dosage on the yield stress of the cement paste plasticized by 0.1 wt.% of PCE**

The time variation in the yield stress obtained for several dosages of tartaric acid is shown in Fig. 12. As with citric acid, it is possible to improve the initial fluidity and extend the workability of CSA cement pastes by combining PCE with tartaric acid. Compare to citric acid, tartaric acid seems to be slightly more powerful to maintain workability. For low dosage up to 0.05 wt.%, the same loss of workability is obtained for both retarder since a similar yield stress of 20 Pa is reached after 98 min and 118 min for 0.025 and 0.05 wt.% respectively. However, from a dosage of 0.075%, tartaric acid becomes slightly more effective than citric acid in slowing the loss of workability of the paste. Indeed, at a dosage of 0.075 wt.%, 138 min are necessary to reach yield stress of 20 Pa with tartaric acid against only 118 min for citric acid. The same value of yield stress is obtained after 158 and 138 min with 0.1 wt.% of tartaric acid and citric acid, respectively. However, depending on the dosage of tartaric acid, a very strong instability of the paste may occur. Indeed, for dosages higher than 0.1 wt.%, a very fast and strong fall of the yield stress is observed. For 0.1 wt% tartaric acid, the yield stress decreases from 4.3 to 0.01 Pa in only 10 min (from 8 to 18 min), resulting in problematic bleeding and sedimentation of cement particles. This was confirmed by slump measurements using the mini-cone test. This phenomenon is further amplified with the acid dosage since the yield stress drops from 11.1 to 0.008 Pa in 20 min for 0.15 wt.% tartaric acid.



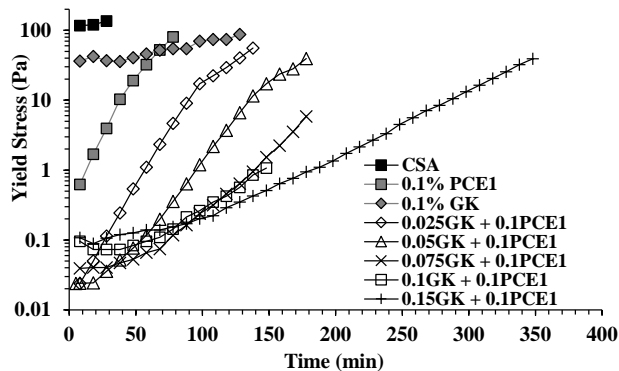
**Fig. 12 – Evolution as a function of time of the yield stress of the cement paste plasticized by 0.1 wt.% PCE and increasing dosage in tartaric acid**

Figure 13 shows the effect of tartaric dosage on the yield stress of cement paste plasticized with 0.1 wt.% PCE. The initial fluidity of the paste is again strongly dependent on the dosage of tartaric acid. Increasing the dosage leads first to an improvement and then to a sudden drop in the fluidity of the paste. As with citric acid, the results seems to suggest that two antagonistic effects occur. At low dosage, the plasticizing effect of tartaric acid and its hydration retarding effect would increase the dispersing ability of PCE to reduce the yield stress. However, as the dosage of tartaric acid increases, strong competitive adsorption may occur, resulting in a negative effect on the fluidity of the paste. Optimal fluidity is achieved at a dosage of 0.075 wt.% tartaric acid, which is significantly higher than that of citric acid (0.025 wt.%).



**Fig. 13 – Effect of tartaric acid dosage on the yield stress of the cement paste plasticized by 0.1 wt.% of PCE**

The same experiments were conducted with potassium gluconate and the results are shown in Fig. 14. Compared to PCE alone, the use of potassium gluconate in combination with 0.1 wt.% PCE leads to an overall decrease in the yield stress of the cement pastes. However, these values obtained for dosages between 0.025 and 0.1% are significantly less dispersed than those obtained with the two other retarders. Indeed, during the first 30 min, the values of the yield stress vary only from 0.02 to 0.1 Pa whereas they vary from 0.02 to 2.5 Pa and from 0.0075 to 4.5 Pa for citric acid and tartaric acid, respectively. This means less sensitivity of the formulations to gluconate dosing compared to citric or tartaric acids and therefore better robustness. Moreover, the addition of gluconate to CSA cement paste leads to interesting changes in yield stress over time. Indeed, gluconate seems to improve the maintenance of the fluidity better than the two other retarders. For example, at 0.05 wt.% retarder, a yield stress of 20 Pa is reached after 158 min with gluconate against only 118 min for citric and tartaric acids. At this time, the paste admixed with gluconate exhibits a yield stress of only 2 Pa, which is 10 times less.



**Fig. 14 – Evolution as a function of time of the yield stress of the cement paste plasticized by 0.1 wt.% PCE and increasing dosage in potassium gluconate**

Figure 15 represents the effect of gluconate dosage on the yield stress of the cement pastes. In contrast to citric and tartaric acids, the addition of gluconate results in an improvement in initial fluidity compared to PCE alone, regardless of dosage in the range tested here (between 0.025 to 0.15 wt.%). Again, the addition of gluconate to cement paste plasticized with 0.1 wt.% PCE leads first to a reduction followed by an increase in the yield stress, with an optimum dosage between 0.025 and 0.05 wt.%. However, the effect of gluconate dosage on the initial fluidity is low since the yield stress is between 0.02 and 0.1 Pa when the dosage increases from 0.025 to 0.15 wt.%. For comparison, the initial yield stress ranges from 0.2 to 4.7 Pa and 0.0075 to 11 Pa with a range of 0.025 to 0.1 wt.% citric acid and tartaric acid, respectively. This could be the result of the strong retarding power of gluconate, which even at low dosage limits sufficiently the precipitation of hydrates, and thus the PCE entrapment, for PCE to be effective. Then, as the gluconate dosage increases, competitive adsorption between PCE and gluconate occurs but to a lesser extent. Indeed, as described in Table 2, the Ca-gluconate complexes have the lowest charge density of the three retarders, if any, and a value closer than that of PCE. Thus, despite its small size, competitive adsorption may be less favorable for gluconate than for the two other retarders, hindering PCE adsorption to a lesser extent.

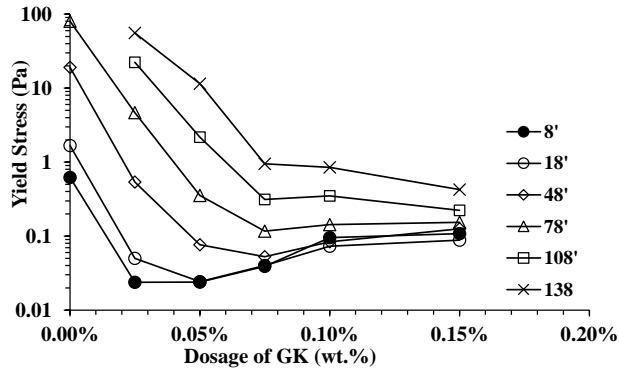


Fig. 15 – Effect of potassium gluconate dosage on the yield stress of the cement paste plasticized by 0.1 wt.% of PCE

### FURTHER RESEARCH

Adsorption measurements should be performed to quantify the extend of competitive adsorption between PCE and tartaric acid or gluconate. Mechanical investigations could also be useful to determine the best combination (PCE + retarder).

### CONCLUSIONS

In order to extend the use of sulfoaluminate cements to larger-scale applications, the influence of PCE, three different retarders and their combination on the hydration and rheology of a commercially available CSA was investigated. Based on the results of this experimental investigation, the following conclusions are drawn:

1. The three retarders tested delay the hydration of CSA cement when introduced alone. Among them, tartaric acid seems to be slightly more effective than citric acid. However, potassium gluconate results in a more significant retardation of CSA hydration and can be classified as the most powerful retarder.
2. When retarders are combined with 0.1 wt.% PCE, additional delay was noticed. However, for all retarders, the final retardation was not the linear combination of the individual retardations, implying interactions between the both admixtures.
3. The initial fluidity of the cement pastes was improved by combining retarder and PCE. However, an optimum dosage of retarder was found. For a dosage higher than this optimum, competitive adsorption between the retarder and PCE occurs, leading to an increase in the yield stress of the pastes. For lower dosage, a synergetic effect of the two admixture is observed since an improvement of the fluidity is observed.
4. Potassium gluconate prolongs the workability of CSA pastes plasticized with PCE, while tartaric acid results in a very high rheological instability. Citric acid shows an intermediate behavior. Moreover, the yield stress of the pastes seems to be less sensitive to the dosage of gluconate, making it the best retarder.

Adsorption measurements could provide useful information on the mechanism of action of retarders, as well as an explanation for the retarding power of sodium gluconate. This will be part of a future work.

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