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Hydration and rheology of sulfoaluminate cements (CSA) in presence of polycarboxylate superplasticizers (PCE) and citric acid

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ABSTARCT

It is admitted that the cement industry contributes for about 5-7% of the total man-made CO2 emissions. A possible way for decreasing these CO2 emissions is the development of alternative clinkers with lower proportion of limestone in the raw materials. Calcium sulfoaluminate cements (CSA) are regarded as a promising low CO2 alternative to Portland cements. Generally, with a sufficient amount of calcium sulfates, the main hydration product of these cements is ettringite, which strongly affects the workability of CSA pastes. Polycarboxylate superplasticizers (PCE), combined with retarders, can be used with the aim to decrease the yield stress and the viscosity of this type of pastes. However, the multitude of components of these cements makes it difficult to understand the effect of these additives on the hydration process and on the properties of pastes. The aim of this work is to provide a better understanding of the: (i) effect of the molecular structure and the dosage of PCE on the hydration and rheology of CSA (ii) effect of citric acid on the dispersing effectiveness of PCE . Three PCEs, with the same chemical structure but different molecular structure, were investigated. Vicat tests and isothermal calorimetry were used to describe the hydration process. While, Rheological properties were characterized with mini-cone tests. Adsorption measurements were carried out with Total Organic Carbon analyzer and ion chromatography. The results reveal a competitive adsorption between citric acid and PCEs, which decreases the dispersing effectiveness of the latter.

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1. INTRODUCTION

Since the 19th century, ordinary Portland cement (OPC) has become the most used material in the world. Annual worldwide Portland cement production is approaching 5.9 Mdt/year (William 2018). Unfortunately, the production of Portland cement accounts for about 5-7% of the total man-made CO_2 emissions (Damtoft et al. 2008). One of the low CO_2 alternatives to Portland cement is calcium sulfoaluminate cement (CSA) mainly composed of ye'elimite ($C_4A_3\$$), belite (C_2S) and anhydrite ($C\$$). Thanks to its high early strength and fast setting, CSA has been used in fast construction engineering (Qian et al. 2014), offshore and corrosion resistance engineering and emergency repairs (Guo et al. 2012). Smaller amount of limestone in the raw materials (Scrivener et al. 2018), lower calcination temperature and the ease of grinding (Glasser & Zhang 2001) make CSA much greener than OPC and thus a potential alternative to OPC.

The mechanism of CSA hydration depends on the cement clinker composition (Sahu et al. 1991) and particularly on the amount and reactivity of calcium sulfate they contain. The main hydrated phase of CSA is ettringite ($C_6A_3\$H_{32}$), which results from dissolution and precipitation processes of anhydrite and ye'elimite phases. Generally, the hydration process of CSA is described by the following reactions (Zhang 2000):

$$C\$ + 2H \rightarrow C\$H_2 \quad (1)$$

$$C_4A_3\$ + 2C\$H_2 + 34H \rightarrow C_6A_3\$H_{32} + 2AH_3 \quad (2)$$

CSA are known for their poor workability and short setting time (Tan et al. 2017), which requires the use of superplasticizers and retarders. Polycarboxylate ether (PCE) superplasticizers, known as high-range water reducers, are one of the most used admixtures in concrete. They adsorb onto particles surface inducing their dispersion thanks to steric hindrance (Flatt et al. 2009). Garcia-Maté et al. (2012) studied the interaction of a commercial PCE superplasticizer with CSA. They found a very strong increase of workability at a dosage of 0,1% of PCE. Sun et al. (2011) and Chang et al. (2009) investigated the influence of synthesized PCE superplasticizers on the rheology and hydration of a commercial CSA. At low PCE dosages, a strong increase of workability was observed. However, a quick loss of workability of CSA-PCE system was seen over time (Winnefeld 2012). Retarders, such as citrate, gluconate, tartrate, sodium, borax, can be used to improve the fluidizing effect of PCE on CSA paste because these retarders delay the formation of hydration products and thus reduce the consumption of free water and PCE (Tan et al. 2017).

It is well known that the use of several admixtures in concrete can cause undesired interactions. In PCE-citric acid system, competitive adsorption risk may occur between highly charged citrate and PCE. Plank & Winter (2008) investigated the competitive adsorption between polycarboxylate superplasticizers and retarders in cementitious self-levelling underlayments based on ordinary Portland cement (OPC), calcium aluminate cement (CAC) and anhydrite. They found that citric acid, which is highly charged, prevents the adsorption of PCE and hence affects workability. The aim of this work is to investigate the effect of the combination of citric acid and PCE on rheology and early age hydration of CSA.

2. MATERIALS AND METHODS

2.1 Binder

A commercial calcium sulfoaluminate-belite cement (CSA), provided by Italcementi Group, was investigated. The chemical composition of the cement was obtained by X-Ray fluorescence (XRF), while phase composition was determined by X-Ray diffraction and quantified using Rietveld algorithm, as shown in table 1.

2.2 Admixtures

Three comb-type polycarboxylate superplasticizers (PCE1, PCE2 and PCE3), provided by Chryso, were used for this study. All the polymers have the same chemical structure, i.e. polymethacrylic acid backbone and grafted side chain of polyethylene oxide (Figure 1a). On the contrary, they have a different molecular structure. Main characteristics of the PCEs, given by the manufacturer, are listed in

Table 2. The charge density of PCEs was measured experimentally by conductimetric titration with NaOH. A schematic illustration of the molecular structure of PCEs, obtained from structural data of the Table 2, is given in Figure 1b.

In order to delay the hydration of CSA, a commercial citric acid (99.5% Honeywell) was used. In this paper citric acid will be noted as CA.

Table 1. Properties of CSA cement

Chemical composition (%)	O	Ca	Al	S	Si	F	Mg	Fe	K	Cl
	43.4	27.3	12.3	7.8	3	1.8	1.5	0.8	0.4	0.1
Phase composition (%)	$C_4A_3\$$		C_2S		C$		Other			
	49.4		8		21.9		20.7			

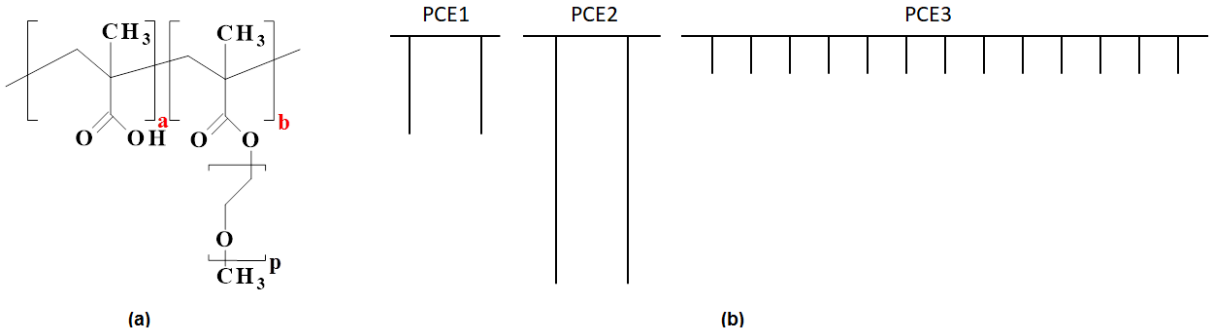


Figure 1. (a) Chemical structure of PCE1, PCE2 and PCE3 (b) Schematic illustration of the molecular structure of PCE1, PCE2 and PCE3 based on data given in Table 2

Table 2. Main characteristics of PCE1, PCE2 and PCE3

	Solid content (%)	Mw (g/mol)	Charge density (mmol/g)	P	N (=a+b)	n	Backbone conformation
PCE1	20	48300	0,79	45	5	12	FBW
PCE2	25	138600	0,3	114	5	15	FBW
PCE3	30	119000	0,96	17	2,5	115	SBW

FBW = Flexible Backbone Warm; **SBW** = Stretch Backbone Warm according to Gay & Raphael (2001)

2.3 Paste preparation

For all tests, cement pastes were prepared with Millipore water at a fixed water-to-cement ratio (W/C) of 0.4. PCE dosage intended was 0.05% and from 0.1% to 0.4% by weight of cement at 0.1% increment. The added amount of citric acid was 0.2%, 0.4% and 0.6% by weight of cement. Pastes were mixed according to the standard NF EN 196-1 except pastes prepared for calorimetry tests.

2.4 Hydration

2.4.1 Setting measurements

Initial and final setting time are useful to understand the effect of admixtures on the hydration of cement paste. In our study, Vicat test was used to determine the setting time. The test was conducted with an auto-Vicat (Ibertest) according to EN 196-3 standard.

2.4.2 Heat release measurements

The heat evolution during cement hydration was measured using an isothermal heat flow calorimeter (Calvet calorimeter C 80, SETARAM) at a constant temperature of 25°C. The paste was prepared by mixing cement, admixtures and water, for 30 seconds by hand, then for 1 min at 500 rpm. A small stirrer carried out the mixing. Samples of 1.5g approximately were placed into the calorimeter. The heat flow was recorded for 48 hours.

2.5 Rheology

The plastic yield stress τ_0 is an important parameter to describe the rheological behaviour of cement paste. One cheap and fast method to assess the value of yield stress is the mini-cone test. The test consists of measuring the spread flow of the cement paste using a mini-slump-cone (40 mm in height, 66 mm in top diameter, and 74.3 mm in bottom diameter). Once prepared, the cement paste was poured into the cone, and the cone was vertically removed. The spread flow of the paste was considered to be the diameter of the spread paste. The measurements were realised each 10 min, from 8 min until there was no spread. The paste was mechanically mixed for 30 seconds, at 140 rpm, before each measurement.

The spread flow of the paste can be linked to the yield stress according to (3) (Zimmerman et al. 2009).

$$\tau_0 = \frac{225\rho g V^2}{128\pi^2 R^5 (1+\frac{225}{128\pi}\sqrt{3}VR^{-3})} - \lambda\frac{R^2}{V} \quad (3)$$

Where τ_0 is the yield stress, ρ = paste density, V = volume of the cone, R = radius of the paste spread and λ is a constant linked to the liquid vapour interfacial energy and the wetting angle on the plate. In this paper, λ is fixed at 0.003 (Dallas et al. 2015).

2.6 Adsorption

The adsorption amount of polymer on cement was measured according to the depletion method. The quantification was done by calculating the difference of concentrations of the polymer in the initial solution and in the interstitial solution. The interstitial solution was extracted by double centrifugation of the cement paste at 8 min, 18 min and 38 min after the start of mixing. The first centrifugal separation was carried out at 5000 rpm for 10 min using the Multifuge 3SR+ centrifuge (Thermofischer) and the second one was set out at 14500 rpm using the miniSpin plus centrifuge (Eppendorf) for 5 min. When citric acid was combined with PCE, the interstitial solution was extracted at 8 min, 18min, 38min, 78 min and 118 min.

When the PCE was introduced alone, the non-adsorbed polymer remaining within the interstitial solution was quantified by means of Total Organic Carbon (TOC) measurements (Vario-TOC Cube Elementar). Once obtained, the supernatant was diluted 10 times by adding 0.1 mol/l HCL solution in order to remove inorganic carbon (carbonates) from the samples. The adsorbed amount of superplasticizer was calculated from reference measurements of aqueous polymer solutions.

When combining citric acid with PCE, quantitative analysis of non-adsorbed citrate remaining in the interstitial solution was performed by ion chromatography (IC) (DIONEX ICS 5000+, column CS12A, conductimetric detector). A gradient of KOH concentration was used as eluent. The samples were prepared by diluting the supernatant 100 times using 0.01mol/l HCL solution. Quantification of PCE adsorption was deduced by subtracting the IC results out of the TOC ones. In order to validate IC measurements, adsorption of only citric acid was quantified by, IC and TOC measurements. A good correlation between both methods was found.

The Langmuir model was used for the characterization of adsorption curves. According to the Langmuir model, the adsorption equilibrium can be expressed as follow:

$$\tau = \tau_{\max}\frac{K.c}{1+K.c} \quad (4)$$

Where τ is the amount of admixture adsorbed (mg/g), τ_{max} is maximum amount adsorbed (mg/g), K is the Langmuir constant (l/g) and c is the concentration of admixture in the interstitial solution (g/l).

3. RESULTS

3.1 Hydration

3.1.1 Setting time

The initial and final setting times of CSA with and without admixtures (PCE1, PCE2, PCE3 and CA) are presented in figure 2a as a function of admixture dosage. The initial and final setting time of CSA paste without admixtures is around 40 min and 50 min respectively, indicating the fast setting of CSA. Additionally, with the incorporation of admixtures, the initial and final setting times increase with the dosage. Compared to reference sample, and at dosage of 0.2 wt%, PCE1, PCE2 and PCE3 delayed the initial (final) setting time by 68%, 46% and 41% (67%, 37% and 41%) respectively. According to these results, PCE1 is more efficient than PCE2 and PCE3, and it is even clear with a dosage of 0.4 wt% (initial setting time is delayed by 146%, 69% and 52% when PCE1, PCE2 and PCE3 are introduced respectively). Moreover, the setting kinetics of cement paste change with the dosage in PCE. At a dosage of 0.2 wt% and 0.4 wt%, the setting duration of PCE1 based paste is 16 min and 98 min respectively. Citric acid has a significant effect on initial and final setting time. At a dosage of 0.2 wt% citric acid delayed, both, the initial and final setting time by almost 200%. However, setting kinetics do not change with the citric acid dosage. Results are discussed in the discussion section.

In order to investigate the combined effect of citric acid and PCE, a dosage of 0.2 wt% of citric acid was combined with 0.2 wt% of PCE1 or PCE2. Figure 2b shows that initial and final setting times are about 4 times more than the reference sample. Moreover, the sum of the delay induced by PCE1 (PCE2) in 0.2PCE1 (0.2PCE2) and by CA in 0.2CA is different than the delay induced by their combination in 0.2CA+0.2PCE1 (0.2CA+0.2PCE2). This shows the non-additivity of the effect of citric acid and PCE on setting times, implying interactions between citric acid, PCE and CSA.

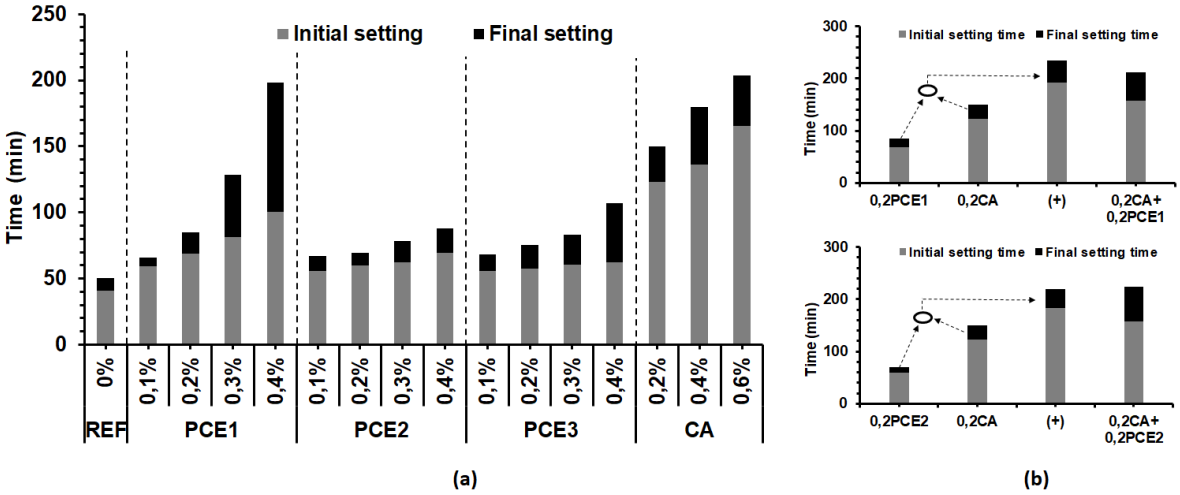


Figure 2. (a) Initial and final setting times of CSA in a function of the dosage of PCEs and CA (b) Initial and final setting times of CSA in presence of CA and PCE1 (PCE2) at a dosage of 0.2wt%

3.1.2 Calorimetry

The hydration kinetics of CSA in presence of PCE and/or citric acid was investigated by isothermal calorimetry. The curves were shifted to the right when increasing the dosage in admixtures. Therefore, only heat flow curves obtained with dosage in admixtures of 0.2 wt% are plotted in Figure 3a. The initial peak refers to the rapid initial dissolution of CSA phases. Because of the external mixing and the sensitivity of the calorimeter, the initial peak can be misinterpreted. For this reason, the initial peak was not considered in this study. After the induction period, all samples present a main hydration peak related to the formation of ettringite (Winnefeld, 2012). The reference sample presents a very short induction period around 40 min of hydration, while addition of admixtures delays the hydration of the

paste. At 0.2 wt%, citric acid increases the induction period by 2h. This show the hydration retardation effect of citric acid. Additionally, PCE1, PCE2 and PCE3 increases induction period by 40 min, 36 min and 20 min respectively. The combination of citric acid with PCE1 at a dosage of 0.2 wt% each, increases the induction period by 2.2 hours. This result confirms the non-additivity of hydration delay of citric acid and PCE. A slight difference is seen between the effect of PCE1 and PCE2 when citric acid is present.

The cumulative heat curves for samples at dosage of 0.2 wt% are plotted in figure 3b. In general, the cumulative heat of CSA is believed to be proportional to its hydration degree, since the hydration of CSA is dominated by ye'elimite dissolution and precipitation of ettringite and $Al(OH)_3$ (Zajac et al. 2016). The hydration of CSA progresses slowly in the first 40min and then accelerates between 40min and 8h. PCEs and/or CA slow down the hydration of CSA pastes. Additionally, the slope of the 0.2CA curve is similar to that of CSA curve, which means that citric acid stops the hydration for a while, and then starts again in the same way as the reference sample. The opposite trend was observed when PCEs are used. PCEs delay hydration of CSA by slowing down its hydration process.

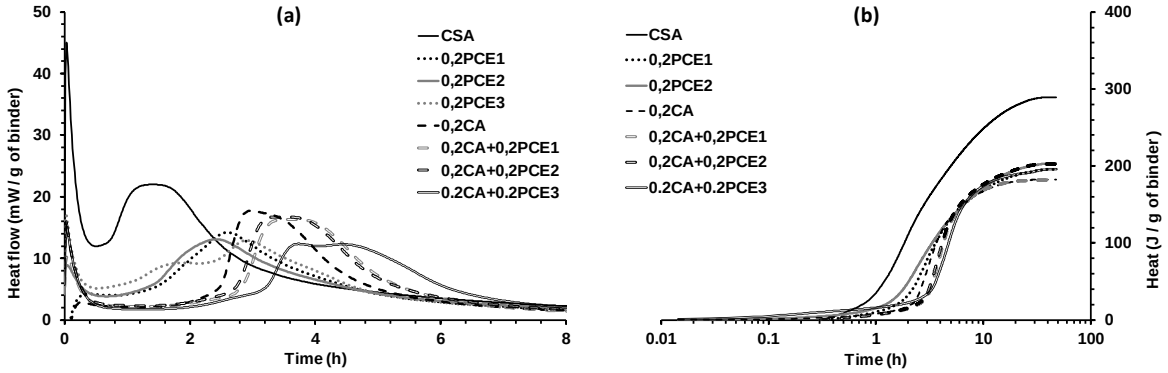


Figure 3. (a) Heat flow of CSA in presence of PCE and CA during 8 hours of hydration, (b) Cumulative heat of CSA in presence of PCE and CA during 48h hours of hydration

3.2 Rheology

Yield stress of the cement paste (W/C=0.4) with various dosages of PCE (0.05, 0.1, 0.2, 0.3 and 0,4 wt%) at 8min of hydration time are depicted in figure 4a. The yield stress of CSA paste without admixture reaches values higher than 200 Pa after 8min of hydration, which explains the necessity of using superplasticizers with this type of cement. The yield stress decreases with the increasing dosage in PCE. At 0.05 wt%, only PCE1 reduces the yield stress from 200 Pa to 20 Pa. At 0.1%, both PCE1 and PCE2 reduce significantly the yield stress from 200 Pa to less than 10 Pa, while 0.4 wt% of PCE3 is needed to reduce yield stress to less than 10 Pa. According to these results, small amount of PCE1 and PCE2 is needed for the improvement of CSA paste workability, while more than 0.4 wt% of PCE3 is required to have significant improvement. In addition to that, PCE1 has the greatest dispersing effectiveness.

Figure 4b, shows the evolution of yield stress within time for the different admixtures used with dosage of 0.2 wt%. As noted above, the use of PCE1 and PCE2 decreases significantly the initial yield stress of the paste. However, a fast slump loss with time, characterised by an increase in yield stress, was remarked when PCEs are used alone. When citric acid is introduced alone in the cement paste, a slight decrease in the initial yield stress was noticed. In addition, citric acid slowed down the increase of yield stress within time. The combination of citric acid (0.2 wt%) with PCE1 (PCE2) (0.2 wt%) decreases the initial yield stress compared to CSA. The yield stress then decreased throughout time to reach a minimum equal to the initial yield stress obtained when PCE1 (PCE2) was introduced alone. Additionally, the combination of citric acid with PCE slows down the slump loss with time. It should be noted that the effect on yield stress induced by the combination of citric acid and PCE is not additive.

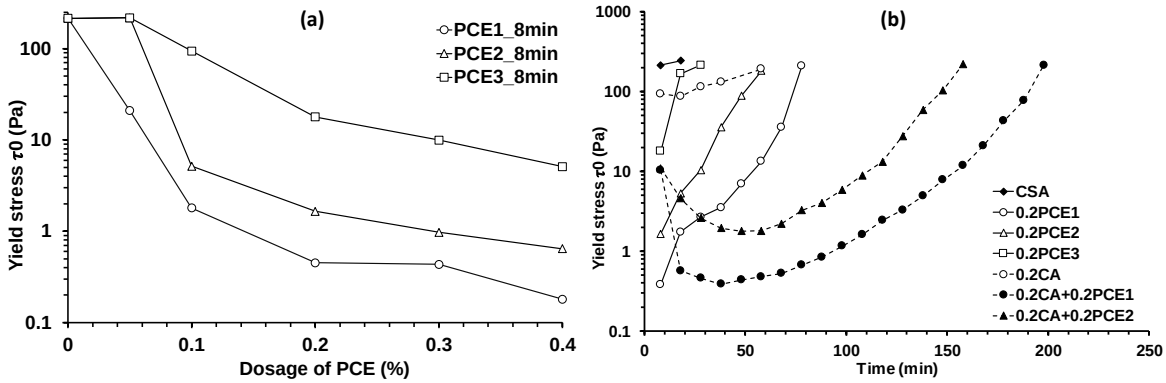


Figure 4. (a) Yield stress as a function of PCE dosage (b) Yield stress as a function of Time

3.3 Adsorption

Adsorption isotherms were used to explain the differences in dispersing effectiveness of admixtures. The results are displayed in figure 5. The Langmuir model correctly represented the isotherms obtained experimentally. At 8min of hydration time, the maximum amount of PCE1 adsorbed was higher (0.91 mg/g of cement) than that of PCE2 (0.67mg/g of cement) and PCE3 (0.89 mg/g of cement). However, the maximum amount of PCE3 adsorbed tended to be higher than that of PCE2, while the affinity to CSA (the slope of the linear part of the curve) of PCE2 (1.77) was much higher than that of PCE3 (0.27).

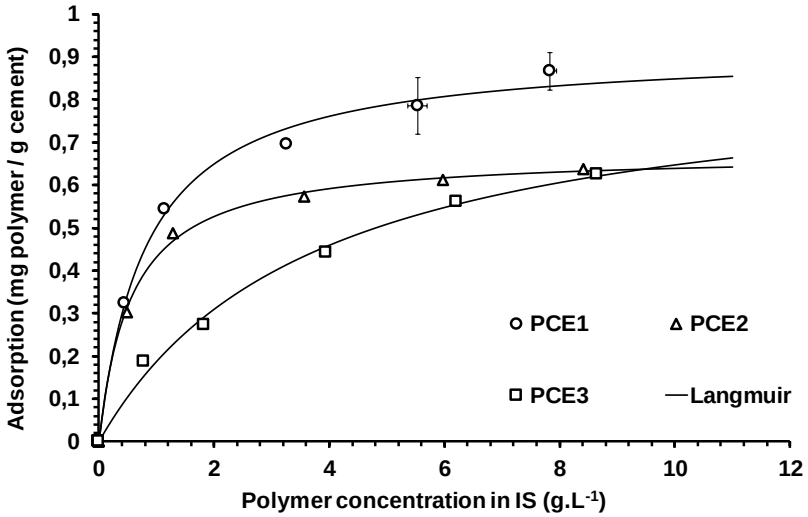


Figure 5. Adsorption isotherms of PCE1, PCE2 and PCE3 obtained at 8min

Figure 6 shows the evolution within time of the percentage in admixture adsorbed for PCE1, PCE2 and citric acid initially introduced at dosage of 0.2wt% in PCE-system, CA-system and PCE+CA-system. The percentages of PCE1 and PCE2 adsorbed at 8 min were around 35% and 29% respectively. Additional 16% of PCE2 adsorbs on the CSA based systems between 8 min and 38 min, whereas only additional 8% of PCE1 was adsorbed during the same time. This shows the faster consumption of PCE2 compared to that of PCE1. At 8min of hydration, citric acid adsorbed almost completely (97%). However, its adsorption decreased to 87% in PCE1+CA-system. Additionally, the adsorption of PCE1 decreases from 35%, in PCE1-system, to 10% in PCE1+CA-system. These results show that a competitive adsorption between citric acid and PCE1 occurred. In PCE2+CA-system, citric acid was adsorbed almost completely since the beginning of hydration, and then hindered almost completely the adsorption of PCE2 (only 4% of PCE2 was adsorbed at 8min of hydration).

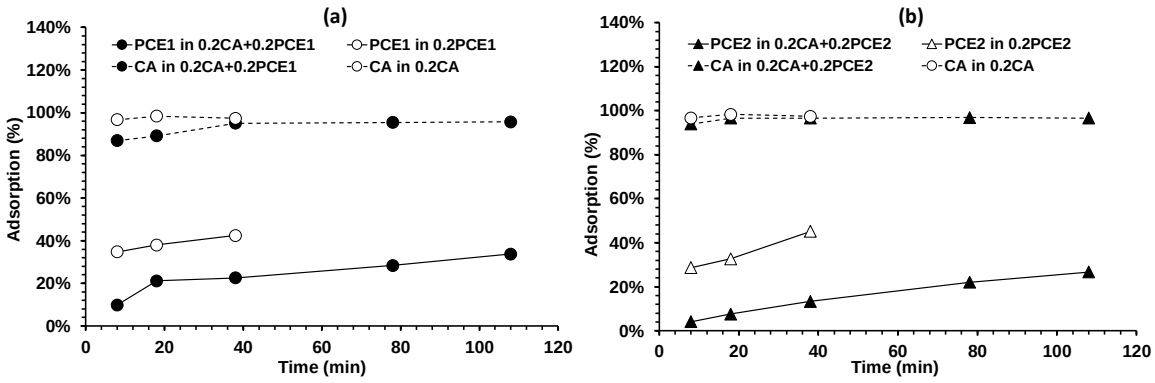


Figure 6. Adsorption of PCE1, PCE2 and CA in PCE-system, CA-system and PCE+CA-system

4. DISCUSSION

In CSA paste, PCEs affect the rheology and the hydration of the paste. On one hand, PCE decreases the yield stress. However, the yield stress increases quickly with time. Additionally, the dispersing effectiveness was higher for PCE1, followed by PCE2 and finally PCE3. On the other hand, PCE delays the hydration of the paste. The hydration retardation is higher for PCE3, followed by PCE1 and then PCE2. The reason of these effects can be summarized as follow:

According to Flatt & Houst (2001), PCE, added to a cement suspension, may be divided into three parts. The first part is consumed by co-precipitation, intercalation or micellization to form an organo-mineral phase (OMP). This part is considered as lost and is no longer available for dispersing cement particles. The second part is adsorbed onto the surface of cement particles and hydrates due to electrostatic interactions, and then side chains reduce inter-particle attractive forces (Van Der Waals) through steric hindrance. The last part consists of the PCE remaining in the supernatant. Only the adsorbed part of PCE reduces particles agglomeration, which decreases the yield stress of the paste. Tan et al. (2017), proposed a dispersion model describing the action mechanism of PCE on CSA paste. They suggested that, during hydration, ettringite would be formed and covered gradually the side chains of PCE, which decreases the dispersive effect of PCE within time until its disappearance when hydration layers cover all the side chains. Taking into account the high reactivity of CSA, the yield stress would increase quickly with time.

Quantifying the dispersing effectiveness of PCE is a difficult task and is further complicated by the hydration reactions of CSA. To overcome this difficulty, some authors have worked on inert systems. Dalas et al (2015) have studied the fluidizing efficiency of PCEs adsorbed on inert calcite suspensions, and at low adsorption amount. They found that the mass of adsorbed PCE was the best parameter to predict the fluidizing efficiency regardless of the PCE structure. Flatt et al. (2009) have studied the interactions of PCE with calcium silicate hydrates and found that, at high adsorption amount, dispersing effectiveness relies on layer thickness of adsorbed PCE, on backbone charge density and on surface coverage. In this case the increase of the side chain length leads to thicken the adsorbed layer rising the dispersing effectiveness. Based on this, the best dispersing effectiveness of PCE1 could be explained by its high adsorbed mass compared to PCE2 and PCE3. Additionally, it was found that PCE1 and PCE2 exhibit the same dispersing effectiveness at 8min of hydration time for the same adsorbed mass corresponding to 0.1 wt% of PCE1 and 0.2 wt% of PCE2. However, at high dosage (0.4%) PCE3 tends to adsorb more than PCE2, while its efficiency is lower than that of PCE2. This comes to the fact that PCE3 exhibited the shortest side chains, which explains its lower dispersing effectiveness.

Based on experimental results obtained, discussion above and taking into account the reactivity of CSA, dispersing effectiveness could be related to several parameters including the adsorbed amount, the layer thickness of adsorbed PCE, the surface coverage and also the quantity of OMP formed and PCE remaining in supernatant. The following interpretation can help in understanding the differences in dispersing effectiveness of these three PCEs. In CSA pastes, at the beginning, PCE adsorbs onto cement grains and first hydrates (ettringite) inducing dispersion. At same amount adsorbed, the longer the side chains are, the better the dispersing effectiveness. When hydration progresses, massive

precipitation of ettringite would occur and the effective side chains would be converted gradually to ineffective side chains. Dispersion effectiveness at a given time lies on effective side chains uncovered by CSA hydrates. Based on this, the small size of side chains of PCE1, compared to PCE2, is compensated by a slower hydration and thus a slower recovery of its side chains.

In presence of citric acid with PCE, the yield stress of CSA paste was lower compared to the reference sample. The Yield stress continues to decrease over time to reach a minimum, and then it starts to increase slowly over time. The presence of citric acid with PCE allows the retention of yield stress over time.

According to Plank & Winter (2008), citric acid forms highly negatively charged complex with Ca^{2+} and adsorb onto the surface of the cement grains. The layer formed is responsible for the hydration delay. In CSA when citric acid and PCE are present at the same time, highly charged complex of citrate compared to PCE, adsorbs almost completely at early age and partly hinder the adsorption of PCE. This can explain the higher initial yield stress of paste containing PCE and citric acid compared to the one containing PCE alone. As hydration progresses, more adsorption sites are available for adsorbing more PCE molecules, which explains the decrease in yield stress. Additionally, citrate complex delays hydration and then reduces the amount of hydrates formed. Consequently, the coverage rate of the side chains by hydrates is decreased, resulting in the retention of yield stress over time. Tan et al (2017) investigated the effect of borax on the dispersing effectiveness of PCE in CSA paste. They found that, depending on the dosage, borax can increase or decrease the dispersing effectiveness of PCE. Small amount of borax can decrease the amount of hydrates formed resulting in an increase of the dispersion, while great amount of borax generates competitive adsorption resulting in a decrease of the dispersion.

5. CONCLUSION

The effect of three different PCE on the hydration and rheology of CSA was investigated. PCE adsorb onto the surface of cement grains inducing their dispersion by steric hindrance. PCE1 exhibit the highest dispersing effectiveness compared to PCE2 and PCE3. In a reactive system, the dispersing effectiveness of PCE that have the same chemical structure relies on adsorbed amount of PCE, the length of their side chains and the hydration delay they induce. At equal adsorbed mass, the longer the effective side chains are the better the dispersing effectiveness. Additionally, the effect of citric acid on dispersion of PCE in CSA was also investigated. Citric acid, which forms highly charged complex compared to PCE, adsorbs almost completely and partly hinders the adsorption of PCE, which decreases the dispersion effectiveness of PCE at early age. However, citric acid delays hydration and then decreases the amount of hydrates formed over time. This leads to retain dispersion effectiveness over time.

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