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# Effect of citric acid and polycarboxylate superplasticizers (PCE) on hydration and rheology of sulfoaluminate cement

R. BELHADI, A. GOVIN, and P. GROSSEAU

**Synopsis:** The production of ordinary Portland cement (OPC) accounts for about 5%-7% of the total man-made CO<sub>2</sub> emissions. One of the low CO<sub>2</sub> alternatives to OPC is sulfoaluminate cement (CSA), mainly composed of ye'elite (C<sub>4</sub>A<sub>3</sub>S), belite (C<sub>2</sub>S) and sulfate source (CS or CS<sub>2</sub>H<sub>2</sub>). Its main hydrated phase is ettringite (C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>). CSA are known for their poor workability and their short setting time, which require the use of superplasticizers and retarders.

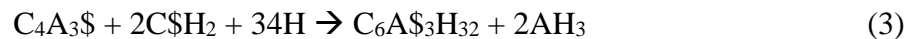
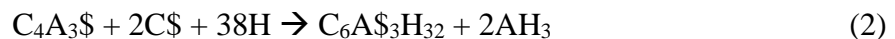
The aim of this work is to investigate: (i) the effect of citric acid and polycarboxylate superplasticizers (PCE) on the hydration and rheology of CSA; and (ii) the effect of citric acid on the dispersing effectiveness of PCEs. Two PCEs, with the same chemical structure and different molecular structure, were studied. Isothermal calorimetry and thermogravimetric analysis (TGA) were used to describe the hydration process, while rheological properties were characterized with a flow test. Adsorption measurements were carried out with total organic carbon analyzer and ionic chromatography. The results show that the combination of citric acid and PCE allows better retention of workability over time. However, a competitive adsorption between citric acid and PCE decreases the initial dispersion.

**Keywords:** CSA, citric acid, competitive adsorption, dispersing effectiveness, hydration, polycarboxylate superplasticizer (PCE)

## INTRODUCTION

Cement industry is one of the largest industrial sources of CO<sub>2</sub> emissions worldwide. The production of Portland cement accounts for about 5%-7% of the total man-made CO<sub>2</sub> emissions [1]. Sulfoaluminate cement (CSA), mainly composed of ye'elite (C<sub>4</sub>A<sub>3</sub>S), sulfate source (CS or CS<sub>2</sub>H) and small amount of belite (C<sub>2</sub>S), is one of the potential alternatives to Portland cement that allow reducing CO<sub>2</sub> emissions. CSA is widely used in small-scale repairs such as fast construction engineering, offshore and corrosion resistance engineering and emergency repairs [2-3]. However, many obstacles prevent more widespread usage of this type of cement, especially in larger scale placements [4].

The mechanism of CSA hydration depends on the cement clinker composition and particularly on the amount and reactivity of calcium sulfate they contain [5]. The main hydrated phases of CSA are ettringite (C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>), monosulfoaluminate (C<sub>6</sub>A<sub>3</sub>H<sub>12</sub>) and aluminium hydroxide (AH<sub>3</sub>), which results from dissolution and precipitation processes of sulfate source (anhydrite or gypsum) and ye'elite phases. With a sufficient amount of calcium sulfate, only ettringite and AH<sub>3</sub> are formed according to the following equations [6-7-8].



Due to their poor workability and short setting time, CSA need to be admixed with superplasticizers and retarders to allow their use in larger scale [9]. In modern concrete, Polycarboxylate ether (PCE) are the most used superplasticizers. They adsorb onto particle surfaces inducing their dispersion through steric hindrance [10]. However, their dispersing effectiveness decreases quickly over time [11]. According to Dallas et al. [12], the dispersing effectiveness of PCE relies on the adsorbed amount of the later, while Flatt et al. [10] linked the dispersion effectiveness of PCE to their molecular structure, more specifically to the length of their side chains.

One way to overcome the quick loss of workability of systems containing PCE is combining the later with retarders (citrate, gluconate, tartrate, sodium, borax...) because these retarders delay the formation of hydration products and thus reduce the consumption of free water and PCE [9]. However, the combination of several admixtures in concrete can cause undesired interactions. Competitive adsorption may occur between highly charged citrate and PCE and affects the dispersing effectiveness of the later. Plank & Winter [13] 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 decreases the workability. The aim of this work is to investigate (i) the effect of PCE and citric acid on the hydration and rheology of CSA; and (ii) the effect of citric acid on the dispersing effectiveness of PCE.

# MATERIALS AND METHODS

## Binder

A commercial CSA was investigated. Table 1 shows the chemical composition of CSA obtained by X-Ray fluorescence (XRF) and the phase composition determined by X-Ray diffraction and quantified using Rietveld algorithm.

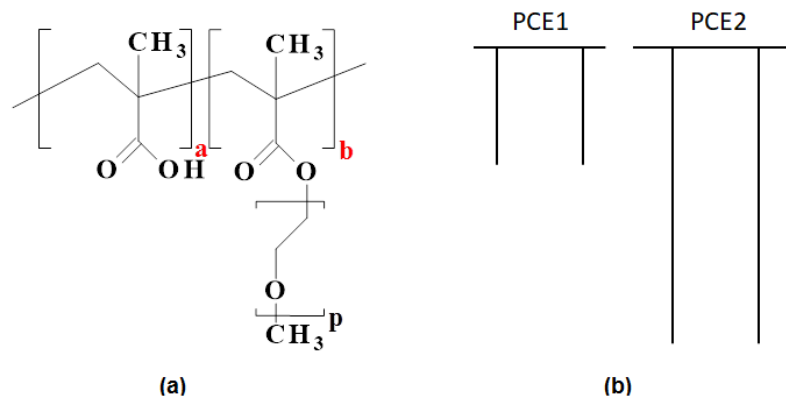
**Table 1**—Chemical and phase composition of CSA

Chemical composition (%)	O	Ca	Al	S	Si	F	Mg	Fe	K	Cl
	43.3	27.3	12.3	7.8	3	1.8	1.5	0.8	0.4	0.1
Phase composition (%)	C <sub>4</sub> A <sub>3</sub> S		C <sub>2</sub> S		C\$		Other			
	49.4		8		21.9		20.7			

## Admixtures

Two comb-type polycarboxylate superplasticizers (PCE1 and PCE2), with the same chemical structure, i.e. polymethacrylic acid backbone and grafted side chain of polyethylene oxide (Figure 1a), were used for this study. Their molecular structure is different since PCE2 exhibits longer side chains than PCE1. 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.

A commercial citric acid (99.5% Honeywell) was used. In this paper, citric acid will be noted as CA.



**Fig. 1**— Schematic illustration of the molecular structure of PCEs

**Table 2**— Main characteristics of PCEs

	Solid content (%)	Mw (g/mol)	Charge density (mmol/mol)	P	N (=a+b)	n	Backbone conformation
PCE1	20	48300	38.16	45	5	12	FBW
PCE2	25	138600	41.58	114	5	15	FBW

FBW = Flexible Backbone Warm according to Gay & Raphael (2001) [14]

## Paste preparation

Cement pastes were prepared with Milli-Q water at a fixed water-to-cement ratio (W/C) of 0.4. The dosage of PCE was from 0.1% to 0.4 % by mass of cement with 0.1% increment, while CA was introduced at a dosage of 0.2 wt%. Pastes were mixed according to the standard NF EN 196-1 excepted pastes prepared for calorimetry tests. The solvent exchange technique was used for stopping the hydration. A 50 ml of isopropanol was added to the crushed sample, and then the suspension was vacuum filtered. The retentate was rinsed once with isopropanol and twice with diethyl ether. Finally, the residue was dried in an oven at 40°C, grounded in a mortar to below 100 μm, and then stored in a desiccator over silica gel until analysis.

### Mini slump test

The test consists of measuring the spread 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, as the diameter of the spread paste. The measurements were realized 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 yield stress of the paste was calculated from the spread value as follow [15]

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

where  $\tau_0$  is the yield stress,  $\rho$  = paste density,  $V$  = volume of the cone,  $R$  = radius of the paste spread and  $\lambda$  is a constant linked to the liquid vapor interfacial energy and the wetting angle on the plate. In this paper,  $\lambda$  is fixed at 0.003 [12]

### Isothermal calorimetry

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 thanks to a small stirrer. Samples of 1.5g approximately were placed into the calorimeter. The heat flow was recorded for 48 hours.

### Thermogravimetric analysis (TGA)

TG measurements were carried out on samples for which the hydration was previously stopped. Around 150 mg of sample was introduced into a TG 92 SETARAM for determining the weight loss as a function of temperature. The temperature range was 30-900°C with a heating rate of 10°C/min under He atmosphere. The software Fityk was used to fit DTG curves and integrate the peaks area. The latter correspond to the amount of hydrates formed. Results were normalized to 100 g of paste.

Per 100 g paste:

$$hydrate_{paste} = \frac{hydrate_{measured}}{(1 - H_2O_{bound})(1 + \frac{W}{C})}$$

where  $H_2O_{\text{bound}}$  was calculated from the difference between the mass loss of sample dried at 105 and 600 °C and  $\frac{w}{c} = 0.4$ .

## Adsorption

The amount of polymer adsorbed 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 CA and PCE were combined, 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.

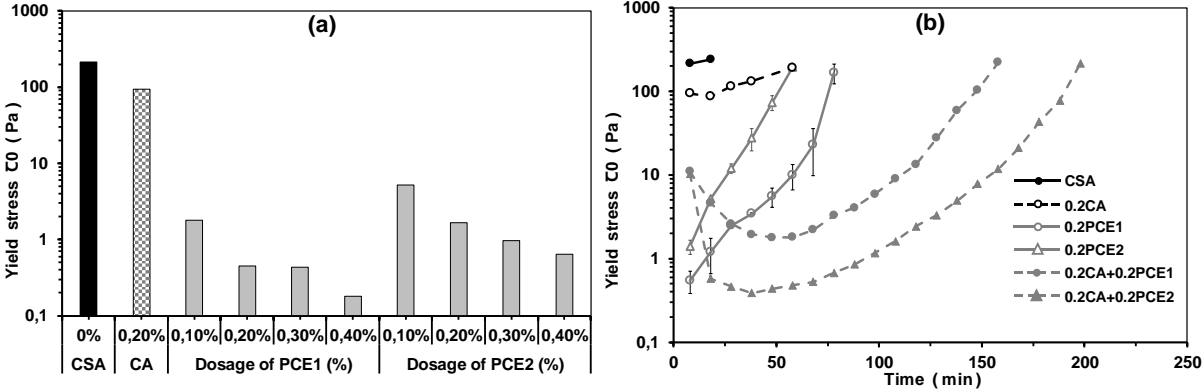
## Results

### Yield stress

Figure 2a shows the yield stress of CSA paste and CSA pastes containing (i) 0.2 wt% of CA; and (ii) from 0.1 wt% to 0.4 wt% of PCE1 and PCE2 after 8min of hydration. The yield stress of CSA paste made without admixture is more than 200 Pa, which shows the poor workability of this paste. The yield stress decreases with the increasing dosage in PCE. At 0.1 wt%, PCE1 reduces the yield stress to 2 Pa, while PCE2 reduces the latter to 5 Pa. At 0.4 wt%, both PCE (1 and 2) reduce significantly the yield stress to less than 1 Pa. This shows that only small amount of PCE1 and PCE2 is needed for the improvement of CSA paste workability. In addition to that, the dispersing effectiveness of PCE1 is higher than that of PCE2.

Figure 2b shows the evolution of the yield stress within time for the different admixtures used with a dosage of 0.2 wt%. PCE1 and PCE2 decreases significantly the initial yield stress of the paste. However, a fast increase in yield stress is noticed over time. On the contrary, CA decreases slightly the initial yield stress, but retain it over time. By combining CA (0.2 wt%) with PCE1 (PCE2) (0.2 wt%), the initial yield stress of the paste decreased compared to CSA without admixtures. Additionally, the yield stress decreases throughout time to reach a minimum equal to the initial yield stress obtained when PCE1 (PCE2) was introduced alone. Then the yield stress starts to increase slowly over time. This shows that the combination of CA

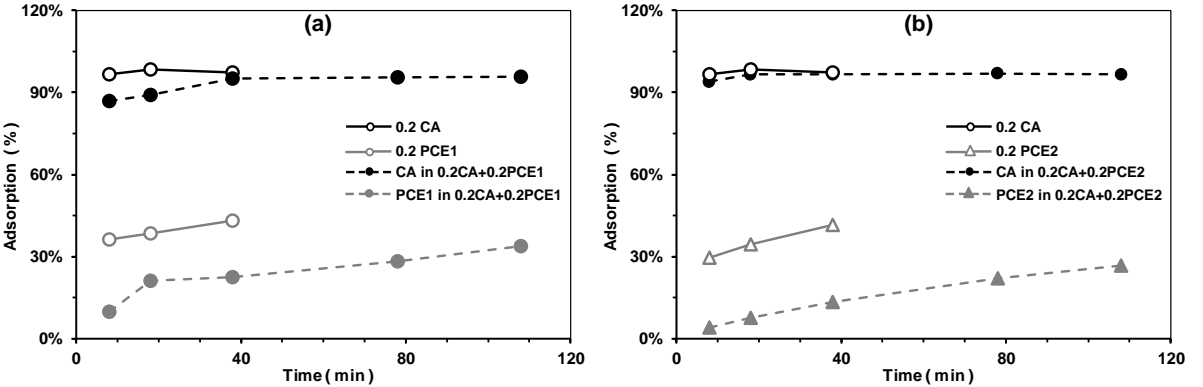
with PCE slows down the slump loss within time. It should be noted that the effect on yield stress induced by the combination of CA and PCE is not cumulative.



**Fig. 2.** (a) Yield stress at 8min as a function of admixture’s dosage (b) yield stress as a function of time

**Adsorption**

Figure 3 shows the evolution within time of the percentage in admixture adsorbed for PCE1, PCE2 and CA initially introduced at a dosage of 0.2wt% in PCE-system, CA-system and PCE+CA-system. After 8 min of hydration, PCE1 and PCE2, introduced alone, adsorb at a percentage of 35% and 29%, respectively. Citric acid adsorbed almost completely (97%) after 8 min of hydration. However, its adsorption decreased to 87% in presence of PCE1. Additionally, the adsorption of PCE1 (PCE2) decreases from 35% (29%), in PCE1-system (PCE2-system), to 10% (4%) in presence of citric acid. These results show that a competitive adsorption between citric acid and PCE occurred, which explain the higher initial yield stress of the paste containing both citric acid and PCE compared to the paste containing only PCE. At 40min of hydration, the adsorbed amount of PCE in presence of CA is lower than its adsorption when introduced alone. However, the yield stress of the paste containing both CA and PCE at 40min is lower than that of the paste containing only PCE1. This shows that CA improved the dispersing effectiveness of PCE.



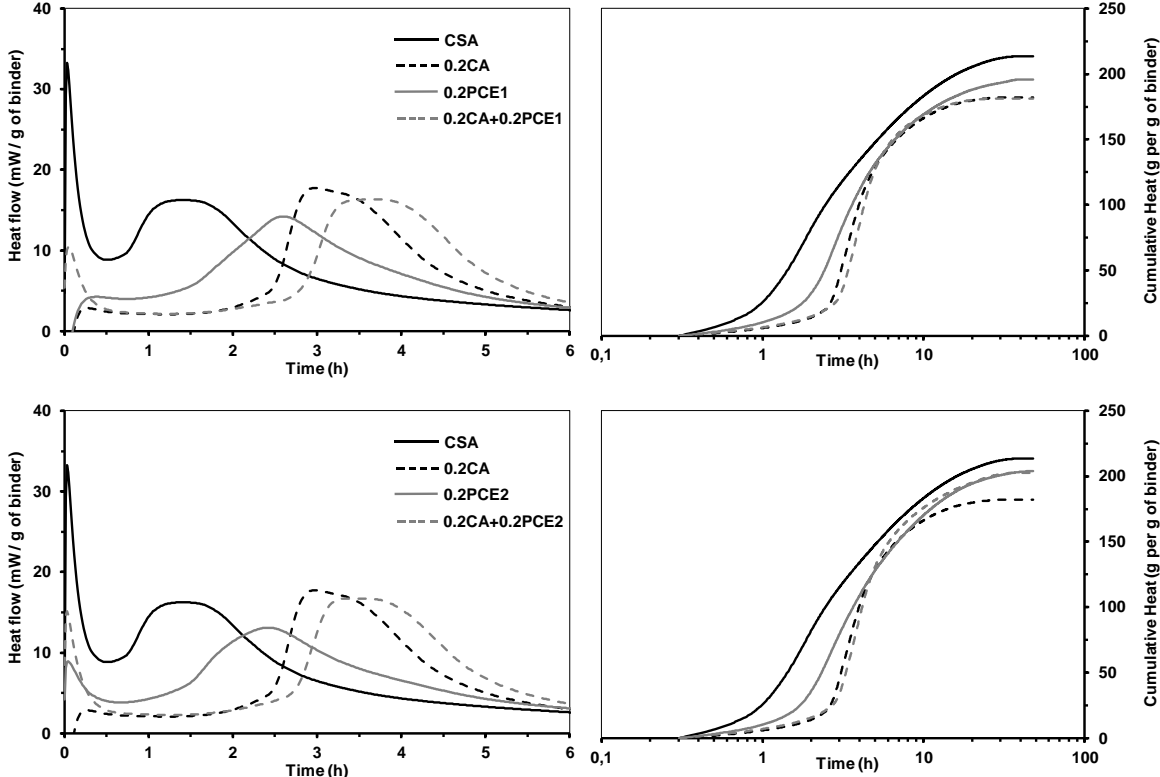
**Fig. 3.** Adsorption within time of PCE1, PCE2 and CA in PCE-system, CA-system and PCE+CA-system

**Isothermal calorimetry**

The heat flow and the cumulative heat curves of CSA pastes made with 0.2 wt% of PCE1, PCE2 and CA are plotted in Figure 4. After contact with water, CSA phases dissolves rapidly which

lead to high amount of heat released in the first seconds to minutes. This means that the intensity of the initial peak should be high. However, some experiments revealed an endothermic behavior. The reason behind this endothermic behavior is related to the external mixing and the sensitivity of the calorimeter. 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 acceleration of ettringite and  $\text{AH}_3$  formation [15]. CA lengthens the induction period by 3.47 times than the reference sample. This shows the retardation effect of CA on CSA cement. PCEs has less effect on the induction period than citric acid. PCE1 delays slightly more the hydration than PCE2. When combining citric acid with PCE1 (PCE2), the induction period was lengthened by 3.89 (3.78) times than the reference sample but the delayed effect was not additive. When citric acid was present in the paste the pic intensity was almost the same as the reference sample, while in presence of PCE the intensity of the pic was lower than the reference sample. This shows that PCE lowers the hydration kinetics while citric acid mainly increases the induction period.

The hydration of CSA is dominated by the dissolution of ye'elimite and anhydrite, and the formation of ettringite and  $\text{Al}(\text{OH})_3$  at early age. This makes the cumulative heat proportional to hydration degree at early ages. Before 4 hours of hydration, samples containing admixtures exhibit less cumulative heat than the reference sample, which highlights the hydration delay induced by these admixtures. After 4 hours of hydration, a quick increase of the cumulative heat of sample containing citric acid until it almost joins the reference. In the contrary, cumulative heat of samples containing PCE increases slowly after 4 hours of hydration to join the reference. This shows that citric acid and PCE have different acting mechanisms on the hydration of CSA.

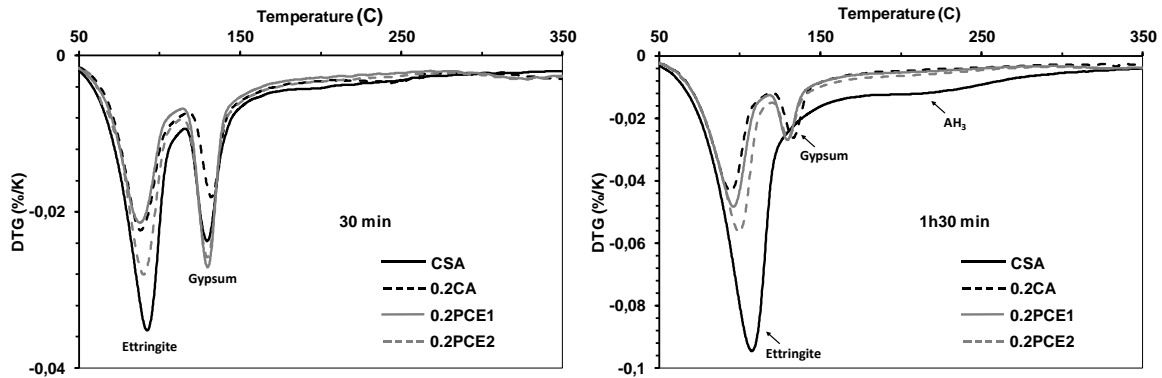


**Fig. 4.** Heat flow and cumulative heat of CSA made with PCE1, PCE2 and CA at a dosage of 0.2 wt%, as a function of time



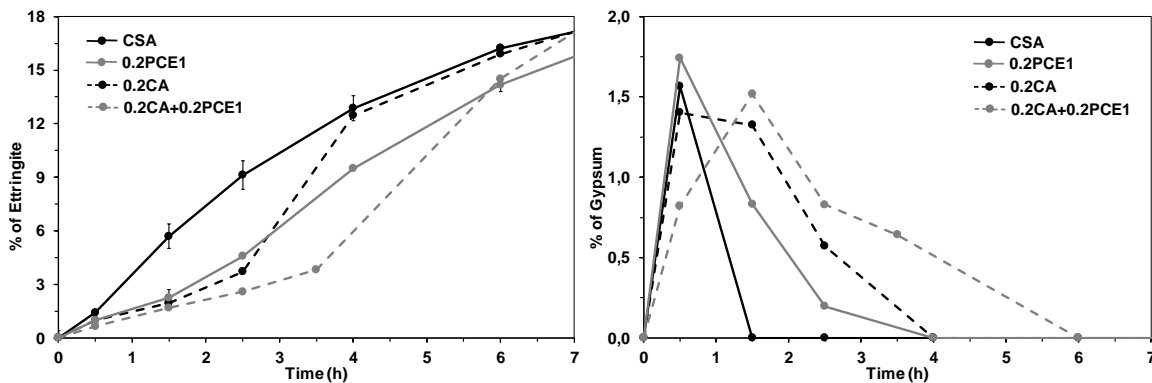
## Thermogravimetric analysis

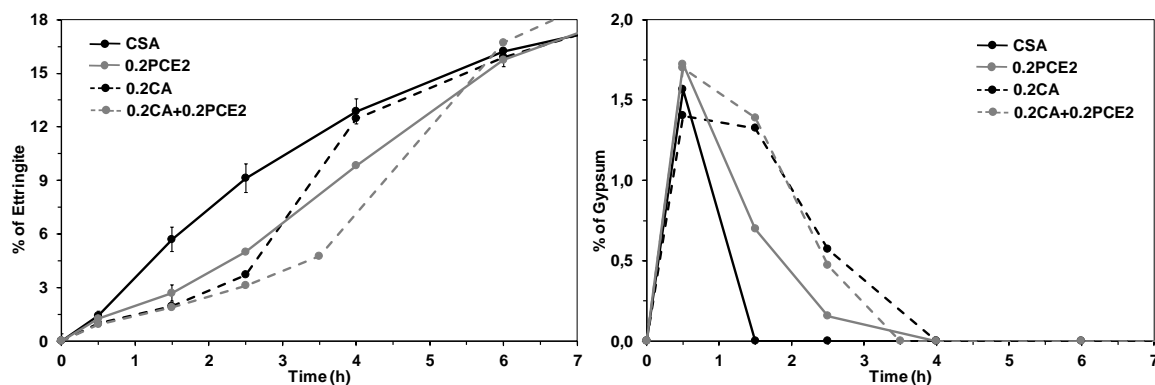
Figure 5 shows the DTG curves of pastes containing admixtures at a dosage of 0.2 wt% and after 30min and 1h30min of hydration. The first pic is related to the decomposition of ettringite (temperature range 60°C\_120°C) and the second one originates from the decomposition of gypsum (temperature around 140°C). The decomposition of  $AH_3$  occurs within the temperature range of 180°C\_300°C [16].



**Fig. 5.** DTG curves of CSA pastes admixed with CA, PCE1 and PCE2 after 30min and after 1h30min of hydration.

Figure 6 shows the amount of ettringite and gypsum present in samples containing CA, PCEs and both (CA+PCE) at a dosage of 0.2 wt%. The amount of ettringite was lower for samples containing admixtures. Before 4h, the amount of ettringite was almost the same for samples containing CA or PCEs. After 4h, the formation of ettringite increases quickly for samples containing CA to join the reference sample, while it increases slowly for samples containing PCEs. This is in agreement with the calorimetric results and shows that PCEs changes the hydration kinetics, while CA blocked the hydration for a while and then it resumes in the same way as the reference sample. Furthermore, gypsum was formed and then consumed during the hydration. In the case of CA, more amount of gypsum was formed and was slowly consumed over time. When PCEs were used, the amount of gypsum formed was the same as the reference sample, but its consumption was slower. After 4h of hydration, all gypsum was consumed with ye'elinite to form ettringite. The combination of CA with PCE decreases significantly the amount of ettringite formed over time. In 0.2CA+0.2PCE1, the depletion of gypsum was extended by 2 hours compared to the 0.2CA and 0.2PCE1. It should be noted that the delayed effect on formation of hydrates is not additive when combining citric acid with PCEs.





**Fig. 6.** Amount of Ettringite and Gypsum over time of pastes containing CA, PCE1, PCE2, CA+ PCE1 and CA+PCE2

## Discussion

The workability of pastes containing citric acid and two PCEs having the same chemical structure but different molecular structure was investigated using the mini-slump test. It was found that PCEs improved the initial workability of CSA pastes with a better dispersing effectiveness of PCE1 compared to PCE2. However, a quick loss of workability was seen over time. Flatt & Houst reported that PCE, added to a cement suspension, might be divided into three parts [17]. The first part forms an organo-mineral phase (OMP) by co-precipitation, intercalation or micellization. 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, resulting in a decrease in the yield stress of the paste. Based on this, the dispersing effectiveness of PCE on CSA lies on the adsorbed amount of PCE and the steric hindrance induced by PCE's side chains. According to Tan et al. [9], during hydration of CSA, 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, this model explains the quick loss of workability of CSA pastes containing PCE. To understand the differences in dispersing effectiveness of PCEs regarding their molecular structure, Dalas et al. have studied the fluidizing efficiency of PCEs adsorbed on inert calcite suspensions, and at low adsorption amount [12]. They found that the mass of adsorbed PCE was the best parameter to predict the fluidizing efficiency regardless of the PCE structure. Furthermore, Flatt et al. 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 the surface coverage [10]. In this case, the increase of the side chain length leads to thicken the adsorbed layer rising the dispersing effectiveness. In our case, the PCE1 exhibit shorter side chains than PCE2 but the adsorption amount of PCE1 was higher than that of PCE2. Although the PCE2 side chains are longer, they may adopt different configuration than PCE1's side chains on the surface of the particles, leading to a better dispersing effectiveness of PCE1 compared to PCE2. The combination of PCEs and citric acid decreases the quick loss of workability over time. However, it decreases the initial workability compared to pastes containing only PCEs. According to Plank & Winter, citric acid forms highly negatively charged complex with  $\text{Ca}^{2+}$

and adsorb onto the surface of the cement grains [13]. These complexes decrease the rate of nucleation and growth of hydrates. When combining citric acid with PCE, 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 leads to 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. This is in agreement with the results found by Tan et al. concerning the effect of borax on the dispersing effectiveness of PCE in CSA paste [9]. They found that, depending on the dosage, borax could increase or decrease the dispersing effectiveness of PCE. Small amount of borax could 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 in the dispersion.

## **Conclusion**

The effect of the molecular structure of PCEs on their dispersion effectiveness was investigated. PCE1 with shorter side chains and PCE2 with longer side chains were used in this study. Both PCE1 and PCE2 improved the initial workability of CSA pastes with a better dispersing effectiveness of PCE1 compared to PCE2. However, a quick loss of workability was seen over time. On the contrary, citric acid improved slightly the initial workability but retain it over time. The combination of citric acid with PCE decreases the quick loss of workability. However, it decreases the initial workability compared to pastes containing only PCEs. The adsorption of PCEs and the hydration of CSA were investigated to understand the differences in effect of these admixtures. It was found that PCE1 adsorbs more than PCE2. Additionally, citric acid forms highly charged complex that 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. Consequently, less side chains were covered and workability was retained over time.

## **References**

- [1] Damtoft JS, Lukasik J, Herfort D, Sorrentino D & Gartner EM (2008). Sustainable development and climate change initiatives. *Cement Concrete Research*, Volume 38, Issue 2, pp115–127.
- [2] Qian J, You C, Wang Q, Wang H & Jia X (2014). A method for assessing bond performance of cement-based repair materials. *Construction Build Materials*, volume 68, pp307-313.
- [3] Guo W, Sun N, Qin J, Zhang J, Pei M, Wang Y & Wang S (2012). Synthesis and properties of an amphoteric polycarboxylic acid-based superplasticizer used in sulfoaluminate cement. *Journal of Applied Polymer Science*, volume 125, pp283-290
- [4] Lisa E. Burris & Kimberly E. Kurtis (2018). Influence of set retarding admixtures on calcium sulfoaluminate cement hydration and property development. *Cement and Concrete Research*, volume 104, pp105-113.

- [5] Sahu S, Havlica J, Tomkova V & Majling J (1991). Hydration behaviour of sulfoaluminate belite cement in the presence of various calcium sulfates. *Thermochimica Acta*, volume 175, issue 1, pp45-52.
- [6] Zhang L (2000). Microstructure and performance of calcium sulfoaluminate cements. University of Aberdeen, Scotland.
- [7] C.W. Hargis, A.P. Kirchheim, P.J.M. Monteiro & E.M. Gartner (2013). Early age hydration of calcium sulfoaluminate (synthetic ye'elimite) in the presence of gypsum and varying amounts of calcium hydroxide. *Cement and Concrete Research*, volume 48, pp105-115.
- [8] S.W. Tang, H.G. Zhu, Z.J. Li, E. Chen & H.Y. Shao (2015). Hydration stage identification and phase transformation of calcium sulfoaluminate cement at early age. *Construction and Building Materials*, volume 75, pp11-18.
- [9] Tan H, Guo Y, Zou F, Jian S, Ma B & Zhi Z (2017). Effect of borax on rheology of calcium sulfoaluminate cement paste in the presence of polycarboxylate superplasticizer. *Construction and Building Materials*, Volume 139, pp277-285.
- [10] Flatt RJ, Schober I, Raphael E, Plassard C & Lesniewska E (2009). Conformation of Adsorbed Comb Copolymer Dispersants. *Langmuir* 2009, Volume 25, Issue 2, pp845-855.
- [11] Winnefeld F (2012). Interaction of superplasticizers with calcium sulfoaluminate cements. Published as part of supplementary papers of the tenth International conference on superplasticizers and other chemical admixtures in concrete held in Prague, Czech Republic, 28-31 October 2012.
- [12] Dalas F, Pourchet S, Nonat A, Rinaldi D, Sabio S & Mosquet M (2015). Fluidizing efficiency of comb-like superplasticizers: the effect of the anionic function, the side chains length and the grafting degree. *Cement and Concrete Research*, volume 71, pp115-123.
- [13] Plank J & Winter Ch (2008). Competitive adsorption between superplasticizer and retarder molecules on mineral binder surface. *Cement and concrete Research*, volume 38, pp599-605
- [14] Gay C & Raphael E (2001). Comb-like polymers inside nanoscale pores. *Colloid Interface Science*, volume 94, pp229-236.
- [15] Zimmermann J, Hampel C, Kurz C, Frunz L & Flatt RJ (2009). Effect of Polymer Structure on the Sulfate-Polycarboxylate Competition. Published as part of proceedings of the ninth ACI International conference on superplasticizers and other Chemical Admixtures in Concrete held in Seville, Spain, 13-17 October 2009.
- [16] B. Lothenbach, P. Durdzinski & K. De Weerd (2013). A practical guide to microstructural analysis of cementitious materials. Taylor & Francis Group, pp177-211.
- [17] Flatt RJ & Houst YF (2001). A simplified view on chemical effects perturbing the action of superplasticizers. *Cement and Concrete Research*, volume 31, Issue 8, pp1169-1176.