



# Effets des superplastifiants de types polycarboxylates et de l'acide citrique sur l'hydratation et la rhéologie des ciments sulfoalumineux-bélitique

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# Hydration and rheology of sulfoaluminate-belite cements (SAC) in presence of polycarboxylate superplasticizers (PCE) and citric acid

R. Belhadi\*, A. Govin & P. Grosseau

Mines Saint-Etienne, Univ Lyon, CNRS UMR 5307 LGF, Centre SPIN, Département PMMG, F - 42023 Saint-Etienne France  
 \* rachid.belhadi@emse.fr

## 1. Context

**SAC** + **PCE** + **Citric acid (CA)**

- + Greener than OPC
- Poor workability
- Fast setting
- Dispersing effectiveness
- Hydration delay
- Rheological properties

Dispersing effectiveness of PCE may be affected by :

- Reactivity of SAC
- Competitive adsorption between Citric acid and PCE

## 2. Objectives

Understand the :

- Effect of the chemical structure of PCE on the hydration and rheology of reactive SAC
- Effect of combination of citric acid with PCE on hydration and rheology of reactive SAC

## 4. Methods

## 3. Materials

Commercial SAC (i.tech ALI CEM)	Phase composition of SAC (%)	$C_4A_3\$$	$C_2S$	$C\$$
Citric acid (99,5% Honeywell)	49,3	15,1	23,5	
3 polycarboxylates ethers (PCE1, PCE2 and PCE3)				

	Mw (g/mol)	Charge density (mmol/g)	P	N	n
PCE1	48300	0,79	45	5	12
PCE2	138600	0,3	114	5	15
PCE3	11900	0,96	17	2,5	115

PCE structures:

PCE1: [CH2]n-C(=O)-CH(OH)-C(=O)-CH2-

PCE2: [CH2]n-C(=O)-CH(OH)-C(=O)-CH2-CH2-

PCE3: [CH2]n-C(=O)-CH(OH)-C(=O)-CH2-CH2-CH2-

## 5. Results

### Setting-Time

**Initial Setting**: SAC (black line) has the shortest setting time (~40 min). CA (red line) delays setting significantly (~140 min at 0.4 wt%). PCEs (orange, green, purple lines) show intermediate setting times (~60-80 min).

**Final Setting**: SAC (black line) has the shortest final setting time (~50 min). CA (red line) delays final setting (~180 min at 0.4 wt%). PCEs (orange, green, purple lines) show intermediate final setting times (~80-100 min).

Annotations: Short setting time of SAC without admixtures. CA delays significantly the Initial and Final setting times. % in PCE → Initial & Final setting: PCE1 > PCE2 ≈ PCE3. PCE + CA → Initial & Final setting: PCE+CA > CA > PCE. PCE1 + CA ≈ PCE2 + CA.

### Spread flow / Yield stress

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

Yield stress  $\tau_0$  (Pa) vs Time (min). SAC shows the highest initial fluidity ( $\tau_0$ ). PCE1 shows the lowest initial fluidity ( $\tau_0$ ). Workability retention over time is observed for CA + PCE.

Annotations: Initial  $\tau_0$  with PCE1 < PCE2 < PCE3. Dispersion efficiency of PCE1 > PCE2 > PCE3.

### Adsorption

**PCE**: Langmuir-like curves for PCE1, PCE2, and PCE3. PCE1 has the highest affinity for SAC.

**PCE + CA**: Adsorption of CA decreases PCE adsorption. CA adsorption increases over time.

Annotations: Affinity of PCE with SAC: PCE1 > PCE2 > PCE3. Maximum adsorption: PCE1 > PCE3 > PCE2. Explain the better dispersing efficiency of PCE1 and the lowest dispersing efficiency of PCE3.

## 6. Conclusions & Perspectives

<b>PCE</b>	<b>Setting time</b> : PCE1 > PCE2 ≥ PCE3 <b>Dispersing effectiveness</b> : PCE1 > PCE2 > PCE3 <b>Adsorption</b> : PCE1 > PCE2 > PCE3	<b>CA</b>	<b>Setting time</b> : CA > PCE <b>Adsorption</b> : CA > 97% >> PCE	<b>CA + PCE</b>	<b>Setting time</b> : PCE + CA > CA > PCE <b>Adsorption</b> : CA > 87% > PCE & PCE < PCE alone <b>Effect</b> ↗ Initial fluidity compared to PCE alone ↗ Workability retention over time
TGA & DRX are required to follow the hydration	Rheological properties	The amount of PCE consumed by intercalation	CA reduces the amount of ettringite at early age	Hypothesis	

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