

## Retarding cement hydration by increasing temperature

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### Biography:

**Dr. Marta Palacios**, Ph.D. in Chemistry, is a senior researcher at Eduardo Torroja Institute for Construction Science. Her research interests include the impact of chemical admixtures on rheological properties and hydration of cementitious materials.

**Dr. Daniel Sanz-Pont** obtained his PhD working on mix design, hydration and material properties of aerogel with calcium sulphate binders. His research paper entitled “Anhydrite/aerogel composites for thermal insulation” (Nov 2015) published in *Materials and Structures* was selected by the RILEM’s Board-of-Editors as one of the ten “outstanding papers” for 2016. Currently he works as a postdoctoral researcher at ETH Zurich on aerogel-based ultra-high performance thermal insulation via Digital Fabrication and on chemical admixtures and mix design of cementitious binders and mortars.

**Dr. Ratan Mishra** obtained his PhD in Polymer Engineering in the area of development of Interface force field (IFF) for the molecular dynamics simulations of construction minerals and inorganic-organic hybrid structures. His research has been also focused on multi-scale modeling of chemical admixtures to increase the energy efficiency of clinker particle grinding and reactivity of cement. He received the Sandmeyer Award 2016 from the Swiss Chemical Society and a 2017 Outstanding Collaborator Award from Sika Corporate Research, Switzerland

**Federica Boscaro** is a Ph.D. student of the group of Physical Chemistry of Building Materials at the Institute of Building Materials at ETHZ. Her project is focused on the development of compatible superplasticizers for low clinker concrete.

**Dr. Delphine Marchon** obtained her Ph.D. working on cement hydration and chemical admixtures. More specifically, she focused on the delay of cement hydration induced by comb-shaped polycarboxylate superplasticizers with respect to their molecular structure.

**Lex Reiter**, is a Civil Engineer working in the field of digital fabrication with concrete. His work focusses on the control of hydration and hardening kinetics for novel processes such as layered extrusion and slipforming.

**Dr. Sara Mantellato** is chemist and has great experience on chemical admixtures. In particular, her research is focused on the governing mechanism of the flow loss of superplasticized cementitious materials.

**Prof. Dr. Robert Flatt** is Professor of Building Materials at ETHZ. Before that he was Principal Scientist at Sika Technology AG and postdoctoral researcher at the Princeton University. He owns a master in Chemical Engineering and a PhD from EPFL. He has received various awards among which the *RILEM Robert L'Hermite Medal*, the *Ross C. Purdy* and the *Brunauer* awards from the American Ceramic Society, as well an *Outstanding Research Contribution in the Broad Area of Chemical Admixtures* presented at the 10<sup>th</sup> International Conference on Superplasticizers and Other Chemical Admixtures.

## ABSTRACT

Specific polymer structures at particular dosages have been identified to be able to delay cement hydration as temperature increases. The aim of the present work is to understand the underlying mechanisms involved behind this unexpected phenomenon. In particular, hydration kinetics of chemically admixed cement pastes at different temperatures have been related to the mineralogical changes in pastes, chemical composition of the pore solution and rheological properties.

Results have demonstrated a dramatic increase in the low- concentration elements (Si, Al, Mg and Fe) in the pore solution of admixed samples hydrated at room temperature. At this temperature, nano-particles (polymer aggregates involving complexes and/or organo-aluminates) have been detected. In contrast, nano-particles are not present at higher temperatures, when the delay of hydration is observed. This could lead to a higher amount of free polymer in the pore solution leading to a greater delay of silicates hydration.

**Keywords:** chemical admixtures, cement hydration, rheology, pore solution

## INTRODUCTION

It is well-known that kinetics of cement hydration can be modified by parameters such as chemical and mineralogical composition of cement, temperature and chemical admixtures [1], [2], [3]. In particular, the rate of hydration of cement increases with the raise of temperature, leading to higher early strength. Pore solution composition, morphology and microstructure of hydration products are directly linked to the curing temperature. An increase of the apparent density of C-S-H and a more heterogenous precipitation of hydration products have been obtained as temperature rises [4] and, above 50 °C, AFm phases are more stable than ettringite [5].

Nowadays, comb-copolymers superplasticizers (PCEs) are essential components of concrete to increase its fluidity while maintaining low water/cement ratio, enhancing its mechanical strength and durability. However, PCEs cause a strong retardation that depends on the molecular structure and dosage of polymer [1], [6], [7]. The mechanism involves the inhibition of the silicates dissolution by the polymer adsorption on the reactive sites [1]. While, the retardation of PCEs on cement hydration has been widely studied, very few studies have been performed regarding the influence of the temperature on the hydration

kinetics of superplasticized cements. This can be extremely relevant in applications such as mass concrete, pre-casting or even well cementing.

In the present study, for the first time, it will be shown that it is possible to delay cement hydration as the temperature increases by using specific dosages and structures of comb-copolymer superplasticizers. An extensive investigation of the pore solution composition, rheological properties and microstructure has been performed to identify the mechanism behind such unexpected behaviour.

## **RESEARCH SIGNIFICANCE**

For the first time, polymer structures able to delay cement hydration as temperature increases have been identified. Understanding the mechanism involved behind this unexpected behavior will give new insights into the design of more robust cement grouts usually used in the construction of geothermal- and/or oil- wells.

## **EXPERIMENTAL PROCEDURE**

### **Materials**

A commercial Portland cement CEM I 52.5R provided by Holcim was used. Table 1 shows the mineralogical composition of the cement determined by Rietveld analysis of the X-ray diffraction (XRD) patterns.

Nine non-commercial PCE polymers were synthesized. Two different synthetic routes were used; six of the PCEs were synthesized by copolymerization and three by esterification on

pre-formed backbones, named RM and RG, respectively in Table 2 [8], [9]. RM and RG notations refer to the random and regular distribution of the side chains along the backbone obtained, respectively, by copolymerization and esterification. After synthesis, the polymers were ultrafiltrated to remove impurities. All the backbones are based on polymethacrylic acid (PMA) and the side chains on polyethylene glycol (PEG) with different lengths, 1000, 2000 and 5000 Da. The molecular weight of these comb copolymers was determined by Gel Permeation Chromatography (GPC) using a Agilent 1260 Infinity equipment with PSS Suprema columns ( $0.8 \times 30$  cm, particle size 10  $\mu\text{m}$ ).  $\text{Na}_2\text{HPO}_4$  0.067 M at a flow rate of 1 mL/min was used as eluent and PEO/PEG were used as calibration standards. Table 2 also shows the calculated charge density of these polymers.

## **Experimental Process**

**Pastes preparation.** Cement pastes were prepared by mixing 50 g of cement with 14 g of ultrapure water at 23 °C for 3 minutes at 500 rpm with a blade stirrer (Eurostar power control visc, IKA). Admixtures were added to the mixing water (direct addition) in different dosages in the range between 0 and 20 mg polymer/ g cement.

### **Characterization**

*Hydration kinetics.* 5 g of cement pastes were poured immediately after mixing in glass ampoules and inserted in an isothermal calorimeter TAM Air (TA Instruments) set at 23 °C, 45 °C, 60 °C and 70 °C.

*Rheological properties.* Cement pastes rheology was measured with a MCR501 (Anton Paar) rheometer by using a serrated coaxial cylinder. The used method lasted 6 minutes and it consisted in an initial pre-shear at  $100\text{s}^{-1}$  during 1 minute, a shear rate continuous ramp from

0 to 100 s<sup>-1</sup> over 2.5 minutes followed by a final reversed ramp from 100 s<sup>-1</sup> to 0 s<sup>-1</sup> over 2.5 minutes. Flow curve tests were performed at 23 °C and 70 °C.

*Characterization of the pore solution.* Cement pore solutions were obtained after 1h of hydration by filtration of cement pastes hydrated at 23 °C and 70 °C using an Accelerated Solvent Extraction System (ASE 350-Dionex). Temperature was kept constant during the extraction process. Pore solutions were filtered through a membrane filter Sartorius 0.45 µm and immediately acidified to prevent the precipitation of hydrates with HCl 0.05 M and 2% (w/w) HNO<sub>3</sub> solutions for TOC and ICP measurements, respectively.

The total organic carbon content in pore solutions was determined by SHIMADZU TOC-V CSH total organic carbon (TOC) analyser. The amount of adsorbed polymer on cement was measured by depletion method [10]. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Thermo iCAP 6300 was used for quantifying the ionic composition of cement pore solutions according to the methodology proposed in the literature [11].

The presence of nanoparticles in the filtered pore solutions were analyzed by dynamic light scattering (Malvern Zetasizer Nano ZS). Measurements were conducted at 25 °C. The wavelength of the incident laser was 633 nm and the scattered light was detected at a constant angle of 173°. For reference purposes, DLS measurements were also performed on the pure PCE in a synthetic pore solution, prepared according to [12].

*Measurement of the specific surface area of pastes.* Hydration was stopped by solvent exchange with isopropanol at room temperature and specific surface area was measured using a BET multi-point nitrogen physisorption apparatus (Micromeritics Tristar II 3020). Samples were previously degassed during 16 h at 40 °C under nitrogen flow [13], [14].

## EXPERIMENTAL RESULTS AND DISCUSSION

### Hydration kinetics

Figure 1 shows the influence of the temperature on the hydration kinetics of cement pastes containing a fixed dosage of 2PMA1000-RG (1.6% active polymer by weight of cement (bwc)). At 23 °C, the addition of PCEs leads to a delay in the time of appearance of the maximum peak associated to the silicates hydration (see Figure 2), as PCE adsorbs on the reactive sites of C<sub>3</sub>S, blocking its dissolution [1]. In contrast, at temperatures higher than 45 °C and dosages above 1% active bwc, an unexpected delay of cement hydration is observed, as shown in Figure 2. To the best of our knowledge, this is the first time that this phenomenon has been described in the literature. Additionally, an inversion of the aluminate (sharp peak) and silicate peak occurs with the increase of the temperature. However, taking this into account is beyond the scope of the paper and we have only considered the overall features of the main peak regardless of this modification.

To understand the role of the polymer structure on the retardation, the delay of the silicates peak in pastes hydrated at 70 °C with respect to 23 °C, has been plotted as a function of the total number of carboxylate groups, as adsorption of PCEs onto cement particles occurs through electrostatic interactions [15]. Figure 3 reveals that for all those polymers synthesized by copolymerization, the retardation increases linearly with the number of added carboxylic groups. In contrast, PCEs synthesized by analogous esterification lead to a massive retardation (up to 150 h for 3.2PMA1000-RG), increasing quadratically with the number of anionic charges introduced.

To gain insight into the mechanism involved in this unpredicted behavior, the impact of two PCEs on the rheology has been studied. In particular, 4PMA1000-RM and 2PMA1000-RG synthesized through two different synthetic routes.

### **Rheological properties of cement pastes**

At 23 °C, both admixed pastes present a shear-thickening behavior, with an increase of the apparent viscosity as shear rate increases, as shown in Figures 4a and 5a. Moreover, pastes containing 2PMA1000-RG have a higher degree of shear-thickening behavior that increases with polymer dosage (see Figure 4a). This shear thickening behavior at 23 °C could be related to a higher volume fraction of solid particles in the suspension, and consequently a higher packing, mainly when 2PMA1000-RG is added [16]. On the contrary, at 70 °C, admixed pastes behave as shear-thinning fluids, reaching a Bingham behavior at the maximum polymer dosages used (see Figures 4b and 5b). Furthermore, at both studied temperatures, pastes containing 1.6% of 2PMA1000-RG show yield stress values of 2 Pa, inferring that both systems are well dispersed.

Figure 6a illustrates an unusual rheological behavior of a cement paste containing 1.6% of 2PMA1000-RG under a temperature cycle, illustrated in Figure 6b. In particular, the initial shear-thickening fluid at 23 °C is transformed into a Bingham fluid after keeping the paste at 70 °C for 15 minutes. Moreover, the shear-thickening behavior is recovered once the paste has treated again at 23 °C (approaching to the initial curve), concluding the almost reversibility of the physical-chemical process occurring at the molecular level.



## **Analysis of the pore solution**

As shown in Figure 7, the addition of 1.6% of PCE to cement pastes dramatically increases the concentration of Al, Mg, Si and Fe in the pore solution at 23 °C and 70 °C, rising, respectively, by a factor of 1000 and 2000 for Al and Mg. Furthermore, a much higher increase of these elements is observed at 23 °C, and mainly in the case of 4PMA1000-RM polymer.

TOC analysis (see Table 3) confirms that for both PCEs, polymer adsorption decreases with the increase in temperature. In addition, 4PMA1000-RM, with a higher charge density, adsorbs at least twice compared to 2PMA1000-RG. Radical copolymerization typically leads PCEs to a gradient distribution of side chains along the backbone (and consequently of the charge units), while PCEs synthesized by esterification present a more uniform distribution of polyethyleneglycol side chains [9], [17]. Therefore, the higher adsorption of 4PMA1000-RM compared to 2PMA1000-RG would be explained by both a higher mean charge density of the former and the presence of fragments in the polymer with a shorter distance between the anion groups that favors its adsorption.

TOC measurements confirm that at 1 h of hydration, more than 80% of the polymer initially added remains in solution at both tested temperatures. However, the state of the polymer in the pore solution depends on the temperature as confirmed by DLS measurements. In particular, in the cement pastes hydrated at 23 °C, free polymer has not been detected in the interstitial fluid; on the contrary nanoparticles with a size around 700-800 nm are measured. Moreover, the amount of nanoparticles in the pore solution is significantly higher with the addition of 4PMA1000-RM, as confirmed by the higher intensity of the scattered light. In contrast, at 70 °C the amount of nanoparticles in solution is dramatically reduced, being possible to detect at this temperature free polymer as evidenced by the signal appearing at

around 10 nm. The nanoparticles detected at 23 °C could be (i) nano-hydrates (nano-ettringite, nano-AFm and/or C-S-H), whose growth is inhibited by the adsorbed PCE [11], [18], [19], and/or (ii) polymer aggregates involving intramolecular complexes between polymers and multivalent cations) [20], although their exact nature has not been identified yet. In any case, the formation of these nanoparticles seem to be less favourable at 70 °C. The presence of these nanoparticles in the interstitial fluid at 23 °C would lead to an increase of the packing fraction of the suspension and consequently the shear thickening behavior observed in Figures 4a and 5a. In contrast, the absence of these nanoparticles at 70 °C is in agreement with the Bingham behavior as shown in Figures 4b and 5b.

### **Specific surface area of admixed pastes**

Table 4 shows a significant influence of the temperature and polymer molecular structure on the specific surface area (SSA) of cement pastes. For instance, at 3 h of hydration, SSA of pastes containing 4PMA1000-RM polymer is two and three times higher at 23 °C and 70 °C, respectively, compared to pastes containing 2PMA1000-RG. Several studies [1], [21], [22] have confirmed that, at room temperature, the addition of superplasticizers favors ettringite nucleation increasing the SSA of cement pastes. This effect is enhanced with the increase of the charge density of the PCEs, that explains the higher SSA measured for pastes containing 4PMA1000-RM.

### **Underlying mechanism of retardation at high temperatures**

It has been previously shown that PCEs with different molecular structure slow down cement hydration as temperature increases. This occurs at polymer dosages higher than 1% active bwc and mainly in the case of PCEs with a more homogenous distribution of the side chains

along the backbone (obtained by esterification). The high stability of the studied PCEs in strong alkaline conditions and at different temperatures have been confirmed by SEC, concluding that the possible hydrolyzation of the PCEs is not involved in the cement reaction inhibition. Recent studies have proved that polymer adsorption cause inhibition of silicates dissolution by blocking the reactive surface areas [1]. In the studied delayed pastes, more than 80% of the polymer remains in solution, as measured by TOC measurements, however clear differences have been detected in the chemical composition of the pore solution with the temperature by ICP. At 23 °C, the polymer is consumed in the formation of nanoparticles (see Figure 8) that could be nano-aluminate hydrates or polymer aggregates, in agreement with the high concentrations of Al and Mg of the pore solution. The presence of these nanoparticles would explain the shear-thickening behavior of admixed cement pastes at 23 °C (see Figure 4). On the contrary, at 70 °C, most of the polymer is free as concluded from DLS measurements and the lower concentrations of Al, Si, Mg and Fe compared to pastes hydrated at 23 °C. Consequently, at 70 °C, most of the polymer in solution is free to progressively adsorb on the silicate phases, inhibiting its dissolution. On the contrary, at 23 °C, the polymer in solution is consumed in the formation of nanoparticles, leading to lower delaying effect.

It still remains unclear why 2PMA1000-RG leads to a further retardation than 4PMA1000-RM. This could be related that during mixing (always at 23 °C) a higher specific surface area is found for the latter as ettringite precipitation is favored with the increase of the charge density of the polymer. In this situation, ettringite offers a bigger surface for the polymer to adsorb, leaving less polymer available to slow down silicates dissolution compared to 2PMA1000-RG; however this should be further studied.

## CONCLUSIONS

1. PCEs with specific molecular structures lead to a massive delay of cement hydration as temperature increases. This occurs at polymer dosages higher than 1% active bwc and mainly when PCEs synthesized by esterification are added.
2. The temperature has a direct impact on:
  - a. The rheological properties of the cement pastes. At 23 °C, admixed pastes show a shear-thickening behavior, while at 70 °C they behave as Bingham fluid. This would indicate a higher packing particle fraction in the former.
  - b. The chemical composition of the pore solution. At 23 °C, concentrations of Al, Mg, Fe and Si dramatically increases when PCEs are added. At this temperature, polymer is consumed in the formation of nanoparticles. On the contrary, at 70 °C the polymer is free, leading to the significant delay of cement hydration.

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## TABLES AND FIGURES

**Table 1- Mineralogical composition (%w/w) of Portland cement determined by Rietveld analysis of the XRD patterns.**

C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Gypsum	Hemihydrate	Quartz	Calcite
67.3	6.7	6.6	12.4	3.0	2.5	0.6	0.9

**Table 2: Molecular characteristics of the superplasticizers used.**

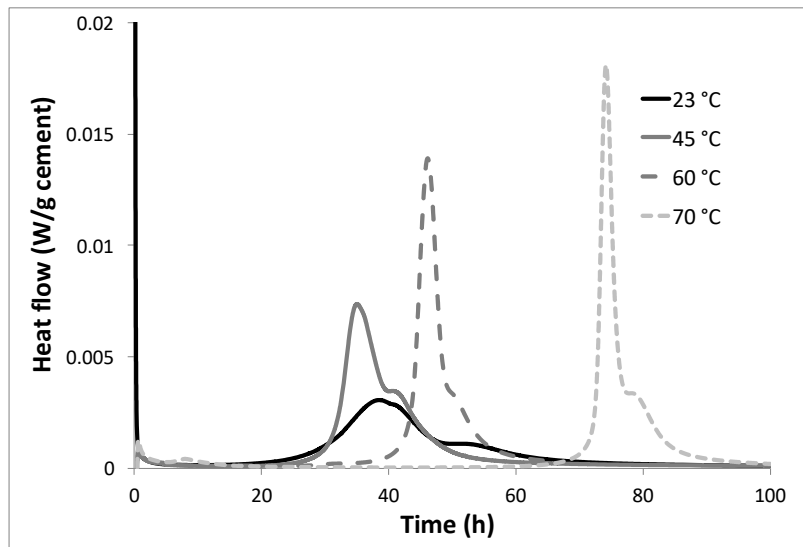
Synthesis route	Polymer	C/E	Side chain (g/mol)	Mw (g/mol)	# COO <sup>-</sup> (mmol/g polymer)
Copolymerization	4PMA1000-RM	4	1000	26000	2.80
	2.5PMA1000-RM	2.5	1000	34000	1.92
	4PMA2000-RM	4	2000	38000	1.65
	2.5PMA2000-RM	2.5	2000	40600	1.09
	4PMA5000-RM	4	5000	111000	0.74
	2.5PMA5000-RM	2.5	5000	106100	0.47
Analogous esterification	2PMA1000-RG	2	1000	22200	1.58
	3.0PMA1000-RG	3.2	1000	23500	2.35
	3.4PMA3000-RG	3.4	3000	54500	1.00

**Table 3. Polymer adsorbed after 1h of hydration at 23 °C and 70 °C (initial polymer dosage = 16 mg polymer/g cement)**

Polymer	Temperature	mg polymer adsorbed/g cement
2PMA1000-RG	23 °C	0.92
	70 °C	0.26
4PMA1000-RM	23 °C	2.77
	70 °C	1.81

**Table 4. Specific surface area of admixed samples (containing 16 mg polymer/g cement) after 3h of hydration at 23 °C and 70 °C.**

Polymer	Temperature	SSA (m <sup>2</sup> /g cement)
2PMA1000-RG	23 °C	2.24
	70 °C	1.36
4PMA1000-RM	23 °C	4.01
	70 °C	3.99



*Fig. 1- Calorimetry curves of cement pastes in presence of 1.6% 2PMA1000-RG at different temperatures*



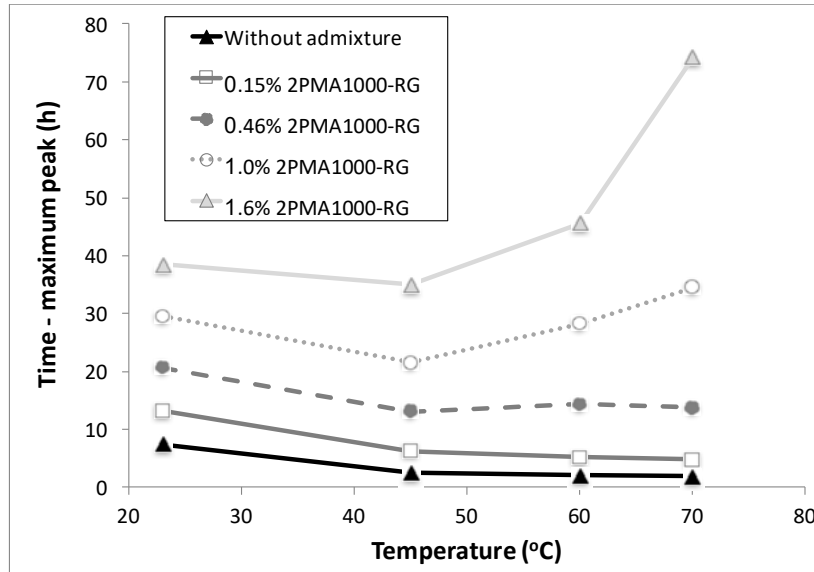


Fig. 2- Effect of 2PMA1000-RG on the time of appearance of the maximum peak in the calorimetry curve

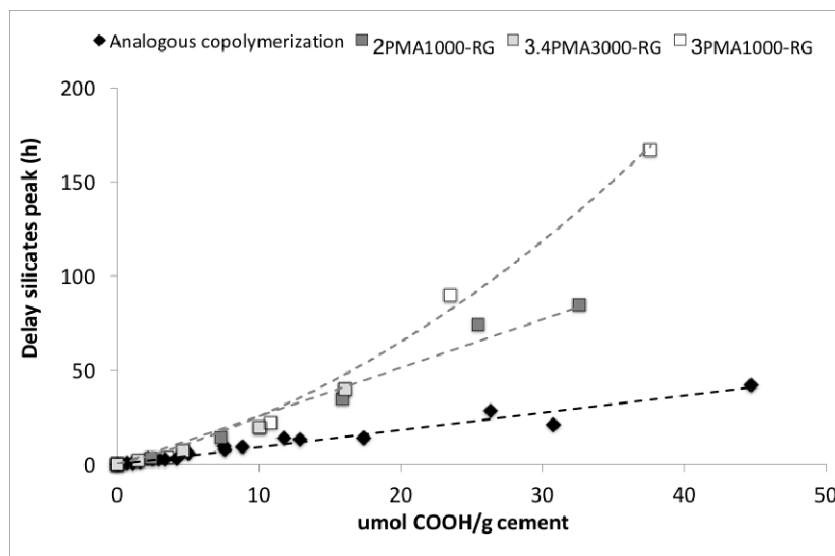


Fig. 3- Delay on the time of appearance of the maximum peak in pastes hydrated at 70 °C compared to 23 °C, as a function of the amount of carboxylic groups for the nine studied polymers

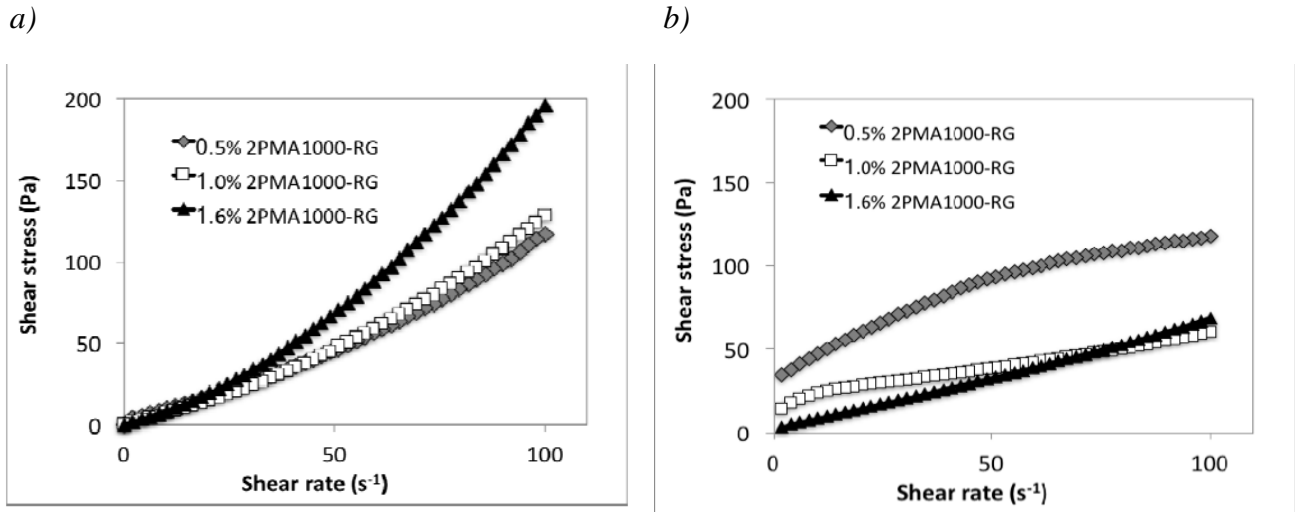


Fig. 4- Flow curve of cement pastes containing 2PMA1000-RG at (a) 23 °C and (b) 70 °C

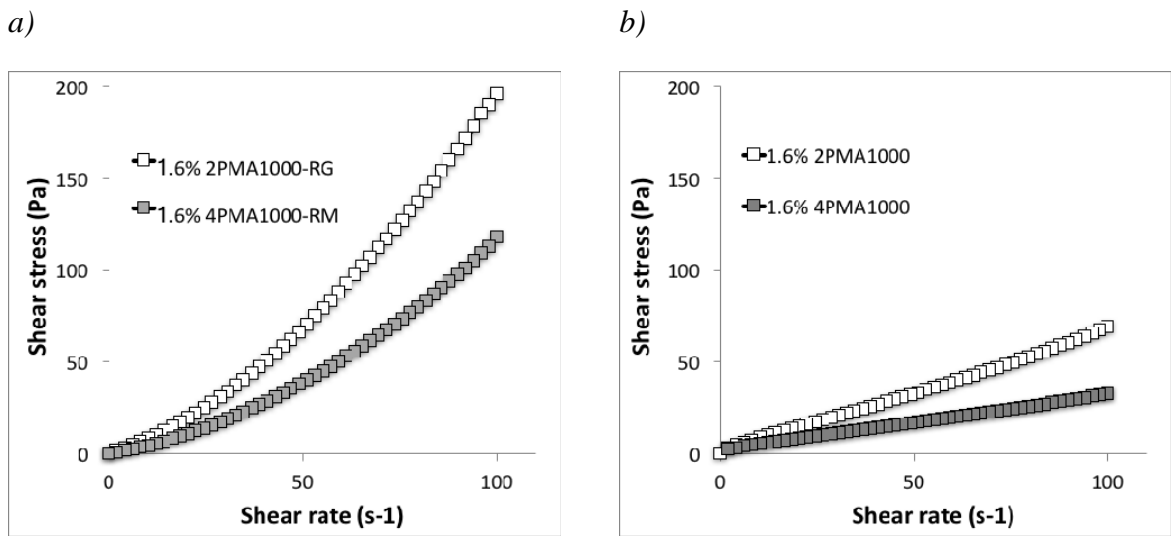


Fig. 5. Flow curve of cement pastes containing 1.6% of 2PMA1000-RG and 4PMA1000-RM at (a) 23 °C and (b) 70 °C

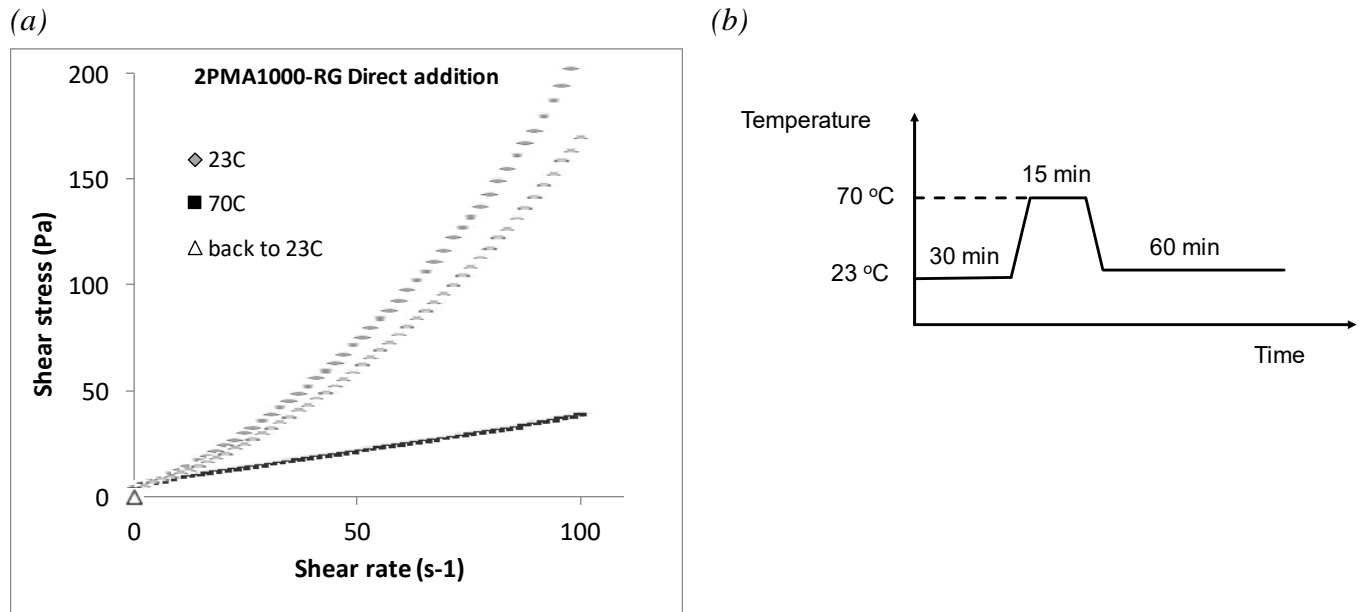


Fig. 6 - (a) Flow curve of cement paste containing 1.6% of 2PMA1000-RG during the cycle temperature illustrated in (b).

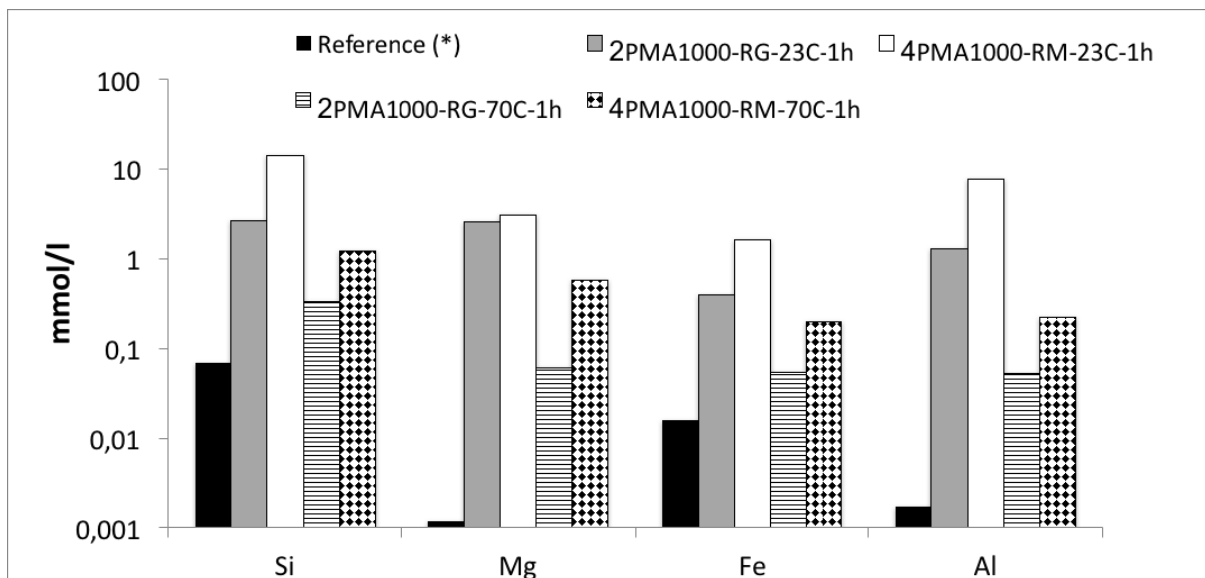
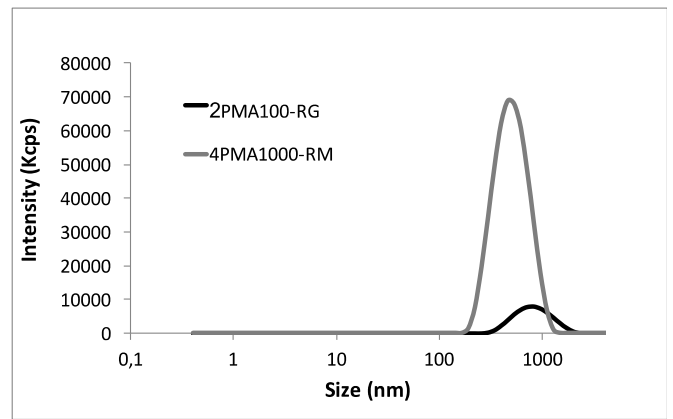
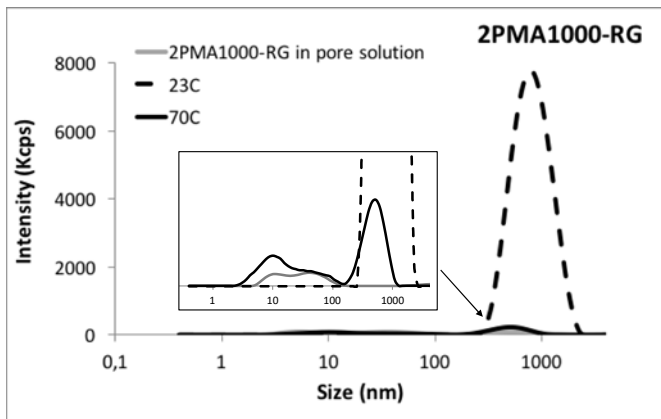


Fig. 7- Chemical composition of the pore solution in a cement paste without admixture [11], and in presence of 1.6% 2PMA1000-RG and 4PMA1000-RM. (\*) Reference refers to a free-polymer cement paste



(a)

(b)

Fig. 8- Intensity size distribution of pore solutions from cement containing (a) 1.6% 2PMA1000-RG and (b) 1.6% 4PMA1000-RM