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# Diphosphonated comb-like copolymers synthesis as suspensions dispersants and their resistance to ionic competition phenomenon

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## A B S T R A C T

The dispersive action of synthesized comb-like copolymers including phosphonated or diphosphonated functions has been investigated using rheology and stability measurements. These investigations were performed by using calcite suspensions able to mimic the early-age behavior of cement paste. In addition, adsorption measurements were conducted to relate the adsorbed amount of copolymer to the effects on dispersion. The effectiveness of the studied copolymers was evaluated in different ionic media. It appears that diphosphonated structures with the shortest chain length are the most effective even in the context of ionic competition phenomenon.

### Keywords:

Superplasticizers

Calcite suspension

Adsorption

Dispersion

Amino-bisphosphonic acid

Ionic competition

## 1. Introduction

Superplasticizers or high range water reducers (HRWR) are used as admixture for cementitious materials. These admixtures allow increasing the workability of fresh concrete without increasing the water content and thus improving durability and mechanical behavior of hardened concrete [1,2].

Polycarboxylates (PCEs) are the most effective water reducer used in concrete. Their structure consists of a main chain bearing carboxylic acids and poly(ethylene oxide) (PEO) side chains. Carboxylic acids are assumed to be fully deprotonated in highly alkali environment but anionic moieties, which are negatively-charged, adsorb on the positively charged surface of cement particles. Furthermore, PEO side chains generate steric repulsion improving the dispersion of particles and avoiding their agglomeration. In fact, the formation of agglomerates tends to trap some of the water that will no longer be available to improve the fluidity of the fresh material.

Despite a high dispersive action, these superplasticizers may, however, lose their effectiveness in certain media [3–5], and lead to undesired side effects such as retardation of cement hydration [6]. For example, it was found that superplasticizer can react with cement phases to form organo-mineral phases (OMP) [5,7]. Furthermore, the adsorption of superplasticizer can be reduced due to the ionic

competition phenomenon induced by high concentration of ions such as sulfates [8].

By tailoring macromolecular parameters such as side chain length monomers ratio and their distribution along carbon backbone [9], it is possible to design copolymers able to maintain their dispersive action in different media [10]. In addition, it has been shown that comb-like copolymers including phosphonic acids moieties are less sensitive to the loss of adsorption efficiency induced by sulfates [11]. Amino-bisphosphonic acid such as the commercial superplasticizer from Chryso referred as Optima 100 is among copolymers containing bisphosphonic acids. This copolymer seems to have high dispersive action and to reduce the side effects related to admixture/cement incompatibilities. Despite these considerations and the fact that amino-bisphosphonic is relatively more efficient than conventional PCE [12,13], this pattern has never been transposed onto a comb-like copolymer structure.

The aim of this paper is to investigate the dispersive action of synthesized comb-like copolymers bearing amino-bisphosphonated moieties. The dispersive action is evaluated using rheology measurements and colloidal stability with Turbiscan. The amount of adsorbed polymer is determined by total organic carbon analysis (TOC) to relate it to effects on dispersion. The resistance to ionic competition is investigated by using different sulfate and nitrate concentrations. The results of this paper will help to understand the effect of superplasticizers on the dispersion of mineral suspensions, especially in the presence of ionic competition phenomenon.

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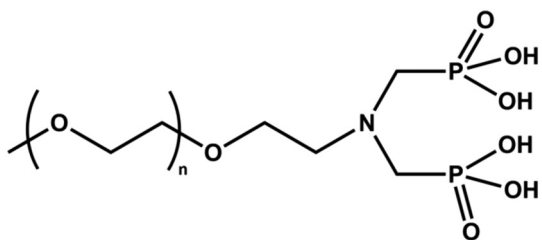


Fig. 1. Chemical structure of commercial superplasticizer (Optima 100).

## 2. Experimental

### 2.1. Materials

The synthesis of copolymers was performed by using different reagents. Poly(ethylene glycol) methyl ether methacrylate of 950 g/mol "MAPEG<sub>950</sub>" and 4,4'-Azobis(4-cyanovaleric acid) (ACVA) were purchased from Sigma-Aldrich. Dimethyl(methacryloyloxy)methyl

phosphonate (MAPC1(OMe)) was purchased from Specific Polymers. Thioglycolic acid (TA) was provided by Acros. Reagents were used as received without any further purification. Dimethyl(methacryloyloxy)methyl phosphonate (MAPC1(OMe)) was hydrolyzed into (methacryloyloxy)methyl phosphonic acid MAPC1(OH) and Tetramethyl ((2-hydroxyethyl)azanediy)bis(methylene))bis(phosphonate) (methacrylate monomer bearing amino-bisphosphonic acid) "MANP2" was synthesized according to Chougrani procedure [14].

A pure commercial superplasticizer (optima 100) provided by Chryso was used as reference copolymer. The chemical structure of this copolymer consists of a single poly(ethylene oxide) chain terminated by a diphosphonated function [15] (Fig. 1).

The new synthesized superplasticizers were tested on calcite suspensions in different ionic media by adding sodium sulfate or sodium nitrate. The calcite BL was supplied by OMYA France. Sodium nitrate and calcium hydroxide were provided by Panreax AppliChem, and sodium sulfate was purchased from Prolabo. The measured density of calcite was of about 2.75 g/cm<sup>3</sup> and specific surface area was 1.25 m<sup>2</sup>/g. Calcite particles are of monomorphous angular shape. The particle size

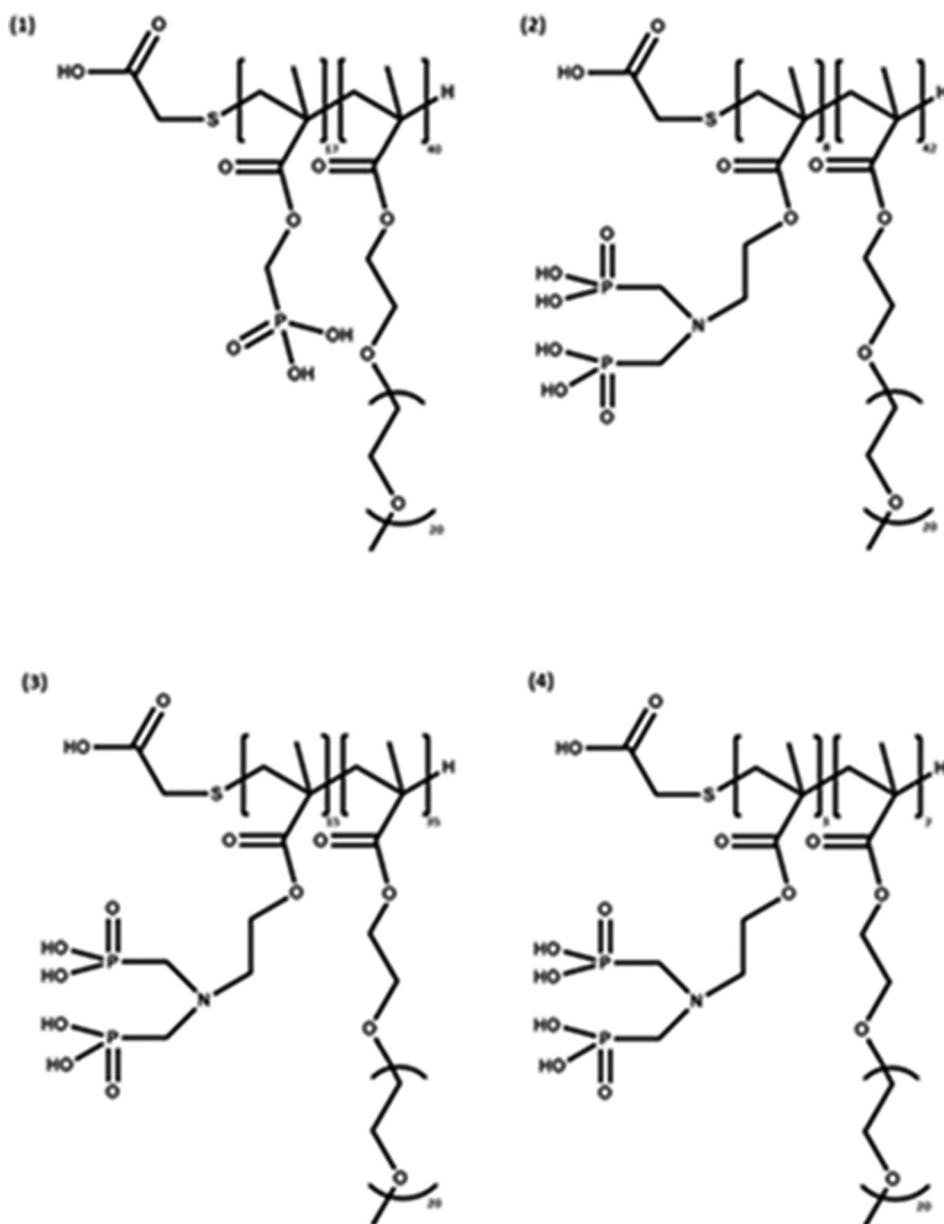
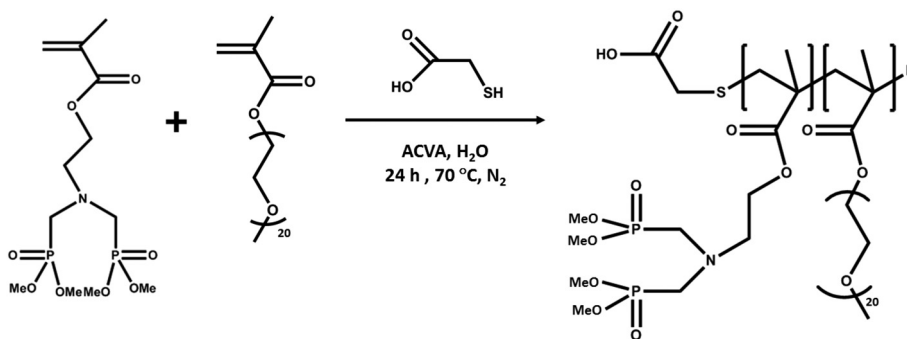


Fig. 2. Chemical formulae of random copolymers: Stat PCE-30P (1), Stat PCE-15 diNP (2), Stat PCE-30 diNP (3), Stat PCE-30 diNP DPn 10 (4).



**Scheme 1.** General procedure for diphosphonated comb-like copolymers synthesis.

distribution was determined by a laser granulometer S13320 from Beckman Coulter Company. Calcite exhibited particle size distribution ranging from 0.1 to 30  $\mu\text{m}$ , with a main mode of about 8  $\mu\text{m}$ . Calcite suspensions are commonly used as a model material to overcome the complexity of cementitious materials [8]. In fact, physical properties of calcite suspensions are close to that of cement pastes. It has to be kept in mind that the use of calcite suspensions cannot account for the effects of early stages of hydration that occur in the case of cementitious materials (Fig. 2).

## 2.2. Synthesis of copolymers

The synthesis of four statistical comb-like copolymers was performed. Three copolymers with amino-bisphosphonated acid and a reference copolymer with monophosphonated were synthesized using the procedure presented in Scheme 1. The amount of reactants used is summarized in Table 1.

MAPEG<sub>950</sub>, phosphonated monomer, thioglycolic acid and distilled water were introduced in a 250 mL three-neck round bottom flask and kept under nitrogen flux. The mixture was heated at 70 °C and 1% of ACVA (according to moles of monomers) was added to the solution. After 24 h of reaction, the solution was cooled and complete conversion was checked with <sup>1</sup>H NMR analysis. Water was then eliminated by lyophilization. Copolymers were collected as white powder and finally dried under vacuum until constant mass.

For the three diphosphonated structures, an additional step was necessary for hydrolyzing N(CH<sub>2</sub>(P)(O)(OCH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> moieties to N(CH<sub>2</sub>(P)(O)(OH)<sub>2</sub>)<sub>2</sub>. Diphosphonated copolymers were dissolved in dry dichloromethane in a 250 mL three-neck flask kept under nitrogen flux. Trimethylsilyl bromide (TMSBr) was added dropwise with a dropping funnel (2 eq. per phosphonate function to treat). After 12 h of reaction, dichloromethane was eliminated and methanol was added for 3 h. Methanol was then eliminated, and the product was dried under vacuum until constant mass. Total conversion was checked with <sup>31</sup>P NMR, whose signal was shifted from 26.5 ppm to 10.7 ppm for N(CH<sub>2</sub>(P)(O)(OH)<sub>2</sub>)<sub>2</sub> moieties.

**Table 1**  
Amounts of reactants used for random copolymers synthesis.

Reference	MAPEG <sub>950</sub> mmol	Thioglycolic acid mmol	Phosphonated monomer mmol	ACVA mmol	Water mL
Stat PCE-30P	42.18	1.11	17.94 MAPC1	0.8	140
Stat PCE-15 diNP	29.82	0.70	5.26 MANP2	0.36	40
Stat PCE-30 diNP	26.24	0.79	11.84 MANP2	0.4	50
Stat PCE-30 diNP DPn 10	12.19	1.74	5.27 MANP2	0.19	30

Copolymers were finally solubilized in distilled water to reach a 100 g/L concentration and accurate mass concentrations of these aqueous solutions were determined with thermobalance analysis.

Chemical characterization of synthesized copolymers was carried out by <sup>1</sup>H and <sup>31</sup>P NMR spectra recorded in deuterated chloroform with a 400 MHz NMR spectrometer from Bruker Company.

## 2.3. Sample preparation

Calcite suspensions were prepared using limewater to ensure alkaline conditions (pH  $\approx$  12.8) close to cement pore solution. Molar concentrations and ionic strengths were evaluated using the freeware Phreeqc [16] (Table 2). Ionic salts were added to a milk of lime obtained with an excess of lime Ca(OH)<sub>2</sub> in deionized water. Then, the milk of lime containing ions is filtered through a Büchner funnel with a sintered glass disc, resulting in a totally clear limewater containing ions. Note that the formation of gypsum is taken into account by Phreeqc calculations. The solution is re-filtered if precipitated solid particles due to carbonation and/or formation of gypsum are detected.

Calcite suspensions were mixed in a beaker using a magnetic stirrer according to the following sequence: (1) aqueous solution of superplasticizer is added to the freshly prepared ionic solution according to the amount of liquid required, (2) calcite is added with the respect of liquid to solid ratio (L/S) of 0.5, which corresponds to mass fraction  $\phi_m$  of 66.7% and volume fraction  $\phi_v$  of 43%, (3) the suspension is kept under magnetic stirring for at least 10 min before being diluted. Superplasticizer dosage corresponds to the mass of polymer added by the mass of calcite.

## 2.4. Methods

### 2.4.1. Adsorption by total organic carbon

The adsorbed amount of polymer was calculated by subtracting the amount of free polymer from the total amount initially added to the sample. The amount of free polymer in the pore solution extracted from calcite suspensions was measured with the total organic carbon (TOC) analysis using a Vario TOC Cube from Elementar. In this study, adsorption isotherms have not been determined. In fact, calcite suspensions were prepared with a single dosage (0.5%) due to the limited amounts of polymers synthesized. However, the 0.5% dosage allows marked adsorption difference between superplasticizers to be exhibited.

Calcite suspension is centrifuged (at 7000 rpm during 7 min) after 10 min of magnetic stirring. Supernatant liquid is filtered with 0.45  $\mu\text{m}$  PTFE filter. Part of this solution (4 ml) is diluted with deionized water with a factor of 5, and then acidified with some drops of concentrated sulfuric acid to prevent carbonation. Different concentrations of ethanol are used to calibrate the device. All the tests were performed in triplicate. The TOC analyzer is calibrated with unadmixed calcite suspension to take into account the amount of organic carbon in calcite. The standard deviation of TOC measurement is of about  $\pm$ 2.3%.

**Table 2**

Quantities of salts to add in order to reach targeted ionic strength.

Ionic strength mmol/L	NaNO <sub>3</sub>					Na <sub>2</sub> SO <sub>4</sub>				
	Mass to add g/L	[Na <sup>+</sup> ] mmol/L	[NO <sub>3</sub> <sup>-</sup> ] mmol/L	pH <sub>measured</sub>	σ <sub>measured</sub> mS/cm	Mass to add g/L	[Na <sup>+</sup> ] mmol/L	[SO <sub>4</sub> <sup>2-</sup> ] mmol/L	pH <sub>measured</sub>	σ <sub>measured</sub> mS/cm
66	Limewater: 4 g of Ca(OH) <sub>2</sub> /L (excess)								12.8	11.4
171	9.4	110	110	13	17.05	7.1	95.3	37.37	13.3	16.75
855	65	760	760	13.1	54.3	48,3	595	225	13.3	65

#### 2.4.2. Stability measurements

Stability was investigated with a Turbiscan MA 2000 from Formulacion. This device is composed of a light source ( $\lambda = 860$  nm) moving along a glass tube with a step of 40  $\mu$ m. The light transmitted across the sample is collected by a transmission detector (0° from incident beam) whereas backscattered light is analyzed by a backscattering detector (135°). Evolutions of transmitted and backscattered lights are plotted as a function of column height and time, and are linked to mean diameter of particles and solid volume fraction from the Lorentz and Mie theory. It is thus possible to access information about mesostructural organization of suspensions and dispersion/agglomeration phenomena.

Dilution with a factor of 3/10 (corresponding to mass concentration of 20 wt%) is performed in order to accelerate the particle migration. After 5 min of magnetic stirring, 7 mL of diluted suspension is pipetted into the Turbiscan cell. The analysis is started as soon as possible in order to record the initial sedimentation. Turbiscan analyses last 30 min with a scan every minute.

#### 2.4.3. Rheological measurements

Rheological measurements were carried out using an experimental Couette rheometer AR2000 ex from TA instruments equipped with a four blades vane geometry. Calcite suspensions were prepared with a L/S ratio of 0.36 corresponding to volume fraction of about 51%. Due to the limited amounts of synthesized polymers, a single dosage of 0.05% was used. Even if it would be possible to work at higher doses, it would lead to very fluid calcite suspensions that do not make it possible to compare superplasticizers.

Calcite suspensions were mixed during 10 min at 500 rpm. The procedure consists of yield stress measurement by stress growth [17,18]. After a strong pre-shear phase (60 s<sup>-1</sup> during 30 s) followed by a resting time (30 s), a small rotational velocity corresponding to a shear rate of 0.006 s<sup>-1</sup> was applied to the vane geometry. On the shear rate versus strain curve obtained for yield stress measurement, it can be noted that the stress begins to increase linearly with the strain (elastic behavior in the solid regime) to reach a peak followed by a slow decrease corresponding to destruction of the suspension (viscous behavior in the liquid regime). This peak defines the static yield stress which corresponds to the minimum stress to induce flow.

**Table 3**

Macromolecular parameters of synthesized comb-like copolymers, in addition to Optima 100. Mn and DPn of comb-like copolymers are theoretical calculated according to reactants amount.

Reference	% MAPEG <sub>950</sub>	% anionic functions	Nature of anionic function	Number of (CH <sub>2</sub> -CH <sub>2</sub> -O) per PEO chain	DPn	Mn (g/mol)
Stat PCE-30P	70	30	Phosphonic acid	20	57	41,000
Stat PCE-15 diNP	85	15	Amino bisphosphonic acid	20	50	43,000
Stat PCE-30 diNP	70	30		20	50	38,000
Stat PCE-30 diNP DPn 10	70	30		20	10	7600

Diphosphonated poly(ethylene oxide) superplasticizer			
Reference	Nature of anionic function	Number of (CH <sub>2</sub> -CH <sub>2</sub> -O) per PEO chain	M (g/mol)
Optima 100	Aminobisphosphonic acid	44	2200

### 3. Results and discussion

#### 3.1. Comb-like copolymers synthesis

In this study, four comb-like copolymers have been designed by  $\alpha$ radical copolymerization of MAPEG<sub>950</sub> (having constant number of 20 CH<sub>2</sub>-CH<sub>2</sub>-O per side chain) with either MAPC1 or MANP2. Their macromolecular parameters are summarized in Table 3. Thioglycolic acid, a chain transfer agent, was used to control efficiently molecular weights. Stat PCE-30P, the first comb-like copolymer, exhibits monophosphonic acid as anchor groups, whereas both Stat PCE-15 diNP and Stat PCE-30 diNP show 15% and 30% amino-bisphosphonic acid moieties, respectively. All these three comb-like copolymers have the same chain length, i.e. same degree of polymerization (close to 50). It should be noted that Stat PCE-30P and Stat PCE-15 diNP have the same number of phosphonic acid units per chain, and twice less than Stat PCE-30 diNP. Concerning Stat PCE-30 diNP DPn 10, this macromolecule has the same structure than Stat PCE-30 diNP, but with a shorter chain length; its degree of polymerization is about 10. For this structure, the role of terminal acid coming from thioglycolic acid moieties (Scheme 1) may be not negligible, considering the fact that, statically, there are only three acidic functions per macromolecule (contrary to macromolecules with a DPn close to 50 which have, statically, 15 acidic functions per macromolecule).

These four comb-like copolymers will be used as superplasticizers and compared to Commercial superplasticizer; the latter is not a comb-like copolymer but a poly(ethylene oxide) chain terminated by an amino-bisphosphonic acid. This commercial molecule is described as a very effective superplasticizer, with good compatibility with every kinds of cement [15]. Although this smaller molecule of "only" 2200 g/mol (18 times less than Stat PCE-30P, for example) is supposed to behave very differently and to adopt another conformation at particle surfaces than conventional PCE, it is interesting to compare the performance of the amino-bisphosphonated function, especially at high ionic strength.

#### 3.2. Adsorption

TOC analysis allows determining amount of copolymer adsorbed on calcite particles. The knowledge of this quantity is useful to understand superplasticizer efficiency. A direct correlation between adsorption and

dispersive action was established [19]. It was also found that including phosphonic acid moieties does not necessarily improve adsorption efficiency compared to conventional PCE; but it may reduce the loss of adsorption efficiency in the presence of competitive anions such as sulfates [11]. According to Bishop et al. [20], the adsorption decreases as the rate of phosphonic functions increases due to the possibility of polymer-Ca<sup>2+</sup> formation.

Fig. 3 presents the adsorbed amount of superplasticizers in different media. It can be seen that copolymers does not adsorb in same proportions in limewater. Stat PCE-30P is adsorbed almost three times more than Stat PCE-30 diNP (0.98 and 0.35 mg adsorbed per gram of calcite, respectively). A decrease of adsorption is observed for each copolymer as ionic strength increases. This decrease is more pronounced with sulfate and is less marked for diphosphonated structures than monophosphonated or Optima 100. At high sulfate concentration (I = 855 mmol/L), diphosphonated structures are adsorbed in similar proportions. Stat PCE-30 diNP DPn10, which is the copolymer with the shortest molecular weight structure, shows even higher adsorption than other structures. It reflects the resistance to ionic competition phenomenon. This may be related to good adhesion and complexation

properties exhibited by amino-biphosphonated copolymers [14,21] due to their higher charge density per anchoring groups (compared to MAPC1 moieties). Stat PCE-30 diNP DPn 10 exhibits a good resistance to ionic competition phenomenon. It can be noted that this copolymer is assumed to have the same charge density than Stat PCE-30 diNP, the difference is only the terminal —COOH of thioglycolic acid chain transfer agent.

### 3.3. Impact on suspensions stability

Stability was characterized by Turbiscan MA 2000. This device is able to detect nascent destabilization phenomenon in concentrated suspensions and gives information about the mesostructure organization. By using laser granulometry analyses, two populations of particles were detected: the first population in turbid supernatant corresponds to finest calcite particles with diameters between 0.7 and 8 μm and a main mode of 3 μm, the second population in opaque sediment consists of a large variety including finest and largest particles from 0.5 to 30 μm with a main mode of 10 μm.

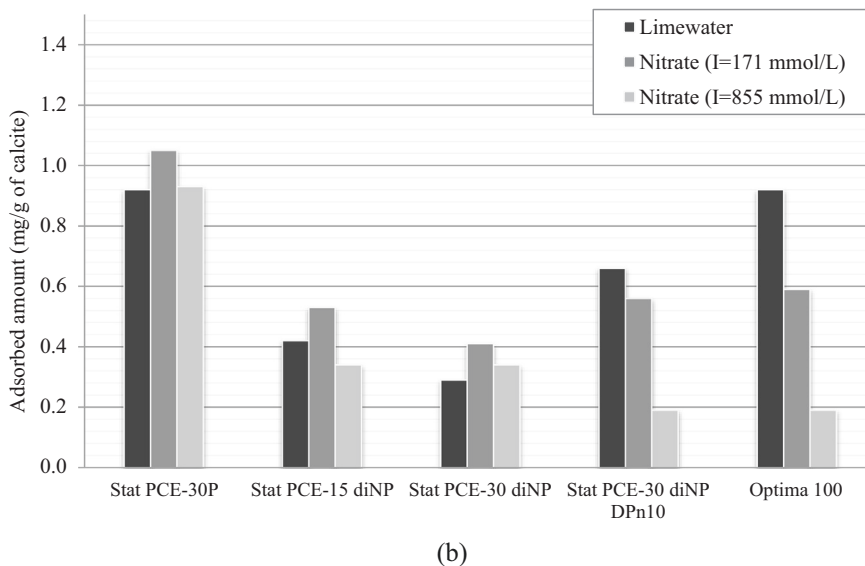
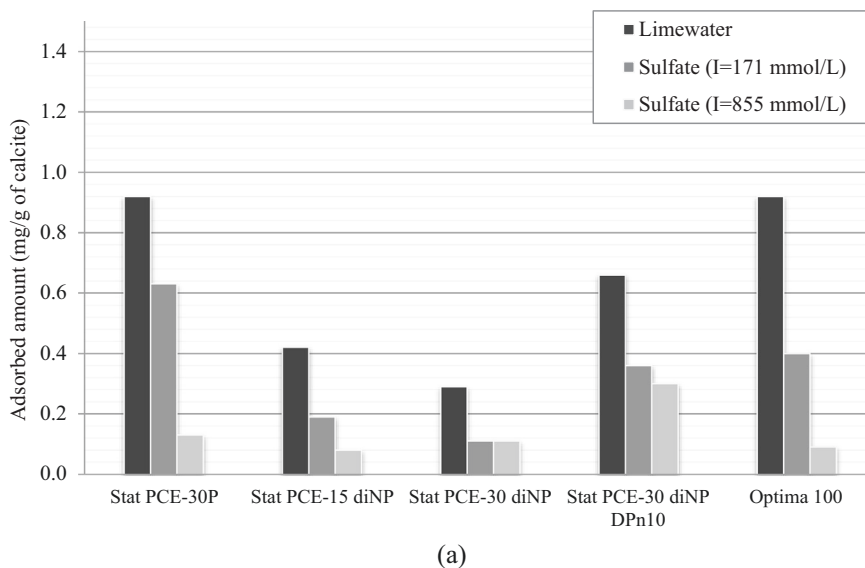


Fig. 3. Amount of adsorbed superplasticizer in the presence of sulfate (a) and nitrate (b).



**Table 4**  
Required dosage to reach  $T_{30} = 0\%$  in different environments and for different SP.

Environment	Ionic strength mmol/L	Stat PCE-30P	Stat PCE-15 diNP	Stat PCE-30 diNP	Stat PCE-30 diNP DPn 10	Optima 100
Limewater	66	0.1	0.05	0.05	0.05	0.05
NaNO <sub>3</sub>	171	0.1	0.05	0.05	0.05	0.05
	855	0.1	0.1	0.1	0.05	0.05
Na <sub>2</sub> SO <sub>4</sub>	171	0.1	0.5	0.2	0.1	0.05
	855	0.2	0.5	0.5	0.1	0.5

**Table 5**  
Required dosage for the Stability Index to reach the plateau at 50 area units.

Environment	Ionic strength mmol/L	Stat PCE-30P	Stat PCE-15 diNP	Stat PCE-30 diNP	Stat PCE-30 diNP DPn 10	Optima 100
Limewater	66	0.1	0.1	0.1	0.1	0.1
NaNO <sub>3</sub>	171	0.2	0.1	0.1	0.1	0.1
	855	0.2	0.1	0.1	0.1	0.1
Na <sub>2</sub> SO <sub>4</sub>	171	0.2	1	0.2	0.1	0.1
	855	0.5	1	0.5	0.2	0.5

### 3.3.1. Impact on fine particles dispersion

Evolution of transmission light intensity as function of superplasticizer dosage is characterized using  $T_{30}$  index. This index

corresponds to the mean transmission in the column at  $t = 30$  min. Sediment remains opaque during analysis and  $T_{30}$  cannot therefore give information about it; but it allows studying dispersion of finest particles in turbid supernatant.

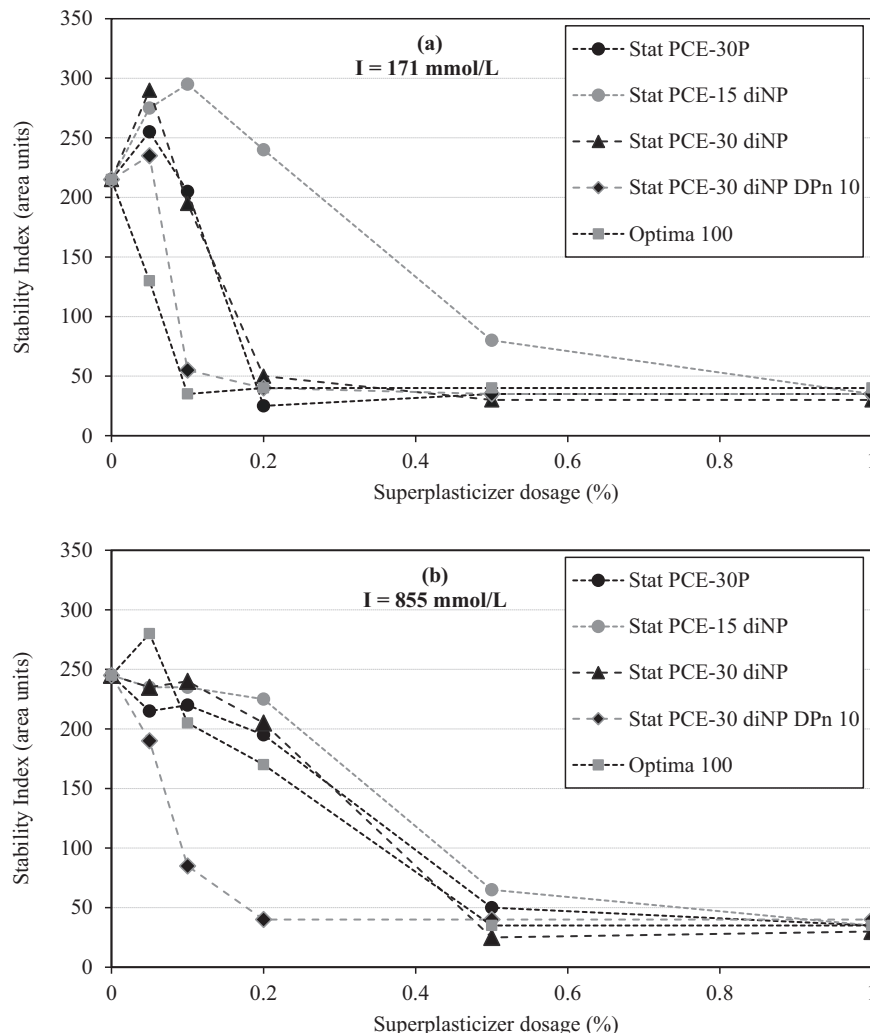
Adding superplasticizer leads to dispersion of finest particles. With increasing superplasticizer dosage, sedimentation is very slow and turbid supernatant becomes fully opaque. Table 4 presents the dosage required to make the supernatant opaque, i.e.  $T_{30}$  equal to 0%. It thus represents the dosage needed to stabilize finest particles in suspension.

In limewater, the dosage required to stabilize finest particles is of about 0.05 except for Stat PCE-30P which is of about 0.1%. Increase of ionic strength tends to increase this required dosage as shown for Stat PCE-15 diNP and Stat PCE-30 diNP. Commercial superplasticizer seems to maintain its dispersive action except at high ionic strength in the presence of sulfate.

As shown in Table 4, it appears that Stat PCE-30 diNP DPn 10 is the best admixture for stabilizing finest particles since it requires only 0.1% to stabilize finest particles in suspension. It is in accordance with adsorption results where Stat PCE-30 diNP DPn 10 seems to be less sensitive to ionic competition compared to Stat PCE-30P or Commercial superplasticizer (Fig. 3).

### 3.3.2. Impact on global particles dispersion

Study of transmission intensity in supernatant can only give information about finest particles with diameter lower than 8  $\mu\text{m}$ . To investigate all populations of settling particles, backscattered light evolution



**Fig. 4.** Evolution of Stability Index as a function of superplasticizer dosage in the presence of sulfates at (a)  $I = 171$  mmol/L and (b)  $I = 855$  mmol/L.

is required. Monitoring this evolution is therefore relevant for characterizing global stability of suspension. We thus chose to define a stability index corresponding to the area between curves at  $t = 0$  and  $t = 6$  min on backscattered profiles. This stability index allows the evaluation of stability of calcite suspensions by following the particles settling. It increases with increasing of destabilization. For a low stability index, suspensions can be considered as stable.

Without any admixtures, the stability index is close to 200–250 area units and decreases with dosage increasing. The intermediate state in terms of stabilization corresponds to a stability index between 100 and 70 area units with opaque supernatant and slowed sediment front evolution. At high dosage, evolution of this index becomes monotonous and reaches a stability plateau at approximately 50 area units. This value is defined as the stability threshold below which the suspension can be considered as stable. Table 5 presents dosages needed to reach this stability threshold.

As shown in Table 5, all superplasticizers exhibits similar stability threshold in limewater and in the presence of nitrate. However, in the presence of sulfate, there is marked difference between superplasticizers. Fig. 4 presents the stability index evolution as a function of superplasticizer dosage. It can be noted that higher dosage is required to reach the stability threshold in the presence of sulfate. For instance,

Stat PCE-15 diNP needs a dosage of 1% to stabilize particles which is in accordance with adsorption results (Fig. 3) and  $T_{30}$  evolution (Table 4). Indeed, Stat PCE-15 diNP is slightly more sensitive to ionic competition than Stat PCE-30 diNP, and it is also unable to stabilize finest particles at dosages lower than 0.5% in the presence of sulfates. This behavior may be attributed to the low content of anchoring groups and the high content of MAPEG<sub>950</sub> moieties. Maybe a higher quantity of PEO side chains is detrimental to dispersion efficiency.

For Stat PCE-30P, Stat PCE-30 diNP and Commercial superplasticizer, the stabilization threshold is reached for a dosage of 0.1–0.2% at low ionic strength and of 0.5% at high ionic strength. Stat PCE-30 diNP DPn10 maintains its dispersive action even at high sulfate concentration. This is in accordance with finest particles dispersion, for which this short comb-like copolymer was able to disperse at low dosage (0.1%). This indicates that a shorter chain length allows reducing ionic competition effects.

### 3.4. Impact on rheological behavior

The yield stress is the shear stress below which the material stops flowing. According to Roussel et al. [22], the yield stress is a very

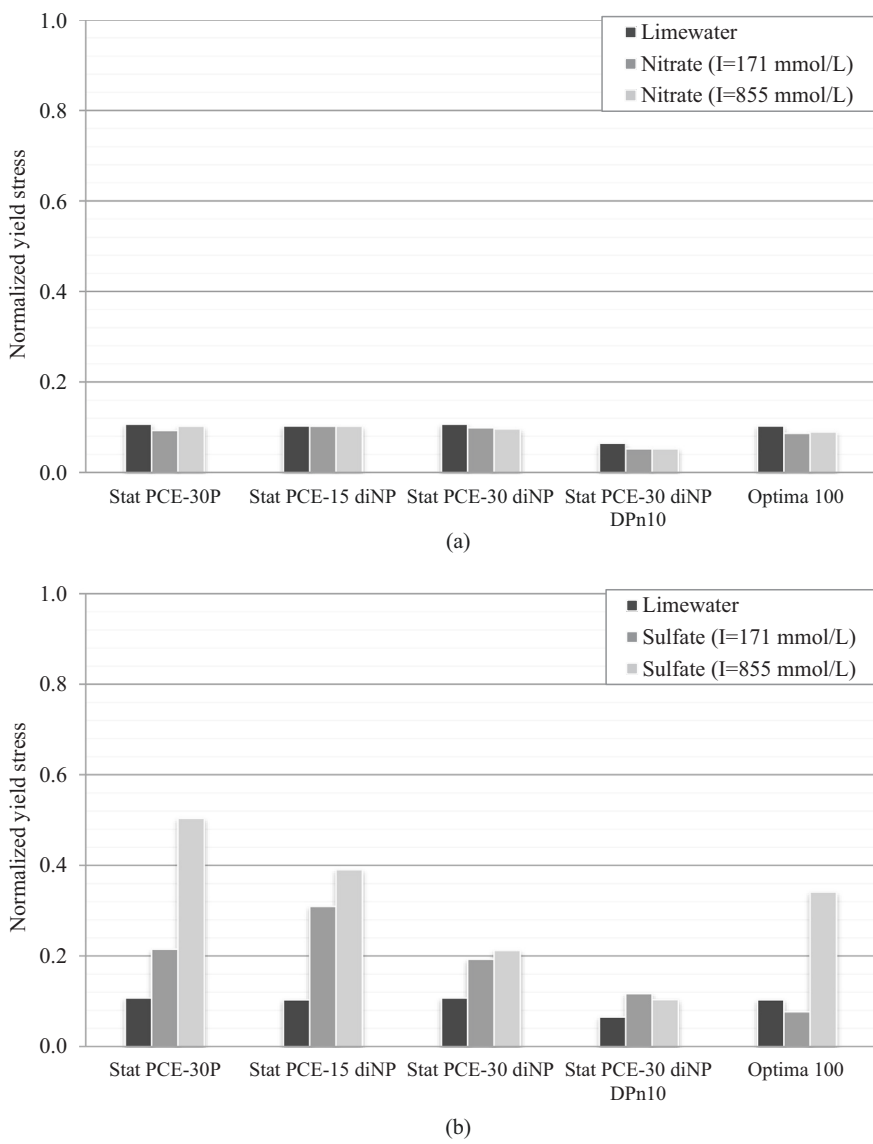


Fig. 5. Normalized yield stress measured in the presence of nitrate (a) and sulfate (b).



relevant parameter to describe the effect of superplasticizers on the fluidity or workability.

As displayed in Fig. 5, adding a dosage of 0.05% of superplasticizer allows reducing the yield stress by a ratio of about 90 compared to unadmixture suspension. In addition, the yield stress increases with increasing of ionic strength in the presence of sulfate. The change in the yield stress could result from a modification of dispersion state affecting the network of interaction between particles. It therefore appears that the increase in the ionic strength makes superplasticizers less effective in terms of fluidity improvement due to ionic competition phenomenon. Diphosphonated structures such as Stat PCE-30 diNP seem to be enough resistant to this phenomenon. The difference between Stat PCE-30 diNP and Stat PCE-15 diNP indicates that the number of anionic functions should be considered in the context of high sulfate concentration.

By comparing Stat PCE-30P and Stat PCE-30 diNP which have the same monomers ratio and the same chain length, the structure bearing amino-bisphosphonic acid, i.e. Stat PCE-30 diNP, seems to be more effective. This comparison may indicate that amino-bisphosphonic acids are more powerful anchoring moieties than monophosphonic acids, and makes macromolecular structures more resistant to ionic competition. This could be due to higher charge density of MANP2

moieties compared to MAPC1 ones. In fact, MANP2 possesses good adhesion and complexation properties [14,23].

The shortest macromolecule, i.e. Stat PCE-30 diNP DPn 10, maintains its dispersive action at high sulfate concentration. The resistance of this copolymer to ionic competition phenomenon shows a strong interest for the synthesis of short comb-like copolymers. Yamada et al. [24] found that shortening polycarboxylates backbone length enhanced their dispersive action. This could be due to the conformation of polymer. Indeed, small macromolecule can probably reach more easily particle surface saturated by competitive ions. Commercial superplasticizer is very effective in terms of fluidity improvement except in high sulfate concentration.

### 3.5. Characterization of efficiency gains of superplasticizers

In order to compare superplasticizers performances, three parameters,  $\omega_d$ ,  $\omega_f$  and  $\omega_a$ , are defined.

$\omega_a$  is an index of adsorption, which is the ratio between the adsorbed amount of copolymer and the mass of initially polymer added during TOC experiment preparation.

$\omega_f$  is a fluidification index and is the ratio between the yield stress of admixture suspensions and the yield stress of unadmixture suspension.

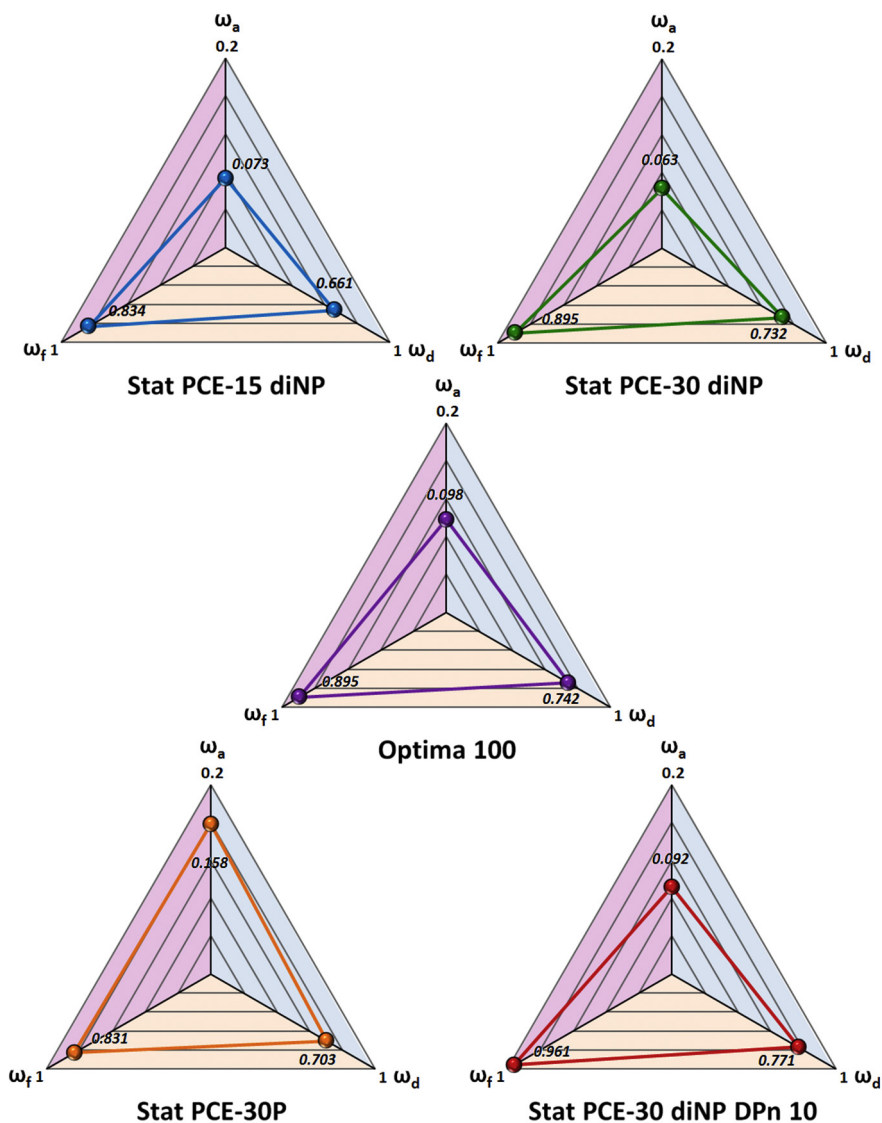


Fig. 6. Values of  $\omega_a$ ,  $\omega_d$  and  $\omega_f$  for the studied superplasticizers.

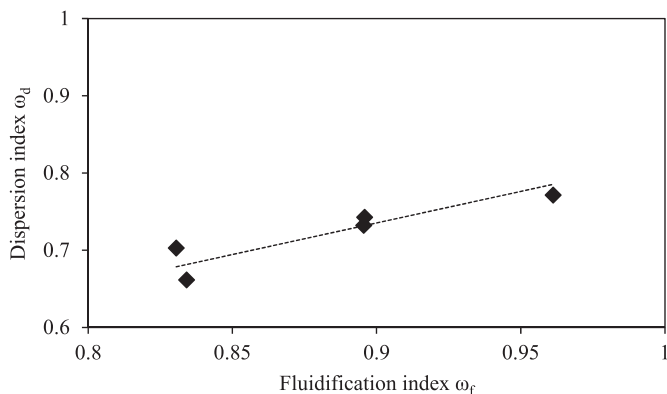


Fig. 7. Possible correlation between dispersion ( $\omega_d$ ) and fluidity ( $\omega_f$ ).

$\omega_d$  is a dispersion index obtained from the stability index. It is defined as follows:

$$\omega_d = 1 - \frac{A_{SP}}{A_0} \quad (1)$$

where:  $A_{SP}$  corresponds to the area under the stability index versus dosage curve.  $A_0$  corresponds to the area which would be obtained with a fictive superplasticizer, so ineffective that it would not induce any changes in stability index whatever the dosage.

As shown in Fig. 6, it appears that Stat PCE-30 diNP DPn 10 is the best admixture for dispersing and fluidizing calcite particles. Commercial superplasticizer and Stat PCE-30 diNP display the same effectiveness.

Possible correlations between adsorption, stability and rheology could be established. According to Dalas et al. [19], a linear relation exists between adsorption and fluidification. In this study, the correlation is difficult to establish. For example, Stat PCE-30P, which is the most adsorbed on calcite particles, does not have the best dispersive action (stability and fluidity improvement). It has to be kept in mind that adsorption measurements performed in this work are not sufficient to find this correlation. In fact, no adsorption plateau could be determined. The chosen dosage could be at the plateau for some polymers, whereas for others, it could be not yet at the plateau. More details related to the polymer conformation and surface coverage are needed to find a possible correlation.

Furthermore, as shown in Fig. 7, a possible correlation between stability and rheology could be established.

#### 4. Conclusion

The dispersive action of synthesized comb-like copolymers including amino-bisphosphonated functions was investigated using adsorption, rheology measurements and colloidal stability in different media subjected to ionic competition phenomenon. The results of this paper will help to understand the effect of superplasticizers on the dispersion of mineral suspensions, especially in the presence of ionic competition phenomenon. The following conclusions were drawn:

- Copolymers including amino-bisphosphonated seem to be more effective than monophosphonated copolymers even in ionic competition context.
- The role of fine particles seems very important. In fact, as the rate of phosphonic acid increases, the dispersion of the fines particles increases leading to the fluidity improvement.
- The chain length represented by the degree of polymerization (DPn) appears to be an important parameter to improve the effectiveness of comb-like copolymers. Structures with the shortest chain length (DPn close to 10) are more effective in terms of dispersive action, and more resistant to ionic competition phenomenon.

Although chemical synthesis of diphosphonated comb-like copolymers is more complicated than conventional polycarboxylates, such structures may present a great interest for concrete admixtures with very high ions concentration in pore solution.

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#### References

- [1] C.A. Anagnostopoulos, Effect of different superplasticizers on the physical and mechanical properties of cement grouts, *Constr. Build. Mater.* 50 (2014) 162–168, <https://doi.org/10.1016/j.conbuildmat.2013.09.050>.
- [2] M. Courtial, M.N. De Noirfontaine, F. Dunstetter, M. Signes-Frehel, P. Mounanga, K. Cherkaoui, Effect of polycarboxylate and crushed quartz in UHPC: microstructural investigation, *Constr. Build. Mater.* 44 (2013) 699–705, <https://doi.org/10.1016/j.conbuildmat.2013.03.077>.
- [3] S.K. Agarwal, I. Masood, S.K. Malhotra, Compatibility of superplasticizers with different cements, *Constr. Build. Mater.* 14 (2000) 253–259, [https://doi.org/10.1016/S0950-0618\(00\)00025-8](https://doi.org/10.1016/S0950-0618(00)00025-8).
- [4] P.-C. Nkinamubanzi, S. Mantellato, R.J. Flatt, 16 – Superplasticizers in practice, in: J.C. Aitcin, R.J. Flatt (Eds.), *Science and Technology of Concrete Admixtures*, Woodhead Publishing 2016, pp. 353–377. *Sci. Technol. Concr. Admixtures* <https://doi.org/10.1016/B978-0-08-100693-1.00016-3>.
- [5] R.J. Flatt, Y.F. Houst, A simplified view on chemical effects perturbing the action of superplasticizers, *Cem. Concr. Res.* 31 (2001) 1169–1176, [https://doi.org/10.1016/S0008-8846\(01\)00534-8](https://doi.org/10.1016/S0008-8846(01)00534-8).
- [6] D. Marchon, R.J. Flatt, 12 – Impact of chemical admixtures on cement hydration, in: J.C. Aitcin, R.J. Flatt (Eds.), *Science and Technology of Concrete Admixtures*, Woodhead Publishing, 2016 <https://doi.org/10.1016/B978-0-08-100693-1.00012-6>.
- [7] A. Habbaba, Z. Dai, J. Plank, Formation of organo-mineral phases at early addition of superplasticizers: the role of alkali sulfates and  $C_3A$  content, *Cem. Concr. Res.* 59 (2014) 112–117, <https://doi.org/10.1016/j.cemconres.2014.02.007>.
- [8] S. Pourchet, I. Pochard, F. Brunel, D. Perrey, Chemistry of the calcite/water interface: influence of sulfate ions and consequences in terms of cohesion forces, *Cem. Concr. Res.* 52 (2013) 22–30, <https://doi.org/10.1016/j.cemconres.2013.04.002>.
- [9] S. Pourchet, S. Liautaud, D. Rinaldi, I. Pochard, Effect of the repartition of the PEG side chains on the adsorption and dispersion behaviors of PCP in presence of sulfate, *Cem. Concr. Res.* 42 (2012) 431–439, <https://doi.org/10.1016/j.cemconres.2011.11.011>.
- [10] J. Plank, E. Sakai, C.W. Miao, C. Yu, J.X. Hong, Chemical admixtures – chemistry, applications and their impact on concrete microstructure and durability, *Cem. Concr. Res.* 78 (2015) 81–99, <https://doi.org/10.1016/j.cemconres.2015.05.016>.
- [11] F. Dalas, A. Nonat, S. Pourchet, M. Mosquet, D. Rinaldi, S. Sabio, Tailoring the anionic function and the side chains of comb-like superplasticizers to improve their adsorption, *Cem. Concr. Res.* 67 (2015) 21–30, <https://doi.org/10.1016/j.cemconres.2014.07.024>.
- [12] R. Morini, *Rhéologie de suspensions concentrées de carbonate de calcium en présence de fluidifiant*, Université de Nice Sophia Antipolis, 2014.
- [13] M. Mosquet, Y. Chevalier, S. Brunel, J.P. Guicquero, P. Le Perche, Polyoxyethylene diphosphonates as efficient dispersing polymers for aqueous suspensions, *J. Appl. Polym. Sci.* 65 (1997) 2545–2555, [https://doi.org/10.1002/\(SICI\)1097-4628\(19970919\)65:12<2545::AID-APP24>3.0.CO;2-Y](https://doi.org/10.1002/(SICI)1097-4628(19970919)65:12<2545::AID-APP24>3.0.CO;2-Y).
- [14] K. Chougrani, B. Boutevin, G. David, S. Seabrook, L. Cedric, Acrylate based anticorrosion films using novel Bis-Phosphonic Methacrylates, *J. Polym. Sci. A Polym. Chem.* 49 (2008) 511–512, <https://doi.org/10.1002/pola>.
- [15] J. Seurre, B. Pellerin, J.P. Bigas, *Admixture System for Prefabricated Concrete*, 2010.
- [16] U.S.G. Survey, PHREEQC Interactive, Version 2.17.5.4799, a Computer Program for Speciation, Batch-reaction, One-dimensional Transport and Inverse Geochemical Calculations, 2018.
- [17] F. Mahaut, S. Mokéddem, X. Chateau, N. Roussel, G. Ovarlez, Effect of coarse particle volume fraction on the yield stress and thixotropy of cementitious materials, *Cem. Concr. Res.* 38 (2008) 1276–1285, <https://doi.org/10.1016/j.cemconres.2008.06.001>.
- [18] A. Perrot, T. Lecompte, H. Khelifi, C. Brumaud, J. Hot, N. Roussel, Yield stress and bleeding of fresh cement pastes, *Cem. Concr. Res.* 42 (2012) 937–944, <https://doi.org/10.1016/j.cemconres.2012.03.015>.
- [19] F. Dalas, S. Pourchet, A. Nonat, D. Rinaldi, S. Sabio, M. Mosquet, Fluidizing efficiency of comb-like superplasticizers: the effect of the anionic function, the side chain length and the grafting degree, *Cem. Concr. Res.* 71 (2015) 115–123, <https://doi.org/10.1016/j.cemconres.2015.02.001>.
- [20] M. Bishop, S.G. Bott, A.R. Barron, A new mechanism for cement hydration inhibition: solid-state chemistry of calcium nitrilotris(methylene)triphosphonate, *Chem. Mater.* 15 (2003) 3074–3088, <https://doi.org/10.1021/cm0302431>.
- [21] Y. Catel, M. Degrange, L. Le Pluart, P.-J. Madec, T.-N. Pham, F. Chen, W.D. Cook, Synthesis, photopolymerization, and adhesive properties of new bisphosphonic acid monomers for dental application, *J. Polym. Sci. A Polym. Chem.* 49 (2009) 511–512, <https://doi.org/10.1002/pola>.

- [22] N. Roussel, A. Lemaître, R.J. Flatt, P. Coussot, Steady state flow of cement suspensions: a micromechanical state of the art, *Cem. Concr. Res.* 40 (2010) 77–84, <https://doi.org/10.1016/j.cemconres.2009.08.026>.
- [23] Y. Catel, V. Besse, A. Zulauf, D. Marchat, E. Pfund, T.N. Pham, D. Bernache-Assolant, M. Degrange, T. Lequeux, P.J. Madec, L. Le Pluart, Synthesis and evaluation of new phosphonic, bisphosphonic and difluoromethylphosphonic acid monomers for dental application, *Eur. Polym. J.* 48 (2012) 318–330, <https://doi.org/10.1016/j.eurpolymj.2011.09.020>.
- [24] K. Yamada, T. Takahashi, S. Hanehara, M. Matsuhisa, Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer, *Cem. Concr. Res.* 30 (2000) 197–207, [https://doi.org/10.1016/S0008-8846\(99\)00230-6](https://doi.org/10.1016/S0008-8846(99)00230-6).