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Multi-method approach to study influence of superplasticizers on cement suspensions

L. Ferrari [a,b,*], J. Kaufmann [a], F. Winnefeld [a], J. Plank [b]

[a] Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstr. 129, 8600 Duebendorf, Switzerland
[b] Technische Universität München, Department of Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany

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ABSTRACT

Superplasticizers are widely used in concrete processing to increase the rheological properties of hardening pastes. In this study, different techniques (rheology, adsorption, atomic force microscopy—AFM, and ζ-potential) are used to characterize the impact of polycarboxylate-ether based superplasticizer (PCE) on particle suspensions. Results obtained with two cements and two inert powders (MgO and calcite) show that superplasticizer efficiency is strongly influenced by polymer architecture and by the ionic species present in solution. Additionally, experiments performed with AFM and ζ-potential contributed to characterize dispersion forces exerted by superplasticizers at the solid–liquid interface. The application of plateau AFM-tips coated with platinum reveals that dispersion forces depends on the presence of ions in solution, and that multilayer formation occurs with certain superplasticizer types. A further conclusion includes the idea that the PCE has a lubricating effect between adjacent particles and PCE increases surface wettability.

1. Introduction

Polycarboxylate-ether based superplasticizers (PCEs) are widely used in different industrial fields to improve the rheological properties of particle suspensions. Especially in cement application, their addition allows a reduction of the water-to-cement (w/c) ratio, thus strongly increasing the workability of the fresh mixtures and the performances of the hardened pastes, mortars or concretes. Despite their widespread utilization, these polymers are currently still the subject of many studies, because details about their working principles lack of a full understanding. Indeed, sometimes unpredictable incompatibility with certain cements was observed [1–3].

A multi-method approach is required to understand different aspects of superplasticizer behavior in fresh cementitious suspensions. The workability of a particulate mixture is usually characterized by detecting its rheological properties [4,5]. Apparent yield stress and viscosity, which describe the fluid's internal resistance to flow, are the two main macroscopic parameters which are used to quantify the effects of PCE addition to the suspensions. A further key factor, to quantify the efficiency of a superplasticizer, is to investigate how much polymer is really interacting and remaining on the particle surfaces. The adsorption behavior on colloid surface may be determined by means of total organic carbon (TOC) measurements [6,7]. Moreover, the detection of the ζ-potential enables to study the influence of superplasticizers on particle charges and to analyze the effect of electrostatic dispersion forces acting between them [8].

Houst et al. [9] recently collected results, obtained with many techniques, to asses the adsorption behavior and the rheological properties of different systems, and to model superplasticizer action at the solid–liquid interface. Studies from Plank et al. [10–12] highlighted the influence of different polymer architectures and their interaction with cementitious systems. They showed that short side chains, resulting in a high polymer charge, perform strong adsorption especially on positively charged particles. Other studies by Zingg et al. on pure cement phases confirmed that ettringite is the cement phase which most adsorbs superplasticizers [13].

Additionally to this variety of techniques, atomic force microscopy (AFM) was applied in the past to measure in liquid the dispersion forces due to PCE [14]. In order to obtain reliable results with this technique, substrates that are smooth, flat and non-reacting are a prerequisite. Since these characteristics can not be provided by cement, the use of inert model systems is necessary to enable these kinds of force measurements. Spherical probes of magnesium oxide approaching MgO substrates were used to simulate a cement-like colloidal particle [15]. It was proposed that, for a more complete understanding of the measured force–distance curves, additional studies on the polymer adsorption and the ζ-potential are required [16]. This investigation revealed that the standard AFM tips, composed of silicon nitride, are positively charged, and so they adsorb PCE.

In the present study, a multi-method approach involving all these experimental techniques (rheology, adsorption, ζ-potential, and AFM) is reported, in order to contribute to a more general

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[*] Corresponding author at: Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstr. 129, 8600 Duebendorf, Switzerland. Tel.: +41 58 765 43 60; fax: +41 58 765 40 35.
E-mail address: lucia.ferrari@empa.ch (L. Ferrari).

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understanding of the influence of superplasticizers on cement suspensions. The aim of this work is to separately analyze different behaviors of PCEs, from a macroscopic to a nanoscopic point of view. In a first moment, a series of superplasticizer architectures was tested on two cements with different chemical compositions, and on two model powders (magnesium oxide and calcite), in water or in synthetic cement pore solution. Experiments about rheological properties and PCE adsorption were performed on these systems. In a second moment, the focus was shifted toward the characterization of the electrostatic and steric dispersion forces, detected respectively by ζ-potential and AFM. The use of an AFM device restricted the set of the used materials to magnesium oxide only. Steric forces were detected by means of an AFM technique applying plateau tips coated with platinum. This new tool reasonably permits to probe the liquid–solid interfaces with a non-adsorbing, neutral tip, which prevents the adsorption of PCE on the AFM tip, due to its negative zeta potential [17].

2. Materials

2.1. Superplasticizers

Different polycarboxylate superplasticizers composed of methoxy-polyethylene-glycol side chains attached on a poly-methacrylic-acid backbone were tested in this study (see Fig. 1). One of the aims is to understand the influence of anionic charge density, side chain length and side chain density on the interaction between PCE and particles at the liquid–solid interface, in order to capture the efficiency of different polymer architectures. Table 1 reports superplasticizer properties, while Fig. 2 illustrates their architectures. The first number in the name of superplasticizer, here called p, refers to the number of polyethylene oxide (PEO) units and it represents the side chain length, while the second one, n, refers to the number of anionic functional groups. M_n is the number-average molecular weight, M_w is the mass-average molecular weight, and their ratio M_w/M_n represents the polydispersity index. Superplasticizers with high side chain density ($n=1.5$ and $n=3$) were synthesized as described in [10], 45PC12 was synthesized according to [12], and 23PC6 was synthesized following the process explained in [18]. Main chain length (MCL) and side chain length (SCL) were estimated according to [19]. Charge density (CD) is calculated as the ratio between the moles of anionic charge and the molar mass of each PCE unit.

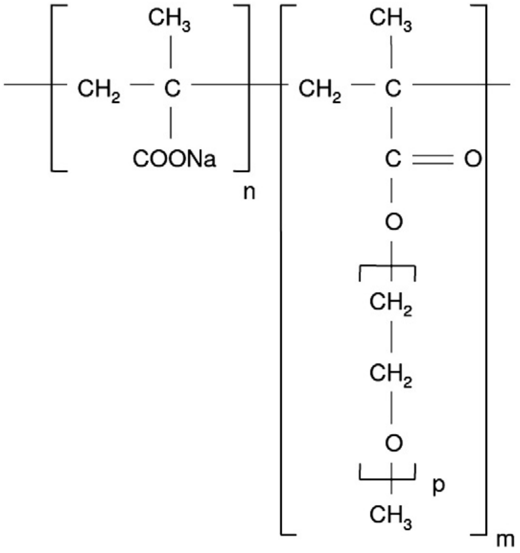

Fig. 1. Chemical structure of the studied PCE.

Table 1
Characteristic properties of PCE.

$pPCn$ [a]	M_n [b] (g/mol)	M_w [c] (g/mol)	PDI [d]	MCL (nm)	SCL (nm)	CD [e] (mmol/g)
8.5PC1.5	121,700	520,400	4.3	130.4	2.4	2.6
8.5PC3	25,800	106,000	4.1	36.3	2.4	4.2
23PC6	7600	18,900	2.5	8.3	6.4	3.7
45PC1.5	35,000	161,300	4.6	10.0	12.5	0.8
45PC3	50,100	156,700	3.1	21.7	12.5	1.4
45PC12	11,800	342,500	2.9	12.5	12.5	3.9
111PC1.5	57,100	98,000	1.7	7.0	30.9	0.3
111PC3	53,000	149,100	2.8	10.2	30.9	0.6

[a] p = number of PEO groups, n = number of carboxylic groups.
[b] M_n = number-average molecular weight.
[c] M_w = mass-average molecular weight.
[d] $PDI = M_n/M_w$ = polydispersity index.
[e] CD = charge density.

2.2. Cements and model powders

To study the influence of different superplasticizer architectures on particle suspensions, two kinds of cements and two almost inert model-powders (magnesium oxide and calcite) were used (see Table 2). Magnesium oxide was used in the past to model cement suspensions, due to their similar isoelectric points [20], while calcite is ordinarily used as a mineral constituent of common building materials. The BET value of MgO is significantly higher than the other three powders. Furthermore specific surface area of cement changes during the first minutes of hydration, generally increasing. Considering all these aspects, at least for the inert powders, adjustment of the water-to-powder ratio was empirically considered to compensate the increase of water demand with the increase of BET values.

Particle size distributions were obtained by laser diffraction measurements (Mastersizer X, Malvern, UK), and surface areas were derived from BET theory measuring nitrogen sorption (SA 3100, Beckman Coulter, Fullerton, CA).

Table 3 reports the chemical compositions of the cements (by polarized X-Ray fluorescence), while the main clinker phases were estimated by the Bogue calculation (Cement N (wt.%): $C_3S=58$, $C_2S=14$, $C_3A=6$, $C_4AF=11$; Cement HS (wt.%): $C_3S=47$, $C_2S=15$, $C_3A=1$, $C_4AF=18$). Since many studies showed the affinity between ettringite and superplasticizers [1,7,8,21], the two cements were selected with different C_3A contents in order to test the influence of ettringite formation on the effect of PCE performance. The amount of ettringite formed was measured by thermogravimetric analysis. 10 min after preparing the paste the hydration was stopped by solvent exchange with isopropanol and washing with ether. The quantity of ettringite was then calculated by the water loss between 50 °C and 125 °C determined by means of thermogravimetric analyses. The ettringite contents after 10 min were 2.7% for cement N and 1.1% for cement HS, which is related to the respective content of C_3A in the cement.

The decision of testing inert powder allows to control the influence of ionic species on the behavior of the different superplasticizers, and permitted the comparison with the AFM measurements on model substances. On the other side, the cements were mixed with deionized water and the two model powders were treated with deionized water or a synthetic solution simulating a typical ionic composition of the cement pore solution after 1 h of hydration for a w/c ratio of 0.5 [22]. Table 4 reports the chemical composition of the synthetic pore solution, of the two cements and of the inert powders after 10 min of hydration analyzed by ion chromatography system (ICS-3000, Dionex Corporation, Sunnyvale CA, USA). The synthetic pore solution represents well the ionic composition of the standard cement N, while for cement HS with low C_3A content the concentration of sulfate and potassium ions is reduced.

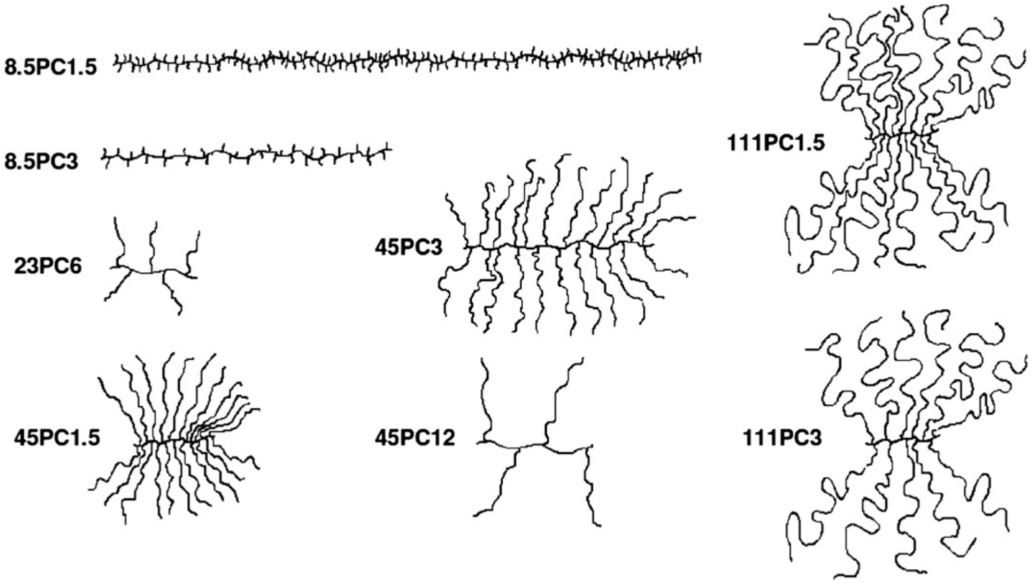

Fig. 2. Schematic representation of PCE architecture.

3. Methods

3.1. Rheology

Rheological measurements were performed using a Paar Physica MCR 300 rheometer with concentric cylindrical geometry. A rotating bob was lowered to the measuring position, and shear stress was detected recording a flow curve with shear rates increasing from 10 up to 100 s^{-1} and decreasing from 100 down to 10 s^{-1}. Apparent yield stress was estimated interpolating the data of the return curve following the Birmingham model (see Fig. 3).

For each powder, different volume fractions were tested. For the two cements the w/c ratio was kept constant at 0.36, while for the model powders the w/p ratio was adjusted in order to find the right paste consistence displaying apparent yield stresses around 27 ± 5 Pa in absence of superplasticizer. These water-to-powder ratios were highly different, 1 for MgO and 0.32 for calcite. Consequently, PCE was added at a constant dosage of 1 mg/g of solid and the new apparent yield stress was recorded. All the suspensions were mixed by a commercial electronic mixer for 1 min, then the addition of PCE was done and the paste was mixed for an additional minute prior to the measurement. The temperature was kept constant at 20 °C using a water bath during the tests, and no segregation of particles was observed. Some additional experiments applying higher dosages (2 and 4 mg/g) of 8.5PC3 and 45PC3 to MgO suspensions were performed in order to test the effect concentrations higher than 1 mg/g of solid.

Table 2
Characteristic properties of powders used for PCE tests.

Material	Name	Blaine (cm^2/g)	BET (m^2/g)	Density (g/cm^3)	% volume diameters (μm)		
					d_{10}	d_{50}	d_{90}
Cement N	CEM I 42.5 N	3150	0.94	3.11	2.8	17.1	52.74
Cement HS	CEM I 42.5 N HS	4050	1.21	3.11	2.9	14.2	45.3
Magnesium oxide	Magnesia 298 (MgO 99.5%)	–	5.77	3.51	1.8	7.4	65.3
Calcite	Nekafill 15 ($CaCO_3$ 90.9%)	–	1.33	2.71	1.5	12.4	103.0

3.2. Adsorption

Adsorption measurements were performed to detect the quantity of superplasticizer adsorbed on the solid particles. This value is usually determined by the solution depletion method. After mixing the powder with the solution containing the polymer, the amount of superplasticizer remaining in the solution can be measured by separating the liquid phase from the suspension. The consumed polymer is estimated to be the difference in concentration before and after contact with the powder.

Volume fractions and superplasticizer dosages were the same as used for the rheological experiments. Ten minutes after mixing, the samples were centrifuged and the liquid part was removed and filtrated through a 0.45 μm nylon filter. Then a Sievers 5310 Laboratory TOC-Analyzer was used to determine the total organic carbon (TOC) of the remaining liquid phase, which gives direct information about the amount of remained polymer. TOC content of the pore solution without superplasticizer was considered as background to calculate the consumed PCE. The solution depletion method explained does not allow to detect whether the polymer really adsorbs on the particle surface or if the polymer remains simply trapped between the particles after the centrifugation. The term 'consumed' instead of 'adsorbed' is hence preferred to avoid false statements.

3.3. ζ-potential

The electrokinetic potential of colloidal systems is called ζ-potential. It represents the potential difference between the dispersion medium and the stationary layer of water molecules and ions attached to the dispersed particle. In other words, it may be interpreted as particle charge measured on a slip plane usually composed by the species adsorbed in proximity of the surface.

Table 3
Chemical composition (wt.%) of cements.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	CO_2	Total amount
Cement N	62.6	19.0	4.5	3.1	2.2	0.21	0.82	3.3	2.1	97.8
Cement HS	59.8	17.9	4.3	5.9	2.4	0.59	0.82	3.1	2.7	97.5

Table 4
Chemical composition of the solutions extracted from the mixtures after 10 min of hydration (mmol/L).

	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	OH^-	pH
Synthetic pore solution	200	40	444	<0.1	10	104	12.8
Cement N	237	37	449	<0.1	14	121	13.0
Cement HS	124	58	216	<0.1	11	99	12.9
Magnesium oxide	6	4	0.4	15	0.2	0.4	10.7
Calcite	0.5	0.4	0.3	0.2	0.4	0.1	9.4

Actually, it does not represent the charge directly detected on the particle surface; hence it is highly influenced by the presence of ions or charged polymers in solution.

All the ζ-potential data were collected with a ZetaProbe instrument (Colloidal Dynamics Inc., North Attleboro, MA), which works on the basis of the electroacoustic method. The motion of particles in suspension driven by an electrical field is recorded as dynamic mobility, from which the software calculates the ζ-potential.

The aim of measuring ζ-potential is to detect changes in particle charges according to superplasticizer concentration. The adsorption of the negatively charged backbone on the solid particles forms an additional slipping layer which influences particle charge. A change in particle charge is the first indication that the adsorption process is occurring, and it gives information about electrostatic dispersion forces eventually taking place at the particle surfaces. To detect these effects of powder–polymer interaction, 8.5PC3 and 45PC3 were titrated up to a concentration of 5 mg/g of solid to a relatively diluted suspension (wt = 5%) of magnesium oxide using deionized water or synthetic pore solution, respectively.

3.4. Atomic force microscopy

AFM force measurements in liquid solution containing superplasticizers were performed by a commercial instrument (Nanoscope IV, Veeco Digital Instruments, Santa Barbara, CA). This atomic force microscope consists of a cantilever with a sharp tip (probe) at its end, which is used to scan the specimen substrate. When the tip approaches the sample substrate, forces between the tip and the sample lead to a cantilever deflection, which is measured using a laser spot reflected from the top surface of the cantilever into a photodiode. This deformation gives information about substrate topography and the force interacting between the tip and the substrate. A schematic representation of AFM general setup and the translation of a deflection signal into a force–distance curve, using the cantilever spring constant, are presented elsewhere [16]. The distance = 0 is determined as the point of the raw deflection–distance curve in which the deflection of the cantilever becomes linear. The linearity of the cantilever deformation versus the distance indicates the position in which the tip is in a static position in contact with the substrate, thus the movement of the scanner is fully converted in the cantilever deformation.

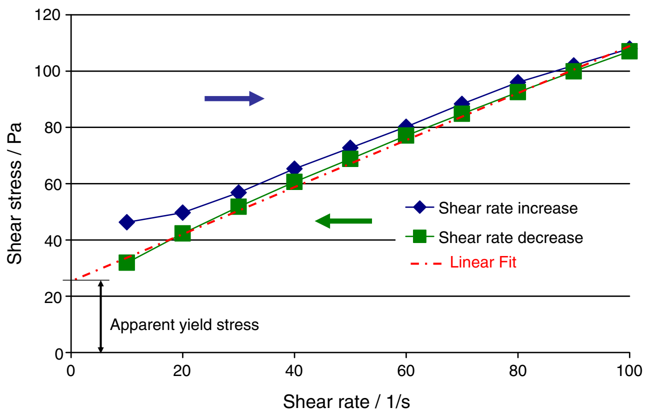

Fig. 3. Typical example of flow curve.

Since it was previously measured that the silicon nitride showed a high affinity with superplasticizers [16], a commercially available plateau tip (NanoAndMore GmbH, Wetzlar, D) coated with a platinum layer of 20 nm of thickness was used here to probe the dispersion forces (see Fig. 4 from NanoAndMore GmbH).

In this way it was possible to approach the substrate covered with superplasticizer with a neutral and flat surface. The idea is to prevent superplasticizer adsorption on the probe. The coating process influenced the elasticity of the cantilever, and this effect was taken into account by measuring the spring constant after the sputtering process.

Water or artificial cement pore solutions containing different amounts (1, 2 and 4 g/L) of superplasticizers (8.5PC3 and 45PC3), which correspond to the concentrations used for the rheology and adsorption experiments, were flushed into a fluid cell and the forces were then detected.

4. Results and discussion

Results and discussion are divided into two parts. In Section 4.1, the influence of eight different superplasticizer architectures on the rheology and on the adsorption behavior of two kinds of cements and inert model suspensions is analyzed. In Section 4.2, a more detailed study on two representative PCEs is provided, focusing on the origin of the dispersion forces directly interacting among the particles. This second analysis is based on experimental results obtained with MgO powder and MgO substrates for AFM experiments. This restriction is dictated by the use of AFM in liquid environment.

4.1. Influence of superplasticizer architecture on suspensions

With this first set of results, a wide range of polymer architectures is discussed to test their influence on rheological properties and adsorption, relating them to the presence of ions in solution.

4.1.1. Rheology

The apparent yield stresses of suspensions holding the same dosage (1 mg of PCE per g of solid) of different superplasticizers are reported in Figs. 5 and 6.

Differences in superplasticizer side chain length and in side chain density affect the collected data significantly, on cements and on

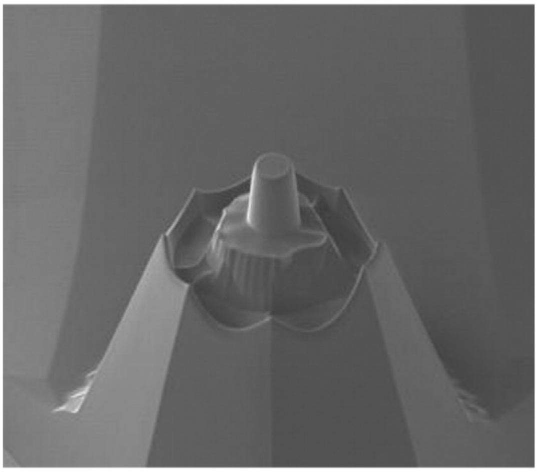

Fig. 4. Image of the AFM-tip. Plateau diameter = 1.8 μm.

model powders. Generally, low charge density confers low apparent yield stresses to the cement suspensions. For instance, 8.5PC3 and 45PC3 have the same density of grafted side chains, but 8.5PC3, because of higher charge density, enables more effective rheological properties. On the other side, comparing 45PC3 with 45PC12, i.e. superplasticizers with same side chain length but different charge densities, the higher charge of 45PC12 brings a significant contribution to improve the rheology of the mixture, leading to a lower apparent yield stress in all the considered suspensions.

The two kinds of cement show generally different behaviors, although the same w/c ratio was used for the mix. Cement N, despite its lower Blaine value and lower BET surface area in dry conditions, provides higher apparent yield stresses in comparison to the cement HS. Accordingly, the cement HS presents different fineness and smaller particle size distribution. In principle, these features of cement HS would lead to a loss of workability, due to the larger area in contact with water; though it allows a more compact packing of particles within the mixture which usually provides good fluidity. On the other side, the reactions occurring at the first minutes of hydration change the total surface area of the cement particles [23], thus misleading the discussion of the influence of specific surface area on cement rheology. Indeed, due to its high content of C_3A, cement N produces more ettringite. The needle-shaped crystals of ettringite [24] at the early age of hydration contribute to increase the total surface area of the cement particles in the paste, influencing the rheological properties of the mixture. As consequence of these facts, the hydration process plays an important role in influencing the flowability of the cement paste.

Looking at results obtained with inert powders (Fig. 6), they show a significant difference between suspensions prepared with pore solution and suspensions prepared with water. Especially in the calcite system, the measurements performed with water show a drastic decrease of the apparent yield stress after the superplasticizer addition, even for those PCEs which do not have strong influence in the other systems (111PC1.5 and 111PC3). This comparison between the different inert mixtures reveals that the presence of ions in the solution disturbs the PCE efficiency.

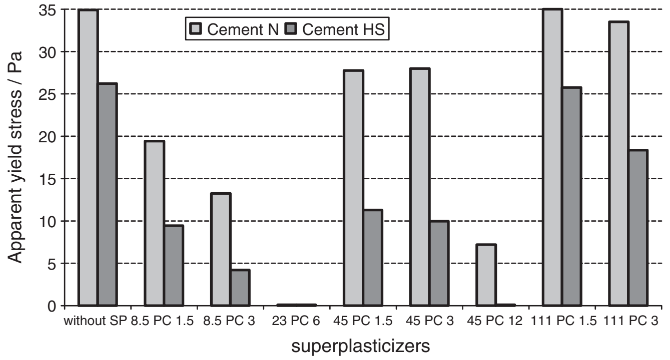

Fig. 5. Apparent yield stress of cement suspensions mixed with water and different superplasticizers (1 mg of PCE per g of solid).

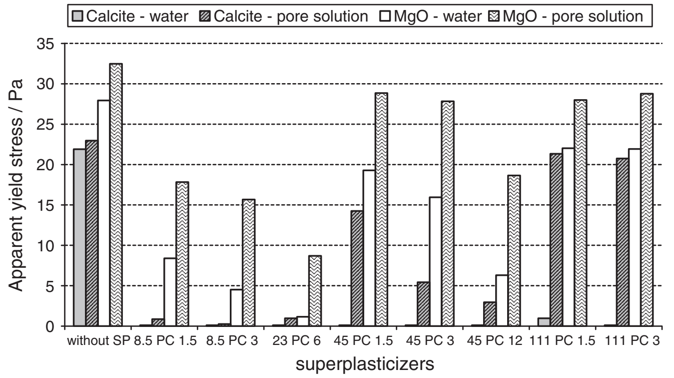

Fig. 6. Apparent yield stress of inert powder suspensions mixed with water or synthetic cement pore solution containing superplasticizers (1 mg of PCE per g of powder).

4.1.2. Adsorption

The adsorption ratios of suspensions with the same dosage of superplasticizers (1 mg of PCE per g of solid) are shown in Table 5. Three different normalizations are provided: adsorption per unit weight of powder (mg/g), adsorption per surface BET unit area of dry powder (mg/m^2) and adsorption ratio between PCE added and PCE consumed (%). Each of this normalization is in principle correct, and they take into account different aspects of the adsorption process. These data provide more information to the reader and allow a more complete understanding of the adsorption phenomenon. The normalizations emphasize the difficulties of a direct comparison of the adsorption data due to the differences in specific surface area. However some trends can be observed and the discussion is led according to the different types of PCE architecture, to the two kinds of cement and to the influence of ions.

In each liquid–solid system, higher charge density of PCE enables stronger adsorption in particle suspensions. Indeed, 111PC1.5 and 111PC3 afford rather poor adsorption compared to 8.5PC1.5 or 23PC6. This is also due to the high molar mass of the side chains, which results in a lower molar charge density. The concept to supply high charge density and long side chains at the same time is to reduce the

Table 5
Adsorption of superplasticizer on tested powders.

	Cement N			Cement HS		
	Per weight (mg/g)	Per surface area (mg/m^2)	Adsorption ratio (%)	Per weight (mg/g)	Per surface area (mg/m^2)	Adsorption ratio (%)
8.5PC1.5	0.66	0.70	67	0.61	0.51	63
8.5PC3	0.63	0.67	61	0.55	0.45	54
23PC6	0.65	0.69	66	0.62	0.52	64
45PC1.5	0.30	0.32	31	0.15	0.12	15
45PC3	0.40	0.43	39	0.34	0.28	33
45PC12	0.49	0.52	49	0.45	0.37	45
111PC1.5	0.01	0.01	1	0.01	0.01	1
111PC3	0.02	0.02	2	0.06	0.05	1
	Calcite–water			Calcite–pore solution		
	Per weight (mg/g)	Per surface area (mg/m^2)	Adsorption ratio (%)	Per weight (mg/g)	Per surface area (mg/m^2)	Adsorption ratio (%)
8.5PC1.5	0.67	0.50	66	0.32	0.24	32
8.5PC3	0.46	0.34	47	0.18	0.13	18
23PC6	0.40	0.30	50	0.41	0.31	51
45PC1.5	0.54	0.40	52	0.27	0.20	26
45PC3	0.61	0.46	62	0.25	0.19	26
45PC12	0.38	0.28	37	0.29	0.22	29
111PC1.5	0.27	0.20	27	0.09	0.06	9
111PC3	0.32	0.24	31	0.18	0.13	17
	MgO–water			MgO–pore solution		
	Per weight (mg/g)	Per surface area (mg/m^2)	Adsorption ratio (%)	Per weight (mg/g)	Per surface area (mg/m^2)	Adsorption ratio (%)
8.5PC1.5	0.84	0.15	80	0.74	0.13	71
8.5PC3	0.86	0.15	79	0.61	0.11	56
23PC6	0.64	0.11	81	0.52	0.09	66
45PC1.5	0.50	0.09	52	0.21	0.04	21
45PC3	0.45	0.08	47	0.24	0.04	25
45PC12	0.69	0.12	65	0.47	0.08	45
111PC1.5	0.01	0.01	1	0.01	0.01	1
111PC3	0.23	0.04	21	0.01	0.01	1

grafting density. Indeed, 45PC12 in comparison to 45PC3 generally performs stronger adsorption on the tested suspensions.

Regarding cement mixtures, cement N adsorbs slightly larger amounts of PCE in comparison to cement HS, despite the double amount of sulfate presence in the extracted pore solution. In the first 10 min of hydration, the ettringite formed from C_3A phase allows adsorption properties to the cement suspensions. More ettringite is formed, more PCEs are required to obtain a high workability. Furthermore, ettringite formation increases the specific surface area if cement, providing more available surface for PCE adsorption.

On the other side, regarding the inert powders, the adsorption is strongly influenced by the presence of ions in the suspensions. In general, the ions present in the pore solution have the tendency to interfere with the adsorption process, reducing the amount of consumed polymer in both systems treated with pore solution. It was shown that sulfate ions, with their high negative charge, compete with PCE to occupy the surface of positively charged particles [25], affecting the adsorption of the polymer on grain surface. Thus, among all the ionic species present in solution, sulfates are the most likely candidates to interfere with the adsorption process.

4.1.3. Discussion about superplasticizer efficiency

To obtain a similar initial apparent yield stress in suspension without superplasticizer, very different solid fractions had to be used. This significant difference is probably due to different particle size distributions, which may create disparity in the water demand. Indeed, MgO has a d_{50} value that is much smaller than the one of the other three powders, and also its specific surface area (BET) is nearly five times larger than the other ones. This means that, at the same weight, the area at the solid–liquid interface is five times more, hence increasing the water demand. This fact is the main reason why a higher water-to-powder ratio was required for MgO in order to obtain similar apparent yield stresses.

Different superplasticizer architectures achieve differences in adsorption and in rheological properties. Generally, high charge density is responsible for high adsorption, which then leads to low apparent yield stresses. Long side chains reduce the molar charge density of the polymer, and this effect creates some difficulties in the adsorption process, since it is mainly driven by electrostatic attraction between the negatively charged polymer and the positively charged particles. By theory, longer side chains should exert higher steric repulsion between two particle surfaces, thus affording more effective rheological properties, and higher performance in cement pastes. However, the superplasticizer with the longest side chain does not produce the best performance in fresh mixtures, probably owing to their poor adsorption.

Regarding the two cements used here, cement N contains a larger amount of C_3A, which forms ettringite during the early hydration. The ettringite is directly related to PCE adsorption, due to the increase of the available positively charged surface area. However, rheological properties clearly show the tendency of having low apparent yield stress in suspension prepared with cement HS. Indeed, whenever there is a substantial quantity of ettringite formed, more PCEs are required to provide fluidity to the suspension, because the large surface area of ettringite adsorbs much polymer. Thus, on one side this hydration product negatively impacts the rheological properties, but on the other side it provides a strong adsorption. This effect suggests the idea that large amount of adsorbed PCE does not necessarily imply low apparent yield stresses.

The use of inert powders to test rheology and adsorption clearly shows a strong influence of ions on superplasticizer behavior, reducing the PCE action when the liquid–powder mix is prepared with pore solution. Actually, it is reasonable to imagine that many ionic species in the suspension and the pH may influence the ζ-potential of the particles, consequently negatively affecting the adsorption ratio, resulting in worse rheological properties.

A comparison between all these data suggests the idea that another aspect of PCE efficiency has to be considered. Calcite treated with water and PCE shows a drastic decrease of the apparent yield stresses, which does not match with similarly strong adsorption of superplasticizer. In a previous publication [16], the adsorption of PCE has been detected on the same calcite–water system used here, but the suspensions were prepared with a much lower solid content. There, the results displayed that superplasticizer interaction with calcite powder is very poor. The increase of adsorbed polymer according to the increase of particles in suspension suggests the idea that in certain cases superplasticizers are not really sticking on particles, but they remain trapped and framed between two adjacent particle surfaces. This effect may give less friction and less pressure among particles, thus affording a more compact packing of the solid grains. This allows effective rheological properties even without specific attachment of the polymer on the particles.

4.2. Detailed analysis of dispersion forces

In this second part a detailed analysis of the dispersion forces owed to superplasticizer is presented. Since some experiments were performed using the AFM, it was necessary to limit the set of previously used materials to inert materials. However, calcite was not considered because of its poor ability to adsorb superplasticizer in diluted systems, which is the case of the AFM set-up, thus reporting low force ranges [16]. Thus all the measurements were performed on magnesium oxide. The variety of superplasticizer structures tested also was reduced to only two kinds, 8.5PC3 and 45PC3, in order to focus on the effect of different side chain lengths, different charge densities, and different PCE concentrations.

4.2.1. AFM

Force–distance curves measured with AFM are displayed in Fig. 7, which reports plots for the curves collected with 8.5PC3 and 45PC3 in concentrations of 1, 2 and 4 g/L in water or synthetic cement pore solution. Without superplasticizer, an attraction between the tip and the substrate was observed.

One of the most evident differences between these two plots is the change in dispersion forces occurring at different concentrations when superplasticizer 8.5PC3 is used. Opposite to this, measurements performed with 45PC3 show no apparent impact on repulsion between the tip and the substrate as a result of higher polymer concentration in solution. Accordingly, all the curves collected in water (empty markers) and in pore solution (filled markers) overlap. For interpretation of the force curves, some assumptions were made. For instance, one possible explanation for this effect is the probable formation of multi-layers of 8.5PC3, which accumulate on the MgO substrate. For a PCE possessing low charge density and long side chain, i.e. 45PC3, the interaction with particles may be weak, so after the formation of a first layer of PCE on the particle surface, the other side superplasticizer remains in the solution not producing the accumulation of many layer of PCE. These differences in dispersion forces by varying the concentration of PCE was already directly observed with highly charged superplasticizers, and similar conclusions about multilayer formation were made [27]. AFM images scanned in air on substrates with depositions of PCE provide a further confirmation of this accumulation of superplasticizer on the substrate [28].

A second observation is related to experiments done in pore solution, which display a significant reduction of dispersion force values, compared to results obtained in water. It shows once again the strong influence of ions on the effect of superplasticizer. The reduction of the force ranges in presence of ions was already observed in the literature. Sindel et al. (1999) speculated that the presence of electrolytes disrupts hydrogen bonds required to form an extended polymer conformation [26], and Kirby and Lewis (2004) attributed the shrinkage of polyelectrolytes in high ionic strength solution to

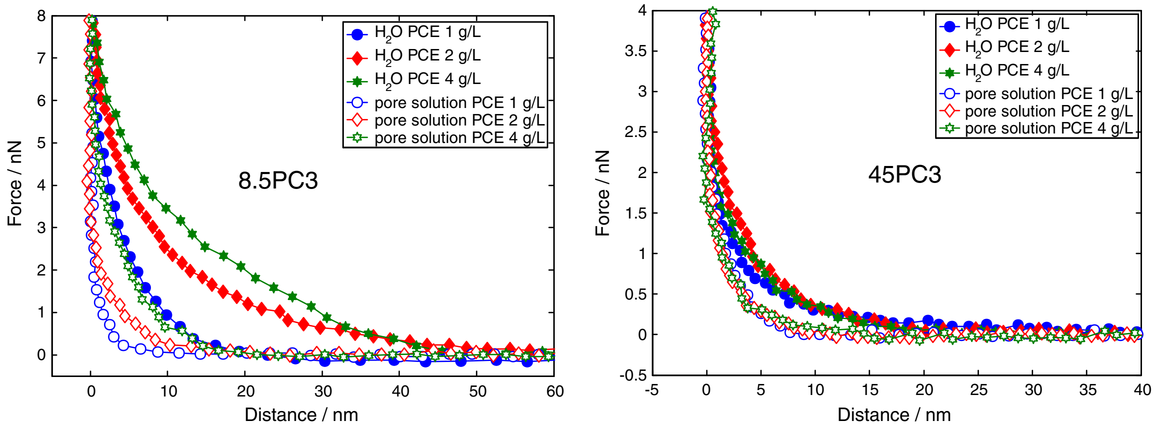

Fig. 7. AFM force measurements.

reduced intersegment repulsion between screened COO^- groups [5]. Both interpretations can in principle be true and can explain the decrease of the force ranges.

4.2.2. Adsorption

Adsorption isotherms obtained on magnesium oxide at increasing concentrations of superplasticizer are reported in Fig. 8.

As expected from previous discussions, short side chains afford high charge density, hence strong adsorption on solid particles. Indeed, the isotherm curve of 8.5PC3 displays a higher adsorption, compared to the one obtained with 45PC3. The presence of ions in solution influences the interaction superplasticizer–powder, thus lowering the adsorption of both PCEs. However, highly anionic 8.5PC3 is much more affected by ions than 45PC3.

4.2.3. ζ-potential

In order to evaluate the possibility of electrostatic forces interacting between particles coated by superplasticizer molecules, ζ-potential measurements were performed. Fig. 9 shows particle charge values at different concentrations of superplasticizers.

Adsorption of 8.5PC3 on MgO enables to change the particle ζ-potential from positive to negative. On the other side, 45PC3, which has a lower charge density, brings the MgO particle to values of ζ-potential around zero.

In this set of measurements, the presence of ions in solution highly affects the conductivity of the suspensions (deionized water = 0.7 mS/cm, pore solution = 35 mS/cm), and consequently it affects particle charges. Indeed, measurements of ζ-potential show that titration of superplasticizers is highly different according to the used solution. When the measurements are performed in synthetic pore solution, the initial value of MgO particles is negative, and it remain almost constant during the PCE titration.

4.2.4. Rheology

It is known that a higher dosage of PCE gives more effective rheological properties to cement pastes. For consistence, apparent yield stresses obtained with MgO suspensions in water and pore solution with different concentrations of 8.5PC3 and 45PC3 are provided in Fig. 10.

Differences in side chain length and in ionic composition of the solution again affect the efficiency of PCE. Indeed, addition of 8.5PC3 to a suspension grants lower apparent yield stress compared to the addition of 45PC3. However, when exceeding a certain PCE dosage (4 mg/g of solid), this difference is not that significant any more: the apparent yield stress values are similar, with the exception of 45PC3 in pore solution.

On the other hand, the measurements obtained in pore solution display poor rheological properties, compared to the suspension mixed with deionized water. This fact reveals that the presence of ions, maybe mainly of sulfates, reduces superplasticizer performance, reasonably disturbing the adsorption of polymer on the particles, and thus the dispersion force as well.

4.2.5. Discussion about dispersion forces

As shown in the previously discussed data, differences in superplasticizer architecture produces different results on adsorption and rheological properties. In addition to these observations, superplasticizer dosage highly influences apparent yield stress data,

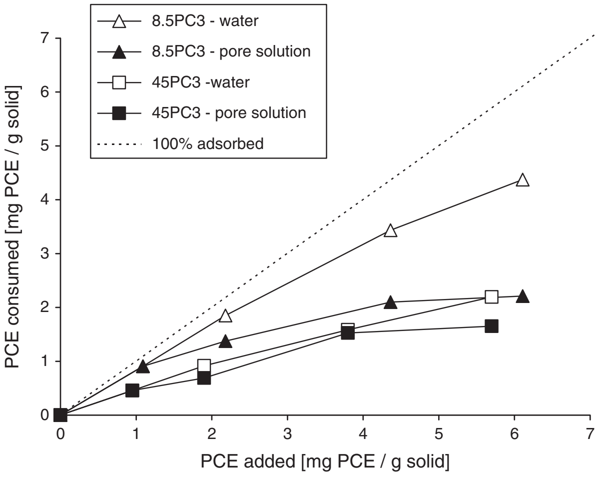

Fig. 8. Adsorption isotherms for different PCEs in MgO suspensions prepared with water or synthetic cement pore solution.

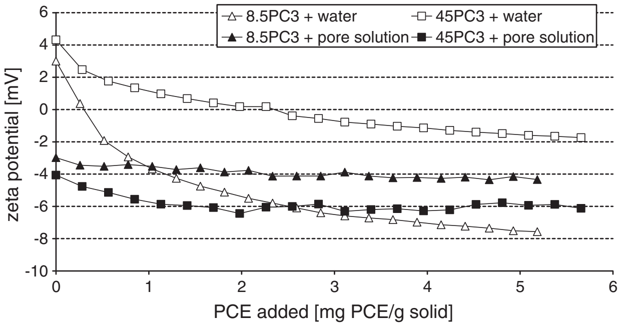

Fig. 9. ζ-potential of MgO at different concentrations of superplasticizer in deionized water or in pore solution.

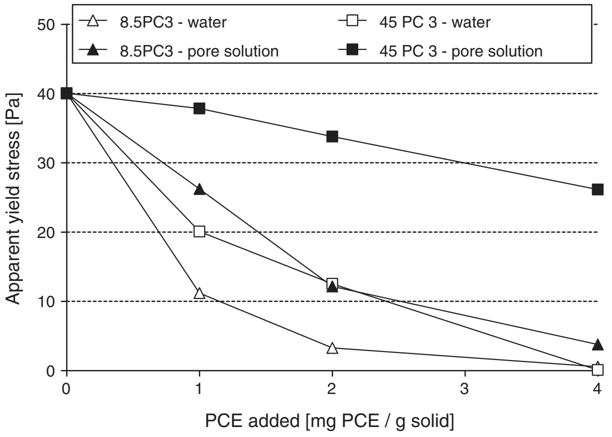

Fig. 10. Apparent yield stress of MgO suspensions at different PCE concentrations.

even in systems where the dispersion forces did not increase with PCE concentration (see data collected with 45PC3). In other words, even when the dispersion forces, steric and electrostatic, do not increase with increase of dosage of superplasticizer, the rheological properties of the suspensions improve. Hence, from microscopic point of view, no differences occur at the surface level of individual particles. However, probably a larger amount of particles is covered by superplasticizers, and this fact reduces the apparent yield stresses of the paste. In any case, it is possible to conclude that shorter side chains afford higher performances in adsorption and rheology. Furthermore, AFM results show that they provide stronger dispersion forces that increase with the concentration of PCE in solution.

On the other side, ionic species in solution disturb superplasticizer behavior in each aspect analyzed here: adsorption on particle, dispersion steric forces, ζ-potential, and consequently rheology. The adsorption of sulfate ions on positive particles influences the ζ-potential, which influences the adsorption process. The ions in solution also affect the steric dispersion forces by reducing force ranges and intensities, thus influencing the rheology. Of course, in an actual cement suspension, there is no possibility of avoiding the interaction superplasticizer–ions, but we find these results to present a good starting point to understand cases of unexpected incompatibility between PCE and cement.

5. Conclusions

This study shows that superplasticizer architecture affects the efficiency of PCE. Generally, the addition of PCE to a particle suspension provides more effective rheological properties, thus reducing the apparent yield stress of the mixture. The results elucidate that high polymer charge affords strong adsorption of the superplasticizer, then high dispersion forces, and thus good rheology. The AFM measurements also show that certain PCE architectures lead to dispersion of local forces which vary with the concentration of superplasticizer in solution.

Tests on two kinds of cement with different amounts of ettringite formed after 10 min of hydration reveal that this hydration product strongly affects the workability of the cement paste, by increasing the surface area of the cement particles and providing high adsorption of superplasticizer.

Tests on inert powders clarify that the presence of different ion species in solution may impede PCE adsorption, and so the apparent yield stress values. The use of an AFM plateau tip coated with platinum reveals that dispersion forces are also affected by high ionic strength.

Another aspect emerging from this multi-method analysis concerns the idea that rheological properties are not only depending on PCE adsorption and PCE dispersion forces. Our analysis starts from macroscopic observations, i.e. rheological measurements, and it zooms in focusing on details of superplasticizer behavior at the solid liquid interface, i.e. adsorption and dispersion forces. However, suspensions of calcite treated with water, where adsorption and the dispersion forces are not optimal, give surprisingly low apparent yield stress values. This observation could potentially be explained by the existence of a third effect, namely the filling of the interstitial spaces between neighbor particles, to avoid their direct contact and lubricating their surfaces, in order to reduce the friction between adjacent particles. Furthermore, it is expected that properties of the liquid also are affected by PCE presence: if the water–solid interface is energetically convenient, it increases the wettability of particle surface and the water will have the tendency to distribute around particles. More research in this direction is hence needed.

Concluding, major reason of incompatibility phenomena has been clarified and additional information was elucidated by this study. However, in order to complete the study on this topic, further investigation is important and indispensable.

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