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Compatibility between polycarboxylate-based admixtures and blended-cement pastes

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ABSTRACT

Compatibility between three structurally different PCEs and four commercial cements: one non-blended cement and three blended cements, was studied by adsorption, zeta potential, rheological and calorimetric methods.

According to the adsorption curve results, the higher the percentage of carboxylates groups in the admixture, the more intensely it is adsorbed on cement pastes. Moreover, admixtures were shown to be adsorbed by the additions as well, being most effectively adsorbed in limestone.

From the rheological point of view, the optimum carboxylate group/ester group ratio for the admixtures used in the present study was found to range from 0.7 to 1.2. The fluidizing effect of the admixtures on cement pastes is conditioned by the presence of mineral additions. Despite the low adsorption rates of the admixtures in slag-blended cements, the inclusion of PCEs generated the steepest declines in the rheological parameters.

The delay of admixtures on cement hydration intensifies with rising PCE dosage. This admixture-mediated retarding effect was also observed to vary depending on the nature of the addition, and was most intense in slag-blended cement.

1. Introduction

The development in recent years of higher performance and self-compacting concretes has been possible thanks to the use of superplasticizers, mainly polycarboxylate-ether superplasticizers (PCEs). These admixtures decrease water content in concrete (up to 40%) much greater than afforded by conventional lignosulfonate-, melamine- or naphthalene-based superplasticizers. This reduction in water content leads to a decline in porosity, thereby raising concrete mechanical strength and durability. These admixtures also improve concrete workability and rheology, facilitating casting in hard-to-reach places, covering reinforcement more effectively [1].

PCE admixtures structure consists in a linear hydrocarbon backbone with carboxylate and ether group side chains. Their adsorption on cement particles, mediated by their carboxylate groups, disperses cement grains as a result of the steric repulsion generated by the long ether group chains [2–4]. Nonetheless, the use of superplasticizers may pose problems in terms of variations in flowability, uncontrolled setting, anomalous rheological behaviour and so on, due in most cases to cement–admixture incompatibility.

Several authors have reported that cement–admixture compatibility depends primarily on factors attributable to both the admixtures and the cements. The factors associated with admixtures that determine their performance and fluidizing effect are their dosage, the manner and timing of inclusion in the mix and their chemical and structural composition [4–8]. The wide variety of formulations in commercial PCE admixtures, however, is largely responsible for the present incomplete understanding of their effect on rheology, hydration and microstructure of cement systems. The factors attributable to cements that affect compatibility, in turn, include their fineness [9], chemical and mineralogical composition, particularly their C_3A content [10–12], and the amount and type of components such as calcium sulphate and alkaline sulphates [13–15].

The partial replacement of cement clinker with mineral additions is an increasingly common practice. The aim is to produce more eco-efficient, less energy intensive cements whose manufacture involves the re-use of industrial by-products such as fly ash and granulated blast furnace slag. The inclusion of such mineral additions may also enhance paste flowability and durability. Of the 27 cements listed in the existing European standard on the subject (EN 197-1:2000), 26 contain some manner of mineral addition.

Consequently, one factor that may affect cement–admixture compatibility is the presence of mineral additions, since

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admixtures may interact not only with cement, but also with these other components. Nonetheless, very few studies have been conducted on the compatibility of blended cements and PCE admixtures.

Prior studies [12,16] have shown that the rheological changes induced by PCEs on fly ash-blended cements are very similar to the changes observed in non-blended cement. However Li et al. [17] found that the adsorption of PCEs on fly ash-blended cement pastes (with 20% of fly ash) was less intense than in non-blended cement pastes.

Sahmaran et al. [18], in turn, studied the effect of replacing 15–30% of cement with fly ash and limestone powder in self-consolidating mortars containing PCEs. According to these authors, the fluidizing effect of these admixtures was greater in the mortars made with blended than with non-blended cement. Magarotto et al. [19] concluded that limestone-blended cements adsorb greater amounts of PCEs and present better retain of workability than non-blended cements. Palacios et al. [20] concluded that PCEs induce greater flowability in slag-containing pastes than in unblended paste and that this effect is enhanced with the rising percentage of slag in the pastes. These findings concur with the results reported by Hamada et al. [21], who found that the dosage of PCE admixtures required to attain a given flowability was much lower in granulated slag than in other additions or type I cement.

Despite the information obtained from these studies, however, the compatibility between different types of blended cements and superplasticizers, particularly polycarboxylate-based admixtures, is still not fully understood. The present study therefore aimed to ascertain the compatibility between PCE superplasticizers with different structures and blended cements by measuring paste rheology and the changes in their hydration reactions particularly at early ages.

2. Experimental

2.1. Materials

The materials used in this study were:

- Four commercial Portland cements (European standard EN 197-1:2000): One CEM I 42.5R used as a reference, and three blended cements with different content of mineral additions: CEM II/BL 32.5N (limestone-blended cement), CEM II/AV 42.5R (fly ash-blended cement) and CEM III/B 32.5R (slag-blended cement).
- Three mineral additions: fly-ash, limestone and granulated blast furnace slag, which were not the same as the additions present in the blended cements used.
- Three PCE admixtures polyacrilic acid derivatives, named PC1, PC2 and PC3.

Chemical composition and Blaine fineness of the cements (Spanish/European standard UNE-EN 196-6) are given in Table 1. Table 2 lists the mineralogical composition found by Rietveld analysis, along with the amorphous material content in the cements containing slag and fly ash, determined as described by De la Torre et al. [22]. Cement mineralogy is expressed in values normalized to 100% of the crystalline phases, except in cements CEM II/AV 42.5R and CEM III/B 32.5R, where the amorphous content is also included. The percentage of the addition in each case was determined on the grounds of the information in Tables 1 and 2. The percentage of fly ash in CEM II/AV 42.5R was 21%, cement CEM II/BL 32.5R contained 26% of limestone and CEM III/B 32.5R 72% of blast furnace slag.

The soluble sulphate content in these cements at 30 min of hydration was likewise determined, as follows. One gram of cement was mixed with 100 ml of deionized water, stirred for 30 min and filtered. The SO_4^{2-} ion concentration was determined on a Dionex SO_4^{2-} chromatographic instrument (AS14 column, 50-μl loop, 1.20-ml/min flow, eluent: $Na_2CO_3/NaHCO_3$). Table 3 gives the findings and the soluble SO_4^{2-}/C_3A molar ratio for each cement at that hydration time. Table 4, in turn, shows the particle size distribution for the four cements used and the particle size cut-offs for 10%, 50% and 90% of the cement by volume.

The admixtures where characterized using different analytical techniques: FTIR, FT-Raman, ^1H and ^{13}C NMR, GPC and rotational viscosimetry [23]. The functional group estimates were found using the methodology described in the literature [24,25]. Table 5 gives the main physical–chemical characteristics of the three PCE superplasticizers used. Through information given by the manufacturers and the physical–chemical and structural characterization conducted, it is concluded that PC1, PC2 and PC3 have the same length of ether chains (length of PEO chains = 5500 D), but different main chain length (PC1 > PC2 > PC3) and different *C*/*E* ratios, with *C*/*E* (carboxylic/ester groups) values of 1.20, 0.70 and 0.40, respectively. Therefore, the charge density increases from PC1 to PC3 progressively. Table 5 also shows the molecular weight determined for the three PCEs, where the progression of molecular weights is PC1 < PC2 < PC3, in reverse order to the ratio *C*/*E*. Table 6 gives the chemical analysis and Blaine fineness of the fly ash, limestone and granulated blast furnace slag used exclusively in adsorption tests of admixture PC1.

2.2. Tests conducted

2.2.1. Adsorption curves

Twenty grams of cement and 40 g of a solution containing polycarboxylate-based admixture were mixed and stirred for 30 min at 25 °C to determine the adsorption isotherms for the superplasticizers. The suspensions were subsequently centrifuged, the liquid phase was extracted off and the total organic carbon content was found on a SHIMADZU TOC-VCSH/CSN total organic carbon (TOC) analyzer. Admixture adsorption by the cements studied was taken to be the difference between the amount initially added and the amount present in the liquid phase measured by TOC.

2.2.2. Determination of the effect of polycarboxylate-based superplasticizers on the zeta potential of cement suspensions

The effect of different dosages of superplasticizer on the zeta potential of cement suspensions was determined with a Colloidal Dynamics Acoustosizer IIs. Cement suspensions were prepared by mixing 30 g of binder with 160 g of water (solid fraction in the suspension = 0.16). After stirring for 15 min in a magnetic stirrer, the suspensions were placed in a sonicator for 5 min and then in the measuring cell to determine their zeta potential. Polycarboxylate admixture dosages ranging from 0 to 7 mg polymer/g cement were added to these suspensions using an automatic titrator. The zeta potential values were corrected for the pore solution background contribution. Diluted solutions were used in order to study the interaction between PCE-cement from a colloidal chemical point of view.

2.2.3. Rheological behaviour

Paste rheological behaviour was characterized by determining the plastic viscosity and yield stress, using a Haake Rheowin Pro RV1 rotational viscometer fitted with a serrated cylindrical rotor.

The cement pastes were prepared by mixing for 3 min with a blade stirrer 100 g of cement with 40 g of water (liquid/solid ratio of 0.4). Dosages of 0, 0.4 and 1.2 mg PCE/g cement were added to the mixing water. In addition, in CEM III/B 32.5R pastes, dosages of 0.2 mg PCE/g of cement were used, for with the exception of

Table 1
Chemical composition (wt.%) and Blaine fineness of the cements used.

	CEM I 42.5R	CEM II/AV 42.5R	CEM II/BL 32.5N	CEM III/B 32.5R
LOI	3.28	1.77	10.59	0.60
IR	1.04	8.82	1.06	0.44
SiO_2	21.13	16.01	11.84	29.50
Al_2O_3	4.16	6.51	5.20	11.39
Fe_2O_3	3.80	3.81	0.81	1.73
CaO	63.94	58.73	63.16	47.26
MgO	0.13	0.16	0.33	5.67
SO_3	3.06	3.07	4.54	1.11
S^{2-}	–	–	–	1.04
Na_2O	0.25	0.27	0.20	0.27
K_2O	0.74	0.56	0.50	0.71
Total	100.93	99.69	98.75	99.72
Free CaO	1.28	1.34	1.35	0.58
Blaine (m^2/kg)	386.7	387.6	438.7	383.1

LOI (loss on ignition); IR (insoluble residue).

Table 2
Mineralogical composition of the cements used (wt.%).

	CEM I 42.5R	CEM II/AV 42.5R	CEM II/B-L 32.5R	CEMIII/B 32.5R
C_3S	62.5 (±0.2)	51.9 (±0.2)	45.4 (±0.2)	21.5 (±0.2)
C_2S	8.3 (±0.5)	8.5 (±0.1)	10.0 (±0.4)	0.7 (±0.1)
C_3A	4.0 (±0.2)	3.4 (±0.1)	3.6 (±0.1)	1.1 (±0.1)
C_4AF	11.9 (±0.2)	9.5 (±0.2)	8.5(±0.2)	3.1 (±0.1)
CA	–	–	–	–
$C_{12}A_7$	–	–	–	–
FeO	–	–	–	–
$CaCO_3$	3.7(±0.2)	–	26.7(±0.2)	–
$CaSO_4{\cdot}2H_2O$	5.4 (±0.1)	2.4 (±0.1)	1.4 (±0.1)	–
$CaSO_4{\cdot}1/2H_2O$	1.3 (±0.1)	1.3 (±0.2)	2.1 (±0.2)	–
$CaSO_4{\cdot}$	0.6 (±0.1)		1.1 (±0.1)	0.6 (±0.1)
Alkaline sulphates	1.7 (±0.1)	1.3 (±0.2)	1.2 (±0.1)	0.8 (±0.1)
SiO_2	–	0.3 (±0.1)	–	
Other	0.5 (±0.1)		–	0.3 (±0.1)
Amorphous	–	21.3 (±0.2)	–	71.9 (±0.6)

In parentheses, standard deviation.

Table 3
Soluble sulphate content for the four cements.

Cement	g SO_4^{2-}/g cement	Molar ratio SO_4^{2-}/C_3A
CEM I 42.5R	0.027	1.90
Cem II/AV 42.5R	0.030	2.44
Cem II/B-L 32.5R	0.025	1.98
Cem III/B 32.5R	0.011	2.81

Table 4
Particle size for 10%, 50% and 90% of the cement, by volume.

	10% of sample smaller than (μm)	50% of sample smaller than (μm)	90% of sample smaller than (μm)
CEM I 42.5R	2.12	14.27	48.34
CEM II AV 42.5R	1.88	12.61	42.03
CEM II BL 32.5R	1.51	10.69	44.30
CEM III/B 32.5R	1.95	12.10	36.08

admixture PC3, higher dosages induced paste segregation in this slag-blended cement. The pastes were tested according to the evolution of shear rate as shown in Fig. 1. The values shown are the means of at least three different determinations on pastes with the same dosage.

Table 5
Physical and chemical characteristics of the admixtures used.

	PC1	PC2	PC3
Solids content (%) (UNE-EN 480-8)	39.94	39.67	39.74
Rotational viscosity (mPa s)	432.86	865.02	918.08
Carboxylic groups/ester groups (C/E)	1.20	0.70	0.40
Mw (D)	61,000	123,000	189,000
PDI (polydispersity index)	1.70	2.20	2.40
Na content (ppm)	13,200	8375	5625

2.2.4. Conduction calorimetry

Calorimetric measurements were recorded in a TAM Air conduction calorimeter on cement pastes with a w/c ratio of 0.4 and the same dosages of admixture as used for the rheological tests. The pastes were previously stirred with a spatula for 3 min. The test duration was 65 h.

3. Results

3.1. Adsorption curves

One of the factors of particular importance for the study of cement–admixture system compatibility is the amount of polymer adsorbed onto the cement. This can then be related to the effect of the admixture on cement paste rheological properties and the reactions taking place in the paste.

Table 6
Chemical composition of the additions.

	Granulated blast furnace slag	Fly ash	Limestone
LOI	2.72	1.02	40.50
IR	0.64	0.12	–
SiO_2	35.34	42.03	5.60
Al_2O_3	13.65	26.70	1.30
Fe_2O_3	0.39	14.42	0.58
CaO	41.00	9.60	51.10
MgO	4.11	1.87	0.58
SO_3	0.06	0.86	–
S^{2-}	1.91	–	–
Na_2O	0.01	0.34	0.01
K_2O	–	2.44	0.23
Total	99.83	99.40	99.90
	Other components		
Reactive silica	–	37.68	–
Vitreous phase content	99	–	–
Blaine (m^2/kg)	325	336	675

LOI: Loss on ignition; IR: Insoluble residue.

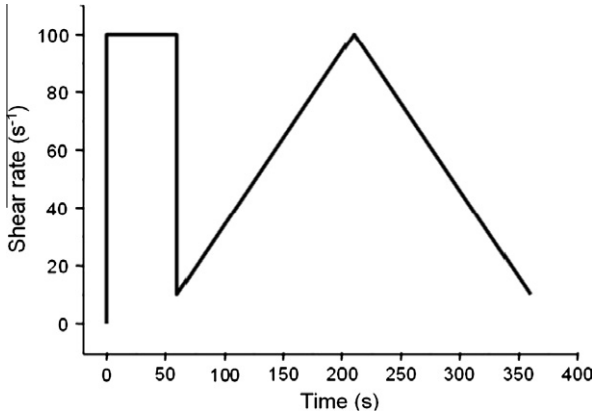

Fig. 1. Rheological test.

The proportion of admixture adsorbed is generally computed from the amount remaining in the aqueous phase after being in contact with the cement. Flatt and Houst [26] concluded that the total admixture present in cement pastes was either adsorbed onto cement particles or consumed in the formation of an organo-mineral phase. Consequently, given that adsorption isotherms do not distinguished between these two forms, the most accurate term for this fraction of superplasticizer is "consumed" admixture.

Fig. 2 shows the isotherms for the three superplasticizers "consumed" by the four cement suspensions. Here the amount of polymer added per gram of solid was plotted against the amount consumed and the resulting curve was fitted to an exponential equation [27]. Three regions can be identified in these isotherms: a linear region, a region where the amount consumed rose non-linearly and a flat region with a maximum or "plateau value" after which adsorption is scantly affected by higher dosages of polymer. Table 7 gives the maximum value in the linear range, the slope of the linear region and the "*plateau values*" of each curve. According to the data shown in this table, the slope in the linear region generally ranges from 0.70 to 0.99. The only exception is slag-blended cement CEM III/B 32.5R and admixture PC3, with a value of 0.55 that infers that admixture PC3 has less affinity for this substrate.

The isotherms for CEM I 42.5R show the effect of differences between the admixtures on adsorption. PC1 generally exhibited the highest values, followed by PC2 and, with significantly lower values, PC3. These curves also revealed the effect of the additions present in the cements on the adsorption values of the three admixtures. In CEM II/AV 42.5R, they were similar to the values for the reference cement, CEM I 42.5R. The adsorption values for CEM II/BL 32.5R, blended with limestone, were slightly higher. Lastly, slag-blended CEM III/B 32.5R adsorbed significantly smaller amounts of the admixtures. Nonetheless, this cement adsorbed PC3 at a rate similar to the rate at which it was adsorbed by the other three cements.

3.2. Effect of PCE superplasticizers on the zeta potential of cement suspensions

The zeta-potential values for the cements studied are given in Table 8. The results show that zeta potential for the four cement suspensions was slightly positive. A very slight decline in the zeta potential was observed with the inclusion of PCE admixtures, to values close to 0 mV (see Fig. 3). As a general rule, at dosages higher than 0.5 mg admixture per g of cement the zeta potential remained constant. The inclusion of any of the admixtures generated similar effects on the zeta potential, regardless of the type of superplasticizer and cement to which it was added.

3.3. Rotational rheometer tests

According to the hysteresis cycles shown in Fig. 4, all the pastes are totally deflocculated and behaved like Bingham fluids, for in all cases the shear rate descent curves could be fitted to the Bingham equation (see Eq. (1)) in which the *y*-intercept is associated with the yield stress (τ_0) and the slope with paste plastic viscosity (μ):

$$\tau = \tau_0 + \mu\dot{\gamma} \quad (1)$$

Fig. 5 shows the variation in cement paste for yield stress and plastic viscosity in the presence of the superplasticizers studied. Table 9 gives the percentage reduction of the yield stress for each cement and admixture dosage compared to the value of this parameter in a paste with no admixture. The findings show that all superplasticizers mainly reduce the yield stress of cement paste and the higher the dosage, the greater was the reduction, while their effect on plastic viscosity is less important.

The declines in yield stress in CEM I 42.5R illustrated the effect of the structural differences in the admixtures on yield stress. PC1 and PC2 appeared to have a similar effect on cement paste flowability, which was perceptibly greater than found for admixture PC3. For this cement, admixtures PC1 and PC2 reduced plastic viscosity much more intensely than PC3. Indeed, paste viscosity was unmodified by this third admixture.

The pastes made with CEM II/AV 42.5R were modified most significantly with a 1.2-mg/g cement dosage of admixture PC1, with reductions of yield stress by up to 96% compared to paste with no admixture. PC2 was less effective in this regard, and PC3 reduced this rheological parameter by 25%. The inclusion of admixtures PC1 and PC2 in CEM II/BL 32.5R pastes, induced declines in the yield stress of 85%. In both cements, admixture PC3 performed differently, as it had no effect neither on yield stress nor in plastic viscosity.

In CEM III/B 32.5R, dosages of only 0.2 mg of admixtures PC1, PC2 and PC3 per g of cement reduced the yield stress by 78–83%, whereas higher dosages caused paste segregation. The greatest impact on CEM III/B 32.5R was achieved with PC3, which at a dosage of 1.2 mg PC/g of cement reduced the yield stress by 82%. All the admixtures except PC3, in turn, induced a steep decline in CEM III/B 32.5R paste viscosity at very low concentrations of admixture (0.2 mg polymer/g cement).

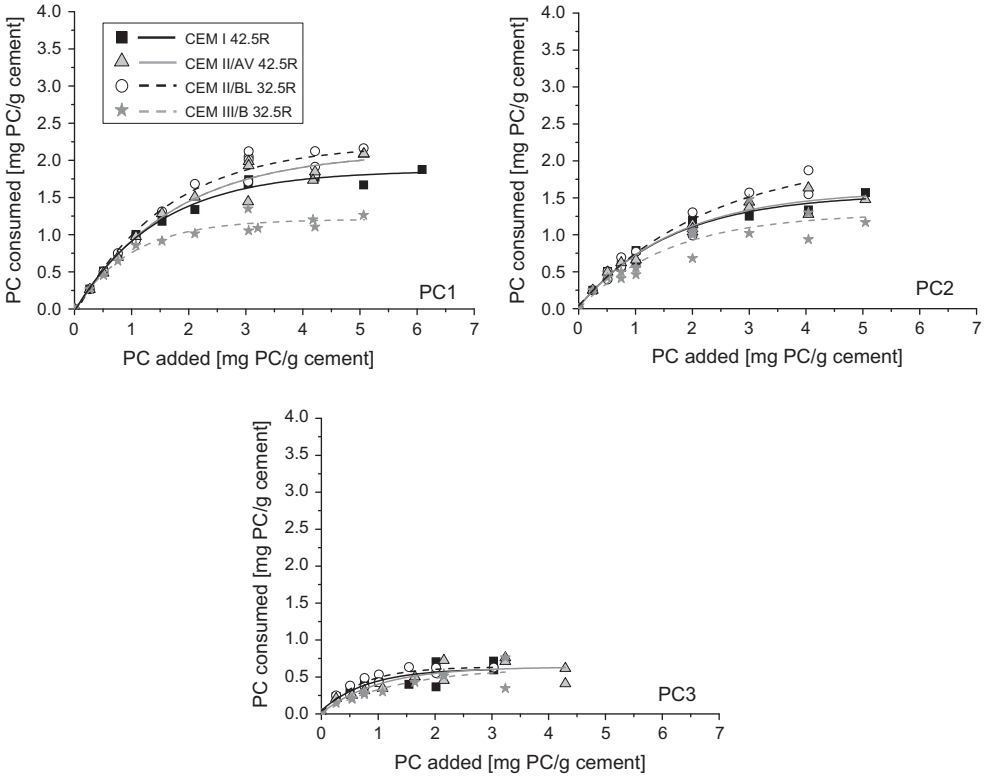

Fig. 2. Isotherms for the three PCE admixtures adsorbed by four cements.

Table 7
Adsorption data for the four cements and three superplasticizers.

	CEM I 42.5R	CEM II/AV 42.5R	CEM II/BL 32.5R	CEM III/B 32.5R
PC1				
Linear range (mg initial polymer/g cement) from zero to	1.00	1.00	0.75	0.75
Slope	0.94	0.92	0.98	0.87
Plateau value*	1.83	2.11	2.17	1.21
PC2				
Linear range (mg initial polymer/g cement) from zero to	0.50	0.50	0.50	0.50
Slope	0.99	0.97	0.80	0.85
Plateau value*	1.45	1.55	1.75	1.26
PC3				
Linear range (mg initial polymer/g cement) from zero to	0.50	0.25	0.50	0.25
Slope	0.70	0.79	0.80	0.55
Plateau value*	0.61	0.63	0.63	0.61

* mg polymer uptake/g cement.

Table 8
Zeta potential of cement suspensions.

Cement	CEM I 42.5R	CEM II/AV 42.5R	CEM II/BL 32.5R	CEM III/B 32.5R
Zeta potential (mV)	+1.1 ± 0.4	+1.3 ± 0.6	+1.3 ± 0.6	+1.4 ± 0.4

3.4. Conduction calorimetry

Fig. 6 shows the heat flow rate during hydration of cements CEM I 42.5R, CEM II/BL 32.5R, CEM II/AV 42.5R and CEM III/B 32.5R in the presence and absence of PC1, PC2 and PC3. The calorimetric data obtained from an analysis of these calorimetric curves are shown in Table 10.

The calorimetric curves and data show that as a rule the presence of admixtures retarded the main calorimetric signal, and the higher the dosage of admixture, the longer was the delay. The longest delays were induced by PC2. PC1, in turn, increased signal intensity more than any of the other admixtures.

The calorimetric profiles for cements CEM I 42.5R, CEM II/BL 32.5R and CEM II/AV 42.5R were characterized by a predominant signal associated with the mass precipitation of the main reaction products (C–S–H gel and $Ca(OH)_2$) and a shoulder that may be attributed either to the conversion of ettringite to monosulphoaluminate [28] or the renewed ettringite formation [29]. In CEM II/BL 32.5R pastes the flow rate peak time was slightly earlier than in CEM I 42.5R and CEM II/AV 42.5R. This was attributed to the finer

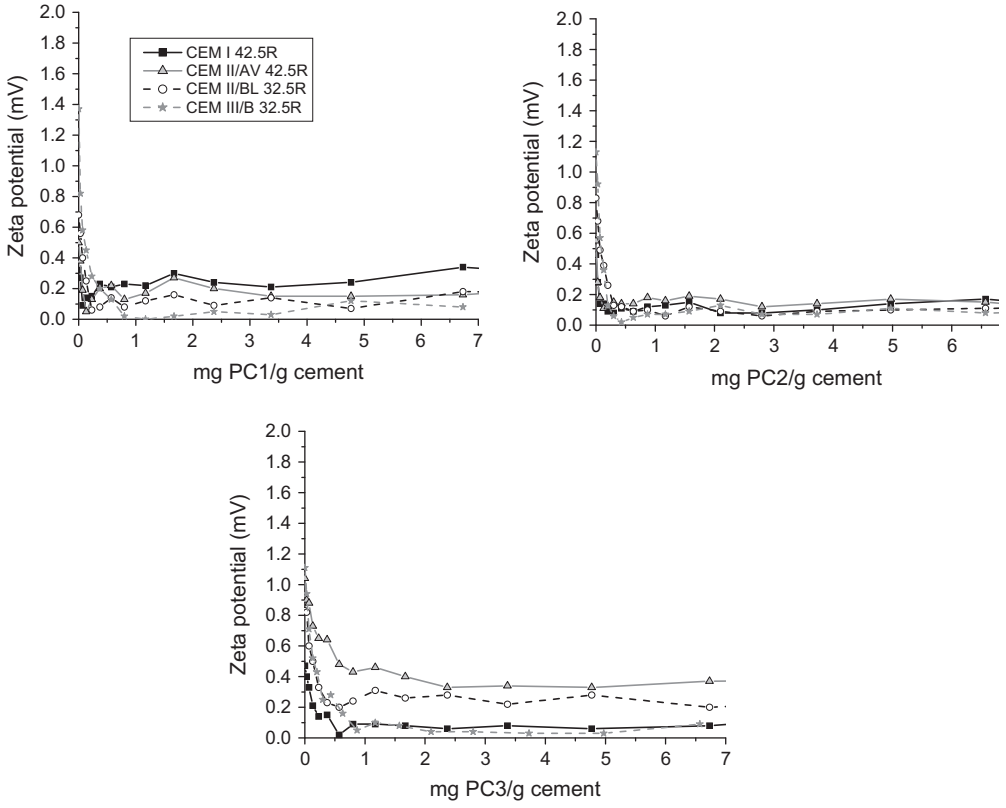

Fig. 3. Zeta potential values for four cements and three superplasticizers.

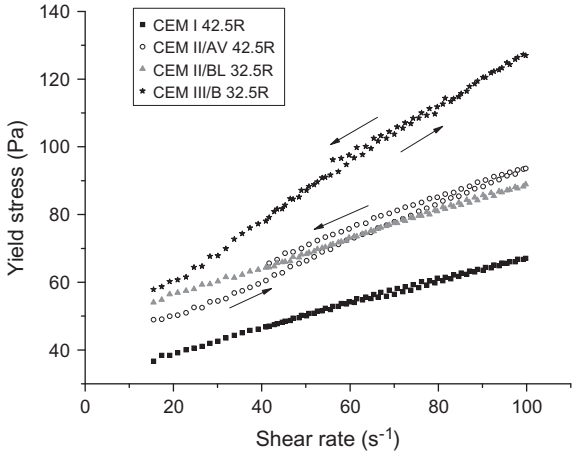

Fig. 4. Hysteresis cycles for the four cement pastes without admixtures.

grain of this cement as a result of the presence of limestone and the early age formation of carboluminate hydrates. The inclusion of 0.4 mg of the three admixtures per g of cement and of 1.2 mg PC3/g of cement barely modified the calorimetric curve in any of the cement pastes. The longest extension of the induction period, with delays of 1.1–1.7 h, was recorded for PC2, at a dosage of 1.2 mg PC2/g of cement.

The shape of the calorimetric curve for CEM III/B 32.5R was characteristic of slag-blended cements, with a series of consecutive signals associated with the precipitation of the reaction products, and lower heat of reaction values than in other cements. The inclusion of all the admixtures in these cement pastes at dosages of 0.2 mg PC/g of cement lengthened the calorimetric signal by 0.7–0.9 h. The longest delay in the heat flow peak time in this cement (2.5 h) was attained with 1.2 mg of PC3 per g of cement.

The inclusion of cement paste admixtures raised the heat of hydration. The highest rise was observed when 1.2 mg of PC1 per g cement were included in cements CEM I 42.5R and CEM II/AV 42.5R. The inclusion of 1.2 mg of PC3 per g of cement to cement CEM III/B 32.5R barely altered the total heat after 65 h, while somewhat less heat was accumulated in the pastes containing PC1 and PC2 than in the non-blended sample.

4. Discussion

The compatibility study for the three different PCE admixtures and blended cements with different proportions of their respective mineralogical additions was based on admixture adsorption and the effect of the superplasticizers on cement paste rheology and hydration reactions.

4.1. Effect of PCE admixtures on adsorption and rheological behaviour in non-blended cements

The findings from the tests conducted on CEM I 42.5R can be used to determine the effect of admixture's characteristics on adsorption by non-blended cement pastes and, consequently, paste rheology.

According to the adsorption isotherms shown in Fig. 3, the order of the intensity of admixture adsorption by CEM I 42.5R cement pastes was as follows: PC1 > PC2 > PC3. This confirms that the higher the carboxylate group content in the admixture, the greater is its adsorption (see Table 5), because admixture adsorption by cement particles is mediated by its carboxylate groups [4,13]. Hence, PC1, with the highest *C*/*E* ratio (1.20), was the one most effectively adsorbed [30]. The significantly lower adsorption observed for admixture PC3 is due to its lower carboxylate content.

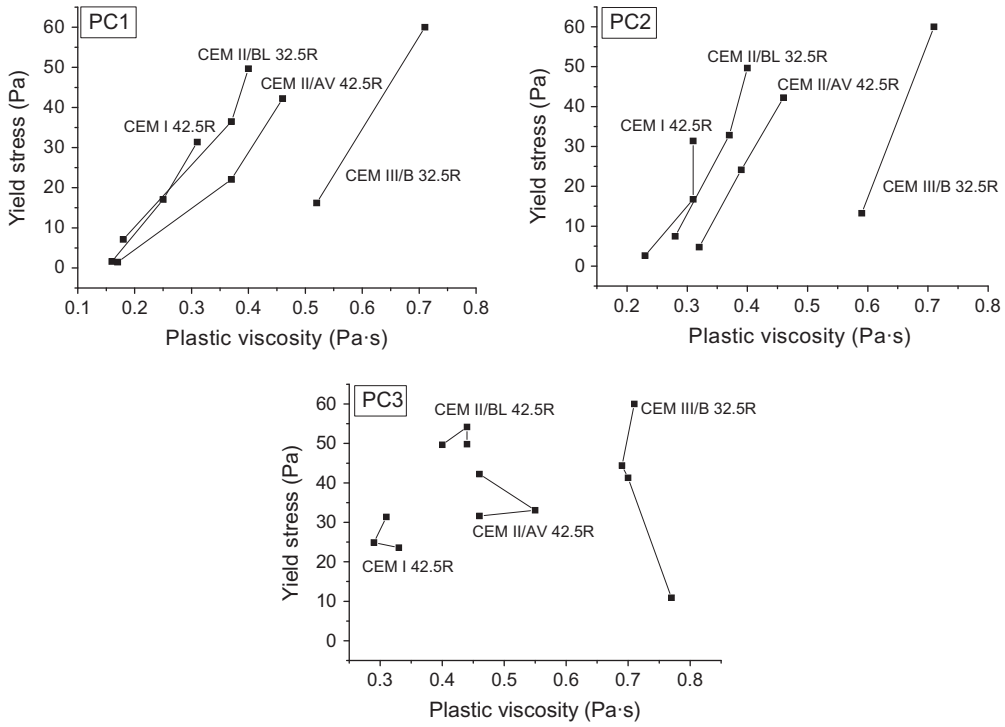

Fig. 5. Plastic viscosity versus shear stress variations in cement pastes containing admixtures.

Table 9
Percentage reduction of the yield shear stress for each cement and admixture dosage— n.d. not determined.

Admixture	Admixture dosage (mg/g cement)	CEM I 42.5R (%)	CEM II/AV 42.5R (%)	CEM II/BL 32.5R (%)	CEM III/B 32.5R (%)
PC1	0.2	n.d.	n.d.	n.d.	83
	0.4	45	47	26	n.d.
	1.2	95	96	85	n.d.
PC2	0.2	n.d.	n.d.	n.d.	78
	0.4	47	42	33	n.d.
	1.2	92	89	85	n.d.
PC3	0.2	n.d.	n.d.	n.d.	26
	0.4	21	22	0	31
	1.2	25	25	0	82

Rheological testing yields information, on the one hand, on plastic viscosity, affording insight into the number and size of the flocs forming in cement pastes, and on the other, on yield stress, which is proportional to the interaction forces between cement particles in the cement paste. CEM I 42.5R rheological behaviour was affected by the incorporation of PCE admixtures, which lowered plastic viscosity and yield stress to levels found to depend primarily on admixture dosage and molecular weight. According to the results shown in Fig. 3, the presence of all the admixtures in CEM I 42.5R pastes led to zeta potential values close to zero. These findings confirmed that the electrostatic contribution to cement particles dispersion was negligible and that steric repulsion was the prevalent mechanism [31].

In CEM I 42.5R pastes (Fig. 5 and Table 9), the greater the molecular weight and lower C/E of the admixtures, the greater was the reduction in yield stress [27]. PC3, however, exhibited differential behaviour, for even though it was the admixture with the highest molecular weight. Its low adsorption rate prevented it from inducing a suitable steric effect.

To further explore the effect of admixture characteristics on paste rheological behaviour, Fig. 7 plots the relationship between the adsorption values of each dosage of each admixture against the normalized yield stress value for each admixture at that dosage. This normalized yield stress depicts the reduction of this rheological parameter with respect to pastes with no admixtures. As Fig. 7a (CEM I 42.5R) shows, when the admixture dosage is 0.4 mg PCE/g of cement, the differences between PC1 and PC2 are small both in terms of the fluidizing effect induced and of the amounts consumed, with values of around 0.4 mg PCE/g of cement (nearly the entire dosage added). Consequently, at these dosages, which correspond to the linear region on the adsorption isotherms (see Table 7), the differences between the admixtures do not condition rheological behaviour. Despite the lower C/E and consequently higher content of side chains in PC3, however, the inclusion of 0.4 mg PC3/g of cement clearly lowered yield stress much less than the other admixtures, due to its lower adsorption values. A compromise was therefore observed to exist between the degree of admixture adsorption and the dispersion induced, which depends on the density of lateral ether chains.

In the admixtures studied and according to the rheological results it may be concluded that the optimal C/E ratio was in the 1.2–0.7 range, which correspond to PC1 and PC2. Previous reports by Platel [32] also inferred the need for a compromise between the carboxylate groups and the grafting ratio (density of PEO units). At dosages of 1.2 mg polymer per g of cement, however, the differences between the admixtures had a decisive effect on the rheological properties of the cement pastes. Even though PC1 had the highest adsorption values, PC2 proved to be the most effective admixture, for it induced a greater reduction in yield stress at lower adsorption values. Here also, the effect of admixture PC3, despite its higher proportion of side chains, was highly conditioned by its low adsorption, for it was the least effective of the three superplasticizers.

In prior studies [12] that used the minislump test to explore paste flowability over time, admixtures PC1 and PC2 were shown

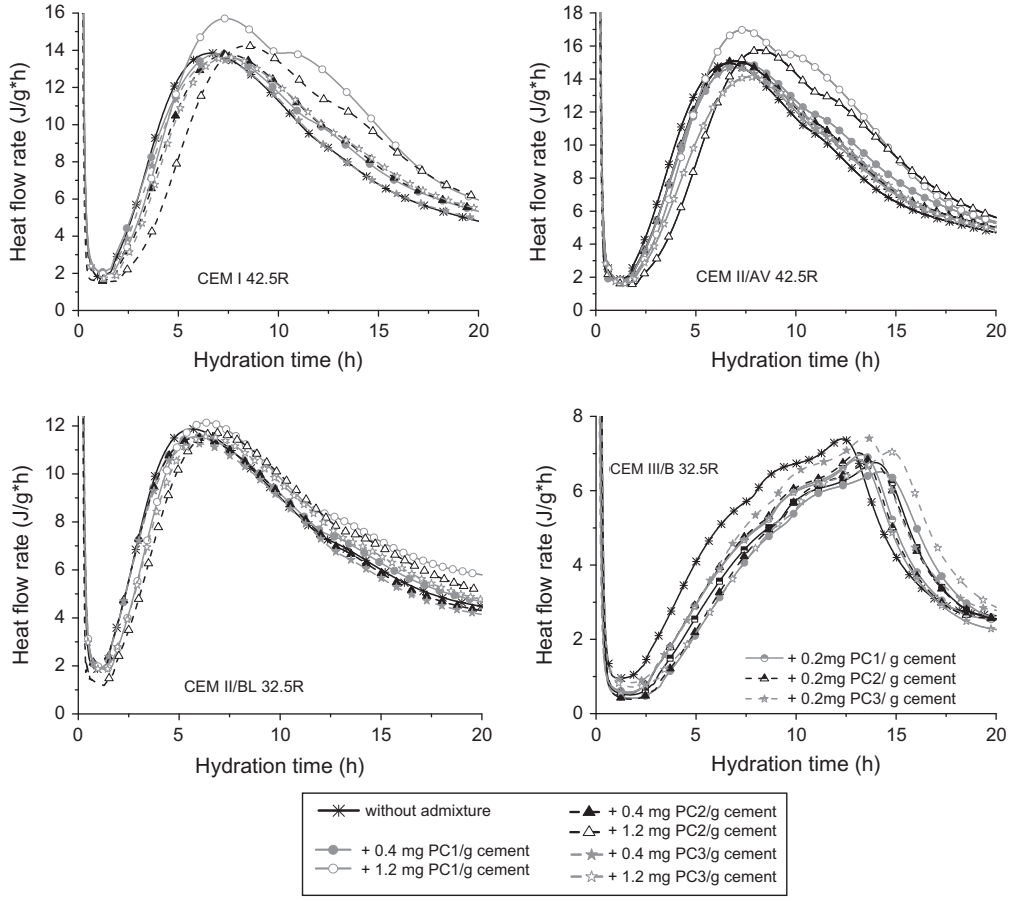

Fig. 6. Conduction calorimetry curves. Heat flow for CEM I 42.5R, CEM II/BL 32.5R, CEM II/AV 42.5R and CEM III/B 32.5R.

to induce a greater fluidizing effect than admixture PC3, and maintain flowability for the 60-min test duration in all the pastes.

4.2. Effect of the presence of mineral additions on adsorption and rheological behaviour in cement pastes

Superplasticizer adsorption depends largely on the presence of soluble sulphates in the solution [13,33,34]. In the presence of optimal sulphate content, C_3A reacts with the sulphates to form ettringite. As a result, the admixtures adsorb not only on aluminate hydrates, but also onto silicate phases, inducing the desired fluidizing effect. If the soluble sulphate/C_3A ratio is low, however, the sulphate content is insufficient to react with the C_3A, which adsorbs or intermingles with PCE admixtures, forming organo-mineral phases and consuming larger amounts of admixture [26,35]. According to Plank et al. [36], at a SO_4^{2-}/C_3A molar ratio of 0.7–2.0 the sulphate content suffices to generate monosulpholuminate and ettringite, on which the admixtures are adsorbed and prevent the formation of the organo-mineral phase. In the four cements studied, the soluble SO_4^{2-}/C_3A molar ratio at 30 min, same time when adsorption isotherms of PCEs were determined, was greater than or equal to 2 (Table 3). Consequently, the differences observed in adsorption could not be attributed to differences in the soluble sulphate content present in the cements.

Fig. 7b and c shows the effect of the different admixtures on cements CEM II/AV 42.5R and CEM II/BL 32.5R, blended with fly ash and limestone, respectively. The patterns for all four superplasticizers were found to be similar to their behaviour in CEM I 42.5R. In CEM III/B 32.5R, which contains slag, the presence of superplasticizers induced steeper reductions in yield stress, despite their low adsorption values in this cement. The inclusion of 0.2 mg of PC1 and PC2 per g of cement in CEM III/B 32.5R (Fig. 7d) lowered yield stress in similar proportions. Consequently, the different characteristics of these three admixtures were not significant on the rheological properties of the cement pastes. Moreover, higher dosages caused segregation. PC3 had a lower fluidizing effect than the other two admixtures, but it reduced yield stress in this cement more intensely than in the other three cements studied.

The study of the effect of the presence of mineral additions in the studied cement CEM II/AV 42.5R, containing fly ash, showed that the consumption values obtained for the three admixtures were similar to the findings in cement CEM I 42.5R. The effect of the presence of fly ash on admixture adsorption in cement CEM II/AV 42.5R was evaluated on the basis of the fly ash adsorption isotherm for admixture PC1 in a synthetic aqueous cement phase [31]. The findings are shown in Fig. 8.

According to our data, polycarboxylate admixtures used in this study are adsorbed not only by cement grains, but by fly ash particles as well. The fly ash, with a positive zeta potential (+2.5 mV) [37], in fact adsorbed admixture at an amount of 0.6 mg PC1/g of fly ash. This dosage was lower than the amount of admixture adsorbed by the non-blended cement (1.8 mg PC1/g of cement). Other authors [27,37] concluded that also with lignosulfonate and PCE type admixtures; these were adsorbed by fly ash at a lower amount than by non-blended cement. Since the fly ash content in cement CEM II/AV 42.5R was low (under 21%), however, total admixture adsorption by the cement did not differ significantly from the amounts observed for CEM I 42.5R.

Table 10
Calorimetric findings for cement pastes.

Admixture	CEM I 42.5R			CEM II/AV 42.5R		
	Heat flow rate peak time (h)	Signal intensity (J/g* h)	Total heat at 65 h (J/g)	Heat flow rate peak time (h)	Signal intensity (J/g* h)	Total heat at 65 h (J/g)
None	6.67	13.9	251	6.64	14.9	253
0.4 mg PC1/g cement	7.04	13.8	262	7.21	15.0	268
1.2 mg PC1/g cement	7.40	15.7	282	7.35	16.9	280
0.4 mg PC2/g cement	7.46	13.7	262	6.99	15.1	258
1.2 mg PC2/g cement	8.40	14.2	268	8.18	15.7	252
0.4 mg PC3/g cement	7.03	13.4	251	7.01	14.7	258
1.2 mg PC3/g cement	7.46	13.7	262	7.68	14.1	251
	CEM II/BL 32.5R			CEM III/B 32.5R		
None	5.67	11.8	224	12.40	7.3	156
0.2 mg PC1/g cement	–	–	–	13.31	6.9	139
0.4 mg PC1/g cement	5.89	11.6	225	14.22	6.7	133
1.2 mg PC1/g cement	6.37	12.1	249	–	–	–
0.2 mg PC2/g cement	–	–	–	13.16	7.0	139
0.4 mg PC2/g cement	5.95	11.5	223	13.73	6.8	133
1.2 mg PC2/g cement	6.82	11.7	243	–	–	–
0.2 mg PC3/g cement	–	–	–	13.12	6.8	134
0.4 mg PC3/g cement	5.95	11.3	220	13.49	7.4	160
1.2 mg PC3/g cement	6.33	11.6	241	14.87	6.8	156

In light of the similarity in the amount of admixture adsorbed by fly ash-blended cement and non-blended cement, the effect of the superplasticizers on the rheological behaviour of the two pastes was likewise similar (see Fig. 5). In both pastes, inter-particle repulsion was primarily steric, as can be deduced from the zeta potential findings (see Fig. 3). Consequently, the inference is that in the cement used, CEM II/AV 42.5R, the presence of fly ash had no effect on either adsorption or rheological behaviour.

Slightly higher amounts of all the superplasticizers studied were adsorbed on the CEM II/BL 32.5R used than CEM I 42.5R. Fig. 8 shows the adsorption isotherm for PC1 with respect to limestone in aqueous cement phase [31]. PCE admixtures may also be concluded to be adsorbed by these limestone particles, with a plateau value of 2.2 mg/g of limestone, due to its high positive zeta potential (+13 mV) [37]. Previous authors [37,38] also reported that PNS and PCS admixtures were adsorbed by limestone pastes. The slightly higher admixture adsorption by limestone than by cement could explain why CEM II/BL 32.5R adsorbs more admixture than non-blended cement. These findings concur with previous reports [15].

Admixtures lowered yield stress less in CEM II/BL 32.5R than in CEM I 42.5R pastes, despite the slightly higher adsorption in the former. Björnstrom and Chandra [39] reported in this regard that the presence of superplasticizer admixtures induced a smaller reduction in yield stress and plastic viscosity in cements blended with limestone than in those without this addition. This lesser fluidizing effect observed in CEM II/BL 32.5R pastes could be attributed to essentially to three factors.

a. Moreover, the Blaine fineness value for CEM II/BL 32.5R (438.7 m^2/kg) is higher than for CEM I 42.5R (386 m^2/kg) due to the presence of limestone. As a result of its greater fineness, this cement would call for more admixture to obtain a given fluidizing effect [30,40].
b. According to the literature [41], hydration takes place at a faster pace in limestone blended cements, where the C_3A phases react with the $CaCO_3$ to primarily form carboaluminates. The C_3S, in turn, although less intensely, would form carbosilicates resulting in more tightly interacting flocs that are more difficult to disperse with superplasticizers.
c. As noted earlier, cement and limestone could compete to adsorb PCE, leaving less superplasticizer available for possible adsorption by cement particles to generate the desired effect.

With respect to CEM III/B 32.5R cement pastes, the adsorption curves of PC1 on the slag (Fig. 8), confirmed that the admixtures were also adsorbed by the slag particles used in this study, despite its negative zeta potential value (−2.7 mV) [20]. These results concur with earlier studies [42]. As the figures shows, the slag adsorbed significantly less admixture (plateu value of 0.40 mg PC1/g slag) than the reference cement. The adsorption values for the admixtures in CEM III/B 32.5R were also smaller than observed in non-blended cement (Fig. 2). Despite the low adsorption of admixtures by CEM III/B 32.5R, however, their effect on the decline in yield stress was significant, even at small dosages. The reason for this differential behaviour by CEM III/B 32,5R is associated with two facts:

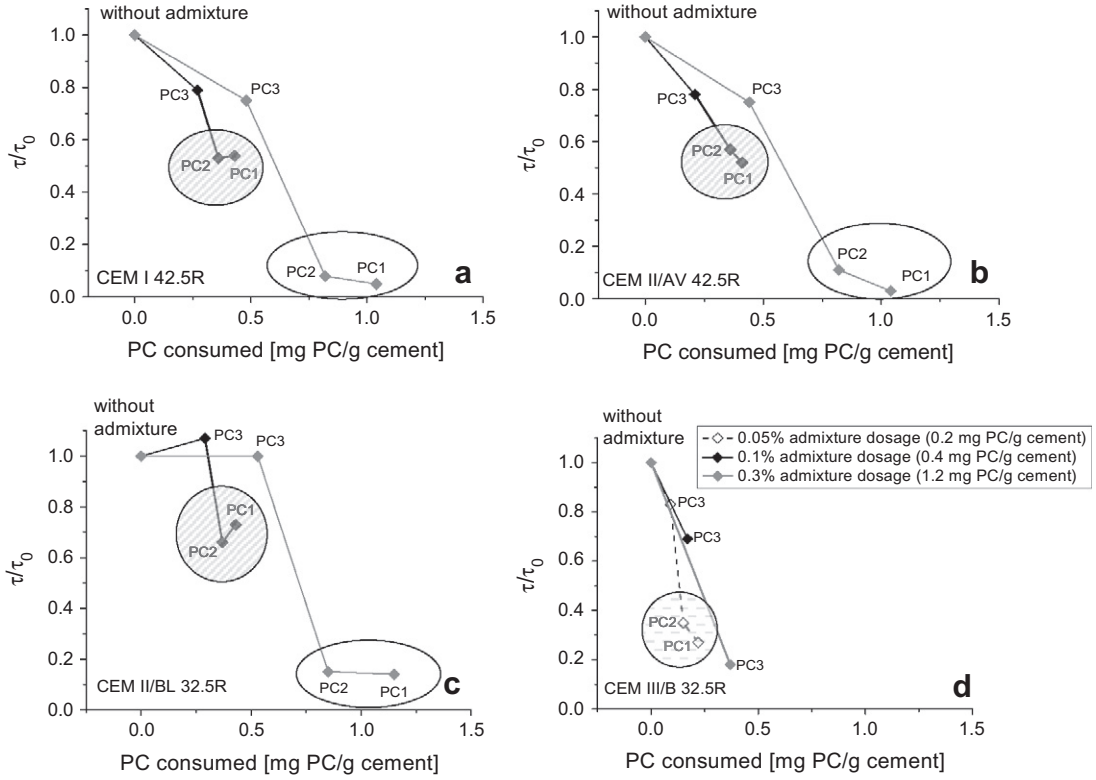

Fig. 7. Adsorption values for each admixture versus normalized yield shear stress.

- With respect with the mineral additions used in this paper, slag adsorbs less admixture and requires less PCE than fly ash or limestone to establish inter-particle repulsion.
- Granulated blast furnace slag accounts for over 70% of this cement, so the low proportion of clinker (26.4%), which was substantially smaller than in the other two blended cements studied. This would account for its low C_3A content (1.1% crystalline). According to the literature [43], C_3A is the mineralogical phase in cement with the highest affinity for admixtures thanks to its highly positive zeta potential, which facilitates adsorption, and the possible formation of an organo-mineral phase [36]. Where the C_3A content is low, then, the admixture is primarily adsorbed by the silicate phases of the clinker and the slag, where it generates the desired dispersing effect. This differential rheological behaviour was identified in previous studies [20].

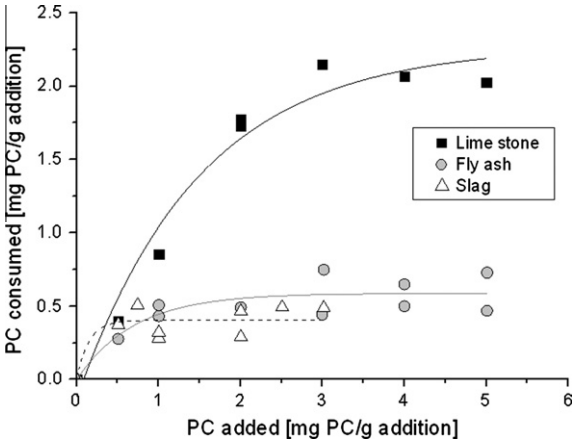

Fig. 8. Adsorption isotherms for admixture PC1 with respect to limestone, fly ash and granulated blast furnace slag.

4.3. Effect of admixture structure on hydration process in non-blended cement

The conduction calorimetry findings showed that the presence of PCE admixtures retarded initial cement hydration, and that the duration of the delay rose with admixture dosage [44]. According to the conduction calorimetry data for CEM I 42.5R, PC2 retarded the appearance of the calorimetric signal associated to massive precipitation of reaction products (see Fig. 6 and Table 10) more than any of the other admixtures. By contrast, PC3 was the admixture that had the slightest effect on hydration reactions, even at dosages of 1.2 mg PC/g of cement, due to its low adsorption as a result of its low carboxylate group content. However, while PC2 was adsorbed less intensely than PC1, it retarded reactions more significantly. Previous studies [45,46] have explained that the delay of the hydration process induced by PCEs could be due to two main reasons (a) their adsorption onto the cement particles and (b) due to the growth kinetics and morphology of early hydrates. However, further studies are needed to establish the mechanism of retardation and the effect of PCE structure on that retardation.

Finally, the presence of all the admixtures raised the total heat of reaction slightly. This may be because the presence of admixtures disperses the flocs, releasing the entrapped water and thereby enhancing hydration [44].

4.4. Effect of admixtures on blended cement hydration

The effect of different characteristics of the superplasticizers on hydration reactions in the three blended cements was similar to their effect on these reactions in the reference cement. Nonetheless, in CEM III/B 32.5R, admixture PC3 retarded hydration significantly more than it did in the other cements due to its fluidizing effect on this slag-blended cement.

The presence of different types and proportions of mineral additions affected cement hydration differently, with and without admixtures. The calorimetric curve for cement CEM II/AV 42.5R, with a fly ash content of 21%, closely resembled the curve for CEM I 42.5R. Since the effect of admixture adsorption on the fly ash impacted neither total superplasticizer adsorption nor its fluidizing effect, the hydration reactions were also unaffected; hence the similarity with CEM I 42.5R.

The calorimetric findings for CEM II/BL 32.5R, in turn, with 26.7% limestone, show that the signal indicating the maximum peak cement hydration in the cement without admixtures appears slightly earlier than in the cements with superplasticizers. This can be partly attributed to the higher Blaine fineness of this cement, very likely as the result of the presence of limestone (see Table 1) [47] and partly, as mentioned above, to the very early age formation of carboaluminate hydrates [41]. The presence of admixtures in these cement pastes affected hydration reactions to a lesser extent than in CEM I 42.5R due to admixture adsorption by the limestone.

Lastly, according to the calorimetric curves for CEM III/B 32.5R (72% slag), its hydration reactions were slower and less exothermal than in the non-blended cement [48]. The presence of admixtures at dosages of 0.2 mg PC/g of cement induced delays in cement hydration of up to 1.5 h, due to its lower adsorption values induces a substantial fluidizing effect.

Finally the presence of all the admixtures raised total heat of reaction slightly in fly ash and limestone-blended cements. Heat of hydration was observed to decline, however, in the cement with slag additions. Given the slower hydration reactions in this slag-blended cement, the reason for such lower values may be that the reactions in the pastes had not finalized after 65 h. According to findings from prior studies, however, at longer hydration times the heat released by slag-blended cements in the presence of PCE admixtures rose, just as it was observed to do in non-blended cements [20].

5. Conclusions

The main conclusions relating to admixture characteristics are the following:

1. The characteristic of the admixtures studied that condition more the effect on their adsorption by blended and non-blended cements is the C/E ratio: the higher that content, the greater the adsorption. By degree of consumption, the three admixtures studied can be ranked as follows: PC1 > PC2 > PC3.
2. The presence of PCE admixtures generally lowers yield stress in cement pastes. The decline in cement paste yield stress strongly depends on the dosage of PCE and C/E ratio. Further to the present results, the optimum C/E ratio for the admixtures used in the present study was found to range from 1.20 to 0.70.

The main conclusions relating to the effect of the presence of mineral additions (fly ash, limestone and granulated blast furnace slag) are:

1. Admixtures used in this study are adsorbed not only by cement particles, but by the mineral additions used as well. Significantly smaller amounts of admixture are adsorbed by both fly ash and blast furnace slag, and slightly larger amounts by limestone, than by the non-blended cement.
2. Adsorption of the three admixtures by CEM II/AV 42.5R is very similar to adsorption of these same superplasticizers by non-blended cement. By contrast, the adsorption values are slightly higher in limestone blended CEM II/BL 32.5R and significantly lower in general in the cement blended with slag, CEM III/B 32.5R.
3. The dispersing effect induced by PCE admixtures in CEM II/AV pastes, which contain fly ash, is similar to the effect observed in non-blended cement pastes. The effect is less significant in CEM II/BL 32.5R than in CEM I 42.5R pastes. Lastly, CEM III/B pastes, with granulated blast furnace slag additions, show the highest rises in flowability, even at admixture dosages as small as 0.2 mg per g of cement.

With respect to the effect of the PCEs on the hydration process of the cements, we can conclude:

1. The delay of admixtures on cement hydration intensifies with rising PCE dosage. In cements containing fly ash, the delay in the hydration reactions induced by admixtures is similar to the delay observed in non-blended cement pastes. These reactions are retarded less in cement blended with limestone, and most significantly in cement pastes containing slag: from 0.7 to 0.9 h at admixture dosages of only 0.2 mg per g of cement.
2. The presence of all the admixtures raises the total heat of reaction slightly. This may be because they disperse the flocs, releasing the entrapped water and enhancing hydration.

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