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Compatibility between superplasticizer admixtures and cements with mineral additions

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ABSTRACT

The incorporation of mineral additions to Portland cement reduces the amount of clinker required in cement manufacture improving the eco-efficiency of this process. They also impact rheology and it may affect the interaction between superplasticizers and cements. The presented study explores the effect of limestone, fly ash and silica fume on Portland cement and the interaction of these additions with naphthalene (PNS)-, melamine (PMS)-, lignosulfonate (LS)- and polycarboxylate (PCE)-based admixtures. The adsorption isotherms, zeta potentials and rheological behaviour of the blended cements were found and compared to the same parameters in non-blended cement. The results showed that cement–superplasticizers compatibility was altered by the physical (specific surface) and chemical (surface charge) characteristics of the mineral additions studied.

1. Introduction

The incorporation of mineral additions to Portland cement reduces the amount of clinker required in cement manufacture improving the eco-efficiency of this process by lowering both greenhouse gas emissions and energy consumption [1]. These additions also enhance mainly the long-term strength and durability of the material obtained. Additions may be natural materials (limestone, pozzolans, schist) or industrial by-products (vitreous granulated blast furnace slag, fly ash or silica fume) with pozzolanic or hydraulic properties [2,3].

Limestone-blended cements have been widely studied. In terms of durability, permeability and strength, they are similar to non-blended cements, while exhibiting high compressive strength when small amounts of limestone are added [4–7]. A final material with the desired properties can only be obtained, however, when the limestone used complies with certain quality, content, and particle size and fineness requirements [8,9]. These characteristics allow the better packing of particles obtaining more compact and hence less porous structures [10].

The use of fly ash in cement compositions is very common because it raises product strength and reduces alkali silica reaction-induced expansion [11–14]. Fly ash fineness determines the properties of the end material, which is more fluid and less porous than non-blended cement pastes [15–18].

In light of its very fine particle size, silica fume has been studied as an addition to densify cement paste. As cements made with this addition exhibit higher compressive strength than non-blended materials, it is used to manufacture high-strength concrete [19–21]. Moreover, it has been observed to act not only as filler or pozzolanic material, but also to improve the cement paste–aggregate interface, which contributes to further improving mortar and concrete strength. Its incorporation also affects fresh cement flowability, however, substantially raising the water demand, and its high early age hydration reactivity increases the heat of hydration and consequently intensifies total shrinkage [22–25].

Cement paste, mortar and concrete microstructure, and in particular the homogeneity, density and porosity of the reaction products, must be closely monitored to attain the desired properties in the hardened material. Fresh cement paste rheology is regarded to be closely associated with the development of mortar and concrete microstructure [26]. Given the direct impact of the presence of mineral additions on such microstructure, and consequently behaviour rheology, an understanding of blended cement behaviour in this regard is imperative. As a rule, the incorporation of mineral additions raises yield stress and to a lesser extent, plastic viscosity, especially in silica fume-blended cements [27–29].

The fresh characteristics of concrete made with Portland cement and rheology can be modified and controlled with superplasticizers. Achieving the steepest decline in the water–cement

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ratio, greatest workability and decreasing the viscosity and the yield stress is, however, contingent upon the compatibility between the admixture chosen and the cement used. The presence of mineral additions such as limestone, fly ash and silica fume may affect the interaction between the superplasticizer and the cement. The performance of additions could be also influenced by admixtures. Conventional superplasticizers such as naphthalene (PNS)-, melamine (PMS)- or lignosulfonate (LS)-based disperse the particles due to a electrosteric mechanism while the PCE form a steric obstacle to any direct inter-particle contact [35–41]. The compatibility of mineral additons with, and affinity for, a given admixture must therefore be determined [3,30–34].

The studies of limestone-blended cements and the superplasticizers have focused primarily on PCE admixtures [42–45]. Magarotto et al. [43] and Banfill [44] determined the importance of the molecular weight and the structure of the PCE on the rheological behaviour and the water-reduction of the limestone-blended cement. Mikanovic and Jolicoeur [46] studied the relationship between particle–superplasticizer interactions, rheology and paste stability on the one hand, and blending, sedimentation and consolidation on the other. Their findings showed that the mechanisms involved in superplasticizer action on limestone and cement type I varied depending on whether the admixture was PCE or PNS. They also observed that while the dispersion effect of the two was similar in water–limestone pastes, the presence of $Ca(OH)_2$ improved the effectiveness of PCE.

The use of fly ash has been reported to improve cement rheology and lower the dose of superplasticizer needed (PCE and PMS) to obtain the desired reological properties [45,47]. Due to the nearly spherical shape and the size of fly ash particles, these cement pastes demand a lower concentration of admixture than limestone blended cements [45].

Silica fume blended cements behave differently from other blended cements due to the mineral surface [48] of this addition. The use of silica fume reduces paste workability. The improvement in reological properties depends on the type of superplasticizer. The PMS dose needed by silica fume-containing cements is similar to the dose required by cement type I to induce the same reological behaviour [47–49]. The molecular architectures of the PCE are critical to the dispersion of the silica fume particles [48].

Despite the importance of admixture compatibility, the interactions between blended cements and superplasticizers have been scantly studied, and the interactions between limestone, fly ash and silica fume particles and superplasticizers have barely been researched at all.

The present study aimed to establish the effect of mineral additions on fresh type II Portland cement pastes containing limestone (CEM II/B-L), fly ash (CEM II/B-V) and silica fume (CEM II/A-D), and to determine the compatibility between these additions and four superplasticizers: naphthalene (PNS), melamine (PMS), lignosulphonate (LS) and polycarboxylate (PCE) polymers. The control used throughout was non-blended CEM I 52.5-R.

2. Materials and methods

2.1. Materials

The characteristics of the commercial CEM I 52.5 R Portland cement used are given in Table 1. The three type II cements studied were prepared in the laboratory: CEM II/B-L, containing (30 wt%) limestone, CEM II/B-V, containing (30 wt%) fly ash and CEM II/A-D, containing (10 wt%) silica fume. The cement constituents were blended in a turbula mixer for 2 h. The chemical composition and specific surface of these blended-cements are given in Table 1. Table 2 lists the chemical composition and B.E.T. specific surface of the mineral additions.

Four commercial superplasticizers were used: a lignosulphonate (LS) derivative, a naphthalene-based compound (PNS), a melamine-based material (PMS) and a polycarboxylate superplasticizing admixture (PCE). The physical–chemical characteristics of the admixtures are given in Table 3.

Table 1
Chemicals composition (wt%), Blaine and BET specific surface of Portland cements. L.O.I.: loss on ignition. I.R.: insoluble residue. $S_{S\ BET}$. Specific Surface Area determined by B.E.T.

wt%	CEM I 52.5R	CEM II/B-L	CEM II/B-V	CEM II/A-D
L.O.I.	2.35	14.83	3.58	2.56
SiO_2	20.51	13.45	28.44	32.58
Al_2O_3	5.37	3.53	14.11	4.25
Fe_2O_3	2.10	1.54	2.93	1.76
MnO	0.02	0.01	0.02	0.02
MgO	3.86	2.79	2.93	3.13
CaO	57.05	57.49	40.79	48.47
Na_2O	0.64	0.56	0.55	0.64
K_2O	1.44	1.02	1.44	1.23
TiO_2	0.16	0.12	0.45	0.14
P_2O_5	0.13	0.12	0.45	0.12
SO_3	6.37	6.16	4.33	5.09
I.R.	0.26	1.48	2.00	2.33
CaO_{free}	1.27	0.10	0.93	0.96
Blaine (m^2/kg)	501.7	524	472.1	559.0
$S_{S\ BET}$ (m^2/g)	1.22	2.11	1.53	2.98

Table 2
Chemicals composition (wt%), Blaine and BET specific surface of mineral additions.

wt%		L	CV	HS
L.O.I.		43.56	6.76	3.96
SiO_2		0.34	46.32	94.29
Al_2O_3		0.04	31.01	0.24
Fe_2O_3		0.11	4.50	0.11
MnO		0.01	0.05	0.02
MgO		0.93	1.29	0.24
CaO		54.56	4.90	0.46
Na_2O		0.36	0.34	0.11
K_2O		–	1.34	0.37
TiO_2		0.01	1.53	–
P_2O_5		0.08	0.98	0.05
SO_3		–	0.98	0.15
$Si_{react.}$		0	36.4	92.7
$S_{S\ BET}$ (m^2/g)		4.38	2.70	20.29
Dv (μm)	1	1.7	14.7	0.31
	2	14.7	36.2	10.48

Table 3
Physical and chemical characteristics of superplasticizers.

Admixture	LS	PNS	PMS	PCE
Solid content (%)	40.1	39.6	41.9	40.9
M_w (Da)	39,230	136,995	78,828	59,596
Mn	16,915	25,695	7315	35,923
Viscosity (mPa.s)	24.28	51.11	31.50	118.20
%C	37.08	43.78	18.65	51.67
%S	5.91	9.13	10.65	0.30
%H	4.89	4.53	3.98	8.14
%N	1.46	0.80	22.17	0.17
Na (ppm)	41,840	31,400	55,280	2820
K (ppm)	390	340	0.2	10
pH	8	8.5	8	4.5

2.2. Methods

2.2.1. Adsorption isotherms

Admixture adsorption isotherms were determined for cements and mineral additions. The suspensions were prepared as described by Perche [50]. The admixtures were dissolved in water and 40 g of each solution were mixed with 20 g of cement. The dosage ranged from 0 to 40 mg of polymer/g of cement for LS, PNS and PMS and from 0 to 2.5 mg of polymer/g of cement for the PCE. The suspensions were stirred magnetically for 30 min at 25 °C and subsequently centrifuged for 3 min to separate the supernatant from the solid. The amount of admixture present in the supernatant was determined with a SHIMADZU TOC-VCSH/CSN total organic carbon analyzer. The amount of admixture consumed was obtained as the difference between the amount initially added and the quantity remaining in the supernatant.