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Viscosity and water demand of limestone- and fly ash-blended cement pastes in the presence of superplasticisers

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HIGHLIGHTS

- Krieger–Dougherty equation could predict the viscosity of blended cement suspensions.
- The use of mineral additions reduced the effectiveness of cement superplasticizers.
- Cement with limestone under 30% had little effect on paste rheology.
- Fly ash lowers the minimum water demand for suitable fluidity.

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ABSTRACT

The rheological behaviour of fresh cement has a direct effect on the microstructural development of mortar and concrete. Inasmuch as the presence of mineral additions impact cement paste rheology and consequently its permanent microstructure and strength, a full understanding of blended cement behaviour should be pursued. The present study addresses the joint effect of mineral additions (limestone and fly ash) and superplasticisers admixtures on the viscosity and water demand of cement pastes.

Cement pastes were prepared with 10, 30 or 50 wt% limestone or fly ash as mineral admixtures. Melamine-, naphthalene- and polycarboxylate-based superplasticisers were used. Paste rheology was studied in terms of variations in yield stress and viscosity with the solids content and amount of mineral additions added. The strength and microstructure of the blended cement pastes were determined at viscosity values of 1.5 Pa·s. in the presence of superplasticisers.

The findings showed that the Krieger–Dougherty equation could be used to determine the effect of solids content on the apparent viscosity of limestone- and fly ash-blended cement suspensions, as well as the effect of superplasticisers. Adding less than 30% limestone to cement had no effect on paste rheology: i.e., the w/c ratios for minimum and optimal workability were similar to the ratios for ordinary cement. However, adding fly ash did lower the minimum water demand, and the optimal amount of water needed for suitable fluidity. The inclusion of 10% of either addition raised paste strength, while higher proportions 30 or 50%) had the opposite effect. The use of mineral additions reduced the effectiveness of cement superplasticisers.

1. Introduction

One of the key factors in the development of concrete microstructure is its fresh state fluidity. Workability is the term traditionally used to define a concrete that can be readily mixed, shipped and placed. Workability is typically determined by means of the slump test, although different concrete mixes with similar slump values have been reported to behave differently during on-site casting. Given the essential role in concrete fluidity played by fresh cement rheology, a detailed study is needed to define the different factors affecting the rheological behaviour of the cement. The physical parameters of cement pastes, which govern their characteristics and physical behaviour under different conditions can be studied on the grounds of their rheology [1–3].

In on-site concrete casting, the general trend is to use binders with a high solids content but low yield stress and viscosity. This combination ensures high performing concretes with no detriment to their workability. Since viscosity and yield stress are generally agreed to be exponentially related to the water/cement ratio, the conditions for obtaining an ideal compromise between solids content and paste fluidity need to be determined [4]. That objective can be attained by controlling both the physical–chemical characteristics of cement pastes and the inter-particulate forces with the addition of superplasticisers to the mix [5–9].

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Mineral additions are used in cement for economic and environmental reasons, as well as to enhance mortar or concrete strength and durability. Mineral additions reduce the amount of clinker needed in Portland cement manufacture. In other words, their presence lowers the high temperature (and energy consumption) required and also mitigates other adverse impacts of cement manufacture. The economic and environmental advantages of the use of this type of cements have fuelled their use the world over. Of the 27 types of common cements listed in European standard EN197-1, 26 contain some manner of mineral addition (such as limestone, fly ash, blast furnace slag, silica fume or burnt shale). The mineral additions chosen for the present study were limestone and fly ash, both listed in European standard EN197-1. Their effect on paste rheology constituted the object of the research conducted.

Limestone-blended cements have been widely studied. Their durability and mechanical strength are similar to the values found in the non-blended cements, and compressive strength remains high at replacement ratios of up to 25% [10–16]. Another mineral addition used in cement compositions is pozzolanic aluminosiliceous fly ash, whose presence in cement has beneficial effects, such as higher late-age mechanical strength. It also affords improved concrete durability by constraining the expansion associated with the reaction between the aggregate and the alkalis in cement [17–20]. Since the use of these mineral additions may also alter paste rheology [5,7,8], further studies are needed to through more light on the subject.

The use of mineral additions has been generally thought to improve end product performance, although it has negative effect on the workability [21,22]. The main reason given for such behaviour is that the large specific surface of these fine powders generates a high water demand. This effect is observed primarily when silica fume is the mineral addition used. It is not always present, however, when other mineral additions are chosen. The literature has reported that some mineral additions lower water demand and raise slump [2,4,11,23,24]. Improved workability and lower water demand in fly ash-blended cements is attributed to the fact that its spherical particles can readily roll over other particles, reducing inter-particulate friction and raising paste fluidity [4,22,25,26]. In limestone-blended cements, however, no consensus has been reached on the effect of the addition on paste fluidity. Some authors have observed improvements in rheological properties, especially yield stress, plastic viscosity and water demand [8,23,27], while others have found cement rheology to be adversely affected by limestone [21,28].

A number of authors [5,8,21,29] studying the effect of superplasticisers admixtures on cement paste rheology, have reported that the adsorption of part of the admixture onto the mineral additions in blended cements alters their behaviour and ultimately their effect.

In other words, the rheological behaviour of fresh cement directly affects the microstructure development and strength behaviour of mortars and concrete. In light of the foregoing, the present study focuses on the joint effect of mineral additions (limestone or fly ash) and superplasticisers on cement paste viscosity and water demand and the concomitant impact on microstructure and strength.

2. Materials and methodology

2.1. Materials

The study was conducted with CEM I 52.5 R commercial Portland cement (hereafter CEM I) and limestone (L) and fly ash (FA) mineral additions. The chemical composition and specific surface of the materials are listed in Table 1. Six blended cements were prepared in the laboratory with CEM I and 10, 30 or 50 wt% limestone or fly ash and respectively labelled CEM 10L, CEM 30L, CEM 50L, CEM 10FA, CEM 30FA and CEM 50FA. Each cement was blended in a mixer for 2 h. Table 2 lists the densities of the cements used.

Table 1
Chemical composition (%,weight) and Blaine fineness of the cement and additions used.

% p.		CEM I 52.5R	L	FA
L.O.I.		2.35	43.56	6.76
SiO_2		20.51	0.34	46.32
Al_2O_3		5.37	0.04	31.01
Fe_2O_3		2.10	0.11	4.50
MnO		0.02	0.01	0.05
MgO		3.86	0.93	1.29
CaO		57.05	54.56	4.90
Na_2O		0.64	0.36	0.34
K_2O		1.44	–	1.34
TiO_2		0.16	0.01	1.53
P_2O_5		0.13	0.08	0.98
SO_3		6.37	–	0.98
Si_{react}		–	0	36.4
Blaine (m^2/Kg)		501.7	–	–
ES_{BET} (m^2/g)		1.22	4.38	2.70
Dv(μm)	10	1.19	0.81	1.80
	50	7.08	3.58	13.81
	90	22.46	35.14	59.33

Table 2
Density values of CEM I 52.5R and blended cements.

	CEM						
	I 52.5R	10L	30L	50L	10FA	30FA	50FA
Density(g/cm^3)	3.15	3.05	2.97	2.93	3.00	2.78	2.60

Table 3
Physical and chemical characteristics of the admixtures used.

Admixture	PNS	PMS	PCE
Solid content (%)	39.6	41.9	40.9
M_w (Da)	136,995	78,828	59,596
Mn	25,695	7315	35,923
Rotational viscosity (mPa·s)	51.11	31.50	118.20
%C	43.78	18.65	51.67
%S	9.13	10.65	0.30
%H	4.53	3.98	8.14
%N	0.80	22.17	0.17
Na (ppm)	31,400	55,280	2820
K (ppm)	340	0.2	10
pH	8.5	8	4.5

Three commercial superplasticisers admixtures were also added: a naphthalene-based (PNS), a melamine-based (PMS) and a polycarboxylate-based (PCE) product. Their physical-chemical characteristics are given in Table 3.

2.2. Methodology

2.2.1. Paste rheology

Cement paste rheological behaviour was determined with a Haake Rheowin Pro RV1 rotational viscometer fitted with a grooved Z38S (Haake) cylindrical rotor to avoid slippage. Behaviour was studied with different solids contents. The solids content in a cement paste, defined as its volume fraction (ϕ), is related to the water/cement (w/c) ratio as shown in following equation:

$$\phi = (\rho_w/\rho_c)(\mathrm{w/c} + (\rho_w/\rho_c)) \tag{1}$$

where ρ_w and ρ_c are water and cement density, respectively.

The cement pastes were prepared by mixing 100 g of cement and the amount of water established for each trial with a mechanical blade stirrer for 3 min. Six milligram of PNS and PMS polymers/g cement and 2 mg of PCE polymer/g of cement were added to the mixing water (the optimal dosages were determined in an earlier study) [5].

In the rheological tests, the cement pastes were subjected to pre-shear at 100 s^{-1} for 1 min, return to a rotor velocity of 0 s^{-1}, re-ramping to 100 s^{-1} in 12 min and lastly a gradual reduction in speed to 0 s^{-1} in a further 12 min. The downward shear rate values were fit to the Bingham equation (Eq. (2)), in which the y-intercept