Cement and Concrete Research 39 (2009) 843–848

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Effect of activation conditions of a kaolinite based waste on rheology of blended cement pastes

P.F.G. Banfill [a,*], O. Rodríguez [b], M.I. Sánchez de Rojas [b], M. Frías [b]

[a] School of the Built Environment, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom
[b] Eduardo Torroja Institute (CSIC), C/Serrano Galvache 4, 28033, Madrid, Spain

ARTICLE INFO

Article history:
Received 11 December 2008
Accepted 9 June 2009

Keywords:
Rheology
Thermal treatment
Cement paste
Waste paper sludge

ABSTRACT

This paper reports the influence of calcining temperature on the rheology of blended cement pastes with 10 and 20% of thermally activated paper sludge as pozzolan at water/binder ratio of 0.5 and 0.4. The kaolinite based waste was activated at different activation temperatures (700–800 °C) and retention times of 2 and 5 h. The yield stress of the blended pastes increased when the activation intensity increased as a result of the increased calcite and free lime content. Due to the stiffness of the blended pastes, a superplasticiser (sodium lignosulfonate) was used in order to reduce the yield stress. The best results could be obtained using the lower calcining temperature (700 °C and 2 h).

1. Introduction

The cement industry is becoming more efficient and is trying, with much success, to employ more industrial by-products and wastes in order to reduce greenhouse gas emissions, mainly of CO_2. In this line of research during recent decades, the cement industry has used these by-products as active additions to commercial cements, which are covered in different international standards [1]. Several papers show the effect of incorporating supplementary cementing materials on the final performance of blended pastes, mortars and concretes [2–7]. Some authors emphasize the importance of determining the rheological properties as one of the ways to predict the later behaviour of the properties of hardened blended cements [8–11].

Rheology of fresh blended cement paste is generally very complex because of the mutual interactions between the cement phases and pozzolan components, it being dependent on several factors of different nature, such as [12]:

- Physical factors (the water/cement ratio, the cement grain shape and size, etc.)
- Chemical and mineralogical factors (the cement composition and its structural modifications due to hydration processes, etc.)
- Mixing conditions (stirrer type and rate, the stirring time, etc.)
- Measurement conditions (the measuring instruments, the experimental procedures, etc.)
- Presence of admixtures.

Generally pozzolanic addition decreases the workability of cement pastes, as, for the same water/cement ratio, the mixed pozzolan/cement requires more water than cement without additions. That is why superplasticisers are commonly employed to improve the rheological behaviour of cement pastes containing these additions [1,13] and the yield stress is reduced to very low values by the dispersion of the flocculated cement particles [14].

This paper is a part of a research project focused on thermally activated paper sludge wastes as pozzolanic addition [15]. Frías et al [16] reported the possibility of recycling industrial waste materials from paper manufacturing companies as an environmentally friendly source of obtaining metakaolin. Vigil de la Villa et al [17] concluded that the composition of activated paper sludge permits its utilization as pozzolanic material, with treatment at 700 °C for 2 h being the best in terms of pozzolanic activity in the activation range of 700–800 °C. Vegas et al [18] also concluded that, when added to Portland cement, activated paper sludges comply with the chemical, physical and mechanical requirements set out in existing standards. Frías et al [19] demonstrated that the main hydrated phase formed during the pozzolanic reaction was CSH gel. With regard to hydration-induced heat evolution of mortars containing activated paper sludge, Rodríguez et al [20] showed that mortars containing activated paper sludge evolved more heat during the first 20 h than Portland cement without addition, due to the high pozzolanic activity shown by the binder. In previous papers, Frías et al [16] and Vigil et al [17] reported that this heat evolution was mainly due to metakaolin and calcite, and the material showed a pozzolanic activity similar to a pure metakaolin and close to silica fume.

The first approach to rheological behaviour of activated paper sludge blended cement pastes was made by Banfill and Frías [21], who focused on treatment at an activation temperature of 700 °C for 2 h, and compared this sludge to a commercial metakaolin. These results were the basis of the current work in which a study in depth was

* Corresponding author. Tel.: +44 131 451 4648.
E-mail address: p.f.g.banfill@sbe.hw.ac.uk (P.F.G. Banfill).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.06.010

Table 1
Activation conditions.

Sample	Temperature (°C)	Retention (h)
APS1	700	2
APS2	700	5
APS3	750	2
APS4	750	5
APS5	800	2

Table 2
Chemical and physical properties of materials.

	Dry paper sludge	Portland cement (PC)	APS1	APS2	APS3	APS4	APS5
SiO_2	18.05	19.7	30.2	33.4	34.9	34.7	35.7
Al_2O_3	10.14	5.6	18.0	19.5	20.2	20.2	20.5
Fe_2O_3	0.55	3.1	0.7	0.8	0.8	0.8	0.8
CaO	19.82	62.4	31.4	32.2	32.7	33.2	33.5
MgO	2.58	1.2	3.7	4.3	4.4	4.3	4.6
K_2O	0.33	0.9	0.3	0.3	0.3	0.3	0.3
Na_2O	0.21	0.3	0.2	0.2	0.2	0.2	0.2
TiO_2	0.25	0.2	0.3	0.4	0.4	0.4	0.4
P_2O_5	0.26	0.1	0.2	0.1	0.1	0.2	0.2
Mn_2O_3	0.10	–	0.02	0.02	0.02	0.02	0.02
SO_3	0.33	3.3	0.27	0.20	0.31	0.50	0.31
Cl^-	0.04	–	0.02	0.02	0.02	0.02	0.02
Loss on ignition	47.62	2.72	14.5	8.5	5.5	5.1	3.4
Specific surface area (BET) m^2/g	–	1.2	9.6	8.7	7.8	7.1	6.0

carried out to give further information on how the activation conditions can affect the rheological properties.

2. Materials and methods

2.1. Materials

The kaolinite based waste used as the starting material for this research was paper sludge from a Spanish newsprint company, which uses exclusively 100% recycled paper as raw material. The dry and organic matter contents were about 60 and 29%, respectively. The raw paper sludge was dried at 105 °C for 24 h in an electric laboratory oven. The batch size received from the paper company was about 200 kg, and was homogenized and dried in sub-batches of about 2 kg. When dry the paper sludge was burnt in an electric laboratory furnace at a heating rate of 20 °C/min and at different activation temperatures: 700, 750 and 800 °C. The samples were maintained at the stated temperature for 2 to 5 h, and then the burnt products were cooled to room temperature in a desiccator. Table 1 shows the designation of the different products and activation conditions. The designations reflect the assumption that the intensity of the activation conditions would be a function of both temperature and time. The validity of this is discussed later in view of the results. All samples were then ground in an agate mortar and pestle and then sieved to less than 45 µm before use, in order to reduce the particle size and to achieve homogeneity.

The cement was an ordinary Portland cement designated as CEM I 42.5R from a Spanish cement producer. The chemical composition (as determined by X-ray fluorescence spectroscopy) of the paper sludges (both initial and activated) and the reference cement are shown in Table 2. The initial dry paper sludge has a high loss on ignition because of the content of calcium carbonate and residual organic matter.

The superplasticiser used in this work was a sodium lignosulfonate (Ultrazine NAF, Lignotech, Norway).

2.2. Granulometric distribution and fineness

The particle size distribution of activated paper sludges (APS) and cement (PC) was determined with a SYPATEC HELOS 12LA laser granulometer [22,23], and the results obtained are shown in Fig. 1. The materials are all bimodal as shown by the distribution density, with two peaks around 7 and 25 µm for cement, and 5 and 30 µm for the sludges. In the activated sludges the maximum at 5 µm increases at the expense of that at 30 µm when the calcining temperature and burning time increase. For the case of Portland cement, the 25 µm peak is more intense than the 7 µm peak and the bimodality is less marked than in the activated sludge.

The specific surface area was determined by measuring N_2 adsorption isotherms with the MICROMETRICS ASAP 2000. The BET data are also shown in Table 2, where it is clearly observed that the specific surface area for the activated products decreased from 9.6 m^2/g

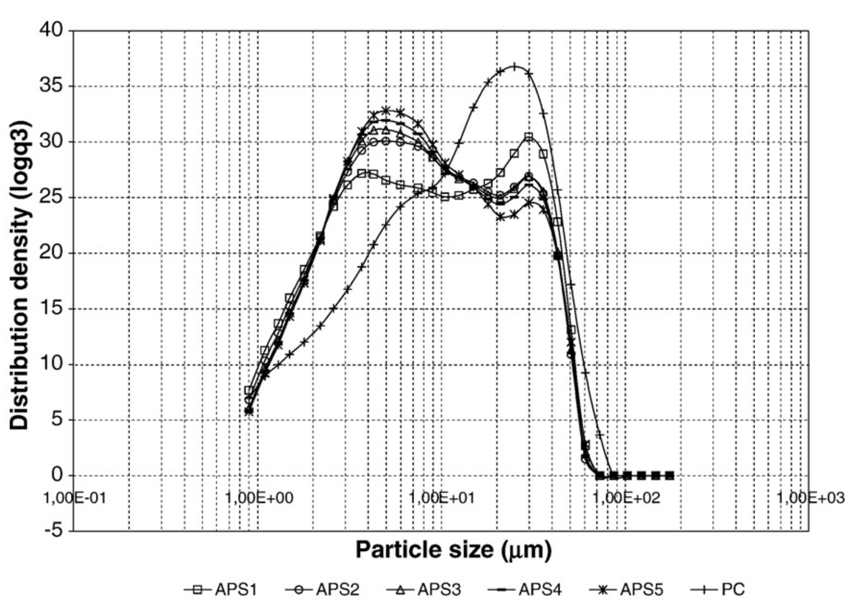

Fig. 1. Particle size distributions of the materials.

Table 3
Programme of experiments.

Water/binder ratio	0.4			0.5		
Superplasticiser (%)	Activated paper sludge (%)			Activated paper sludge (%)		
0	0	10	20	0	10	20
0.3	0	10	20	0	10	20
0.6	0	10	20	0	10	20

(APS1) to 6.0 m^2/g (APS5) with increasingly intense activation conditions, temperature and retention time. While this is contrary to the particle size distribution data, it is because the BET method measures the internal porosity of the particles while laser granulometry measures equivalent external diameter. This decrease is consistent with the findings of Frías et al [16], Rodríguez [15] and Vigil et al [17], who showed that this fact was the consequence of the production of new crystalline phases (α-CS_2) and bigger size aggregates when activation conditions were intensified.

2.3. Equipment and procedures

The rheological measurements were carried out with a TA Instruments model CS500[2] equipped with an interrupted helix impeller rotating in a smooth walled cylinder. This system was used in previous work [9]. The Navigator® software controls the shear rate and the shear stress is measured at predetermined shear rates. Prior calibration with known liquids permits the shear stress and shear rate to be defined in absolute units. The software offers complete flexibility in establishing an appropriate variation of shear rate with time to comply with the requirement that any structure in the paste is broken down to equilibrium before the start of a measurement [10]. Temperature was controlled at 20 °C by circulating water through a jacket surrounding the outer cylinder. The pastes were mixed by hand for 2 min using 100 g of the powders (cement or cement plus activated sludge) and the appropriate quantity of water (containing predissolved superplasticiser if appropriate) to give 0.4 and 0.5 water/binder ratio, and immediately

Table 4
Yield stress of pastes without admixture.

Pastes	w/c = 0.5		w/c = 0.4	
	τ_0(Pa)	R^2	τ_0(Pa)	R^2
PC	10.0	0.9757	42.7	0.9946
PC + 10% APS1	29.9	0.9996	121	0.9738
PC + 20% APS1	47.8	0.9959	–	–
PC + 10% APS2	32.0	0.9998	–	–
PC + 20% APS2	155.0	0.9987	–	–
PC + 10% APS3	42.2	0.9992	–	–
PC + 20% APS3	138	0.9975	–	–
PC + 10% APS4	38.8	0.9981	–	–
PC + 20% APS4	114	0.9956	–	–
PC + 10% APS5	30.7	0.9987	–	–
PC + 20% APS5	182	0.9852	–	–

transferred to the outer measuring cylinder and mounted on the rheometer. When the Navigator® programme started the impeller was automatically inserted and shear measurements started. An initial 10 min preshear at 50 s^{-1} was followed by the test. The flow curve was determined using the preset speed feature available in Navigator® and shear stress measured at each of 20 shear rates from 0.15 to 10 s^{-1} in 60 s and 20 points from 10 to 200 s^{-1} in 60 s. Table 3 shows the experimental plan of this work.

3. Results and discussion

The effect of different activation conditions on the rheological behaviour of blended cement pastes was investigated, due to the importance that these conditions can have on the fluidity of fresh cement pastes and its possible negative consequences on transportation, placement, handling and curing of fresh cementing matrixes.

It was not possible to measure all the combinations in Table 3 because pastes at 0.4 water/binder ratio without superplasticiser were too stiff for the instrument. As described later, these pastes require superplasticiser in order to be measurable. The dosages of superplasticiser (0, 0.3 and 0.6% solids by weight of binder) are consistent with the manufacturer's recommended 0.6%.

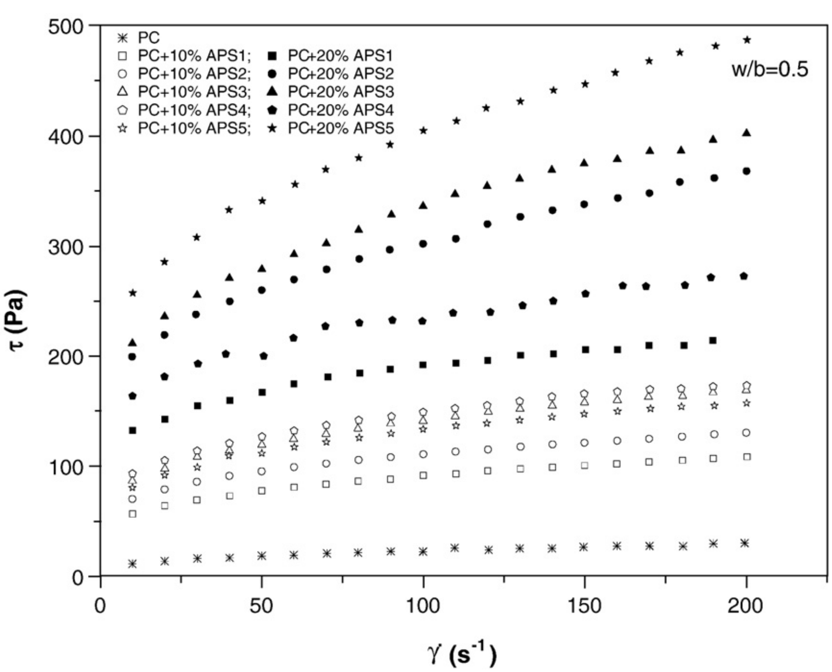

Fig. 2. Flow curves for blended cement pastes without admixture at *w/b* ratio of 0.5. (Points at $\dot{\gamma}<10$ s^{-1} omitted for clarity.).

Table 5
Free lime content calculated by TG.

	Dry paper sludge	APS1	APS2	APS3	APS4	APS5
$CaCO_3$ (%)	35.3	23.84	9.36	5.93	2.39	1.91
Decomposed $CaCO_3$ (%)		8.16	25.94	29.37	32.91	33.39
Free CaO (%)		4.57	14.53	16.45	18.43	18.70

3.1. Rheological behaviour of blended cement pastes without superplasticiser

Fig. 2 shows the flow curves produced for cement pastes containing 10 and 20% of activated paper sludges (APS) without admixture at a water/binder ratio of 0.5. The effect of activation conditions and APS contents on the shear stress of cement pastes analysed at different shear rate is clearly visible.

In this work, the flow curves were analysed by the Herschel–Buckley model (Eq. (1)).

$$\tau = \tau_0 + A\dot{\gamma}^B \quad (1)$$

where τ is shear stress, τ_0 is yield stress, $\dot{\gamma}$ is shear rate and A and B are constants.

The results for yield stress and the regression parameter (R^2), obtained by fitting the data at all $\dot{\gamma}$ to Eq. (1), are shown in Table 4 and suggest a general influence of activation conditions and APS percentages on the fluidity of cement pastes. On one hand, increasing the amount of activated product caused a strong increase in yield stress from 10.0 Pa for the PC paste to 29.9 and 47.8 Pa for 10 and 20% of APS1, respectively. On the other hand, increasing the activation conditions (temperature and retention time in furnace) considerably increased the yield stress for both percentages of APS. For cement pastes containing 10% of APS, yield stress varied from 29.9 Pa for the sample activated at 700 °C/2 h (APS1) to 30.7 Pa at 800 °C/2 h (APS5) and from 47.8 to 182 Pa for the 20% blended cement pastes. It is important to highlight that the yield stresses of the cement pastes containing APS3, APS4 and APS5 in both addition percentages (10 and 20%) showed a clear trend with activation conditions: yield stress increases with increasing activation conditions, as a consequence of the increase of the amount of free lime (see below).

Table 6
Yield stress of blended cement pastes with superplasticiser at $w/b = 0.5$.

Additive content /Pastes	0% SP		0.3% SP		0.6% SP	
	τ_0(Pa)	R^2	τ_0(Pa)	R^2	τ_0(Pa)	R^2
PC	10.0	0.9757	7.45	0.9866	1.48	0.9879
PC + 10% APS1	29.9	0.9996	18.6	0.9953	10.2	0.9946
PC + 20% APS1	47.8	0.9959	45.0	0.9982	41.9	0.9916
PC + 10% APS2	32.0	0.9998	25.5	0.9956	18.0	0.9915
PC + 20% APS2	155	0.9987	126	0.9941	73.5	0.9961
PC + 10% APS3	42.2	0.9992	26.0	0.9972	20.0	0.9934
PC + 20% APS3	138	0.9975	93.9	0.9969	36.3	0.9987
PC + 10% APS4	38.8	0.9981	32.5	0.9961	23.0	0.9921
PC + 20% APS4	113	0.9956	113	0.9840	86.0	0.9972
PC + 10% APS5	30.7	0.9987	25.5	0.9981	20.5	0.9952
PC + 20% APS5	182	0,9852	116	0.9961	65.3	0.9936

From these data, 10% APS1 presents the lowest yield stress, and therefore confers best workability on any products. A possible explanation for this phenomenon is that, in general, cement pastes containing pozzolans (silica fume, some fly ashes, metakaolin etc) have a higher water demand to achieve standard consistency of cement pastes, as tested by existing standard methods [24]. The binders require more water than reference Portland cements due to such factors as high fineness of pozzolans, their mineralogy, reactive silica content and degree of pozzolanic activity [25]. In the case of thermally activated paper sludges there is an additional factor, which plays an important role in a higher water demand. This is the presence of calcium carbonate in blends and some free lime (CaO) coming from decarbonation of the calcite present in the activated products, whose content increases with increasing activation intensity (from 4.6% in APS1 to 18.7% in APS5). Table 5 shows the free lime content, determined by TG analysis of APS, calculating the difference between the content of CaCO3 in the dry and the activated paper sludges, and then transforming each difference into CaO content. This calculation assumes that the calcium carbonate decomposed during activation is completely transformed into free lime (Table 5) leaving some residual calcite. The double effect (physical and chemical) of calcite in cement paste is well known [5], provoking a higher hydration rate of the alite and aluminate phases of cement. As a consequence, monocarbonate is formed [26] and for the particular case of activated paper sludges

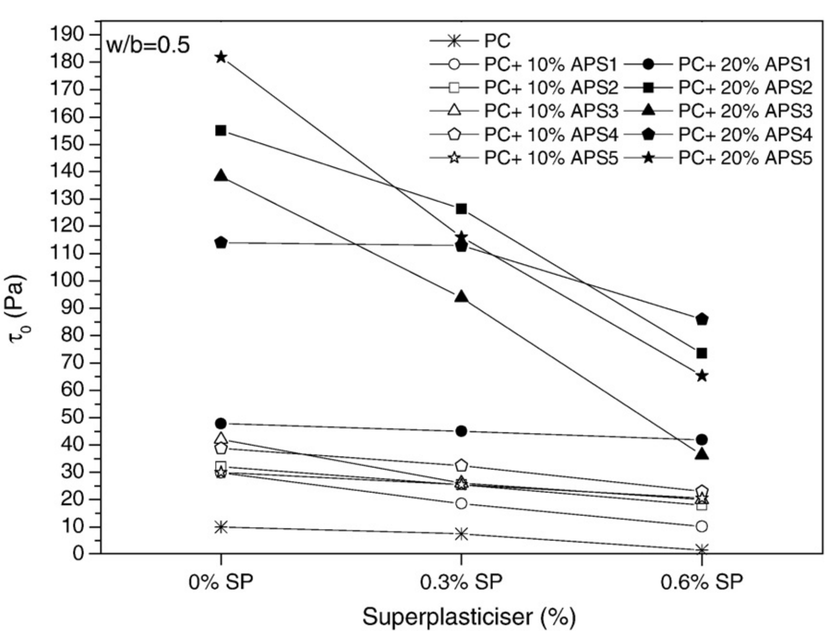

Fig. 3. Effect of superplasticiser on yield stress evolution at $w/b = 0.5$.

(between 700 and 800 °C) hydrotalcite type structures were identified by Frias et al [27] and Rodríguez [15]. Higher free lime content in the APS causes a higher water demand, and therefore the yield stress increases when a constant *w*/*b* ratio is employed.

To sum up, all these factors during the hydration reaction of blended cement pastes increase the water demand that reduces the workability of pastes and produce higher yield stresses when the water/binder ratio was constant at 0.5.

Blended cement pastes at a *w*/*b* of 0.4 were too stiff to test in the rheometer and data could only be obtained for the reference paste and pastes containing 10% of APS1 (Table 4). A reduction of 0.1 in water/binder ratio increased the yield stress by over 400%. From the results shown up to now, it is evident that activation conditions have a significant effect on workability of blended cement pastes containing no superplasticiser.

3.2. Rheological behaviour of blended cement pastes containing superplasticiser

The positive effect of using of admixtures to improve the workability of cement matrices is well known, especially for low *w*/*b* ratios as well as when using active additions [13,14]. For this work, a superplasticiser (Ultrazine NAF) was added to cement pastes at 0.3 and 0.6% solids by weight of binder.

Fig. 3 and Table 6 show the effect of superplasticiser content on the yield stress of blended cement pastes containing 10 and 20% of APS at a water/binder ratio of 0.5. The expected trend for cement pastes of decreasing yield stress with increasing admixture content was observed. The incorporation of this superplasticiser to cement pastes provoked two well-defined behaviours at the different water/binder ratios. A decrease in yield stress at 0.5 *w*/*b* ratio was detected for the cement pastes containing 10% of APS. However, this admixture was more effective in cement pastes containing 20% of APS, giving decreases with increasing admixture content, except for the binder containing 20% of APS1. This is probably because this activated paper sludge has a much higher calcite content than the other APSs, and calcite decreases the effectiveness of superplasticisers [28]. This yield stress trend for this paste is closer to the group of values for pastes containing 10% APS than to the rest of the 20% APS pastes (Fig. 3). Also, the yield stress trend for the paste containing 20% of APS4 is somewhat different from those containing paper sludge wastes activated at higher temperatures (APS3 and APS5). Further investigation is needed to confirm the effect.

Fig. 4 shows the yield stress measurements obtained at water/binder of 0.4. The yield stress of the paste without APS is about four times that at *w*/*b* of 0.5, consistent with 13 datasets summarised by Tattersall and Banfill [14]. To a certain extent this trend also applies to the APS pastes — for example 20% APS1 at 0.6% superplasticiser and 10% APS3 at 0.3% superplasticiser. However, other pastes are much stiffer than this: for example 10% of APS2, APS4 and APS5 at 0.4 *w*/*b* have between 5 and 7 times the yield stress of the equivalent pastes at 0.5 *w*/*b*. In view of this trend it is not surprising that at 0.4 *w*/*b* most of the 20% APS pastes were too stiff to be tested and that superplasticiser is needed to bring the 10% APS pastes within the range of the instrument. 0.3 and 0.6% of admixture made it possible to test blended pastes with 10% of APS, but it was not enough for pastes with 20% of APS except for APS1 (700 °C/2 h).

Figs. 3 and 4 show that the yield stress of paste containing APS is significantly increased above that of the paste without APS and that up to 0.6% of superplasticiser is insufficient to bring this down to the values for the reference paste. In almost all cases the yield stress continuously decreases with increasing % superplasticiser and may be expected to decrease further at higher dosage until saturation coverage of the particle surfaces is achieved, giving minimum yield stress [12,13]. However, this could be at a dosage so much in excess of the recommended 0.6% that other negative effects like set retardation may be observed.

Pastes blended with APS2-5 show steeper reduction with increasing superplasticiser dosage than those with APS1. This is related to the negative effect of the remaining calcite in the activated paper sludge on the effectiveness of the superplasticiser [28].

To summarise these effects, increasing intensity of burning (temperature and time) convert residual $CaCO_3$ to CaO and makes the APS finer. Finer APS with higher CaO increases the water demand and the yield stress of pastes without superplasticiser, thus requiring addition of superplasticiser to give acceptable fluidity. Residual $CaCO_3$ impairs the effectiveness of the superplasticiser added to offset the effect of more intense burning and the lignosulfonate used is not powerful enough to be effective. Thus high intensity activation gives a product with high water demand requiring high dosages of superplasticiser, whereas low intensity activation gives a product with lower water demand which is rather insensitive to the addition of

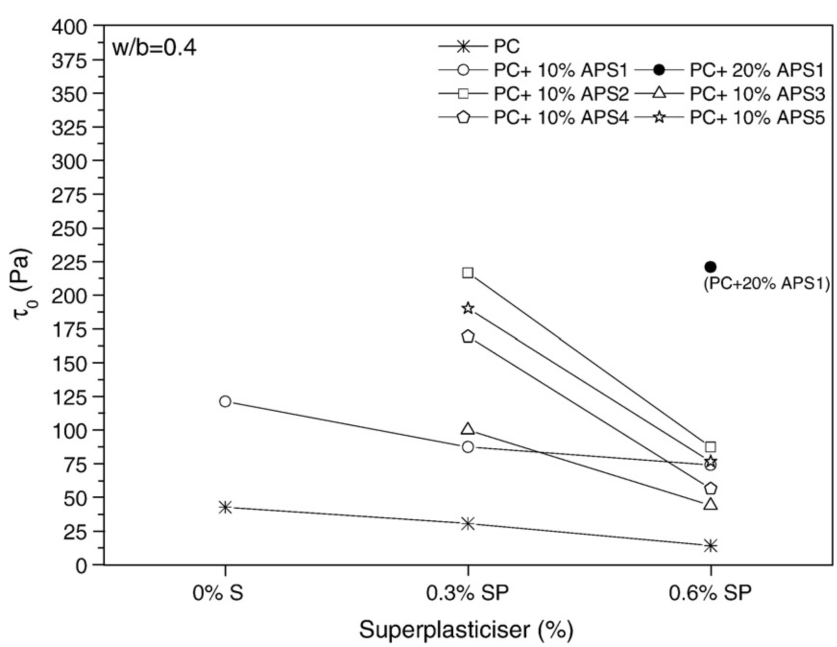

Fig. 4. Effect of superplasticiser on yield stress at *w*/*b* = 0.4.

superplasticiser. Therefore unless a more powerful superplasticiser is used the best results will be obtained using 700 °C for 2 h.

4. Conclusions

- Addition of activated paper sludges in Portland cement increases the yield stress of the blended pastes above the reference paste, due to the calcite and free lime content in APS.
- For a w/b ratio of 0.5, pastes containing activated paper sludge showed a decreasing workability with increasing APS percentage and activation intensity.
- A reduction in w/b ratio from 0.5 to 0.4 produced unworkable pastes, which were too stiff to test, except for the reference and 10% blended cement pastes.
- The effect of superplasticiser in decreasing the yield stress is clearly observed in the blended pastes containing 20% of APS at w/b ratios of 0.5.
- At a w/b ratio of 0.4, up to 0.6% superplasticiser was insufficient to render the pastes containing 20% of APS measurable in the rheometer. This shows that extension of this preliminary investigation to higher admixture contents and/or more powerful superplasticisers is necessary.

Acknowledgements

The authors are grateful to the Spanish Ministries of Education and Science and of Science and Innovation for their financial support in this research (Ref: MAT2003-06479-C03, CTM2006-12551-CO3 and BES-2004-4975) and also to Holmen Paper Madrid, STDI Lafarge Cements (Toledo, Spain) and The Spanish Institute of Cement and its Applications (IECA) for their collaboration in this project.

References

[1] European Standard UNE EN 197-1, Composition, Specifications and Conformity Criteria for Normal Cements, 2000.
[2] B. Pacewska, G. Blonkowski, I. Wilinska, Investigations of the influence of different fly ashes on cement hydration, J. Therm. Anal. Calorim. 86 (1) (2006) 179–186.
[3] B. González-Fonteboa, F. Martínez-Abella, Concretes with aggregates from demolition waste and silica fume. Materials and mechanical properties, Build. Environ. 43 (4) (2008) 429–437.
[4] S. Kourounis, S. Tsivilis, P.E. Tsakiridis, G.D. Papadimitriou, Z. Tsibouki, Properties and hydration of blended cements with steelmaking slag, Cem. Concr. Res. 37 (6) (2007) 815–822.
[5] H.F.W. Taylor, Cement Chemistry, 2nd ed. Thomas Telford, London, 1997.
[6] R. Siddique, Waste Materials and by-Products in Concrete, Springer, Berlin, 2008.
[7] S.N. Gosh, Advances in Cement Technology: Chemistry, Manufacture and Testing, 2nd Edition, TBI, New Delhi, 2002.
[8] M. Heikal, M.S. Morsy, I. Aiad, Effect of treatment temperature on the early hydration characteristics of superplasticized silica fume blended cement pastes, Cem. Concr. Res. 35 (4) (2005) 680–687.
[9] P.F.G. Banfill, The rheology of fresh cement and concrete — a review, in: G. Grieve, G. Owens (Eds.), Proceedings of the 11th International Congress on the Chemistry of Cement, Durban, South Africa, vol. 1, 2003, pp. 50–62.
[10] B. Felekoglu, K. Tosun, B. Baradan, A. Altun, B. Uyulgan, The effect of fly ash and limestone fillers on the viscosity and compressive strength of self-compacting repairs mortars, Cem. Concr. Res. 36 (9) (2006) 1719–1726.
[11] A. Palomo, P.F.G. Banfill, A. Fernandez-Jimenez, D.S. Swift, Properties of alkali activated fly ashes determined from rheological measurements, Adv. Cem. Res. 17 (4) (2005) 143–151.
[12] A. Papo, L. Piani, Effect of various superplasticizers on the rheological properties of Portland cement pastes, Cem. Concr. Res. 34 (11) (2004) 2097–2101.
[13] M.Y.A. Mollah, W.J. Adams, R. Schennach, D.L. Cocke, A review of cement-superplasticizer interactions and their models, Adv. Cem. Res. 12 (4) (2000) 153–161.
[14] G.H. Tattersall, P.F.G. Banfill, The Rheology of Fresh Concrete, Pitman Publishing, London, 1983.
[15] O. Rodríguez, Valorización de un residuo industrial procedente de la industria papelera como material puzolánico, PhD Thesis, Universidad Autónoma de Madrid, Spain, 2008.
[16] M. Frías, M.I. Sánchez de Rojas, O. Rodríguez, R. García Jiménez, R. Vigil de la Villa, Characterisation of calcined paper sludge as an environmental friendly source of metakaolin for manufacture of cementitious materials, Adv. Cem. Res. 19 (1) (2007) 1–8.
[17] R. Vigil de la Villa, M. Frías, M.I. Sánchez de Rojas, I. Vegas, Rosario García, Mineralogical and morphological changes of calcined paper sludge at different temperatures and retention in furnace, Appl. Clay Sci. 36 (4) (2006) 279–286.
[18] I. Vegas, M. Frías, J. Urreta, J.T. San José, Obtaining a pozzolanic addition from the controlled calcination of paper mill sludge. Performance in cement matrixes, Mater. Constr. 56 (283) (2006) 49–60.
[19] M. Frías, O. Rodríguez, I. Vegas, R. Vigil, Properties of calcined clay waste and its influence on blended cement behavior, J. Am. Ceram. Soc. 91 (4) (2008) 1226–1230.
[20] O. Rodríguez, M. Frías, M.I. Sánchez de Rojas, Influence of the calcined paper sludge on the development of hydration heat in blended cement mortars, J. Therm. Anal. Calorim. 92 (3) (2008) 865–871.
[21] P.F.G. Banfill, M. Frías, Rheology and conduction calorimetry of cement modified with calcined paper sludge, Cem. Concr. Res. 37 (2) (2007) 184–190.
[22] M. Frías, M.I. Sánchez de Rojas, Microstructural alterations in fly ash mortars: study on phenomena affecting particle and pore size, Cem. Concr. Res. 27 (4) (1997) 619–628.
[23] M. Frías, M.I. Sánchez de Rojas, M.P. Luxán, N. García, Determination of specific surface area by the laser diffraction technique. Comparison with the Blaine method, Cem. Concr. Res. 21 (5) (1991) 709–717.
[24] European Standard UNE EN 196-3, Methods of Testing Cement — Part 3: Determination of Setting Times and Soundness, 2005.
[25] E. Badogiannis, G. Kakali, G. Dimopoulou, E. Chaniotahir, S. Tsivilis, Metakaolin as a main cement constituent. Exploitation of poor Greek kaolins, Cem. Concr. Compos. 27 (2) (2005) 197–203.
[26] V.L. Bonavetti, V.F. Rahhal, E.F. Irassar, Studies on the carboaluminate formation in limestone filler-blended cements, Cem. Concr. Res. 31 (6) (2001) 853–859.
[27] M. Frías, O. Rodríguez, R. García, I. Vegas, Influence of activation temperature on reaction kinetics in recycled clay waste–calcium hydroxide systems, J. Am. Ceram. Soc. 91 (12) (2008) 4044–4051.
[28] M. Nehdi, Why some carbonate fillers cause rapid increase of viscosity in dispersed cement-based materials, Cem. Concr. Res. 30 (10) (2000) 1663–1669.