Available online at www.sciencedirect.com
ScienceDirect
Cement and Concrete Research 37 (2007) 184–190
Cement and Concrete Research

Rheology and conduction calorimetry of cement modified with calcined paper sludge

P. Banfill [a], Moisés Frias [b,*]

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

Received 13 September 2005; accepted 9 November 2006

Abstract

This paper considers calcined paper sludge as an alternative source of metakaolin, an established supplementary cementitious material. Calcination of the sludge generated in the recycling of newsprint paper at 700 °C yields a product with pozzolanic properties. The effects of this recycled metakaolin on the rheology and conduction calorimetry of cement pastes have been studied and compared to the effects of commercial metakaolin. The effects are similar and the results show that calcined paper sludge has the potential to be used as a supplementary cementitious material. This offers a route for utilising this waste material, as an alternative to the increased environmental burden associated with the production of metakaolin from natural kaolinite resources.

Keywords: Paper sludge; Rheology; Calorimetry; Metakaolin; Blended cement

1. Introduction

Two significant challenges facing the quest for sustainable industrial production in the 21st century are reducing carbon dioxide emissions and reduction or recycling of waste materials. The cement and concrete industry has been a leading proponent of solutions to both of these issues, through using supplementary cementitious materials to reduce the cement content, and hence the carbon dioxide emissions per unit amount of concrete, and incorporating materials in concrete that would otherwise have to be dumped as waste. Such materials range from the long established fly ash and ground granulated blast furnace slag, through the more recent silica fume, metakaolin and rice husk ash to the still-experimental municipal waste incinerator and other ashes. This paper reports a preliminary investigation into the behaviour of paper sludge, a waste material generated in the treatment of recycled paper.

In recent years there has been a worldwide trend towards increased recovery and recycling of wastepaper, which results in significant quantities of sludge as a by-product of the ink removal process. Typically 20–35% of the waste paper feedstock is lost as sludge and this was formerly disposed of by landfill dumping but with increasing environmental pressure and taxation this is no longer acceptable or economic. It is estimated that about 5.8 Mt/year is produced in the European Union [1]. Paper coatings typically use china clay kaolin, so the sludge contains variable quantities of organic material, calcium carbonate and clayey minerals, depending on the process. Pera et al. [1,2] showed that controlled calcination of sludge can produce pozzolanic materials. Calcining this material at around 750 °C removes the organic material and produces a reactive pozzolanic material containing metakaolin and calcite, which is potentially useful in the concrete industry. Above 800 °C decarbonation of the calcite to calcium oxide and pyroprocessing of the clay can yield hydraulic binders like C_2S, C_2AS and CAS_2. Subsequently, Frías et al. [3] reported that the calcining conditions play an important role in the activation of these paper wastes, stating that the most of paper sludges calcined between 700 and 800 °C showed high pozzolanic activity, an activity similar to MK from activation of commercial kaolinite. According to their experimental pozzolanic data and, from the point of view of minimising energy consumption and environmental pollution (due to decarbonation of the limestone

* Corresponding author. Tel.: +34 91 3020440; fax: +34 91 3020700.
E-mail address: mfrias@ietcc.csic.es (M. Frias).

0008-8846/$ - see front matter
doi:10.1016/j.cemconres.2006.11.013

Table 1
Chemical and mineralogical composition of starting paper sludge (%)

Chemical composition (%)		Mineralogical composition (%)	
SiO_2	18.05	Kaolinite	29.2
Al_2O_3	10.14	Calcite	35.3
Fe_2O_3	0.55	Talc	6.85
CaO	19.82	Quartz	6.11
MgO	2.58	Muscovite	1.71
SO_3	0.33	Organic matter (cellulose)	29.20
Na_2O	0.25	Total	100
K_2O	0.21		
TiO_2	0.26		
Loss on ignition	47.62		
Total	99.81		

present in the starting paper sludge under more severe calcination conditions) the best conditions to activate these industrial paper wastes are 700 °C for 2 h duration in the furnace.

Commercial metakaolin is produced from the controlled calcination of kaolinite between 450 and 600 °C by losing the OH lattice water and shows good pozzolanic properties [4–11]. Therefore the question examined in this paper is whether it is possible to use calcined paper sludge as an alternative to metakaolin for use in blended cementitious materials, thus consuming a waste material and reducing CO_2 emissions. The objective of this work was to compare the effect of calcined paper sludge as a supplementary cementitious material on rheology and rate of heat evolution with the effect of metakaolin.

2. Materials

The starting waste sludge for this research came from a Spanish newsprint company which uses 100% recycled paper as its raw material, a process which actually generates about 150,000 t/year of paper sludge wastes at about 50% moisture content. The chemical composition (X-ray fluorescence) and mineralogical composition of the starting sludge is given in Table 1, while the chemical composition for the paper sludge calcined at 700° and 2 h of retention in furnace [3] is shown in Table 2. The very large loss on ignition and high organic content for the starting paper sludge should be noted. The loss on ignition reflects contribution from the decarbonation of calcite and the combustion of cellulose in the furnace above the calcining temperature of 700 °C.

Table 2
Chemical and physical properties of cement, calcined paper sludge and metakaolin

	Cement	Paper sludge calcined at 700 °C and 2 h	Metakaolin
SiO_2	19.48	30.20	51.60
Al_2O_3	5.95	18.00	41.30
Fe_2O_3	2.13	0.70	4.64
CaO	62.96	31.40	0.09
MgO	1.63	3.70	0.16
SO_3	2.28	0.27	–
Na_2O	0.32	0.21	0.01
K_2O	1.18	0.32	0.62
TiO_2	0.21	0.35	0.83
Loss on ignition	3.02	14.53	0.60
Total	99.16	99.68	99.90
Surface area (BET) m^2/g	1.12	8.7	14.4

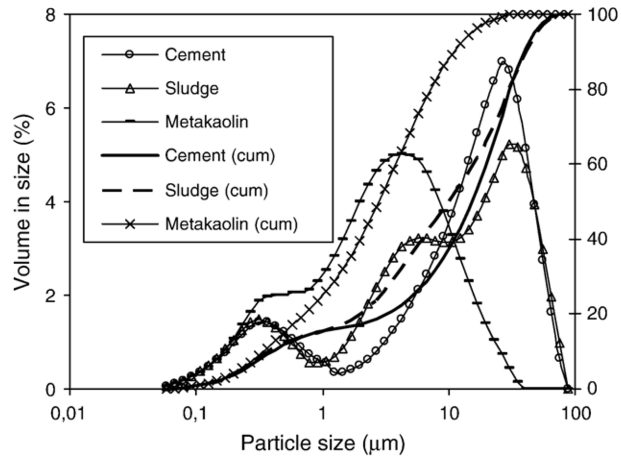

Fig. 1. Particle size distributions of the binder materials.

The cement was a CEM I 42.5N from Cementos Alfa S.A., Spain, and the metakaolin was a commercial grade available in the UK (ECC International, now Imerys). Their chemical composition and certain physical properties are also shown in Table 2. The chemical composition for commercial metakaolin was provided by the supplier company.

The particle size distribution of these materials is shown in Fig. 1, determined with a Malvern Mastersizer® laser granulometer. The volumetric interval distribution (left hand axis) shows that the cement and metakaolin are bimodal with peaks around 0.3 and 25 µm (cement) and 0.3 and 4 µm (metakaolin). The sludge is trimodal with peaks around 0.2, 5 and 28 µm. The cumulative distributions (right hand axis) are consistent with the BET data (Table 2). The superplasticiser used in this work was a

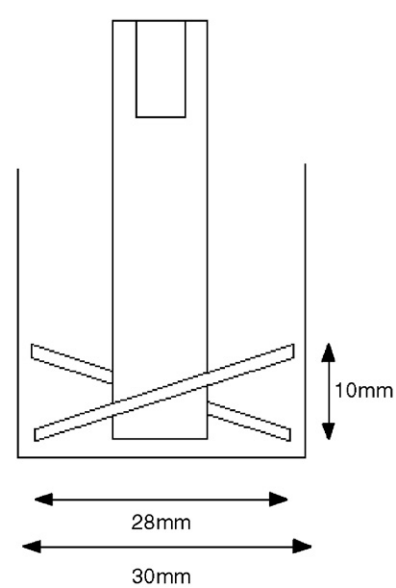

Fig. 2. Geometry of the rheometer measuring system.

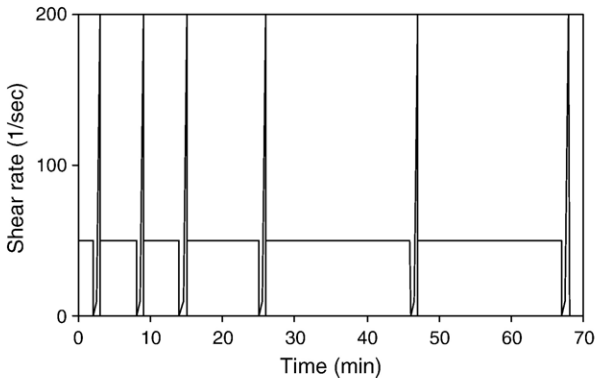

Fig. 3. Variation of shear rate with time.

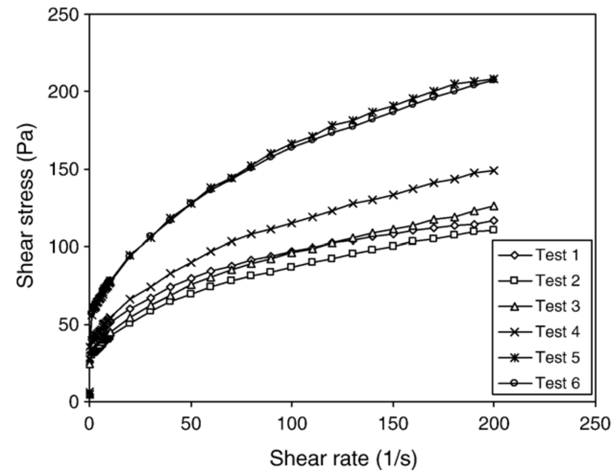

Fig. 4. Typical flow curves for cement pastes without sludge or superplasticiser at water/binder=0.5.

sulfonated naphthalene formaldehyde condensate (YN40, Hodgson Chemicals, Yorkshire).

3. Equipment and procedures

3.1. Rheology

The rheometer was a TA Instruments model CS500[2] operating in controlled shear rate mode and fitted with a specially developed interrupted helix impeller rotating in a smooth walled cylinder (see Fig. 2). This system has been used in previous work on high fluidity grouts and pastes [12,13]. 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 [14]. 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, cement plus calcined sludge, or cement plus metakaolin) and the appropriate quantity of water (containing predissolved superplasticiser if appropriate) to give 0.4 and 0.5 water/binder ratio, and immediately 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. Continuous steady shearing at 50 s^{-1} occurred between repeated measurements of the flow curve, according to the overall schedule shown schematically in Fig. 3. An initial 2 min preshear at 50 s^{-1} was followed by test 1, then 5 min preshear, test 2, 5 min preshear, test 3, 10 min preshear, test 4, 20 min preshear, test 5, 20 min preshear and finally test 6. Allowing for the time taken for each flow curve, tests therefore started at 2, 8, 14, 25, 46 and 68 min. The flow curve was determined using the preset speed feature available in Navigator® and stress measured at each of 20 shear rates from zero to 10 s^{-1} and 20 points from 10 to 200 s^{-1}. This grouping of the measurements at low shear rates combined with the controlled stress measurements in the CSL[2] enhances the precision of direct yield stress determination by emphasising the first deviation of the flow curve from the stress axis. At the end of the measurement cycle the shear rate dropped rapidly from 200 s^{-1} to 50 s^{-1} for the start of the next preshear period, and the data for the flow curve for each test was saved for later analysis. Table 3 summarises the experimental programme of material combinations.

Table 3
Programme of experimental mixes

Water/binder ratio	0.4						0.5					
Superplasticiser %	Sludge %			Metakaolin %			Sludge %			Metakaolin %		
0	0	5	10	0	5	10	0	5	10	0	5	10
0.1	0	5	10	0	5	10	0	5	10	0	5	10
0.2	0	5	10	–	–	–	0	5	10	–	–	–
0.3	0	5	10	0	5	10	0	5	10	0	5	10

3.2. Conduction calorimetry

The rate of heat evolution and the cumulative heat evolved as a consequence of hydration were determined under isothermal conditions at 20 °C in a Wexham Developments JAF calorimeter. 30 g of powder (cement, cement plus calcined sludge, or cement plus metakaolin) were placed in a small plastic bag together with the appropriate quantity of water (containing predissolved superplasticiser as appropriate), sealed and mixed by hand. The bag was carefully placed around the heat sensor and the calorimeter chamber assembled and placed in the water bath. Measurements of temperature difference between sample and water bath, by the small potential difference across the thermal sensor, commenced immediately, but in this method the heat evolution cannot be determined until the sample has reached thermal equilibrium with the water bath and consequently meaningful data were only obtained after about one hour. Hydration was continued for about 40 h, by which time the rate of heat evolution had declined to a low value following the main peak. At the end of the experiment the set up was calibrated

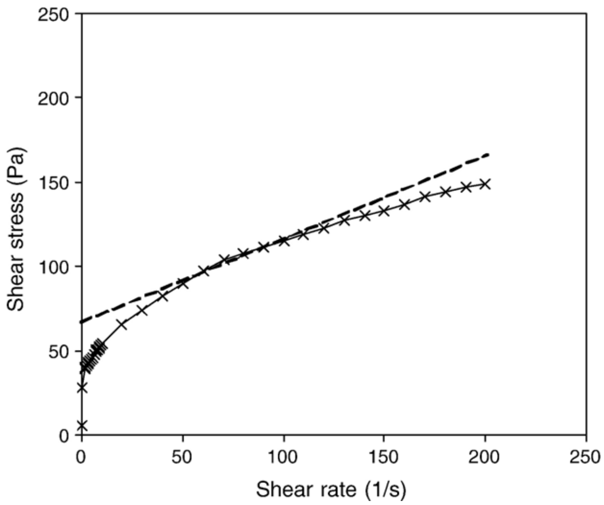

Fig. 5. Evaluation of the yield stress from test 4 in Fig. 4.

using the integral heater in the calorimeter so that the measured voltages were converted to rate of heat evolution. The theory of the method and of the calibration of the unit are given by Forrester [15].

It should be noted that in both rheology and conduction calorimetry the superplasticiser was predissolved in the mixing water, but that the paste is less well dispersed in the latter tests because it was mixed by hand. This lower mixing intensity is likely to cause some retardation relative to the rheology tests.

4. Results

4.1. Rheology

Fig. 4 gives an example of the sort of rheology data produced in the experiment for a cement paste containing no sludge or superplasticiser and at a water/binder ratio of 0.5. The six flow curves correspond to the successive tests (with a period of preshear between each) and it can be seen that the lowest curve in this case is produced by test 2. The shear stress values always dropped slightly from the first test, passed through a minimum (typically on the second test at water/binder = 0.5 and with superplasticiser present, but often on the third or fourth test at water/binder = 0.4) after which they progressively increased as the paste stiffened. Evidently the shear energy input by the first two minutes preshear at 50 s^{-1} was insufficient to break down all the flocculated structure in the paste and further breakdown occurred between the first and the second flow curves. A higher rate of preshear would probably have prevented this [16].

Table 4
Comparison of extrapolated and initial yield stresses from Fig. 4

Test (series)	1	2	3	4	5	6
Age of paste (min)	2	8	14	25	46	68
Extrapolated yield stress (Pa)	62	52	55	66	92	93
Initial yield stress by inspection (Pa)	40	30	32	39	56	57

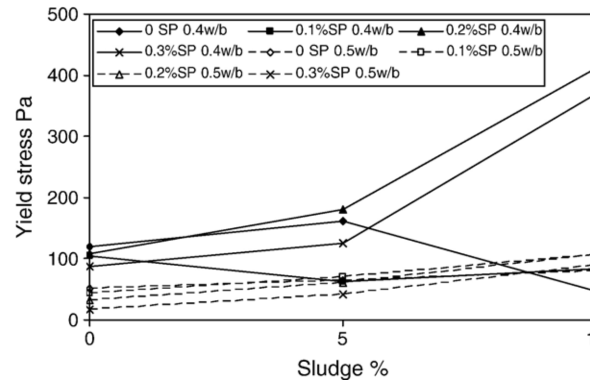

Fig. 6. Effect of sludge content on yield stress.

Fig. 4 also clearly shows the existence of the yield stress in these pastes, but the curves caused some difficulties in analysis. Each flow curve could be analysed by the Herschel–Bulkley equation [17]:

$$\tau = \tau_o + A\ \dot{\gamma}^B \tag{1}$$

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

However, the regression analysis available within the rheometer software to fit this equation proved to be very susceptible to slight differences in the degree of curvature of the flow curve data. This meant that the regression tended to fit the coefficients to the curve rather than to the intercept and gave calculated values of yield stress which did not represent the reality of the data.

This analysis was therefore abandoned in favour of the much more reliable Bingham model:

$$\tau = \tau_o + \mu\ \dot{\gamma} \tag{2}$$

where the symbols have the same meaning and μ is the plastic viscosity. Shown in Fig. 5 is the best straight line through the measured data points for test 4 at shear rates between 55 and 115 s^{-1}. This gives reproducible estimates of the yield stress by extrapolation to the shear stress axis and of the plastic viscosity from the slope of the line. However, this extrapolated yield stress is consistently higher than the initial yield stress, taken as the stress at which the flow curve departs from the shear stress

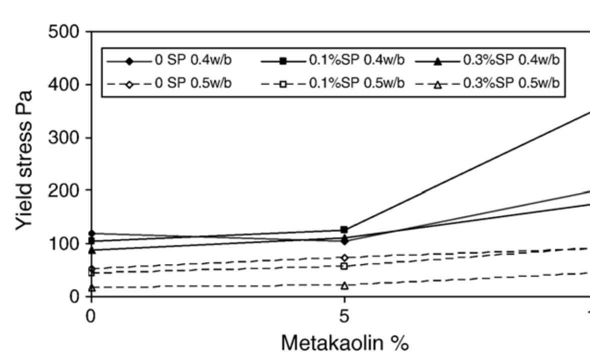

Fig. 7. Effect of metakaolin content on yield stress.

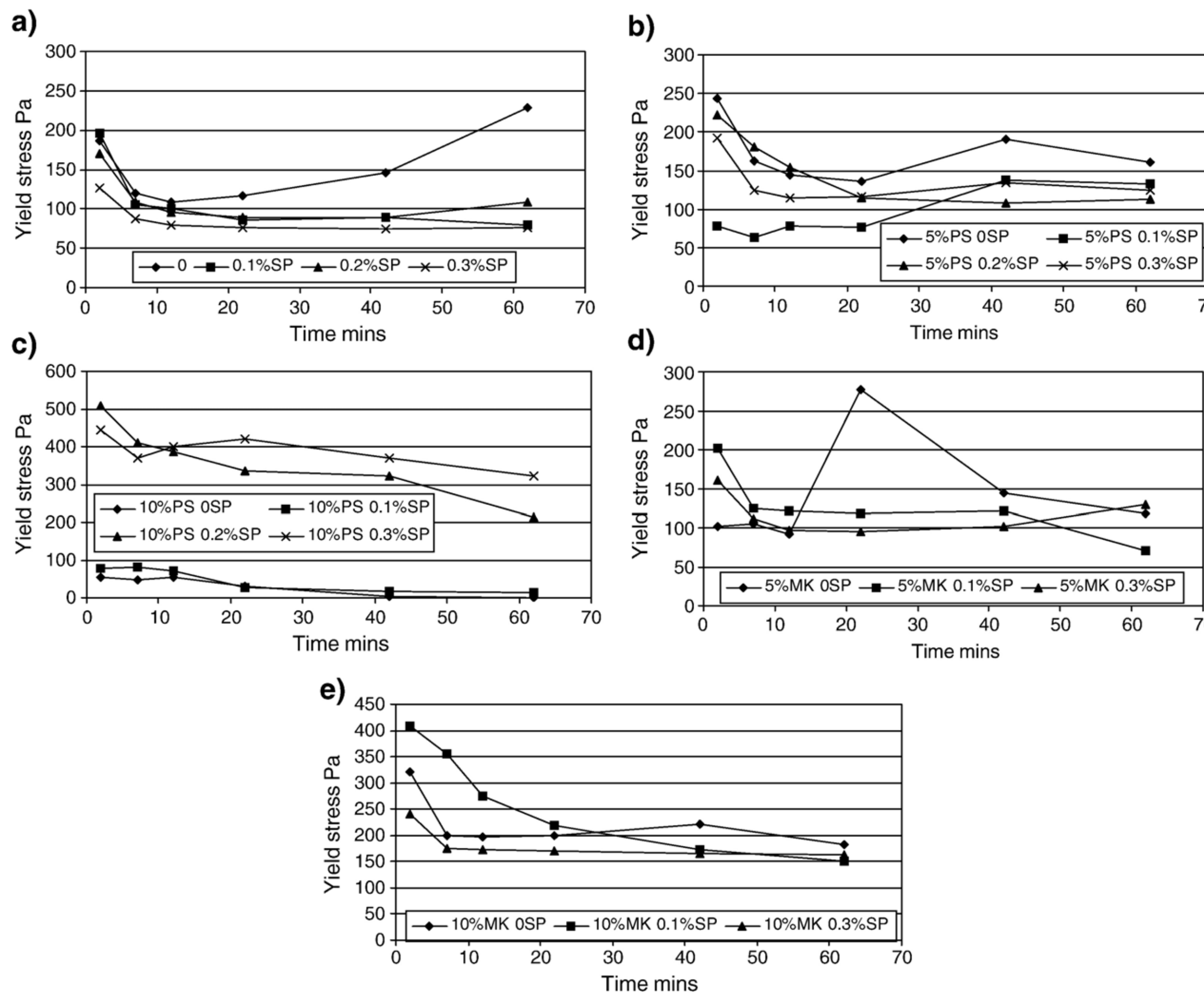

Fig. 8. Variation of yield stress with time for 0.4 water/binder pastes of cement (a) alone, and with (b) 5% sludge, (c) 10% sludge, (d) 5% metakaolin, (e) 10% metakaolin.

axis and which can be estimated by inspection of the data points. Table 4 shows the difference between the two sets of values for the paste shown in Fig. 4. The rest of this paper refers to the extrapolated yield stress and it must be borne in mind that this value is about 60–70% higher than the initial yield stress. The values are at the high end of the range of yield stresses summarized by Tattersall and Banfill [18] which may be the result of this extrapolation combined with a particular feature of the cement used.

Figs. 6 and 7 show the effect of superplasticiser concentration and water/binder ratio on the yield stress of pastes containing sludge and metakaolin respectively. The yield stresses shown are for the second test in every sequence, i.e. the minimum values after the structural breakdown as mentioned above. With no sludge or metakaolin present, the expected trend for cement pastes of decreasing yield stress with increasing superplasticiser concentration was observed. Increasing the amount of sludge and metakaolin caused a smooth increase in yield stress at 0.5 water/binder ratio but the generally rising trend for 0.4 is interrupted by some significant decreases with higher superplasticiser concentrations. These may have been caused by slippage or segregation in the rheometer [18]. The pastes with sludge (Fig. 6) have a generally higher yield stress than the pastes with metakaolin (Fig. 7), despite the lower BET surface area of the former material. This could be the filler effect imparted by limestone filler (from paper sludge) which accelerates hydration of Portland cement clinker grains at early ages, improves the particle packing of the cementitious system, provides new nucleation sites for calcium hydroxide, and promotes the formation of calcium carboaluminates [19]. The yield stress of 0.2% and 0.3% superplasticiser mixes with 10% sludge and 0.4 water/binder ratio is high and suggests that there may be a limit to the amount of sludge that can be used in these blends, while retaining reasonable workability.

Fig. 8a–e show the stiffening of the pastes over 60 min in the form of the change of yield stress. Stiffening is suppressed both by the addition of superplasticiser and by high enough concentrations of sludge or metakaolin. The plain cement paste stiffens as a result of the progress of the hydration reactions consuming free water and producing surface layers of hydration products [20], but the presence of superplasticiser slows down these reactions and the paste stiffens less rapidly, to the extent that in pastes with 0.3% superplasticiser there is no change in yield stress with time after the initial breakdown is complete. A

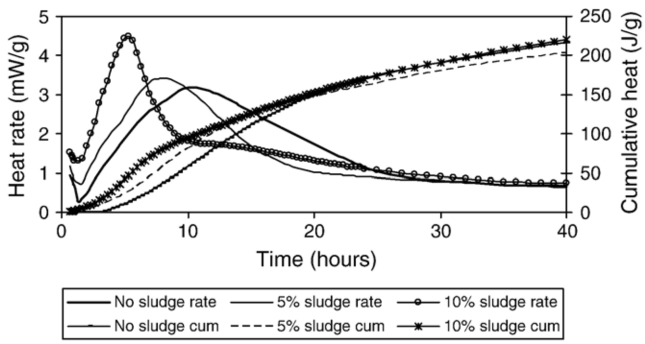

Fig. 9. Typical conduction calorimetry curves showing heat evolution from cement–sludge mixes.

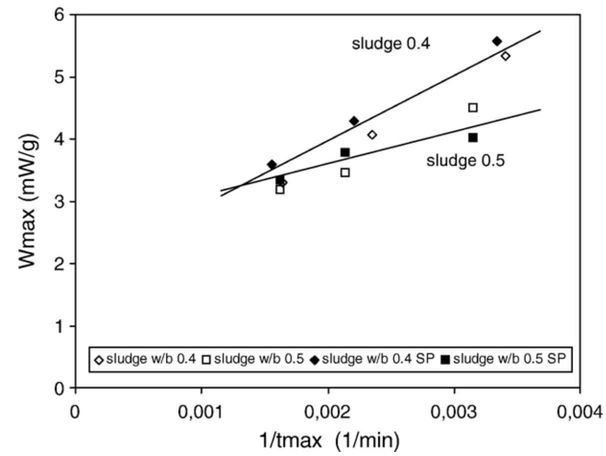

Fig. 10. The effect of sludge and superplasticiser on the heat evolution kinetics.

slight increase in stiffening rate is observed with 5% sludge and metakaolin but not at 10%. This is difficult to explain since it is too early in the hydration process for pozzolanic reactions to be significant. It could be due to the kinetics of adsorption of superplasticiser on fine particles of different types but more work would be needed to clarify this.

4.2. Conduction calorimetry

Fig. 9 shows the typical variation of the rate of heat evolution obtained from the conduction calorimeter. The induction period is clearly seen, followed by the main peak of heat evolution and a period of deceleration, which corresponds to the shallow S shaped curve of the cumulative heat evolution. Table 5 summarises the data for all the tests. Following the presentation style originated by Wilding et al. [21], Fig. 10 shows graphs of W_{max}, the peak heat evolution rate, against $1/t_{max}$, the time to the peak rate. If the hydration kinetics follow the Avrami–Erofeyev form then according to Wilding et al. the data should follow a straight line relationship with points showing acceleration of hydration being further from the origin and points showing retardation being nearer to the origin. Fig. 10 confirms this behaviour for cement plus sludge mixes, with two broad trends in the data corresponding to water/binder ratio of 0.4 and 0.5. However, in the cement plus metakaolin mixes $1/t_{max}$ is effectively constant while W_{max} increases with metakaolin content, so these points are not plotted.

Paper sludge accelerates the hydration of cement paste both with and without superplasticiser, showing more rapid acceleration at water/binder ratio of 0.4 than at 0.5. Two possible explanations for this are, firstly, the reaction between the fine powdered sludge particles and calcium hydroxide released from the cement reduces the concentration of calcium hydroxide in the water and facilitates its further release from the cement, and, secondly, the fine particles provide nucleation sites for hydration products to form. In contrast, metakaolin causes no significant acceleration of the time to the peak heat evolution rate, but it does increase the height of the peak, W_{max}. The total heat evolved after 40 h of hydration is reduced in proportion to the amount of sludge or metakaolin added to the cement blend, because the dominant contribution of cement to the heat evolution is diluted by their presence. Finally, it can be noted that the presence of superplasticiser at 0.3% slightly retards the hydration relative to the equivalent binder blend without superplasticiser.

5. Discussion

The yield stress of a concentrated suspension is primarily the result of interparticle attractions [22] and depends on the size of the interparticle force, the volume fraction of the solid phase, the particle size and particle size distribution [23]. All other factors being equal, the finer the particle size distribution, the higher the number of interparticle contacts per unit volume and hence the higher the yield stress. This is confirmed by the data in Figs. 6 and 7 where increasing sludge and metakaolin content (both of which are finer than the cement) increase the yield stress. However, metakaolin is finer than sludge (Fig. 1) and this predicts a higher yield stress for cement plus metakaolin than for cement plus sludge. This is not observed because the particle

Table 5
Summary of conduction calorimetry results

Water/binder ratio		0.4			0.5		
Superplasticiser %	Sludge %	0	5	10	0	5	10
0		3.30 (10.18)	4.06 (7.08)	5.33 (4.89)	3.18 (10.29)	3.45 (7.01)	4.49 (5.28)
0.3		3.60 (10.73)	4.29 (7.56)	5.57 (5.00)	3.33 (10.73)	3.77 (8.11)	4.01 (5.39)
	Metakaolin %	0	5	10	0	5	10
0		3.3 (10.18)	3.43 (10.18)	–	3.18 (10.29)	3.45 (9.88)	–
0.3		3.6 (10.73)	4.06 (10.40)	–	3.33 (10.73)	3.6 (11.21)	–

Each entry is in the form of peak heat evolution rate in mW/g and time to peak in hours.

shape and chemistry, in particular the tendency to agglomerate, are also important. Notwithstanding the foregoing discussion, the result which has practical importance is that paper sludge increases the yield stress of cement systems by an amount that is not excessive compared to metakaolin, an already established supplementary cementitious material.

The effect of pozzolans on the hydration kinetics of cement is variable [24]. Natural pozzolans accelerate early hydration, while the effect of fly ash and microsilica/silica fume is variable according to their composition. The removal of Ca^{2+} ions from solution by the pozzolan is the suggested reason for the acceleration. The calorimetric data (Fig. 10) is consistent with this and sludge clearly accelerates heat evolution which is reflected by the early stiffening in the rheometer. Once again, the result of practical importance is that paper sludge has no detrimental influence on the heat evolution rate of cement.

6. Conclusions

The effects of calcined paper sludge and metakaolin on the rheology and conduction calorimetry of cement pastes are similar and this work has provided more evidence for the potential use of low concentrations of calcined paper sludge as a supplementary cementitious material. This offers a route for utilising this waste material, as an alternative to the increased environmental burden associated with the production of metakaolin from natural kaolinite resources.

Acknowledgements

We are grateful to the CSIC (Madrid) and the Royal Society (London) for funding this joint investigation.

References

[1] J. Pera, A. Amrouz, Development of highly reactive metakaolin from paper sludge, Advanced Cement Based Materials 7 (2) (1998) 49–56.

[2] J. Pera, J. Ambroise, M. Chabannat, Transformation of wastes into complementary cementing materials, in: V.M. Malhotra (Ed.), Proceedings of the 7th CANMET/ACI Conference on Fly Ash, Silica Fume and Slag in Concrete, ACI SP 199, Madras, India, vol. 2, 2001, pp. 459–475.

[3] M. Frías, M.I. Sánchez de Rojas, J. Rivera, Influence of calcining conditions on pozzolanic activity and reaction kinetics in paper sludge–calcium hydroxide mixes, in: V.M. Malhotra (Ed.), Proceedings of the 8th CANMET/ACI Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolan in Concrete, ACI SP 221, Las Vegas, vol. 1, 2004, pp. 879–892.

[4] J. Pera, E. Bonnin, M. Chabannat, Immobilisation of wastes by metakaolin-blended cements, in: V.M. Malhotra (Ed.), Proceedings of the 6th CANMET/ACI Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolan in Concrete, ACI SP 178, Bangkok, Thailand, vol. 2, 1998, pp. 997–1005.

[5] F. Curcio, B.A. DeAngelis, S. Pagliolico, Metakaolin as a pozzolanic microfiller for high performance mortars, Cement and Concrete Research 28 (6) (1998) 803–809.

[6] M. Chabbanat, C. Girodet, J.L. Bosc, J. Pera, Effectiveness of metakaolin on the freezing resistance of mortars, in: V.M. Malhotra (Ed.), Proceedings of the 5th CANMET/ACI Conference on Durability of Concrete, ACI-SP 192, Barcelona, Spain, Supplementary Papers, 2000, pp. 173–186.

[7] T. Ramlochan, M. Thomas, Effect of metakaolin on external sulphate attack, in: V.M. Malhotra (Ed.), Proceedings of 5th CANMET/ACI Conference on Durability of Concrete, ACI SP 192, Barcelona, Spain, vol. 1, 2000, pp. 239–251.

[8] B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: a review, Cement and Concrete Composites 23 (6) (2001) 441–454.

[9] J. Pera, J. Ambroise, Pozzolanic properties of metakaolin obtained from paper sludge, in: V.M. Malhotra (Ed.), Proceedings of 6th CANMET/ACI Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolan in Concrete, ACI SP 178, Bangkok, Thailand, vol. 2, 1998, pp. 1007–1020.

[10] M. Frías, M.I. Sánchez de Rojas, J. Cabrera, The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin–cement mortars, Cement and Concrete Research 30 (2) (2000) 209–216.

[11] M. Frías, M.I. Sánchez de Rojas, J. Cabrera, The effect of high curing temperature on the reaction kinetics in MK-blended cement matrices at 60 °C, Cement and Concrete Research 33 (5) (2003) 643–649.

[12] D.S. Swift, P.F.G. Banfill, Flow properties of high slag grouts, Final Report for BNFL plc, 2000, p. 95.

[13] D.S. Swift, P.F.G. Banfill, Effects of superplasticizers, powder fineness and solution electrolyte content on the rheology of model paste systems, in: V.M. Malhotra (Ed.), Proceedings of 7th CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures in Concrete, *ACI SP 217*, Berlin, Germany, 2003, pp. 499–512.

[14] 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.

[15] J.A. Forrester, A conduction calorimeter for the study of cement hydration, Cement Technology (May/June 1970) 95–99.

[16] P.F.G. Banfill, D.S. Swift, The effect of mixing on the rheology of cement-based materials containing high performance superplasticisers, Annual Transactions of the Nordic Rheology Society 12 (2004) 9–12.

[17] W.H. Herschel, R. Bulkley, Consistency measurements on rubber benzene solutions, Kolloid Zeitung 39 (1926) 291–300.

[18] G.H. Tattersall, P.F.G. Banfill, The Rheology of Fresh Concrete, Pitman, London, 1983.

[19] V.L. Bonavetti, V.F. Rahhal, E.F. Irassar, Studies on the carboaluminate formation in limestone filler-blended cements, Cement and Concrete Research 31 (6) (2001) 853–859.

[20] J.I. Bhatty, P.F.G. Banfill, A viscometric method of monitoring the effect of retarding admixtures on setting of cement pastes, Cement and Concrete Research 14 (1) (1984) 64–72.

[21] C.R. Wilding, A. Walter, D.D. Double, A classification of inorganic and organic admixtures by conduction calorimetry, Cement and Concrete Research 14 (2) (1984) 185–194.

[22] Flatt R.J., "Interparticle forces and superplasticisers in cement suspensions", PhD thesis #2040, EPFL, Lausanne, 1999.

[23] R. Buscall, I.J. McGowan, P.D.A. Mills, R.F. Stewart, D. Sutton, L.R. White, G.E. Yates, The rheology of strongly flocculated suspensions, Journal of Non-Newtonian Fluid Mechanics 24 (2) (1987) 183–202.

[24] F. Massazza, Pozzolana and pozzolanic cements, in: P.C. Hewlett (Ed.), Lea's Chemistry of Cement and Concrete, 4th edition, Arnold, London, 1998, pp. 471–631.