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INFLUENCE OF THE CALCINED PAPER SLUDGE ON THE DEVELOPMENT OF HYDRATION HEAT IN BLENDED CEMENT MORTARS

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The present study is based on the influence of the addition of a pozzolanic material as a result of the activation of an industrial waste coming from the Spanish paper industry on the heating as well as hydration heat of the cement mortars made with 10 or 20% of active addition.

Once the sludge has been calcined at different temperatures (700–800°C) and stays in furnace (2 and 5 h), the calcined products showed high pozzolanic activity. The maximum activity corresponded to the paper sludge calcined at 700°C for 2 h (S1). Besides, it can be proved that there was an increase both of the heating and also of the hydration heat in the first 23–25 h for both additions (10 and 20% of S1) regarding the reference cement mortar. This behaviour would be related to the influence of different effects: filler and pozzolanic during the first hours of reaction, and by the dilution effect for longer hydration times, mainly when 20% of S1 was added.

Keywords: *heating, hydration heat, paper sludge, pozzolanic activity*

Introduction

The exploitation of any by-product or waste generated in an industrial process has priority nowadays. One of the different ways for recycling the by-products is based on looking for specific applications that can be adapted to their features [1-5].

There is the possibility of including them as an active addition to cement, taking this as one of the most important points in the building sector. According to the present European regulation [6], different active additions may be included.

One of the residues to be added to cement is the paper industry sludge. Nowadays, there is not much bibliography on this line of research. The first studies related to this subject worldwide were carried out by Péra *et al.* [7–8], who pointed at the possibility of adding the sludge to cement as a pozzolanic addition.

The first studies in Spain that dealt with the sludge from the paper industry were carried out by Frías *et al.* [9]. The starting sludge was characterized, showing its high level of organic material (30.3%). The mineral fraction being composed by calcite (35.5%), kaolinite (21%), talc (6.9%), mica (1.7%) and quartz (6.1%). Besides, it was proved that once the sludge has been calcined it shows a high pozzolanic activity as a result of the transformation of kaolinite in metakaolin, mainly.

The evaluation of the heat developed on the cementing matrix is one of the aspects to be taken into account, because of its negative consequence on durability when the developed heat is important.

Relative to the hydration heat, it has been proved that some of the pozzolanic materials react with the calcium hydroxide released during the hydration reaction of Portland cement (PC), increasing the hydration heat at early stages, because of the exothermic reaction that has been produced [10]. This fact turns out to be the more evident with pozzolanic activity increment [11].

So, for example, Frías *et al.* [12], studied the effect of the silica fume (SF) on the hydration heat developed by the mortars made with this type of pozzolanic addition. The results showed that the SF did not provoke a decrease in the heat development proportional to the amount of replaced cement.

Other researches reported the influence of fly ash (FA) on the hydration heat of Portland cement pastes or mortars. This way Pacweska *et al.* [13] concluded that FA with better pozzolanic activity did not show the reduction of heat released observed in another FA addition with lower pozzolanic activity.

On the other hand, Frías *et al.* [14] showed the effect a commercial metakaolin (MK) on the hydration heat, and concluding that the MK produced similar hydration heat values to those of the SF, that is, higher values in relation to the 100% of reference Portland cement.

Other pozzolanic additions have been studied, for example, spent fluid catalytic cracking catalyst (FCC) [15], this kind of by-products when substituted PC, produced higher heat of hydration than PC mortars.

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Therefore, because of the previous experiences and the lack of experimental results on the behaviour of the paper sludge on a Portland cement matrix, the current research is about the influence of thermically activated paper sludge on the development of the hydration heat of the PC mortars elaborated with this kind of industrial residue that comes from the process of paper manufacturing.

Experimental

Materials

The materials used in the research were:

- Ordinary Portland cement (OPC): Commercial cement according to the European regulation [6], the reference cement used was the type CEM I 42,5 R, with a higher or similar clinker to 95%, and which can have 5% of minor components. The chemical and technical properties of OPC used in current paper are shown in Table 1 [16].
- Sand: Spanish standard sand according to CEN EN 196-1 was used [17].
- Paper sludge waste: From Spanish paper industry which uses a 100% recycled paper as raw materials.
- Calcined paper sludges (S). The paper sludge was calcined at different temperatures, and after the calcination mixed with OPC. The calcining conditions are reflected on Table 2.

The chemical composition of both the starting sludge and the calcined one determined by XRF appears on Table 3. These results showed that the paper sludge was composed mainly by silica, alumina and calcium oxide.

The characterization by X-ray diffraction (XRD) is showed in Fig. 1. The quantification of the mineral phases is indicated in Table 4. The initial sludge [18], according to the relative XRD patterns, mainly consisted in kaolinite (21%) and calcite (35%). Other minerals were present in minor proportions, such as phyllosilicates type chlorite and micas (2%), talc (7%) and quartz (6%). An organic matter content of 29% was detected in starting sludge. In the XRD pattern of the calcined samples all kaolinite peaks completely disappeared. Thus the X-ray diffraction analysis indicates that only residual kaolin persist after annealing at 700°C for 2 h; pure metakaolin is obtained from kaolin during the calcination process at 700 and 800°C. The treatment of the dry sludge at 700°C/2 h (S1) showed the calcium oxide formation that has been hydrated ($Ca(OH)_2$), as a consequence of its stay in the atmosphere showing in the diffraction pattern their characteristic spaced two to 4.92 and 2.62 Å. At 700°C/5 h (S2) the treatment continues favouring the decarbonation process and the calcium hydroxide formation that had begun with 2 h treatment. This calcite destruction process was accompanied by the calcium hydroxide formation process which was observed by the increase in the intensity of their reflections. In addition the destruction process of the phyllosilicates was observed. This process finished at 750°C/5 h (S4). Finally, in the calcination to 800°C/2 h (S5) the total destruction of chlorite and calcite is produced since they disappear from the reflections to 14

Table 1 OPC characteristics

Chemical composition/%	
Total CaO	62.44
SiO_2	19.70
Al_2O_3	5.62
Fe_2O_3	3.08
MgO	1.21
SO_3	3.29
K_2O	0.89
Na_2O	0.27
TiO_2	0.24
P_2O_5	0.11
Free CaO	0.52
Na_2O eq=Na_2O+0.658% K_2O	0.86
Loss of ignition (LOI)	2.72
Mineralogical composition/%	
C_3S	67.40
C_2S	8.60
C_3A	9.28
C_4AF	9.97
Other properties	
Compressive strength	
day	R_c/MPa
1	29.45
7	48.54
28	58.14
BET specific surface/m^2 g^{-1}	0.60
Initial setting time/min	127.5
Volume stability/mm	0.50
Density/g cm^{-3}	3.12

Table 2 Calcining conditions

Sample	Temperature/°C	Time/h
S1	700	2
S2	700	5
S3	750	2
S4	750	5
S5	800	2

Table 3 Paper sludge chemical composition

Contents	Starting sludge/%	S1/%	S2/%	S3/%	S4/%	S5/%
SiO_2	18.01	30.20	33.40	34.90	34.70	35.70
Al_2O_3	10.14	18.00	19.50	20.20	20.20	20.50
Fe_2O_3	0.55	0.70	0.80	0.80	0.80	0.80
CaO	19.82	31.40	32.20	32.70	33.20	33.50
MgO	2.58	3.70	4.30	4.40	4.30	4.60
SO_3	0.33	0.27	0.20	0.31	0.50	0.31
K_2O	0.21	0.32	0.29	0.32	0.32	0.33
Na_2O	0.25	0.21	0.16	0.19	0.19	0.20
TiO_2	0.26	0.35	0.39	0.38	0.39	0.40
P_2O_5	0.10	0.19	0.14	0.15	0.16	0.16
Cl^-	0.04	0.02	0.02	0.02	0.02	0.02
LOI	47.62	14.53	8.49	5.47	5.13	3.42
Specific surface/$m^2\ g^{-1}$	–	9.60	8.70	7.80	7.10	6.00
Reactive SiO_2	–	25.20	–	–	–	–

Table 4 Composition of the dry sludge (mass%)

	Organic matter	Phyllosilicates	Kaolinite	Quartz	Talc	Calcite
Dry sludge	28	2	21	6	7	35

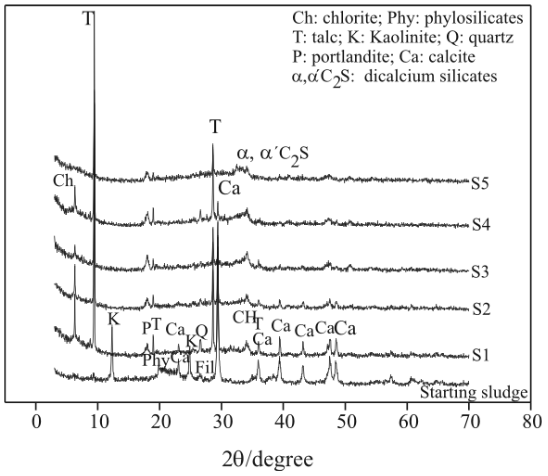

Fig. 1 XRD of starting and calcined paper sludge

and 3.03 Å, respectively. Bicalcic silicates α and α′ began to form (2.75, 2.71, 2.68 and 2.62 Å). The talc along with the new production silicates was the only crystalline phase that was observed at this temperature.

Mixtures

The mixture preparation (OPC+addition) was carried out in a high-speed powder mixer so as to homogenize the mixture. All mixtures were made up by mass to the following compositions (Table 5).

Mortars were prepared with these mixtures, where the sand/binder ratio is 3/1 and the water/binder ratio is 0.5.

To study heat and heating evolution, S1 was used according to the pozzolanic activity data.

Methods

Pozzolanic activity

In order to test the pozzolanic activity of the calcined sludges, an accelerated method was used. It was based on monitoring the reaction between the material and a saturated lime solution at 40 ±1°C for 2 h, 1, 7, 28 and 90 days. At the end of every period, the concentration of CaO in the solution is assessed. The lime

Table 5 Mixtures compositions

Dosage in kg (UNE 80 118)	
OPC/Binder	0.350
Sand	1.050
Water	0.175
Total mass	1.575
Mixtures	
Reference OPC mortar	100% OPC
Binder	90% OPC/10% S1 80% OPC/20% S1

fixed in mM L^{-1} was calculated from the difference between the concentration in the reference saturated lime solution (17.68 mM L^{-1}) and the solution in contact with the sample.

Hydration heat test

The hydration heat was calculated following the method explained in the European standard [19] on the Langavant Calorimeter. This semi-adiabatic method consisted of quantifying the heat produced in the hydration of cement, using a Dewar flask as a calorimeter. In order to carry this out, a mortar made with the cement of this test is manufactured. This was placed in a sealed bottle which in turn is introduced in the Dewar flask. The temperature in the mortar during the hydration was compared to the temperature of a thermically inert mortar (previously mixed, at least 3 months previous to the test, according to the standard) and contained in another flask used as a reference.

Results and discussion

Pozzolanic activity

The results of the pozzolanic activity appear on Fig. 2. All calcined products showed high pozzolanic activity although a slight decrease of the fixed lime with increasing activation conditions was observed, mainly in the S5 (800°C and 2 h). This fact would be related, on one hand, to a loss of specific surface from metakaolinite at high temperature and change their system of reaction [18] and the second hand, to a possible interference of CaO coming from decarbonation process of calcite present in raw paper sludge. This fact was in agreement with the results obtained by Pèra *et al.* [8], who observed a pozzolanic activity decreasing in the product calcined at 800°C, using another pozzolanic test.

In view of the results obtained and taking into account economical and energetic factors, the best condition of activation of kaolinite was at 700°C for 2 h (S1). Consequently, these were the chosen conditions for its subsequent study in the hydration heat.

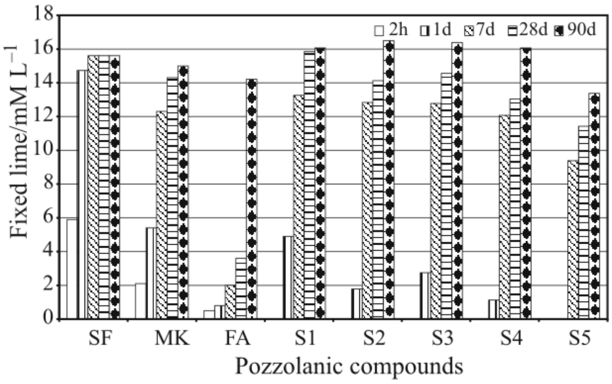

Fig. 2 Pozzolanic activity: fixed lime *vs.* time

Table 6 Pozzolanic compounds composition

Contents	MK	SF	FA
SiO_2	51.60	92.22	42.44
Al_2O_3	41.30	0.10	28.00
Fe_2O_3	4.64	0.62	17.38
CaO	0.09	0.54	7.40
MgO	0.16	0.27	1.38
K_2O	0.62	0.60	1.55
Na_2O	0.01	0.01	0.21
TiO_2	0.83	–	–
SO_3	–	0.18	0.05
LOI	0.60	5.50	1.23
Specific surface/m^2 g^{-1}	15.00	22.20	1.40

Comparing the pozzolanic activity of S1 to other pozzolanic materials used normally in the manufacture of commercial OPC, such as SF, MK and FA, (Table 6), it could be seen that the S1 showed a pozzolanic activity similar to the commercial metakaolin (MK), though minor than the SF activity and higher than FA.

Influence of calcined product (S1) on hydration heat of blended mortars

Heating

The heating is defined as the difference between the evaluated mortar temperature and the inert reference mortar (mixed at least 3 months before the test). This value of heating was used to calculate the hydration heat developed by the tested sample (Eq. (1)).

$$q=\frac{C}{m_c}\theta+\frac{1}{m_c}\int_0^t a\theta \mathrm{d}t \qquad (1)$$

where q=hydration heat (amount of heat given off in J g^{-1} of binder), m_c=mass of cement in the testing specimen in g, t=length of hydration in h, C= total thermal capacity of the calorimeter and testing mortar (J °C), a=global thermic transmission coefficient (J h^{-1} $°C^{-1}$), θ=heating of the testing mortar at the instant t in °C.

Figure 3 shows the evolution of heating for the cement mortars analyzed with 0, 10 and 20% of S1. Results obtained showed how the maximum heating occurred at around 13 to 18 h and depend on the addition percentage. So, the replacement of 10 (15.5 h) and 20% (13.3 h) of S1 by OPC accelerated this maximum with respect to the 100% PC mortar (17.8 h). This behaviour was similar to the effect that produces

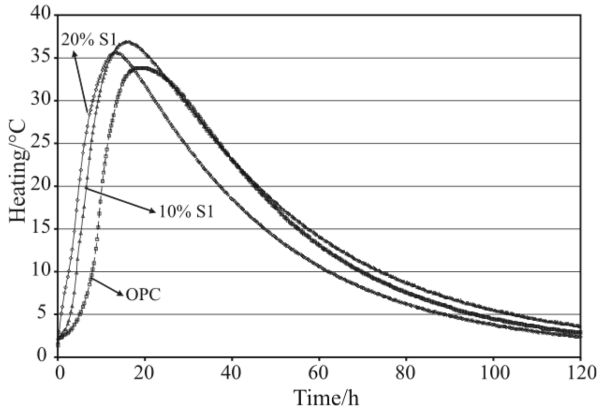

Fig. 3 Heating *vs.* time

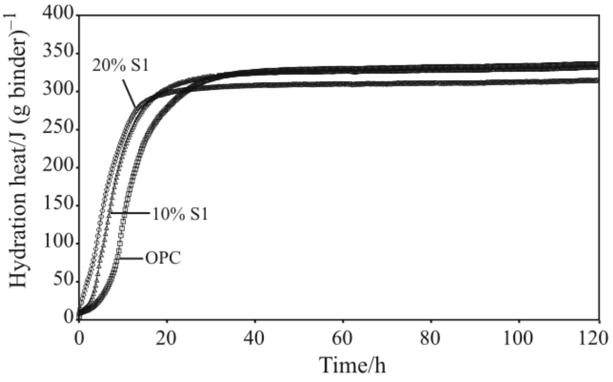

Fig. 4 Additions effect on the hydration heat

other pozzolanic materials as reported Frías *et al.* [14] in blended mortars with different percentages of SF and pure MK.

Also, it is important to note that the S1 blended mortars showed a temperature rise with respect to the 100% OPC mortar. The real maximum temperature reached inside mortar specimen (according to the heating definition, values obtained from Fig. 3 plus 20°C of the inert mortar), for a 10% of addition was 56.9°C, which means an increase of 3.1°C. For a 20% addition, the maximum temperature reached was of 55.7°C, an increase of 1.9°C regarding the reference mortar (53.8°C), and an increase that is less important than for the 10% of addition.

These results indicated the existence of various phenomena to be considered regarding the behaviour of calcined paper sludge in cementing matrixes: 1) Dilution effect (filler) which provokes an acceleration of OPC hydration in the first h of reaction, mainly the alite and aluminates phases [20] and, 2) Pozzolanic effect of S1, that in the first 20 h of reaction, was predominant over dilution effect, increasing the temperature inside mortar. In the case of 20% S1-blended mortar, once reached its maximum value (13.3 h), the heating developed started to decrease; getting lower values than that of the reference mortar, due to that in this case, the dilution effect was the predominant. A typical example where the influence of the pozzolanic reaction was compensated for by the dilution effect can clearly be seen in 10% S1 blended mortar above 24–25 h of reaction.

Hydration heat

Figure 4 shows the evolution of the hydration heat (J g^{-1} of binder) for blended mortars regarding the 100% OPC. Blended mortars with pozzolanic additions usually increase the hydration heat with respect to the reference mortar. During the first 25–35 h, reactions due to the OPC and active pozzolan with calcium hydroxide were strongly exothermic, which makes the ascending slope of the curves very steep; subsequently, the hydration heat began to stabilize and the heat released is of little significant.

In the case of the addition of 10% S1, as product of high activity, it can be seen that the hydration heat increased until about 35 h, the moment when it matches with the hydration heat of the OPC mortar. Taking into account the hydration heat values obtained, it can be seen that the pozzolanic effect predominated in the addition 10% S1, since there were not any values under OPC mortar.

A hydration heat increase regarding OPC mortar until the first 25 h in the curve of 20% S1 can be also detected. From this age onwards, the hydration heat decreased regarding the OPC (this decrease means 6.5%), a smaller value than the replaced cement percentage, since it can be concluded that there was a slight predominance of the replacement effect with regard to the pozzolanic effect.

Figure 5 shows the development of the hydration heat for blended mortars regarding the 100% of OPC. The zero point means the mortar hydration heat at 100% PC. This graphic represents the first 40 h of testing, where an important hydration heat increased usually takes place, since the highest hydration heat values was produced.

In the case of the 10% S1, it could be seen a positive increase until 30 hours, when its effect was the same as the reference mortar. This phenomenon showed that the pozzolanic effect of S1 was predominant, as it was said in the previous section.

For the case of the 20% addition of S1, a similar effect to the mortar with 10% addition could be seen, but in this case it was after 25 hours, when an inflection point between both effects was detected, being the replacement effect (negative values) the predominant one at longer ages.

The appearance of a maximum in relative hydration heat evolution at about 8 h of testing time (Fig. 5) showed a similar behaviour to the SF according

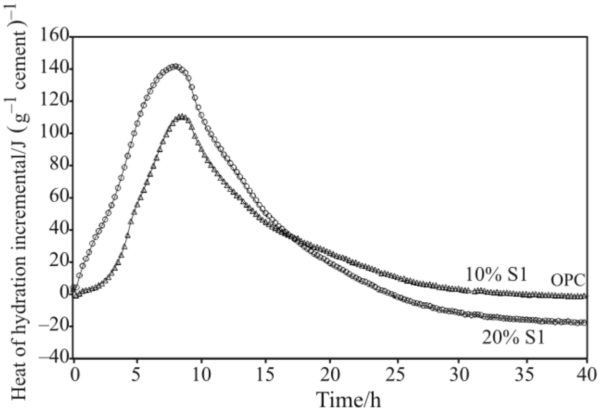

Fig. 5 Heat of hydration incremental *vs.* time

to data published in a previous paper [14]. From those results, in which SF only appeared a maximum (about 8 h), whereas two maxima were identified for MK (8 and 20 h), it can be deduced that this different behaviour was related to the chemical compositions between SF (SiO_2) and MK (SiO_2 and Al_2O_3) (Table 6).

According to data from chemical analysis (Table 2), the calcined paper sludge was formed by SiO_2, Al_2O_3 and CaO, principally. During pozzolanic reaction, gel CSH was formed firstly and being the predominant phase, followed by aluminates ones (tetracalcium aluminate hydrates, hydrotalcites, traces of stratlingite) [21]. However, the evolution of the hydration heat of mortars made with calcined paper sludge (S1) showed a main maximum localised between 8.1 (20% of S1) and 8.5 (10% S1). This fact will confirm that calcined product S1 presents a closer behaviour to that showed by SF.

However, as mentioned previously, S1 also presented aluminium oxide in its chemical composition, therefore the hydration heat evolution should be closer to MK than SF. A priori and taking into account the appearance order of hydrated phases from pozzolanic reaction mentioned above, it is possible to think that SiO_2 would be the responsible of the main maximum in both cases. A tenuous maximum can also be seen faintly in both curves, being the tenuous maximum for the 20% curve a little clearer than for the 10% curve, which could correspond to the presence of reactive alumina in S1. These findings are in agreement with the data published by Lagier and Kurtis [22] which reported that the MK appeared to have a catalysing effect on cement hydration, leading to an acceleration in the reaction rates, an increase in cumulative heat evolved during early hydration, and apparently an increased intensity in heat evolved during certain periods of early hydration. Besides, the OPC used had a high content of Na_2O equivalent (defined as % Na_2O+0.658% K_2O), and when alkali content is increased, the C_3A hydration seems to be suppressed [22].

Conclusions

From the results of the current work it can be concluded that:

- Under any calcination conditions products with pozzolanic activity was obtained. This activity decreased with the temperature rise and the stay time in the furnace. The product with the best activity was S1, with the recommendation of calcining at 700°C during 2 h to carry out the paper sludge activation, for the tested conditions in the present work.
- Regarding the heating, the mortars with 10 and 20% S1 reached a higher heating than the reference mortar as a consequence of the double effect: dilution (cement hydration acceleration) and pozzolanic (hydrated phases formed).
- Both additions suffered a hydration heat increase during the first 20 h regarding the 100% Portland cement.

Taking into account what has been previously exposed, the importance of the evaluation and the study of the influence of pozzolanic activity of the calcined sludge on the development of the heating as well as hydration heat can be clearly seen. Those parameters may play a conclusive part when recycling this kind of industrial by-product, and also which were the best calcination conditions regarding the final application of this blended cement matrix.

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