THE COMBINED EFFECT OF ACTIVATED PAPER SLUDGE AND FLY ASH ON THE TERNARY CEMENT PROPERTIES

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Abstract

This paper presents the main scientific and technical aspects of a pozzolans blend (activated paper sludge (APS) and fly ash (FA)) and its influence on the ternary cement behaviour. Due to the high pozzolanic activity of binary addition, the blended cements (6 and 21%) shows a different behaviour with respect to the control one. The normal consistency water content (up to 10%) and the initial setting decrease in comparison with the control paste. Finally, the compressive strength slightly decreased in the blended cements elaborated with 21% of the pozzolan blend, although the decrease in their strength is lower than the total percentage of cement that is replaced. At 90 days, a recovery of mechanical resistance is observed in the ternary cements as a consequence of the activity developed by the fly ash.

1 Introduction

In the last decades, an increasing preoccupation is arising by the impact generated on the environment, as well as the consequences on the climatic change. Such a concern is promoting that governments and productive sectors sign agreements to optimize the industrial processes to manage the elevated volumes of by-products and wastes generated in the different industrial sectors, which obeys, in great part, to the increase in the quality of life of the present society. The environmental policies, at world-wide level, are more and more strict, prioritizing the re-use of by-products and wastes over the spill. In this context, one of the biggest challenges is the search of strategies that promote the industrial rotation of high volumes of wastes and by-products in the productive cycles. The investigation of these strategies demands exhaustive scientific-technical knowledge of the different trends and the object to provide an added value to the potential applications.

The cement industry, by its own characteristics, is one of the main sectors that contribute to the increase of greenhouse effect gases discharge (CH_4, N_2O, F_6S, CFCs and CO_2). With the approval of the Kyoto Protocol by the European Union (2002/358/CE), the member states agreed to diminish the emissions of greenhouse effect gases (GEG) in the UE in 8 %, which is the equivalent to reduce the CO_2 emissions in 340 Mt. The present situation in Spain, as in the rest of the member states, is far from this objective, since the manufacture of 1 ton of clinker releases approximately 890 kg of CO_2 [1], reason why it forces to buy between 70 and 120 Mt of CO_2 (with an estimation between 20-30 €/t), equivalent to a cost of 0.2 to 0.6 of 3 the gross domestic product (GDP).

The cement industry used 5.7 million tons during the year 2007 of different by-products and industrial wastes as active additions: high furnace slag, ashes, silica fume, industrial pozzolans, etc. These additions improve some of the technical properties of the cements, at the time that produce a significant reduction of environmental impacts associated to emissions and spills. It is expected that the use of additions will increase every year by the direct contribution to the sustainable development [2].

During the last decades, a change in the investigations related to the cement matrices is being observed. In general terms, it can be affirmed that during the XX century most of the scientific-technical studies were focused on binary cements (with an only addition). However, during the last decade, the investigations are being oriented towards the innovation of cements elaborated with more than one addition (II/M, IV and V types) [3]. Thus, this is demonstrated by the elevated number of scientific contributions published in the last years combining mainly three standard products: fly ash and slag, fly ash and silica fume and silica fume and slag [6-19]. The results obtained in cement pastes, mortars and concretes elaborated with ternary cement present a better behaviour than with binary cements (CEM type II).

In addition to the traditionally used pozzolans within the international regulations, investigations concerning the search of new materials that could be inserted in the regulations in a near future also exist. Therefore, it is necessary to carry out pre-normative studies in order to establish the technical bases of use of these new by-products and industrial wastes as supplementary cementitious materials [4-7].

Searching for new sources to obtain metakaolin, it was found the possibility of producing this cement material by thermal activation of the sludge generated in the process of paper manufacture from recycled paper as raw material. In the process of paste and paper manufacture an important volume of non-dangerous solid wastes are produced (1.303.069 tns during 2006 in Spain)

Once reached the objectives proposed in previous research works on the scientific and technical viability of activated paper sludge in type-II cements manufacture, under the category of thermally activated materials (Q), and after the diffusion of the results and consultation to the cement sector, the opportunity to approach a new challenge of investigation was detected. This may generate a great innovatory advance pioneer at world-wide level for the cement sector, consisting of thermal development of ternary cements (types II-M, IV and V) with activated paper sludge. In this type of cements, the activated paper sludge is mixed with other traditionally used pozzolanic addition (fly ash).

2 Materials

The thermally activated paper sludge (APS) used in the present paper was obtained at 700ºC for 2 hours, according to the suitable conditions from the pozzolanic, energetic and environmental points of view [8,9]. The raw paper sludge was provided by the Spanish paper manufacturer Holmen Paper Madrid, S.L, which uses 100% recycled paper as the raw material.

A Spanish fly ash (FA) as pozzolan was used traditionally for the Portland cement manufacture. Previously, each one of the additions was ground with a mortar and pestle and then sieved with a nominal aperture of 90 µm. Latterly, APS/FA mixes were elaborated with proportions of 50/50 by weight [10].

A commercial Portland cement (CEM I 52.5N) was used, according to the existing standard [3].

Ternary cement matrixes (pastes and mortars) were prepared by partially replacing CEM I cement by 0, 6 and 21% of a pozzolan blend (APS/FA).The preparation and curing were carried out according to standardised conditions. For the case of cement mortars a w/b ratio of 1:2 and a binder/sand ratio of 1:3 were used.

3 Results and Conclusions

3.1 *Chemical and mineralogical composition*

Table 1 shows the chemical composition by XRF of materials selected in the present work. The APS mainly contained silica and calcium oxide, silica and alumina for the FA (low CaO content), and finally, silica and calcium oxide for the OPC. The high loss on ignition (LOI) of the APS, at around 27%, was due to the decarbonation process of calcite.

(%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	LOI*
APS	13.90	8.30	0.50	47.12	1.60	0.00	0.30	0.23	0.25	0.20	26.66
FA	55.70	24.00	4.80	2.20	0.90	0.89	2.18	0.46	0.69	0.28	7.60
OPC	20.02	5.71	3.21	58.90	1.73	4.27	1.56	0.77	0.15	0.21	2.58
6%	21.47	6.78	3.16	55.91	1.77	3.66	1.47	0.74	0.17	0.24	3.63
21%	23.99	9.29	3.06	49.28	1.86	3.04	1.49	0.69	0.21	0.24	5.64

*Loss on ignition at 975ºC for 1 hr

Table 1. Chemical composition by XRF of raw materials and blend cements

The semi-quantitative mineralogical composition of the starting APS and FA by XRD is summarized in Table 2. These analyses confirm that the main mineralogical phases in APS were calcite and metakaolinite (from activated kaolinite) and other phyllosilicates such as talc, in minor content. For the FA, the mineral phases consisted primarily of quartz, mullite and hematite.

(%)	Calcite	Metakaolin	Talc	Quartz	Mullite	Hematite
APS	88	7	5	-	-	-
FA	-	-	-	53	34	13

Table 2. Mineralogical composition by XRD

3.2 *Pozzolanic properties*

The fundamental property for a material or an industrial waste product to be used as an active addition in the manufacture of commercial blended cements is its pozzolanic nature. A rapid method of supplying information in the short term is through the use of an accelerated chemical method in the pozzolan/lime system [11]. Figure 1 shows the evolution of the fixed lime, in percentages, with the reaction time up to 90 days of reaction. From the results obtained from the evolution of fixed lime (%) with reaction time, it is confirmed that the mixture of pozzolans (APS / FA) has a high pozzolanic activity, as fixed amounts of lime at short and medium reaction terms.

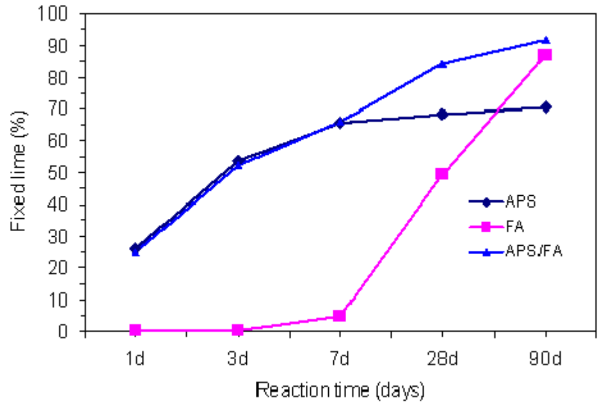

Figure 1. Evolution of fixed lime versus reaction time

Thus, lime fixed percentages of 52, 84 and 92% were determined at 3, 28 and 90 days of pozzolanic reaction. This pozzolanic behaviour is similar to the APS during the first 7 days of reaction.

3.3 *Reaction Kinetics*

From a scientific standpoint, the identification, development and stability of hydrated phases with the reaction time has a direct impact on the subsequent performance of future cement matrices. Different techniques (TG/DTA, F-TIR, XRD, SEM/EDX) were used to study the hydration reaction, so as to semi-quantify of crystalline mineralogical phases up to 90 days of reaction. Table 3 illustrates the semi-quantitative evolution of mineral phases up to 90 days of reaction of cement pastes elaborated with 6 and 21% of replacement. The crystalline reaction products produced during the hydration reaction detected by XRD are portlandite ($Ca(OH)_2$), ettringite (C_4ASH_{32}), α-tetracalcium aluminate 13-hydrate (C_4AH_{13}) and in the spaces between 7.60Å and 7.56Å and 3.85Å and 3.80Å appear diffraction peaks from the layers (0001) and (0002) for the mono carboaluminate hydrate (C_4AcH_{12}) and the (003) and (006) spaces from the LDH compounds.

	APS/FA	0d	1d	7d	28d	90d
C_3S	6%	35	25	17	10	8
	21%	26	18	14	6	3
C_2S	6%	20	12	5	3	2
	21%	14	10	4	1	1
C_3A	6%	10	7	3	3	2
	21%	6	4	2	-	-
C_4AF	6%	6	2	-	-	-
	21%	2	2	1	-	-
Calcite	6%	29	23	14	14	14
	21%	51	33	24	21	21
$Ca(OH)_2$	6%	-	26	42	42	42
	21%	-	26	28	39	42
Ettringite	6%	-	5	12	12	12
	21%	-	7	9	9	9
C_4AH_{13}	6%	-	-	3	5	5
	21%	-	-	3	4	4
C_4AcH_{12}/LDH	6%	-	-	4	11	15
	21%	-	-	16	20	20

Table 3. Semi-quantitative analysis of mineral phases by XRD

The according to the mineralogical evolution, this depends of the replacement grade of blended cements. The ettringite appears at one day of reaction, increasing its content with the hydration time; the C_4AH_{13} was detected at 7 days, staying as traces up to 90 days of reaction, and finally, the content of the C_4AcH_{12}/LDH mixture increased from 7 days to the testing end. In both blended cements, these compounds were the dominant phases (Figure 2) after portlandite and CSH gels. The latter ones were identified by DTA and SEM/EDX, with a Ca/Si ratio of 1.85 (12). Studies carried out by mercury porosimetry confirm that these phases produce a pore size refinement with the increasing pozzolan content and possible beneficial effect on the durability (13).

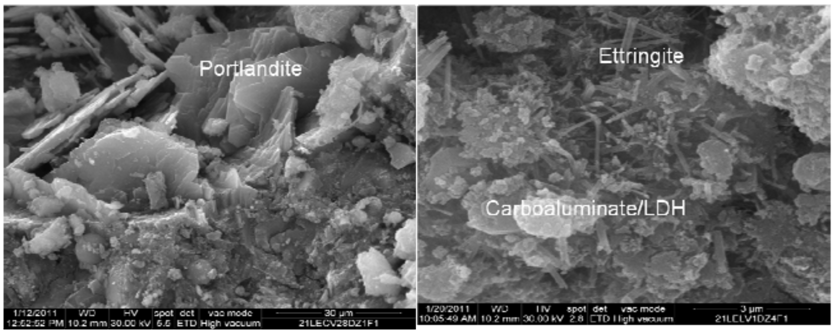

Figure 2. Morphological aspects of hydrated phases

3.4 *Rheological behaviour of cement pastes.*

The influence of this kind of pozzolan blend on the rheological behaviour of new cement pastes was assessed by the standardized tests of normal water consistency (NWC) and initial setting time (IST) (3). Figure 2 summarized the values obtained for the cement pastes with partial additions of 0%, 6% and 21% of ASP and FA mix.

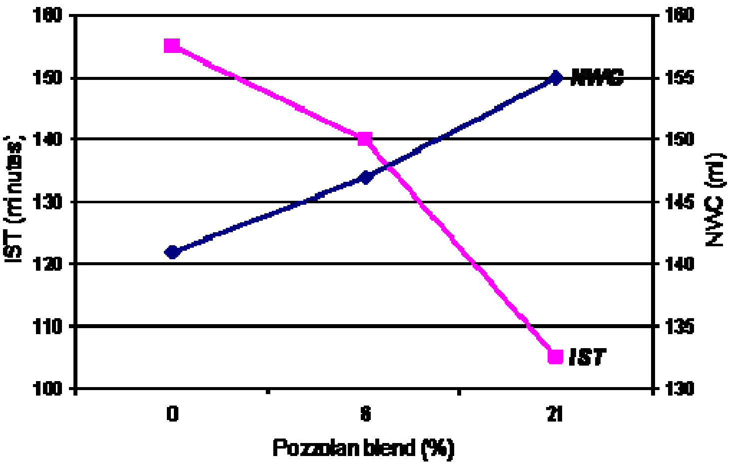

Figure 2. Evolution of NWC and IST versus addition percentages

The results show that the ternary cement pastes elaborated with a mixture of APS and FA (1:1 in weight) requires more water content than to the control paste. Water percentages of 4.2% and 9.9% were obtained for additions of 6 and 21% respectively. Likewise, the joint presence of APS and FA accelerates the initial setting time, passing from 155 minutes in the control paste to 105 minutes in the 21% blended cements.

3.5 Mechanical behaviour of cement mortars.

It is evident from Figure 3 that the incorporation of this pozzolan blend decreased the compressive strength values with respect to the control mortar during the first 28 days of hydration, due to the dilution effect of pozzolans; however, the pozzolanic effect of both pozzolans above 28 days of reaction compensates this strength loss, reaching positive values in cements elaborated with 6% of addition (+2.4%) and losses about 9.2% with additions of 21% of replacement at 90 days of curing, when theses values are compared with reference mortar values.

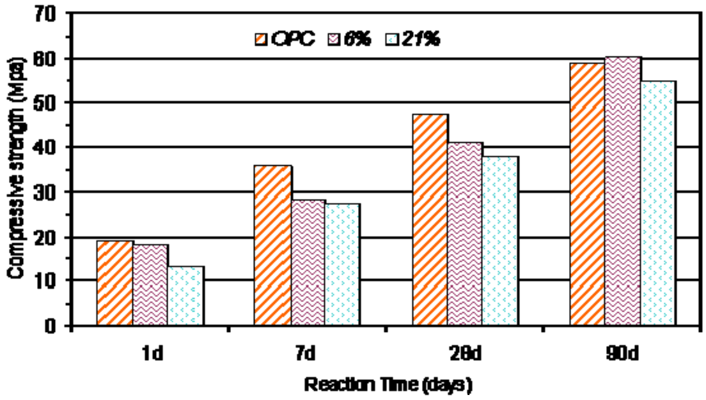

Figure 3. Evolution of compressive strength with the hydration time

4. Conclusions

The main conclusions of this research work can be drawn as follows:

- The mixture of activated paper sludge and fly ash is compatible for the manufacture of future ternary cement.
- Chemically, both pozzolans show a silico-aluminium nature.
- A high pozzolanic activity is reached when ASP and FA are mixed in 1:1 ratios.
- C_4AH_{13}, C_4AcH_{12}/LDH and CSH gels were identified as main hydrated phases in ternary cements, which will have a positive effect on the improvement of the durability of blended cement matrixes.
- The APS+FA blend accelerates the initial setting time of blended cement paste and this one requires additional water in order to get the same normal water consistency that the reference paste.
- The addition of APS and FA up to 21% has a direct influence on the mechanical strength evolution. At 90 days of curing, the strengths obtained are similar or higher than the control mortar in function of the pozzolan content.

From results mentioned above, it is important to note that the combined utilisation of both pozzolans favours the manufacture of more eco-efficient commercial cements.

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References

[1] Horton R. *Factor ten emission reductions: the key to sustainable development and economic prosperity for the cement and concrete industry* in "3rd CANMET/ACI Sustainable Development of Cement and Concrete", San Francisco, USA, (2001).

[2] Sanjuán M.A. Los cementos de adición en España del año 2000 al 2005. *Cemento y Hormigón*, 909, pp. 4-55 (2007).

[3] European Standard EN 197-1. *Cement-Part 1: Composition, specifications and conformity criteria for common cements* (2011).

[4] Frías M., Sánchez de Rojas M.I., Santamaría J., Rodríguez C. Recycling of silicomanganese slag as a pozzolanic material in Portland cements: Basic and engineering properties. *Cement and Concrete Research*, **36** (3), pp. 487-491 (2006).

[5] Sánchez de Rojas M.I., Marín F., Rivera J., Frías M. Morphology and properties in blended cements with ceramics wastes as a pozzolanic material. *Journal of the American Ceramic Society*, **89** (12), pp. 3701-3705 (2006).

[6] Frías M., Villar-Cociña E. Influence of calcining temperature on the activation of sugar-cane bagasse: kinetics parameters. *Advances in Cement Research*, **19** (3), pp. 109-115(2007).

[7] Frías M., Villar-Cociña E., Valencia-Morales E. Characterisation of sugar cane straw waste as a pozzolanic material for construction: Calcining temperature and kinetics parameters. *Waste Management*, **27** (4), pp. 533-538 (2007).

[8] Frías, M., Rodríguez O., Nebreda B., García R., Villar E. Influence of activation temperature of kaolinite based clay wastes on pozzolanic activity and kinetic parameters. *Advances in Cement Research*, **22**(3), pp. 135-142 (2010).

[9] García R., Vigil R., Rodríguez O., Frías M., Study of hydrated phases present in calcined paper sludge/saturated CaO dissolution system cured at 40ºC and 28 days of reaction. *Material Science Engineering A*, **527** (16-17), pp. 3936-3941(2010).

[10]Frías M., Vegas I., Vigil R., García R. Recycling of waste paper sludge in cements: *Characterization and behaviour of new eco-efficient matrices*, in "Integrated Waste Management", Ed. S. Kumar, Volume II, Croatia, pp. 301-318 (2011).

[11]Frías M., Vigil R., Rodriguez O., Goñi S., Vegas I. Evolution of mineralogical phases produced during the pozzolanic reaction of different MK by products: Influence of the activation process. *Applied Clay Science*, **56**, pp. 48-52 (2012).

[12]Goñi S., Frías M., Vegas I., García R., Vigil R. Effect of ternary cements containing thermally activated paper sludge and fly ash on the texture of CSH gel. *Construction and Building Materials*, **30**, pp. 381-388 (2012).

[13]Vegas I., Urreta J., Frías M., García R. Freeze-thaw resistance of blended cements containing calcite paper sludge. *Construction and Building Materials*, **23**(8), 2862-2868 (2009).