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THERMAL ACTIVATION OF A PAPER WASTE AS POZZOLAN FOR THE MANUFACTURE OF CEMENTS

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Abstract

The present work describes the study of a paper waste generated by the paper industry, activated at different temperatures. The results obtained show that these wastes once activated have pozzolanic properties and confirm the scientific and technical viability of the use of this kind of wastes as active additions for the manufacture of Portland cements, according to the current standard.

Keywords: paper sludge, kaolinite, activation, pozzolans.

INTRODUCTION

The amount of domestic and industrial waste generated worldwide is currently increasing alarmingly. In most cases the disposal method employed is land-filling, consuming large areas. Moreover, there is a growing demand for building materials due to the increasing world population. The utilization of industrial waste in the construction sector not only solves waste problems, but also provides new building materials.

The paper industry generates large amounts of waste mainly sludges composed of organic matter and clay minerals (mostly kaolinite). Due to the presence of heavy metals in trace concentrations, these wastes are classified as clean wastes.

Pèra and Amrouz [1] were pioneers in demonstrate that the paper sludge calcined at temperatures between 700 and 800ºC can be incorporated as addition to concrete. At high temperature the kaolinite present in the sludge is transformed into metakaolinite (MK), an amorphous material with composition $Al_2O_3.SiO_2$, which has high pozzolanic activity. Early studies in Spain (M. Frias et al. [2]) showed the influence of the activation conditions.

This paper evaluates the physical, chemical and mineralogical characteristics of a paper sludge activated at temperatures in the range 500-800°C as a function of the hydration time.

EXPERIMENTAL

A. Analytical techniques

Different techniques were used for the characterization of the activated paper sludges. Chemical characterization was carried out by X-ray fluorescence, using a Philips PW 780 equipment. Mineralogical composition was studied by X-ray diffraction (XRD) using the random powder method for the bulk sample. The X-ray diffractometer is a SIEMENS D-500 with a Cu anode.

B. Pozzolanic activity

The pozzolanic activity was studied using an accelerated method. The test consists in putting the activated paper sludge (APS) (1 g) in a lime-saturated solution (75 ml) at 40ºC for 1, 7, 28, 90 and 360 days. The CaO concentration in the solution was analyzed at the end of each period. The combined CaO (mMol/L) is calculated by the difference between the concentration of a standard lime-saturated solution (17.68 mMol/l) and the CaO content in the solution in contact with the APS sample.

C. Materials

The industrial waste used in this research is a paper sludge coming from de-inking process, activated at different conditions. The activation conditions are shown in Table 1.

Table 1. Activation conditions of paper sludge.

Sample	Temperature (ºC)	Residence in furnace (h)
APS1	500	
APS2	550	
APS3	600	
APS4	650	2
APS5	700	
APS6	750	
APS7	800	

All activated paper sludges are mainly formed by silica, alumina and calcium oxide [3-4]. Oxides that mostly contribute to the pozzolanic reactivity are silica and alumina, so it can be expected that these materials show pozzolanic activity, because the sum of these two oxides is above 30% in all cases.

Table 2 shows the presence/absence of the mineral phases identified by XRD of activated paper sludges at different temperatures. Raw paper sludge (RPS) is composed by talc, kaolinite and calcite. Kaolinite is only present in activated paper sludge at low temperature (500ºC). With the increase of the activation temperature kaolinite disappears, and when higher activation temperature is reached (800ºC), a new mineral phase is detected (bredigite), and it can be observed the disappearance of the rest of mineralogical compounds, including calcite that suffers a decarbonation process from 700ºC.

Cement pastes were elaborated with ordinary Portland cement (OPC) CEM I- 42,5 R according to current standard [5].

RESULTS AND DISCUSSION

A. Pozzolanic activity

The results obtained for the combination of lime with the activated sludge are shown in Figure 1, where fixed lime at 1, 7, 28, 90 and 360 days of reaction is represented for each activated paper sludge.

All samples show a high pozzolanic activity in terms of the fixed lime results. However, in first 24 hours it can be clearly observed differences in reaction rates, following the order of decreasing activity:

APS3>APS2>APS1>APS4>APS5>APS6>APS7.

After 7 days of reaction the pozzolanic activities are similar for all activated paper sludges.

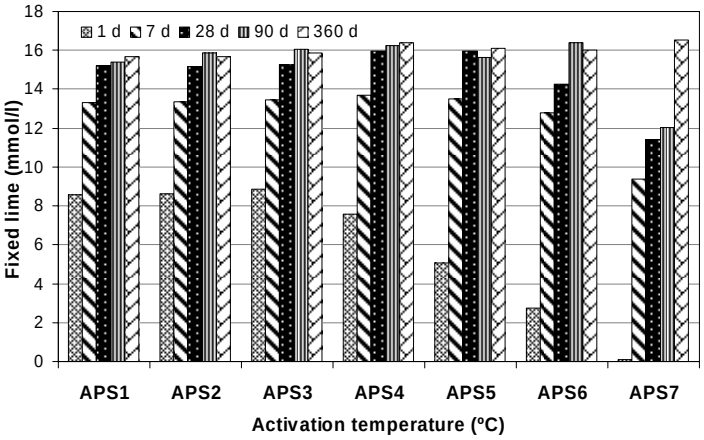

Figure 1. Pozzolanic activity of activated paper sludges.

Although the paper sludge activated at 600ºC shows higher pozzolanic activity at early ages, previous works demonstrated that cellulose is still present within the temperature interval 500-600ºC. Therefore, the paper sludge activated at 650ºC shows better properties [6-9]. Consequently, the following tests in cement pastes will be performed with APS4.

Table 2. Mineralogical composition of activated paper sludges.

	Talc	Kaolinite	Calcite	Quartz	Other phyllosilicates	Bredigite
RPS	x	x	x	tr	x	-
APS1	x	x	x	tr	x	-
APS2	x	-	x	tr	x	-
APS3	x	-	x	tr	x	-
APS4	x	-	x	tr	x	-
APS5	x	-	x	tr	x	-
APS6	x	-	x	tr	x	-
APS7	x	-	-	tr	-	x

B. Physical and chemical specifications of cement pastes elaborated with activated paper sludge

The current standard [5] establishes the physical and chemical specifications that have to fulfill cements for sale. Table 3 shows the results obtained for the requirements: loss on ignition (LOI), insoluble residue (IR), sulphate contain (as SO_3) and chloride (Cl^-) concentration, expressed in percentage per unit of mass of cement, for pastes elaborated with 10% and 20% of APS4. Table 4 shows the results of initial setting time (IST) and volume stability, described in standard UNE-EN 196-3:2005 [10], for the cement pastes containing APS4.

Table 3. Chemical requirements

	LOI	SO_3 (%)	IR (%)	Cl^-(%)
10% APS4	3,95	2,99	1,84	≤0,01
20% APS4	5,17	2,69	2,77	≤0,01
UNE-EN 197-1	≤5,0	≤3,5	≤5,0	≤0,1

The results indicate that cements elaborated with 10% and 20% of APS4 are within the range of chemical requirements under the current standard, except for the loss on ignition in cement made with 20% of APS4, that exceed the upper value, even though this would not be a problem because this value does not correspond to unburnt carbon as happens with fly ash.

The cement elaborated with 10% of APS4 also fulfill the physical requirements and with 20% of APS4 the value of initial setting time is lower than that required in the standard, although the decrease obtained is within the acceptable error of the measurement (± 15 min).

Table 4. Physical requirements

	Initial setting time (min)	Expansion (mm)
10% APS4	112	0
20% APS4	52	1
UNE-EN 196-3	≥60	≤10

C. Mechanical behaviour of pastes elaborated with APS4

The addition of 10 and 20% of paper sludge activated at 650 º C for 2 hours to cement mortars leads to lower values of compressive strength than those obtained for reference mortar (OPC). This decrease becomes smaller with increasing hydration time, reaching values close to the reference mortar. (Table 5).

Table 5. Compressive strength

R_c (MPa)	1 day	7 days	28 days	90 days
OPC	21,94	46,73	60,27	62,55
OPC+10% APS4	20,33	47,19	58,41	61,47
OPC+20% APS4	17,79	43,04	56,83	57,92

CONCLUSIONS

Based on the observations exposed above it can be concluded that:

- Activated paper sludges show a chemical composition based on silica, alumina and calcium oxide, with high loss on ignition due to decarbonation of calcite.
- The mineralogical composition is mainly based on calcite and talc, and minor contents of phyllosilicates and quartz.
- All activated paper sludges show high pozzolanic activity. After 90 days of reaction there are no differences in fixed lime for the APS.
- Cements elaborated with 10% and 20% of waste fulfill the chemical requirements (SO_3 and Cl^-) for the manufacture of cements.
- The cements with APS4 addition fulfill the physical requirements (initial setting time and expansion) according to the current standard, except the paste with 20% of APS that shows a lower value of setting time than the 60 minutes required.

As a general conclusion it can be indicated that activated paper sludge is suitable for addition to Portland cement, but currently are not covered by current standards.

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