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The influence of thermal activation of art paper sludge on the technical properties of blended Portland cements

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ABSTRACT

The influence of the thermal activation (600–750 °C) of a clayey waste (art paper sludge, APS) and the replacement rate of cement by this pozzolan on technical parameters such as normal consistency water, setting time, soundness and compressive strength were investigated. Physical properties of raw materials such as particle size distribution and BET surface areas were also reported. The results have demonstrated that substitution of Portland cement CEM I 42.5 by activated art paper sludge (AAPS) increases normal consistency water and decreases the setting times and compressive strength of the blended cements, with increasing replacement rate, temperature and/or time of activation. However, if APS is properly activated at around 600–650 °C for 2 h, it is feasible to substitute a 10% of cement without adverse effects on technical properties, due to the pozzolanic activity of metakaolinite and set regulator features of calcite, the two major mineral phases present in AAPS.

1. Introduction

One of the most important challenges of modern society is to improve resource efficiency. One aspect of the solution to this problem is the re-use of waste materials as partial replacements for higher embodied energy and commercial value materials. The cement industry has a strong and long established track record with the reuse of numerous types of by-products and wastes from other industries. Such materials have been employed in the cement manufacturing process either as alternative fuels for kiln operation, raw materials in the kiln feed or as partial replacements for final product cement as pozzolanic additions [1–7]. Which of the aforementioned reutilisation routes is most attractive for a given waste depends on its physico-chemical properties such as calorific value, chemical and morphological composition [8].

Art paper sludge (APS) is a residue generated by the de-inking of recycled paper. The sludge consists mainly of water, calcite ($CaCO_3$), kaolinite clay and cellulose fibres. According to European Waste Catalogue APS is considered as an inert waste (03 03 05). The clayey composition and the relatively low heat of combustion of the dried waste (around at 8–9 MJ/kg solids) suggest that, following thermal activation of the kaolinite clay content, exploitation as a pozzolanic addition could be a successful way for its recycling [9]. During thermal activation, the structure of kaolinite is disordered due to the loss of hydroxyl groups at temperatures exceeding 600 °C [10]. Furthermore, the partial substitution of cement by such waste materials contributes to a reduction in the high CO_2 emissions associated with the cement industry. The European commission [8] encourages the reusing and recycling of wastes, assessing to zero the CO_2 emission associated to any additional industrial process necessary for these aims.

Previous studies on the behaviour of thermally activated art paper sludge (AAPS) in chemical environments based on lime and cement binder matrices [11–15] have shown that the thermal activation of APS at temperatures ranging from 500 to 750 °C for periods of 2–5 h results in formation of a highly active pozzolanic material. Furthermore the activated material complies with the chemical requirements (SO_4^{2-} and Cl^- content) for Portland cements [9,16].

The chemical composition of AAPS is sensitive to the thermal treatment applied. Activation at relatively low temperatures (600–650 °C), results in a material mainly composed of metakaolinite and calcite [17], which are two mineral additions widely used in cement manufacturing due to its pozzolanic activity and filler properties, respectively [16]. However, when the activation temperature is greater than or equal to 700 °C, the composition of AAPS shows formation of free lime (CaO) from the de-carbonation of calcite. Upon contact with atmospheric humidity, the free lime will easily convert to portlandite ($Ca(OH)_2$). The interaction between metakaolinite, calcite, free lime, portlandite, water and the anhydrous cement phases present can modify in different

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manners, the common reactions involved in the hydration of Portland cements. For this reason, the present study is focused on the technical properties of common Portland cements, which can be modified by the replacement of 10% or 20% by AAPS. Consequently, this investigation will also attempt to identify the optimum thermal treatment for APS and percentage replacement rate of cement, in the context of standardised technical parameters [16].

2. Materials

The art paper sludge (APS) used for this research was obtained in a paper industry (Holmen Paper Madrid, SL), which processes art paper. Received sludge of approximately 50% by mass of water was dried at 105 °C for 24 h. The dry waste predominantly consisted of kaolinite (27% by mass), and calcite (42% by mass). Phyllosilicates such as chlorite, illite and talc (totaling around 7% by mass) were also detected. An organic matter content of 24% was determined by simultaneous TG/DTA [9]. Further details of material composition can be found in a previous work [17].

APS was activated in a laboratory furnace by different thermal treatments (Table 1) in order to obtain eight activated products (AAPS-*i*, where $i = 1–8$), with diverse chemical and physical properties. The chemical compositions of APS and the eight AAPS are summarised in Table 2.

CEM-I 42.5 *R* type Grey Portland Cement (GPC) was supplied by the Spanish company Cementos Alfa, S.A. Chemical and mineralogical composition of GPC determined according to [18] are summarised in Tables 2 and 3, respectively. Calcite content was determined from the weight loss associated with the peak of de-carbonation of TG–DTA curves (not shown) and free calcium oxide contents were measured by a standardised ethylenglycol method for cements [19].

In order to investigate the influence of each AAPS and the replacement rate on physical performance of GPC, 16 blended cements were prepared applying 2% of replacement (10% and 20% by weight) and the eight types of AAPS.

Table 1
Thermal treatments applied to APS.

Designation of the obtained activated art paper sludge	Temperature (°C)	Retention time (h)
AAPS-1	600	2
AAPS-2		5
AAPS-3	650	2
AAPS-4		5
AAPS-5	700	2
AAPS-6		5
AAPS-7	750	2
AAPS-8		5

Table 2
Chemical composition of materials.

Materials	SiO_2 (wt.%)	Al_2O_3 (wt.%)	CaO (wt.%)	MgO (wt.%)	Fe_2O_3 (wt.%)	SO_3 (wt.%)	K_2O (wt.%)	Na_2O (wt.%)	L.O.I (wt.%)
APS	12.89	8.3	23.2	1.39	0.33	0.18	0.22	0.05	52.98[a]
AAPS-1	20.24	13.11	36.39	2.15	0.52	0.28	0.34	0.08	26.24
AAPS-2	20.65	13.38	37.2	2.2	0.52	0.28	0.34	0.08	24.68
AAPS-3	21.06	13.58	37.81	2.24	0.54	0.29	0.35	0.09	23.36
AAPS-4	21.44	13.87	38.55	2.3	0.54	0.29	0.35	0.09	21.93
AAPS-5	22.32	14.55	40.21	2.35	0.56	0.32	0.37	0.09	18.52
AAPS-6	23.52	15.28	42.51	2.52	0.6	0.33	0.39	0.1	14.03
AAPS-7	25.36	16.45	45.7	2.74	0.63	0.34	0.42	0.09	7.43
AAPS-8	26.22	16.98	47.46	2.82	0.65	0.36	0.44	0.11	4.41
GPC	19.48	5.95	62.96	1.63	2.13	2.28	1.18	0.32	3.02

[a] The high value of LOI of dried APS is approximately the sum of the gases released from pyrolisis of organic fraction (cellulose fibres), dehydroxilation of kaolinite and de-carbonation of calcite.

Table 3
Mineralogical composition of GPC by the modified Taylor-Bogue's method [18].

	Alite (wt.%)	Belite (wt.%)	C_3A (wt.%)	C_4AF (wt.%)	$CaSO_4$ (wt.%)	Calcite (wt.%)	Free calcium oxide (wt.%)
GPC	66.72	5.79	13.09	4.41	3.88	6.08	1.09
Technique used	XRF results applied to modified Taylor-Bogue's method					TG/ DTA	Ethylenglycol method

3. Experimental procedures and methods

Thermal activation of APS was carried out in an air drafted furnace with a heating rate of 20 °C/min from room temperature to the relevant activation temperature (Table 1), which was maintained for either 2 or 5 h. AAPS was then cooled in a desiccator at room temperature, and manually ground until all material passed a 45 μm sieve. AAPS and GPC were then homogenised together in the appropriate proportions for 1 h in a high speed powder mixture.

Laser diffraction spectrometry was carried out with a HELOS 12 LA SYMPATEC instrument based on a He–Ne laser wavelength of 632 nm and a multi-element 31-channel detector. The eight AAPS samples and GPC were suspended in isopropyl alcohol, continuously stirred and pumped inside a closed loop cell. The suspensions were ultrasonically dispersed and subsequently stabilized for 60 and 30 s, respectively prior to the 15 s laser diffraction analysis [20].

Surface-area measurements were made by the BET multipoint method (Model ASAP 2010, Micromeritics Instrument Corp., Norcross, GA) at 77 K submerged in boiling liquid N_2. Surface areas were calculated from the sorption isotherm data using the BET method [21] in a relative pressure (P/P_o) range of 0.003–0.3.

The X-ray fluorescence device used was a Philips PW 780 with an anticathode tube of rhodium of 4 kW. Simultaneous thermogravimetric analysis and differential thermal analysis (TG/DTA), was carried out with a Stanton STA 781 model. Powdered samples between 12–16 mg were heated at a heating rate of 10 °C/min from room temperature to 1000 °C using a N_2 flux of 100 ml/min.

Estimation of the required physical properties, such as normal consistency water requirement, initial and final setting times, soundness of cement pastes and compressive strength of cement mortars were carried out according to the current standards [22,23].

4. Results and discussion

4.1. Normal consistency water and setting times

Technical requirements of common Portland cements, such as setting times, soundness and compressive strength, are stated to their strength class according to the current standard [16] as exposed in Table 4. The influence of each AAPS on the normal consistency water and setting times of blended cements is shown in Figs. 1 and 2. Normal consistency water of blended cements is strongly influenced by the temperature and retention time applied to APS and inversely related to the percentage of replacement applied.

In general, the setting time values of blended cements decrease when there is an increase in temperature and/or time of activation as well as the percentage of APS. The results also indicate two extreme behaviours. Regardless of the AAPS replacement applied, GPC-AAPS-1, 2 and 3 blended cements demonstrate a similar set