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

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	SiO₂ (wt.%)	Al₂O₃ (wt.%)	CaO (wt.%)	MgO (wt.%)	Fe₂O₃ (wt.%)	SO₃ (wt.%)	K₂O (wt.%)	Na₂O (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 pyrolysis 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.%)	C₃A (wt.%)	C₄AF (wt.%)	CaSO₄ (wt.%)	Calcite (wt.%)	Free calcium oxide (wt.%)
GPC Technique used	66.72	5.79	13.09	4.41	3.88	6.08	1.09
	XRF results applied to modified Taylor-Bogue's method					TG/ DTA	Ethylenglycol method

cements were prepared applying 2% of replacement (10% and 20% by weight) and the eight types of AAPS.

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 N₂. 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 N₂ 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

Table 4
Technical requirements for common Portland cements.

Strength class	Setting time		Soundness	Compressive strength (Cs) of mortars cured for 28 days (MPa)
	Initial (min)	Final (h)	Expansion (mm)	
32.5	⩾75	⩽12	⩽10	32.5 ⩽ Cs ⩽ 52.5
42.5	⩾60			42.5 ⩽ Cs ⩽ 62.5
52.5	⩾45			Cs ⩾ 52.5

performance regarding to the control Portland cement (GPC). On the contrary, blended cements elaborated with a 20% of AAPS-6, 7 or 8 show a flash set.

Normal consistency water and setting times are physical properties for the early hydration of the Portland cement. Within minutes following mixing with water, a flocculation of the cement particles takes place [24]. This initial flocculation is brought about by opposite zeta potentials and by weak Van der Waals forces. Therefore, the water demand of a Portland cement is due to several effects directly related with the physical features and chemical composition of the particles.

Physically speaking, water demand depends on the quantity water necessary to fill the interspaces among particles (free bulk water) and the water bound physically at the outer surface and pore walls (physisorbed water) [25]. Obviously, the total particle outer surface area and the space between particles are directly related to particle size distribution. Since all AAPS have a finer particle size distribution than GPC (Fig. 3), the substitution of cement by any AAPS decreases the space among particles in the blended paste reducing the bulk water demand, but at the same time increasing significantly the physisorbed water demand due to the substantial increase in total particle outer surface area.

Regarding to inner surface of pores, BET surface analyses provides information about the total surface area of both the outer particle surface and open and interconnected porosity within particles. The results obtained (Table 5) demonstrate that thermal activation of APS provides a highly porous structure, with a BET surface area 9–12 times greater than GPC. Therefore, the presence of AAPS in the cement matrix significantly increases the area of solid surfaces, explaining the greater water demand of the blended cements relative to the control Portland cement.

However, the variation in water demand and setting time values between the blended cements is not mirrored by the changes in calculated available particle surface areas. Therefore these variations should be attributed to changes in the chemical properties of each AAPS.

As mentioned above, the mineralogy and chemical composition of each AAPS depends on the thermal treatment applied to APS [17]. The absence of the typical endothermic band corresponding
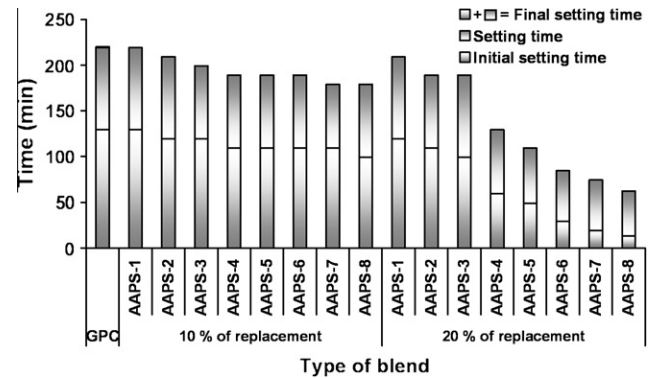
Fig. 2. Setting times of control and blended cement pastes.
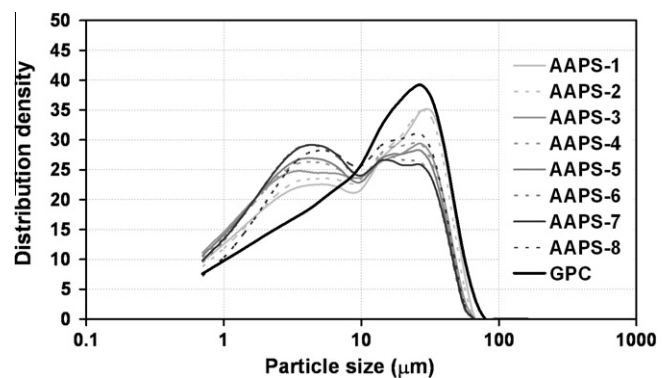
**Fig. 3.** Particle size distribution of materials.

to dehydroxilation of kaolinite between 400 and 600 °C in TG/DTA analyses (Fig. 4) demonstrates that all thermal treatments applied to APS (Table 1) completely transformed kaolinite into the active metakaolinite form. Furthermore, the appearance of an endothermic band between 350 and 450 °C in AAPS-5, 6, 7 and 8, corresponding to the dehydroxilation of portlandite, coupled with the decrease in intensity of the endothermic band between 600 and 800 °C, corresponding to de-carbonation of calcite, demonstrate that when activating APS at 700 °C or above, calcite decomposes to form free lime which in turn forms Portlandite upon contact with atmospheric humidity when each AAPS is ground and handled. Portlandite and calcite contents of each AAPS (Table 5) were determined by the associated weight losses with relevant DTA peaks.
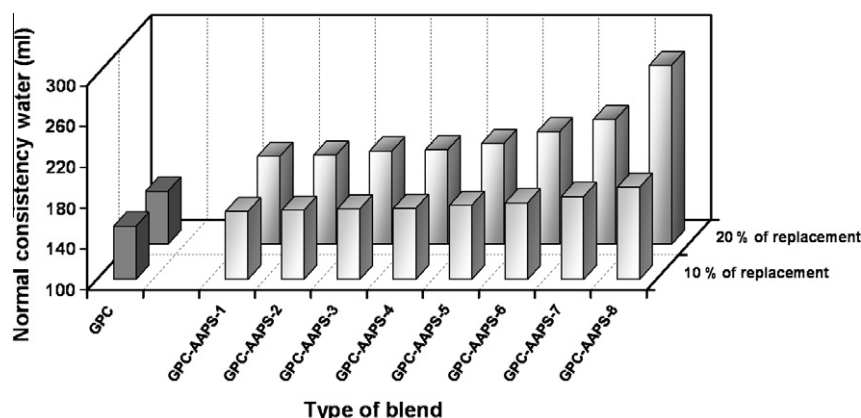
Fig. 1. Normal consistency water of control and blended cement pastes.

Table 5
BET surface area and contents of free calcium oxide, portlandite, real free lime and calcite.

Materials	GPC	AAPS-1	AAPS-2	AAPS-3	AAPS-4	AAPS-5	AAPS-6	AAPS-7	AAPS-8
BET surface area (m^2/g)	1.06	11.33	10.76	9.89	9.21	10.90	9.96	12.11	10.30
Portlandite content determined by TG/DTA (wt.%)	1.17	0.19	0.21	0.12	0.13	3.61	11.80	14.32	18.15
Calcite content determined by TG/DTA (wt.%)	6.08	57.98	53.86	51.24	47.81	42.45	21.24	13.3	4.41
Free calcium oxide content determined by [17] (wt.%, expressed as CaO)	1.09	0.31	0.31	0.35	0.82	7.15	22.50	25.11	26.46
Real free lime content (wt.%)	0.20	0.17	0.15	0.26	0.72	4.42	13.56	14.27	12.72
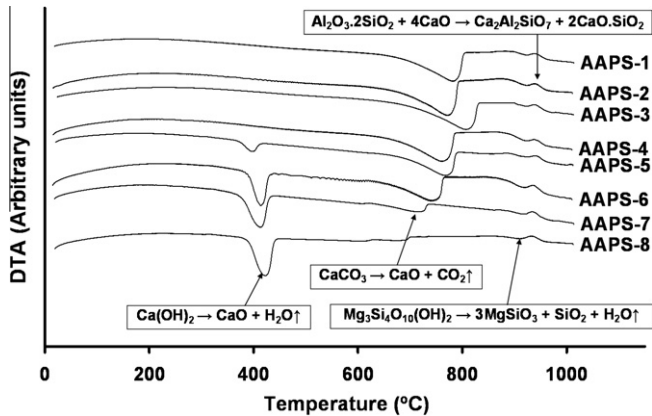
Fig. 4. DTA thermograms of AAPS.

The degree of calcite decomposition and consequently free lime and Portlandite formation increases with increasing time and temperature of activation beyond 650 °C.

The free calcium oxide content is a determining factor for Portland cement performance due to the secondary effects associated with its hydration [16]; therefore, this parameter was evaluated by a standardised method [19] for each AAPS sample and GPC (Table 5).

The ethylenglycol method simultaneously extracts portlandite and free lime. Therefore to obtain the real free lime content it was necessary to subtract the Portlandite results by TG/DTA from the total ethylenglycol results, as is exposed in the following equation.

$$\text{Real free lime(wt.\%)} = \text{Free calcium oxide}_{(\text{Etylenglycol})} - \left[\text{Ca(OH)}_{2(\text{TGA/DTA})} \cdot \frac{Mw_{CaO}}{Mw_{Ca(OH)_2}} \right] \quad (1)$$

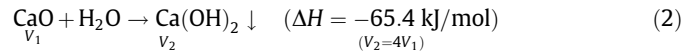where Mw_{CaO} and $Mw_{Ca(OH)_2}$ are 56 and 74 g/mol, respectively.

The results reveal that AAPS-1, 2, 3 and 4 have a similar real free lime content regarding to the control Portland cement, however AAPS-5, 6, 7 and 8 contain an undesirably high amount of this phase.

In addition to hydration of free lime, the formation of *AFt* and *AFm* phases and the hydration of C_3S are also important to the results of tests for normal consistency water requirement and setting time due to their rapid nature.

4.1.1. Hydration of free lime

As mentioned above, free lime content can strongly affect cement performance. A drastic reduction in water availability is caused due to the immediate hydration of free lime, reducing the workability of a paste. Hydration of lime is a highly exothermic reaction that results in a great increase of the temperature of the bulk cement matrix, and implies a four times increment of solid crystalline volume (Eq. (2)), which can break the external barrier of hydrated products that surrounds the unreacted particles,
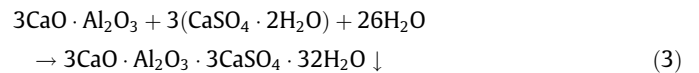
facilitating the ingress of ions [26]. Both phenomena could contribute to an increase of hydration kinetics of any reacting cement phases.

$$\underset{V_1}{\text{CaO}} + H_2O \rightarrow \underset{V_2}{\text{Ca(OH)}_2} \downarrow \quad (\Delta H = -65.4 \text{ kJ/mol}) \quad (V_2 = 4V_1) \quad (2)$$
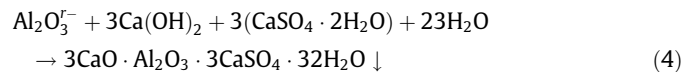
Furthermore, hydration of free lime also results in an increase of the pH of the liquid phase, which affects significantly both the formation and stability of *AFt* and *AFm* phases, as stated below.

4.1.2. Formation of AFt and AFm phases

It is well known that the early hydration of Portland cements is mainly governed by formation of *AFt* and *AFm* phases from the reaction between anhydrous calcium aluminates phases (C_3A and C_4AF). Therefore to produce cement with acceptable setting characteristics, gypsum ($CaSO_4 \cdot 2H_2O$) is usually added to the clinker as a set regulator. The presence of sulphates in the liquid phase delays the C_3A hydration (and presumably ferrite as well), through a barrier of ettringite (Eq. (3)) at the cement grain surfaces [25].

$$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O$$
$$\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \downarrow \quad (3)$$

In case of a blended cement, the reactive alumina ($Al_2O_3^{r-}$) from pozzolanic additions, e.g. metakaolinite, is also involved in the ettringite formation (Eq. (4)) with a reaction rate higher than C_3A [28]. The rapid reactivity of alumina has been demonstrated in a previous study with an AAPS/Calcium hydroxide system, where most of the aluminium nuclei in IV and V-fold coordination from metakaolinite were transformed into hydrated phases with aluminium nuclei in VI-fold coordination within 1 day of hydration, by formation of hydrated calcium monocarboaluminate [29].

$$Al_2O_3^{r-} + 3Ca(OH)_2 + 3(CaSO_4 \cdot 2H_2O) + 23H_2O$$
$$\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \downarrow \quad (4)$$

Obviously, both reactions (Eqs. (3) and (4)) are directly related to sulphate/alumina molar ratio, which is usually employed to optimise the dosage of gypsum of any given cement. However, the most determining factor for the early reactions of Portland cements and hence for the setting times, is the rate at which the relevant ionic species (Ca^{2+}, SO_4^{2-}, OH^- and CO_3^{2-}) are made available at the surfaces of the aluminate and ferrite phases grains, which depends on numerous aspects [27], such as distribution of Al_2O_3 among the clinker phases, the specific surface area and the manner in which gypsum, aluminate and ferrite are ground together. Because 16 new blended cements are prepared from the same GPC, their performance should be attributable only to the substitution effects (10% or 20%) and the chemical properties of each AAPS.

Fig. 5 illustrates the sulphate/alumina and carbonate/alumina molar ratios for GPC and blended cements. These ratios are calculated taking into account the mass fractions of SO_3, CO_3 and Al_2O_3 (Table 2) determined by XRF for GPC and each AAPS, as are exposed in the following equations.

$$\frac{CO_3}{Al_2O_3} = \frac{[CO_3]_{GPC} + [CO_3]_{AAPS-i}}{[Al_2O_3]_{GPC} + [Al_2O_3]_{AAPS-i}} \quad (5)$$
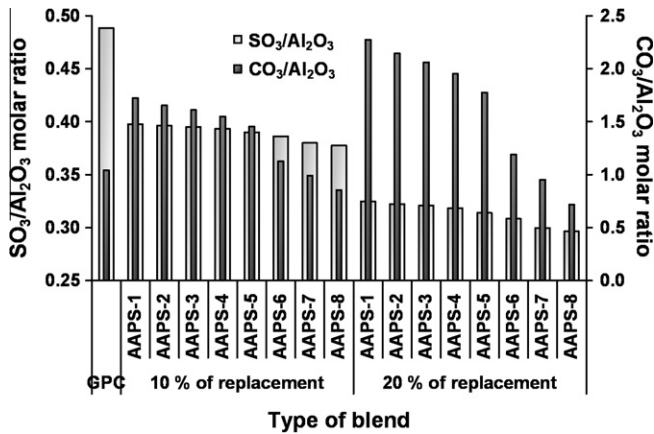
Fig. 5. SO_3/Al_2O_3 and CO_3/Al_2O_3 molar ratios of the blended cements.

$$\frac{SO_3}{Al_2O_3} = \frac{[SO_3]_{GPC} + [SO_3]_{AAPS-i}}{[Al_2O_3]_{GPC} + [Al_2O_3]_{AAPS-i}} \qquad (6)$$

where "i" is the thermal treatment applied.

According to the data in Tables 2 and 5, substitution of cement by AAPS will invariably reduce the sulphate/alumina ratio and, with the notable exception of AAPS-8, increase the carbonate/alumina ratio relative to reference GPC. Some authors [30,31] have confirmed that gypsum could be partially substituted by limestone ($CaCO_3$) as a setting regulator, but that the effects are weaker due the limestone being some 80 times less soluble than gypsum in high pH solutions, typical of hydrating Portland cements [32]. Therefore, in a situation where excesses of both calcite and gypsum are present, C_3A and C_4AF react preferentially with sulphates rather than carbonates. However, if conditions where there is a lack of available sulphate relative to reactive alumina and the local solution pH drops, carbonate anions could play a more significant role in the hydration of alumina bearing phases. The precipitation of carboaluminates around alumina grains, such as monocarboaluminates (Eq. (7)) and hemicarboaluminates (Eq. (8)), would retard hydration and thus setting in a similar manner to ettringite [33].

$$\left.\begin{array}{l} Al_2O_3^{r-} + 3Ca(OH)_2 + CaCO_3 + 8H_2O \\ 3CaO \cdot Al_2O_3 + CaCO_3 + 11H_2O \end{array}\right\} \rightarrow \underset{\text{Hydrated calcium monocarboaluminates}}{3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O \downarrow} \quad (7)$$

$$\left.\begin{array}{l} Al_2O_3^{r-} + 3.5Ca(OH)_2 + 0.5CaCO_3 + 8.5H_2O \\ 3CaO \cdot Al_2O_3 + 0.5Ca(OH)_2 + 0.5CaCO_3 + 11.5H_2O \end{array}\right\} \underset{\text{Hydrated calcium hemicarboaluminates}}{3CaO \cdot Ca[(OH)(CO_3)_{0.5}] \cdot 11.5H_2O \downarrow} \quad (8)$$
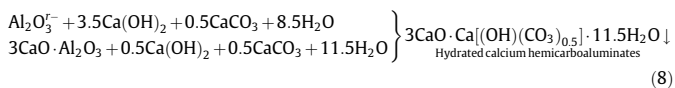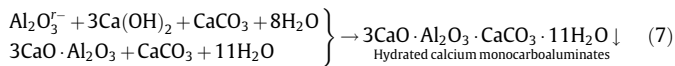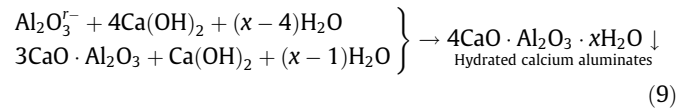
The second effect of substitution of cement by AAPS is the modification of the liquid phase pH during early hydration, by two opposing effects:

1. As the dilution effect associated to the lower content of cement as the pozzolanic reaction of AAPS, result in a lower concentration of portlandite in the liquid phase and thus a lower pH.
2. The variable and temperature of activation dependant contribution of free lime and portlandite from AAPS to the blended matrix will increase the availability of Ca^{2+} y OH^- for the liquid phase and thus the pH.

These factors help explain why blended cements elaborated with a 20% of AAPS-1, 2 or 3 only reduced initial setting time by 30 min, relative to GPC. Although the substitution of cement by either AAPS-1, 2 or 3, resulted in a molar SO_3/Al_2O_3 ratio 1.5 times lower than GPC, the simultaneous increase of carbonate/aluminate ratio (Fig. 5), coupled with the lowering of $Ca(OH)_2$ formation in the liquid phase and thus pH, by both the dilution effect and

$Ca(OH)_2$ consumption by the pozzolanic reaction of metakaolinite in AAPS, permits the formation of carboaluminates. Thus, calcite from AAPS-1, 2 or 3 acts as a set regulator for the large amount of reactive alumina that these activated wastes contribute to the blended cement.

In the opposite case, blended cements elaborated with a 20% of AAPS-6, 7 or 8 with a similar lack of calcium sulphate that those manufactured with AAPS-1, 2 or 3, are not able to solubilise carbonates anions to compensate due to the higher pH of the liquid phase, induced by hydration of free lime and the contribution of portlandite present in AAPS-6, 7 and 8. Without a sufficient retardation of the reactive alumina phases, massive precipitation of plate-like crystals of $C_4(A,F)H_x$ (Eq. (9)) occurred, causing a flash set of the paste [24], as shown in Fig. 5.

$$\left.\begin{array}{l} Al_2O_3^{r-} + 4Ca(OH)_2 + (x-4)H_2O \\ 3CaO \cdot Al_2O_3 + Ca(OH)_2 + (x-1)H_2O \end{array}\right\} \rightarrow \underset{\text{Hydrated calcium aluminates}}{4CaO \cdot Al_2O_3 \cdot xH_2O \downarrow} \quad (9)$$

4.1.3. Hydration of C_3S

When C_3S particles come into contact with water, a membrane C–S–H gel is formed on the grain surface, which permits the inward flow of water molecules and the outward migration of Ca^{2+} and to a lesser extent silicate anions due to the difference in osmotic potential on either side of the membrane. The charge imbalance is addressed by periodic rupturing of the C–S–H membrane and passage of concentrated silicate solution to the bulk liquid phase [34]. Consequently, excess portlandite accumulates on the bulk liquid side of this membrane (Eq. (10)).

$$3CaO \cdot SiO_2 + xH_2O \rightarrow GelC-S-H \downarrow + yCa(OH)_2 \quad (10)$$
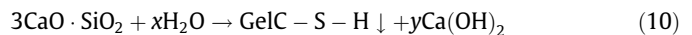
The setting process, i.e. period from initial setting to final setting (Fig. 2), occurs during the acceleratory period of hydration of Portland cement, which is strongly influenced by hydration of alite (C_3S). Alite hydration becomes significant when the liquid phase becomes supersaturated with portlandite. Obviously, that moment is dependent upon the free lime and portlandite contribution of AAPS to the blended cements [35]. Although many studies [36–38] have demonstrated that small amounts of $CaCO_3$ accelerate the hydration of alite, due to the contribution of a higher surface area for the nucleation of new hydrated phases, this fact is not relevant for the GPC-AAPS blended cements, since GPC contains a considerable amount of limestone (Table 3). This fact explains why all the blended cements with a 10% of replacement and those elaborated with a 20% of AAPS-1, 2 or 3, which contain higher contents of calcite relative to GPC (Fig. 5), show little reduction in setting time (Fig. 2). However, the remaining blended cements with 20% AAPS show a significant decrease in setting time, due to the contribution of free lime and portlandite which are particularly evident in AAPS-6, 7 and 8.

4.2. Soundness

The purpose of this accelerated test method [22] is to evaluate in a short period of time, the long term expansion that would take place in a cementitious matrix. Cement expansion is the result of the reactions that involve a rapid precipitation of expansive phases or those that increase the crystalline volume of pre-existing phases. The main expansive reactions are the hydration of free lime and the precipitation of ettringite, which depend on the initial composition and the SO_3/Al_2O_3 ratio of the blended cements.

The decreasing values of the molar SO_3/Al_2O_3 ratio detailed above in Fig. 5 and the results obtained in this test (Fig. 6), demonstrate that an increase in the free lime content is the cause of observed increases expansion. Despite this, all blended cements
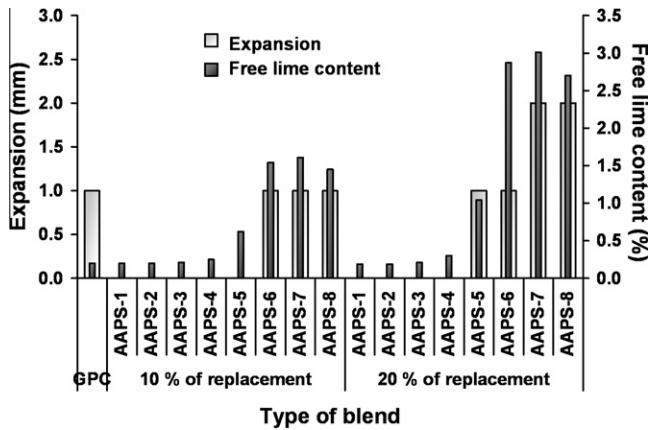
Fig. 6. Expansion and free lime content of the blended cements.

Fig. 8. Compressive strength of GPC and blended cement mortars (for a 20% of replacement of GPC with AAPS).

easily complied with the standardised requirement of expansion $\leqslant 10$ mm [16], which should be attributed to the microstructure of CaO crystals in AAPS [26].

A more detailed analysis of the results shows that although GPC contains a low content of free lime (0.2%) it expands slightly (1 mm), because it has the largest SO_3/Al_2O_3 ratio within the 17 cements studied (Fig. 5), and therefore, generates the largest amount of ettringite.

4.3. Compressive strength of mortars

Compressive strength of GPC and blended cements was evaluated over a period of 720 days using a constant water/binder ratio of 0.5. Figs. 7 and 8 represent the evolution of compressive strength of blended cements for 10% and 20% GPC replacement respectively relative to the control GPC. Both charts demonstrate that the compressive strength of blended cements is a balance among several physical and chemical factors. Physical aspects such as the filler effect of AAPS (positive) and the dilution effect caused by cement replacement (negative) and chemical factors, such as the pozzolanic reaction of metakaolinite in AAPS (positive), the hydration of alite accelerated by the presence of finely ground calcite (positive) and the hydration of free lime (negative), among others.

All blended cement mortars show lower compressive strengths than GPC at one day of hydration, due to both the dilution effect and the free lime content. Blended cements with the higher free lime contents, due to greater activation temperatures and longer
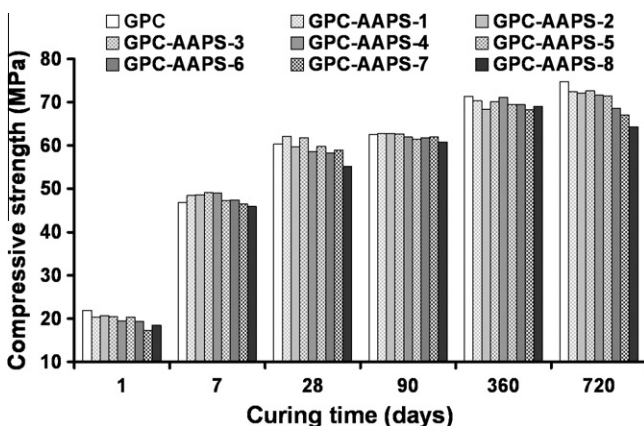
activation times, showed poorer strength development, because of reduced workability as a consequence of the water demand from free lime hydration.

As content of free lime increases, also there is a decrease in the SO_3/Al_2O_3 molar ratio of blended cements, which also reduces the workability of mortars and makes more difficult their consolidation in the mould. Due to this phenomenon, mortars produced with the same blended cements that were shown to exhibit flash setting, i.e. 20% AAPS-6, 7 or 8, induced formation of air-voids, having a marked long term reduction in strength development (Fig. 8), due to the weak microstructure of the *AFm* phases formed in a flash set [24].

The rate of pozzolanic reaction of AAPS and/or hydration of alite catalysed by calcite reaches a maximum at seven days, which equal or even exceed the dilution effect for almost all the blended cement mortars with a 10% of AAPS and those elaborated with a 20% of AAPS-1, 2 or 3, whose samples demonstrate similar or even higher compressive strengths than GPC.

This trend continues up to 90 days of hydration, at which point the pozzolanic reaction has completely finished. Beyond 90 days, the dilution effect becomes apparent again with compressive strengths lower than the control GPC, as a consequence of the large contribution of calcite from some AAPS (Table 5) to blended cement composition. However, in the case of GPC-AAPS-1 to 5, the variation of compressive strength between each blended cement and GPC is always lower than the percentage of replacement applied, which demonstrates that the pozzolanic reaction of these AAPS compensates partially their dilution effect.

Concerning the compressive strength requirement for 28 days of curing, the best mechanical performance is achieved for blended cements containing 10% of AAPS-1, 2, 3 or 4, due to the pozzolanic activity, already demonstrated in previous studies on calcium hydroxide systems [39], the accelerating effect of calcite on the hydration of alite and the low free lime content of these activated wastes.

5. Conclusions

Based on the findings the following conclusions can be drawn:

- The paper sludge wastes can be activated in a broad activation conditions (600–750 °C at 2 and 5 h of retention). However, such conditions have a direct influence on the blended cement properties.
- Regarding to the technical parameters, the substitution of cement by AAPS increases normal consistency water and decreases the setting times of the blended cements, with

Fig. 7. Compressive strength of GPC and blended cement mortars (for a 10% of replacement of GPC with AAPS).

increasing replacement rate, temperature and/or time of activation. This behaviour is due physically to the greater fineness and the higher surface area of AAPS than control GPC, and chemically, because of the hydration of free lime and the low sulphate/alumina ratio of some blended cements.

- The mineralogical composition of AAPS-1, 2, 3 or 4 permits a direct substitution of cement, without being detrimental to the technical properties of the cementitious matrix. This is considered due to the pozzolanic activity of metakaolinite in AAPS and the set regulating features of calcite, which compensate the dilution effect and the lack of gypsum, respectively.
- All blended cements studied comply with the standardised soundness requirement for common Portland cements, despite the presence of significant quantities of free lime in AAPS-5, 6, 7 and 8.
- Optimum compressive strength results were achieved with cement replacement of 10% with AAPS-1, 2, 3 or 4. All blended cements with a 10% of replacement and those that contains a 20% of AAPS-1, 2, 3, 4 or 5, complied with all the technical requirements for Portland cements of 42.5 strength class. Furthermore, these blended cements meet also with the requirements for Portland cement of 52.5 strength class, with the exception of the blended cement with 20% of AAPS-5.
- Optimal activation of APS was found to be 600–650 °C for 2 h (AAPS-1 or 3). The activated material can be considered as a suitable pozzolanic addition for Portland cements. The implementation of 5 h of activation (AAPS-2 or AAPS-4) does not noticeably improve the performance properties of the activated waste, but would imply an increase of economic costs.
- Although AAPS is not specifically mentioned as a pozzolanic addition for Portland cements in the current standards, it could be used to elaborate blended Portland cements CEM II/A-M (L–Q), due to the fact that AAPS is mainly composed of calcite (L) and metakaolinite obtained by thermal treatment (Q).

Acknowledgements

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