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Aging and durability of ternary cements containing fly ash and activated paper sludge

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HIGHLIGHTS

- APS-FA blended cement mortars showed good resistance to freeze/thaw cycles.
- Blended mortars perform better than OPC mortars in marine environments.
- Resistance of blended and OPC mortars to Spanish's plateau conditions are similar.

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ABSTRACT

This research work deals with durability aspects of ternary cements containing 79 wt.% ordinary Portland cement (CEM I), 10.5 wt.% coal fly ash and 10.5 wt.% thermally activated paper sludge. Aging tests were performed to study the resistance of the new ternary cement matrixes to the following aggressive exposure conditions: accelerated freeze/thaw cycles, marine environment and Spanish plateau climate conditions. Ternary cements revealed a high resistance to accelerated freeze/thaw cycles. In addition, after 18 months of exposure, they exhibited enhanced performance under marine conditions and similar resistance to Spanish plateau's climate, compared to ordinary Portland cement.

1. Introduction

A rapid development in the production of less energy intensive cements and concretes with high performance (resistance and durability) is taking place in recent times. This is being accomplished by the use, for example, of industrial wastes or by-products (fly ash, slag, silica fume, rice husk, etc.) with considerable pozzolanic activity. The use of those secondary materials results not only in a better management of both mineral and energy resources but also in improvements on durability and mechanical performance [1–5].

Some studies focused on thermally activated clays as potential sources for pozzolanic materials. In this context, kaolin is the most important clay mineral from which a highly pozzolanic material (metakaolin-MK) can be obtained. In addition, the latter can be obtained from more environmentally friendly sources such as the thermal activation of waste paper sludge. Pioneering studies [6–10] concerning this clayey by-product showed that the controlled calcination of waste paper sludge at 650–700 °C produces the most favorable conditions to obtain a highly reactive metakaolin. Physical and chemical behavior of cements blended with thermally activated paper sludge matrices have been reported in recent years [7,9–14]. The presence of other clayey materials in paper residues (muscovite, talc, chlorite) and the high content of calcium carbonate can act as accelerators in the pozzolanic reaction. Those materials also produce hydrated phases different from those produced with commercial metakaolin [15].

On the other hand, it is well known that coal fly ash is the finely divided residue resulting from the combustion of ground or powdered coal, which is transported from the firebox through the boiler by flue gases. This industrial by-product is used for different applications; among others, for the production of various types of cements [16]. Coal fly ash affects most properties of concrete (workability, segregation, heat of hydration, chloride and sulfate resistance, etc.) [17]. Mostly, the effect is positive at long term;

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however, it also has certain drawbacks. For instance, it slows down strength development.

The first works on the combined effect of both thermally activated paper sludge (APS) and coal fly ash (FA) were carried out by Frias et al. [18–20] and Goñi et al. [21]. They studied reaction kinetics, mechanical performance and durability in ternary cement pastes containing such pozzolanic by-products. The obtained results revealed that the main hydrates resulting from the system APS + FA/$Ca(OH)_2$ were CSH gel, hydrotalcite like structures, C_4AH_{13} and hemicarboaluminate; varying as a function of the nature of the APS. In addition, those ternary cement pastes exhibited enhanced resistance against aggressive media such as Cl^-, sulfates and sea water, when comparing with conventional Portland cement pastes. On the contrary, their behavior when exposed to the action of CO_2 was not so favorable [18–21].

Despite the aforementioned pioneering research works, there is still a lack of knowledge on the response of these ternary cements under other aggressive environments. This was the main motivation for this work, deepening on the combined effect of APS and FA on durability aspects. In particular, freeze/thaw resistance and the consequences of aging under different environmental conditions were studied.

2. Materials and methods

2.1. Materials

Ternary cement mortars were prepared by partially replacing an ordinary Portland cement (CEM I 52.5N) by a mixture of FA and APS. Mixing of the solids took place by shaking in an automatic mixer for 15 min to warranty the homogeneity of the mix. The composition of the binder was 79 wt.% cement, 10.5 wt.% FA and 10.5 wt.% APS. Two different types of APS were used in this work; on the one hand, thermally activated paper sludge at lab scale (LAPS) and on the other hand, paper sludge thermally activated at industrial scale (IAPS). The former (LAPS) was obtained from the company Holmen Paper Madrid, S.L., located in Madrid and using exclusively recycled paper as raw material. This dry paper sludge was thermally activated in the laboratory at 700 °C on the basis of previous works [8–9,22–23]. The latter (IAPS) was a commercial by-product (provided by the Dutch company CDEM) previously activated at roughly 740 °C. IAPS was used as received. The physical properties and chemical composition of the cement and the supplementary by-products are presented in Table 1. The chemical composition was determined by X-ray fluorescence (XRF), the surface area by BET and the reactive silica content by chemical methods according to UNE 80225.

From a mineralogical point of view, thermally activated paper sludge is mainly composed of calcite and talc, see Table 2. Portlandite and quicklime were also identified in the APS residue. While the latter is a direct consequence of the decarbonation process of calcite, portlandite compounds arise from the ulterior hydration of the calcined product during handling. Fly ash is mainly made of quartz, mullite and hematite (Table 2) [24]. Finally, cement has the typical composition of a type I Portland cement with 45 wt.% C3S, 24 wt.% C2S, 10 wt.% C3A and 10 wt.% C4AF as obtained from the chemical composition (Table 1) using Bogue's equations.

Table 1
Physical properties and chemical composition of the cement and supplementary cementitious materials.

	CEM I 52.5N	Fly ash	LAPS	IAPS
Surface area (m^2/g)	1.2	2.3	7.4	8.4
Particle size (μm)	<90	<90	<90	<90
Reactive silica (wt.%)	–	42.7	11.3	9.1
SiO_2 (wt.%)	20.02	55.7	13.9	21.6
Al_2O_3 (wt.%)	5.71	24.0	8.3	14.4
Fe_2O_3 (wt.%)	3.21	4.8	0.5	0.5
CaO (wt.%)	58.90	2.2	47.1	36.5
MgO (wt.%)	1.73	0.9	1.6	2.4
SO_3 (wt.%)	4.27	0.9	0	0.3
K_2O (wt.%)	1.56	2.2	0.3	0.4
Na_2O (wt.%)	0.77	0.5	0.2	0.1
TiO_2 (wt.%)	0.15	0.7	0.25	0.3
P_2O_5 (wt.%)	0.21	0.3	0.2	0.2
Loss on ignition (wt.%)	2.58	7.6	26.7	23.2

Table 2
Mineralogical composition of the raw constituents.

Mineral	LAPS	IAPS	Fly ash
Calcite (wt.%)	96	69	–
Talc (wt.%)	4	2	–
Mullite (wt.%)	–	–	34
Portlandite (wt.%)	–	9	–
Quicklime (wt.%)	–	20	–
Hematite (wt.%)	–	–	13
Quartz (wt.%)	–	–	53

Cement mortars were used for assessing the durability of the ternary cements. The fine aggregate in cement mortars was graded standard sand (>98% SiO_2) [16]. The mix proportions of mortars are based on the specifications and criteria established in UNE EN 196-1 [16] concerning cement test methods. Thus, the mass ratio of water to binder (cement + supplementary material) was 1:2, while the mass ratio of binder to sand was 1:3. Cement mortars were named as TC-0% (containing 0 wt.% supplementary cementitious material), TC-21%L and TC-21%I (21 wt.% addition of supplementary cementitious material with LAPS or IAPS and FA). A previous study on the effect of the percentage of replacement of supplementary cementitious material by cement [25] on the mechanical performance revealed that values higher than 21 wt.% resulted in a notable reduction in the compressive strength (up to 25% compared to the reference cement) after 28 days of curing.

In all cases, the mixing process was carried out according to UNE-EN 196-1 [16]. Test specimens were cured for 24 h in a humidity chamber (>90% relative humidity and 20 °C) and then unmolded and submerged in water at 20 °C for another 27 days, prior to the beginning of the durability tests [26].

2.2. Aging under different exposure conditions

For the study of the effect of aging under different environmental conditions three different scenarios were considered: laboratory conditions, Spanish plateau's climate and marine environment. The samples subjected to laboratory conditions were stored in a room with a constant temperature of 20 °C and over 60% relative humidity. The samples subjected to Spain's plateau climate were placed at a terrace at the top of a building in Madrid. Therefore, they were exposed to both moisture/dryness cycles and natural freeze/thawing cycles with a temperature fluctuation along the year of −7 °C to 40 °C and annual average humidity of 54%. Finally, in order to simulate in the laboratory tidal cycling, a set of samples were submerged in sea water and dried at intervals of 6 h. Sea water was directly obtained from the Cantabric sea in Bilbao's harbor. The ionic composition of the water is contained in Table 3. In order to prevent the excessive growth of algae and maintain the aggressive nature of the water, the water was renewed every 6 months. In this case, temperature varied between about 15 °C and 25 °C along the year.

Damage assessment was carried out at the end of the curing process (28 days), and after both 6 and 18 months of exposure to the different environmental conditions. The damage assessment process consisted of a series of experimental techniques designed for the determination of the internal damage of the diverse materials. Compressive strength, internal pore-size distribution and analysis of the microstructure were determined. For the study of the evolution of the compressive strength as a function of the aging time 40 mm × 40 mm × 160 mm samples

Table 3
Ionic composition of the sea water used to simulate the marine environment.

Ion in the sea water	Concentration
Na^+ (meq/L)	523
Mg^{++} (meq/L)	231
Ca^{2+} (meq/L)	39
K^+ (meq/L)	8
Cl^- (meq/L)	341
SO_4^{2-} (meq/L)	22
HCO^{3-} (meq/L)	5
Br^- (meq/L)	3
Li (ppm)	1
Al (meq/L)	2
V (meq/L)	1
Cr (meq/L)	1
Cu (meq/L)	1
Zn (meq/L)	2
Ga (meq/L)	1
Ge (meq/L)	1
Sr (meq/L)	23
Mo (meq/L)	2