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Physical–mechanical behavior of binary cements blended with thermally activated coal mining waste

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HIGHLIGHTS

- The influence of different percentages of ACMW on the blended cement behavior was evaluated.
- The incorporation of ACMW modified the technical behavior of blended cements.
- The new cements complied to the standard requirements.
- These ACMW can be used as active addition to elaborate future eco-efficient cements.

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ABSTRACT

This research work deals with the technical viability of manufacturing new eco-efficient cement blended with thermally activated coal mining waste (ACMW). The physical–mechanical results obtained in the present work showed that the addition of ACMW (up to 20% of replacement) modified the physical and mechanical properties of the blended cement matrices. The blended cements required a great water demand, slightly accelerated settings times and revealed gain in compressive strengths at early curing times. In general terms, blended cements containing up to 20% ACMW meet the chemical, physical and mechanical requirements set out by the EN 197-1 European standard.

1. Introduction

The problems associated with the accumulation of industrial by-products and waste in refuse pits have traditionally heightened environmental policies that encourage waste recycling as raw material in diverse industrial sectors, which contributes directly to the socio-economic development of a country.

The cement industry is able to absorb industrial waste at different stages of the manufacturing process: preparation of raw materials, use of alternative fuels and blending with pozzolanic by-products. In this line, one of the cement sector's priorities is to find new pozzolans that can be added to clinker during the manufacture of blended cement [1–10]. Metakaolin (MK) is a highly pozzolanic product and collected in the existing European legislation for decades [11]. Frías et al. [12–16] conducted studies on the scientific and technical grounds for the use of alternative resources for MK as new mineral additions to cement. They observed a substantial improvement in the performance of the resulting blended cements.

Aiming to further the use of MK, the valorization of coal mining wastes (CMW) might be a new source for MK-based pozzolans. CMW are generated during the separation of coal from the attached soil and rock (10%) during the mining and subsequent washing (90%). The chemical composition of Spanish coal mining waste is as follows: SiO_2 (43–49%), Al_2O_3 (22–24%, Fe_2O_3 (5–7%), K_2O (2.9–3.2), MgO (1.2–1.5%), TiO_2 (1.1–12 CaO (1.1–2.0%) and S_{total} (0.6–1.4%). The mineralogical constituents are quartz and kaolinite-like clay. These residues for its clayey nature show no ability to react with cement portlandite, but once subjected to a thermal activation process become metakaolinite based products, pozzolan well known for its high pozzolanic activity [17,18].

According to the BP Statistical Review of World Energy data, in Spain, around 10 million tons of CMW were generated in 2009,

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down by 34% from 2000. Despite the decline, over the last decades, vast amounts of this type of waste were accumulated in spoil banks, with a direct impact on huge natural areas [24]. Likewise, in Europe, as a whole, 175 million tons of waste have been stocked in dumps for decades.

The growing problems caused by stockpiling CMW (alteration of the landscape, visual impact, pollution, health hazards, land occupation) call for a study of eco-innovative solutions to valorize such residues by recovering the embedded mineral and energy resources at a low environmental cost. Despite that need, the scant research published worldwide on the subject was focused on its use to fill mine galleries no longer in use, as landfill in road and motorway embankments or in fired brick or pavement manufacture [19–21]. None of these lines of research have been translated into industrial applications.

The conversion of CMW into non-hazardous pozzolanic products for use in the manufacture of new cement matrices constitutes, a priori, a technological and an environmental improvement whose design should simultaneously ensure the pozzolanic activation of CMW, the reuse of the embedded energy resources, the capture/inertisation of harmful particles and the minimization in CO_2 release during the combustion process.

The use of CMW as a pozzolan in cement manufacture is a new line of research barely explored to date. In the first work on the CMW thermal activation in 2006, the characterization of several chinese CMW waste, their activation at temperatures ranging from 700 °C to 1000 °C and the performance of the pozzolanic blended cements obtained at replacement ratios of 20% and 30% were carried out [22]. In 2010, another study based on the behavior of portland cement paste and mortar containing 10 and 20% from the controlled thermal activation (600–800 °C) of CMW taken from Argentine mining basins [23]. Both studies confirmed the possibility of manufacturing a product with certain pozzolanic properties from activated coal mining waste. Frías et al. [24,25], among the coauthors for this research paper, established the initial scientific-technical basis for the pozzolanic reaction in systems composed of calcium hydroxide and thermally activated CMW. Variables such as origin, kaolinite content, activation temperature and rate of pozzolanic reaction, play a significant role in the activation of this waste and its effect on the performance of blended cement. Those authors concluded that the optimal activation conditions occur at 600 °C. The subsequent by-product produced at 600 °C for 2 h contains abundance of pozzolanic MK and octahedral layers from the dehydroxylation of mica that favor the formation of stable crystalline hydrated phases such LDH compounds (phyllosilicate/carbonate) and stratlingite during the pozzolanic reaction.

Despite these early studies, there is still an important scientific-technical gap, so it is important to look into the influence of these thermally activated industrial wastes in the properties of the blended cement matrixes. This new research contribution aims to present and discuss the physical–mechanical performance of blended cements containing CMW thermally activated at 600 °C up to 20% of replacement.

2. Materials and methods

2.1. Materials

Binary cement blends were prepared by partially replacing a conventional Portland Cement (CEM I 52,5N) by CMW thermally activated (in laboratory) at 600 °C for 2 h on the basis of previous works [24,25]. The raw CMW was provided by the Spanish coal Group, Sociedad Anónima Hullera Vasco-Leonesa, located in the province of León. The cement was provided by Financiera y Minera (Italcementi Group). The physical properties and chemical composition of both cement and the coal mining waste activated at 600 °C for 2 h (ACMW) are given in Table 1. The chemical composition was determined by X-ray fluorescence (XRF) using a Philips PW 1404 and X-ray tube of Sc-Mo, while both the fineness and the particle size distribution were determine by means of laser ray diffraction (LRD), using a Sympatec Helos 12 KA spectrometer and isopropyl alcohol as a nonreactive liquid [26].

Table 1
Physical properties and chemical composition of the CEM I 52.5 N and ACMW.

	CEM I 52.5 N	ACMW
100% particles below (μm)	73	73
90% particles below (μm)	35.71	33.32
50% particles below (μm)	12.47	8.33
SiO_2	21.22	58.33
Al_2O_3	6.39	26.09
Fe_2O_3	3.19	4.64
K_2O	1.67	3.09
CaO	61.38	2.16
TiO_2	0.17	1.17
MgO	1.97	0.77
SO_3	0.42	0.27
Na_2O	0.87	0.17
P_2O_5	0.20	0.14
MnO	0.04	0.08
LOI	2.49	3.09

Concerning the mineralogy, the ACMW is mainly composed of quartz, mica hematite and calcite, while the kaolinite is completely transformed into MK. Further details on mineralogical changes were presented in a previous work [24] by the researchers of this investigation line. Finally, cement shows the typical composition of type I Portland cement with 45wt% C_3S, 24wt% C_2S, 10% C_3A and 10wt% C_4AF derived from the chemical composition using Bogue's equation.

2.2. Methods for physical–mechanical characterization

ACMW blended cement matrices (pastes and mortars) were prepared at a water/binder ratio (w/b) of 0.5 and at binder/sand ratio (b/s) equal to 1/3. The OPC was partially (0%, 6%, 10% and 20%) replaced by the ACMW. Blended cements were named as C-0% [1] and C-6%, C-10% and C-20%. In all cases, the test methodology was carried out according to the existing EN 196-1 standard [27].

For the study of the effect of the physical–mechanical performance of the binary blended cements, diverse characteristics were determined: workability, volume stability, flexural and compressive strength, setting times and modulus of elasticity.

- Workability of the binary blended cements was determined by measuring the slump of the fresh mixture on the flow table.
- Setting times and volume stability of the cement pastes, blended with the diverse replacement levels of OPC by ACMW, were determined as per EN 196-3 [28]. It must be highlighted that the w/b ratio, used for the determination of the setting times corresponds to the content of water necessary for normal consistency. Normal consistency is defined as that providing a distance of (6 ± 2) mm between the probe and the base plate of the Vicat apparatus.
- The drying shrinkage was measured on the basis of standard ASTM C 596-7 [29]. For it, four 25 × 25 × 285 mm^3 prisms were fabricated for each blended cement C-0%–C-20%. At the center of the prismatic base, steel cylinders were imbibed. The prismatic specimens were cured for 48 h in a controlled environment of 20 °C and 90% relative humidity. After the first 48 h, bars were remolded and immersed into water for 24 h. At the age of 72 h ± 30 min, the specimens are removed from water, wiped with damp cloth and immediately obtain a length comparator reading for each specimen. The length comparator reading was carried out once a week for 120 days under laboratory conditions (20 ± 3 °C and 60 ± 3%RH).
- Both flexural and compressive strength of the blended cements were determined as per EN 196-1 [27] at 2, 7, 28 and 90 curing days. Prismatic specimens (40 × 40 × 160 mm) were cured in water (20 °C) till the determination of the mechanical strength. In addition, in order to determine the refinement of the microstructure, porosity and pore size distribution in blended cement mortars were performed by using a micrometrics Autopore IV 9500 mercury intrusion porosimeter (MIP) at pressure of 227.5 MPa, sufficient to determine pore sizes of up to 0.0067 μm. The mercury contact angle was 141.3 °C. Samples for MIP measurements were taken from 40 × 40 × 160 mm prism at 2, 7, 28 and 90 days of curing. The average pore diameter values were calculated according to the formula 4V/A.
- The static modulus of elasticity and Poisson's ratio were determined on the basis of the ASTM C 469-02 [30]. For each type of binary blended cement 6 cylindrical specimens of diameter of 100 mm and length of 200 mm were casted and cured in water for 28 days. 3 specimens were used for determination of the compressive strength and the rest for determining the stress–strain curves and, then, the calculation of modulus of elasticity and the Poisson's ratio. The specimens were placed, with the strain-measuring equipment attached (Ibertest) on the bearing block at the testing machine. The specimens were then