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Effect of a high content in activated carbon waste on low clinker cement microstructure and properties

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HIGHLIGHTS

- Blended cements with 20%–50% additions are standard-compliant.
- The binder containing 50% AC qualifies as a low heat cement.
- Drying shrinkage is more intense in high AC content cements.
- Adding 20%–50% AC to cement lowers its mechanical strength.
- Computed tomography shows that the addition raises the intermediate macropore (0.001–0.09 mm^3) volume.

ARTICLE INFO

ABSTRACT

In the context of cement industry sustainability and socio-economic development, one of the primary objectives of the circular economy is the use of industrial waste as a supplementary cementitious material in the manufacture of future eco-efficient binders. This paper reports a first-time study of the effect of large proportions of the activated carbon (AC) waste used in low clinker cements on the properties and structure of the new binders. The behaviour of blended cement matrices prepared with 20%–50% AC as a pozzolan was analysed in terms of their chemical, mechanical and physical (rheology, heat of hydration, drying shrinkage, microporosity) properties. Macroporosity was also assessed with computed tomography (CT). The findings showed that these blended cements meet standard chemical and rheological requirements and that the 50% AC binder qualifies as a low heat cement. Drying shrinkage was observed to intensify with higher percentages of AC. A rise in total porosity was attendant upon pore size refinement, with an increase in the <100 nm fraction. Compressive strength declined with rising replacement ratios. Further to the CT findings, macroporosity (0.001–0.09 mm^3) also increased with AC content, especially in the binders bearing 50% of the addition.

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1. Introduction

World population growth to an expected 9.2 billion by 2050 will entail a steady increase in the consumption of construction materials, cement among them. One of the adverse environmental implications of the manufacture of this artificial material is the release of greenhouse gases, with the emission of CO_2 accounting for 5%–7% of the worldwide total. Sixty per cent of the CO_2 generated is attributable to limestone decarbonation during the industrial process. Cembureau [1] has adopted a low carbon economy strategy, targeting an 80% potential reduction by 2050. With a view to reaching that goal, the cement industry is backing a number of innovative approaches [2], one of which would replace higher percentages of clinker with eco-efficient pozzolans.

On the whole, the wide variety of alternative pozzolans presently known are scientifically and technically apt for use as additions in portland cement manufacture [3–8]. As they have been introduced fairly recently, they are normally added at low replacement ratios, a practice that provides little or no information on the behaviour of low clinker cements.

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One of the lines of research presently pursued is the reuse of kaolinite-based waste as an alternative to metakaolinite, a highly pozzolanic product referenced in international standards on commercial cement manufacture. One such waste is activated carbon [9–10], notorious for the environmental damage caused when stockpiled near the respective coal mine [11].

To date, studies [12–14] have been conducted on how substituting these materials for up to 20% of the cement in binders may alter the kinetics and properties of the pozzolanic reaction. The findings have served to establish the protocol for their use as supplementary cementitious materials (SCMs).

Despite that progress, the effect of high percentages of activated carbon waste (AC) on the behaviour and properties of binary cements is a line of research unexplored by the scientific community. The priority objective of the present study was to gain insight into the chemical, physical and mechanical performance and microstructure of blended cements bearing up to 50% AC.

2. Experimental

2.1. Materials

Activated carbon waste (AC) from coal tailings furnished by an open-pit mine owned by Sociedad Anónima Hullera Vasco Leonesa, sited in the northern Spanish province of León, was activated under energetically, economically and environmentally optimal conditions: in a laboratory muffle furnace at 600 °C for 2 h [15]. Table 1 gives the Rietveld values for the mineralogical phases in both the tailings and the thermally activated waste.

The potential composition of the CEM I 52.5 R [16] Spanish commercial cement used, determined with the Bogue method, was: 41.74% C_3S; 27.95% C_2S; 8.33% C_3A; and 8.79% C_4AF.

Blended cement pastes were prepared with 20%, 30% and 50% AC (hereafter 20% AC, 30% AC, 50% AC). Three prismatic mortar specimens ($4 \times 4 \times 16$ cm) were prepared with a water/binder (w/b) ratio of 0.5 and a sand/cement ratio of 1/3, according to the existing standard. For each hydration time an average value was obtained from 5 compressive strength values.

The sand used consisted in standard sand with a minimum silica content of 98% and maximum particle size of 2 mm. A melanin-based superplasticiser (Sika, Madrid: Sikament FF) was added to lower water demand.

For the shrinkage under the drying condition test, four prismatic specimens ($25 \times 25 \times 285$ mm³) were moulded from OPC, 20% and 50% AC mortars. Six mm diameter stainless steel cylinders were embedded in both ends of the specimens, separated by a calibrated distance of 254 mm. The specimens were stored in the moulds in a humidity chamber for the first 48 h, subsequently demoulded and immersed in water for 24 h, after which the initial measurements were made. Specimen readings were recorded under laboratory conditions (20 °C, 60% RH) with a dial gauge comparator. The test was run for 63 d to ensure that shrinkage had peaked in all the mortars [17].

2.2. Methods and instrumental techniques

AC waste pozzolanicity was evaluated with an accelerated chemical method in which samples were immersed in a saturated lime solution at 40 °C [18]. The lime absorbed at each test age was calculated as the difference between the concentration of the reference solution (17.68 mmol/L) and the CaO content in the problem solution.

The cements were analysed for chemical composition with a Philips PW 1404 X-ray fluorescence (XRF) analyser fitted with an Sc-Mo X-ray tube, a gas scintillation detector and a PR-10 anode.

The mineralogical phases identified in the coal tailings and activated carbon were Rietveld quantified using rutile as the internal standard at a concentration of approximately 5%.

The 90 d cement mortars were studied for morphology under a Hitachi S4800 scanning electron microscope coupled to a Bruker Nano XFlash 5030 silicon drift detector for EDX analysis.

Mortar microporosity and fluctuations in pore size distribution over time were determined on a Micromeritics Autopore IV 9500 mercury porosimeter, with a 60 nm lower limit.

X-ray computed tomography (CT) analyses, conducted on a Nikon XT-H-160 scanner fitted with a W target 0.375 mm Cu filter, were recorded at 708 ms per frame, with a total of four frames and 1100 scans at 155 kV and 57 μA.

Particle size and its distribution were found on a Mastersizer 3000 laser spectrometer using air as the dispersion medium, with particle size ranging from 0.01 to 3500 μm.

Heating and heat of hydration were quantified applying the Langavant semi-adiabatic procedure, pursuant to European standard recommendations [19]. An inert (12 month old) reference cement was placed in the inner bottle of a Dewar vacuum flask and the paste to be tested in the outer. Heating (°C), defined as the difference in temperature between the two, was used to calculate heat of hydration.

3. Results and discussion

3.1. Physical-chemical characterisation of starting materials

The chemical composition of the carbon waste before and after thermal activation at 600 °C given in Table 2 shows that the AC was alumino-siliceous. The sum of the acid oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ accounted for over 86% of the total, a value much higher than the 70% minimum required in the U.S. standard for qualification as a class N pozzolan [20]. It had a reactive silica content of 21.80% and a free lime content of 0.16%. The chemical compositions of the blended cements used in this study, also given in the table, showed that at 1.70% their sulfate and at 0.01% their chloride contents were much lower than the ceilings allowed in the European standards in place [16] ($SO_3 \leq 3.5\%$ or $\leq 4.0\%$ and $Cl \leq 0.1\%$). Binders containing up to 50% AC would consequently meet the chemical requirements for classification as CEM type II or IV cements.

Fig. 1 reproduces the particle size distribution curves for the four cements analysed. A major peak at around 20 μm in all four declined in intensity with rising percentages of AC, while a less intense shoulder at 4 μm grew in intensity with the replacement ratio. Despite these changes in peak intensity, the particle size range was 0.1 μm–100 μm in all the binders. The D_{10}, D_{50} and D_{90} values (particle sizes below which 10%, 50% and 90%, respectively, of the particles lie) are given in Table 3.

3.2. Pozzolanic activity and modelling

The behaviour of activated carbon (AC) waste in a cement matrix depends on its reactivity with the lime released in the hydration reaction. The lime fixed by the AC over time is compared to the values for other types of industrial waste such as fired clay-based products (CW) and paper sludge (PS) in Fig. 2 [21,22]. With a high absorption rate of 40% in the first 24 h and 90% after 90 d, the AC waste exhibited pozzolanicity similar to that of the other two types of waste. The kinetic coefficients for the pozzolanic reaction can be calculated by applying the diffusive kinetic model (Eq. (1)) to the pozzolan/$Ca(OH)_2$ system [23].

Table 1
Coal tailings and activated carbon mineralogical composition (Rietveld, %).

%	Calcite	Kaolinite	Quartz	Mica	Amorphous phase
Tailings	15	14	29	25	17
AC-600	10	–	35	20	35

Table 2
XRF-determined chemical composition (%) of starting materials and blended cements.

%	Tailings	AC	OPC	20% AC	30% AC	50% AC
SiO_2	49.79	56.63	20.80	30.67	35.42	43.19
Al_2O_3	21.77	25.29	5.70	11.13	14.06	18.64
Fe_3O_2	4.07	4.64	2.89	3.16	3.19	3.35
CaO	3.84	4.20	58.99	45.34	37.77	25.51
MgO	0.64	0.77	1.89	1.58	1.45	1.21
Na_2O	0.13	0.17	0.93	1.58	1.29	0.94
K_2O	2.74	3.09	1.36	1.34	1.60	2.28
SO_3	0.27	0.27	4.11	1.69	1.62	1.16
TiO_2	1.07	1.17	0.15	0.29	0.37	0.54
P_2O_5	0.13	0.14	0.26	0.19	0.19	0.17
Cl^-	<0.01	<0.01	0.02	<0.02	<0.02	<0.02
LOI	15.18	3.09	2.79	2.92	2.93	2.95