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Effect of activated coal mining wastes on the properties of blended cement

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ABSTRACT

The large volumes of coal waste generated world-wide in mining operations are mostly deposited in refuse dumps, to the severe detriment of the surrounding groundwater and soil. After calcination under controlled conditions, this waste has been shown to exhibit high pozzolanicity, making it apt for use as an addition in the manufacture of blended cements.

The present paper describes the first detailed study designed to evaluate the behavior of coal tailings from different sources. After activation at 650 °C for 2 h, this waste was used to manufacture blended cements containing 10 and 20 wt.% of the addition. Inclusion of this pozzolan did not affect the initial setting time, although the compressive strength of the blended mortars declined, by 4.7–8.3% in the 10% and by 9.76–14.9% in the 20% material. Nonetheless, the activated carbon waste (ACW) blends complied with all the requirements for Type II/A cement in the existing European legislation.

1. Introduction

The intensification of environmental pollution in recent years has heightened society's awareness of the problems associated with the accumulation of industrial by-products and waste in refuse pits. One example of that awareness is the institution of environmental policies that encourage waste recycling as raw material in industry.

The cement industry is a prime contributor to the rise in CO_2 levels in the atmosphere. At the same time, however, it is better able than many others 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 the third respect, one of the industry's priorities is to find pozzolans that can be used in lieu of the materials conventionally added to clinker during cement manufacture [1–10]. Metakaolin (MK) is one such standard pozzolan, but its use has been largely constrained for social, economic and environmental reasons.

Aiming to further the use of MK, prior research focused on paper sludge as an alternative source of the mineral. Frías et al. [11–13] conducted studies on the scientific and technical grounds for its use as a new addition, and observed a substantial improvement in the performance of the resulting blended cements.

The valorization of coal tailings might be a new source of metakaolin-based pozzolans in the near future. According to Haibin and Zhening [14], this mining waste has become a primary environmental concern in China, where yearly production since 2007 is estimated at 315 million tonnes and where around 4.5 billion tonnes of such waste is stockpiled in pits. Many green industrial uses have been found for coal tailings: man-made eco-parks, power generation, fly ash in building materials, pipelines, electricity generation. In Spain, attendant upon the country's total 11 million-tonne coal output in 2009 was the generation of about 2 million tonnes waste. In Europe as a whole, 175 million tonnes of waste have been accumulating in dumps for decades, with the concomitant adverse economic, social and environmental impact.

The absence of suitable management of these pits often pollutes the surrounding soil and prevents the potential use of minerals required for other industrial purposes [15]. Despite these circumstances, the use of tailings as a pozzolan in cement manufacture is a new line of research barely explored to date.

The only review article in the literature, authored by Bealtramini et al. [16], describes the technical behavior of cement matrices bearing coal tailings activated at 600 or 800 °C. Subsequently, Frías et al. [17] studied reaction kinetics in terms of activation temperature (600–700 °C) in the activated coal waste (ACW)/calcium hydroxide system. They observed that the optimal tailing activation was attained by incinerating the material at 650 °C for 2 h.

Given the scant information available and the heterogeneity of coal waste, the present study aimed primarily to analyze the properties and technical behavior of blended cement pastes and mortars (10% and 20%) containing wastes from several mining sites, activated as described above, and ascertain whether they conformed to the European standard on the manufacture of commercial Type II/A cements.

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2. Experimental

2.1. Materials

2.1.1. Raw coal waste

Three samples of coal waste were used. Two were supplied by Picalin, an industrial group: coal sludge waste (CW1) generated during coal washing and coal gangue (CW2). The third sample, also coal gangue waste (CW3), was furnished by Santa Lucia Hullera, another industrial group. The chemical compositions of the raw waste are given in Table 1. Total organic carbon (TOC) was highest in CW1 (15.08%), followed by CW3 (2.48%) and CW2 (2.22%). Due to the presence of organic matter, the thermal activation of contributes to CO_2 emissions, although in lower proportions than Portland clinker manufacture (800 kg of CO_2 per t of clinker). Mineralogically, these waste contained illite (45–69%), kaolinite (20–27%), quartz (7–16%) and calcite (0–12%), with the percentage composition varying depending on the source (Table 2).

2.1.2. Thermally activated coal waste

Further to prior findings [17], the coal waste were thermally activated (ACW) at 650 °C for 2 h in a laboratory furnace to eliminate the carbon present and ensure that all the kaolinite would convert into metakaolinite. All the activated products were agate mortar-and-pestle ground to a particle size of under 45 μs. The chemical composition of the ACW is given in Table 3.

2.1.3. Cements

- The CEM I 52.5 R ordinary Portland cement (OPC) (as defined in the existing European standard) used was supplied by the Lafarge Cement Company's plant at Villaluenga de la Sagra (Toledo, Spain). All the cement particles were under 63 μm. The chemical composition of the OPC is given in Table 1.
- The blended cements were prepared in a high-speed powder mixer to guarantee homogeneity. The blends were calculated by weight, with ACW/OPC ratios of 0/100, 10/90 and 20/80. These replacement levels were adopted on the grounds of the ratios allowed for Type II/A cements (6–20%) [18].

2.2. Standard methods

2.2.1. Setting test

The rheological behavior of the blended cement pastes was assessed as described in standard EN 196-3 [19], using a Vicat apparatus to determine normal consistency and setting times.

2.2.2. Expansion test

The soundness of the blended cement pastes was found with a Le Chatelier test apparatus to the procedure specified in the European standard presently in effect [19].

2.2.3. Compressive strength

The effect of these additions on the mechanical behavior of new cements was ascertained as per standard EN 196-1 [20], which describes the methodology for testing mortar components, preparation, curing and strength. Blended cement mortar specimens measuring 4 × 4 × 16 cm were prepared with a sand/binder ratio of 3/1 and a water/binder ratio of 0.5.

Table 2
Mineralogical composition of raw coal mining waste (XRD).

	CW1	CW2	CW3
Illite	69	52	45
Kaolinite	20	22	27
Quartz	7	15	16
Calcite	–	2	12
Chlorite	4	3	–
Feldspars	–	4	–
Dolomite	–	2	–

Table 3
Chemical composition of ACW.

	Chemical composition (%)		
	ACW1	ACW2	ACW3
SiO_2	56.40	61.92	52.34
Al_2O_3	26.34	20.23	19.50
Fe_2O_3	6.42	6.77	8.35
CaO	1.06	2.00	8.41
MgO	1.07	1.57	1.21
K_2O	4.02	3.78	2.65
Na_2O	0.17	0.53	0.20
TiO_2	1.21	1.01	0.85
P_2O_5	0.20	0.15	0.17
MnO	0.06	0.10	0.14
SO_3	0.65	0.11	0.49
LOI	2.38	1.81	5.61
Trace elements (ppm)			
Cr	190	308	228
Cd	<DL	<DL	<DL
Ni	56	57	43
Pb	11	10	5
Zn	27	37	46

2.3. Characterization

Different techniques were used for chemical, physical, mineralogical and morphological characterization. Chemical composition was studied with a Philips PW-1404 780 X-ray fluorescence analyzer fitted with an Sc–Mo anticathode tube. Color parameters were quantified with a Minolta CM-2500d portable spectrophotometer able to determine the L^* a^* b^* color space (L^* being lightness and a^* and b the chromaticity coordinates) defined by the CIE (Commission internationale de l'éclairage) in 1976 [21]. Fineness was analyzed by laser ray diffraction (LRD) on a Sympatec Helos 12 KA spectrometer using isopropyl alcohol as the non-reactive liquid [22]. Material mineralogy was determined with X-ray diffraction (XRD) using random powder mounts for the bulk sample and oriented slides for the <2-μm fraction. The samples were analyzed with a SIEMENS D-500 Cu anode diffractometer operating at 30 mA and 40 kV (2-mm divergence slit; 0.6-mm reception slit; 2θ goniometer; step size: 0.04; count time: 3 s).

Table 1
Chemical composition of raw materials (XRF).

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	LOI
OPC	20.16	4.36	2.52	63.41	2.21	0.35	0.91	0.21	0.14	3.57	1.99
CW1	43.70	21.35	5.57	0.89	0.77	0.11	0.16	1.05	0.16	1.02	25.18
CW2	57.20	18.69	6.25	1.86	1.42	0.46	3.59	0.95	0.14	0.08	9.28
CW3	46.86	17.15	7.67	7.60	0.99	0.15	2.40	0.78	0.16	0.34	15.80

3. Results and discussion

3.1. Chemical composition of blended cements

Fig. 1 shows the XRF findings for the activated coal waste blended cements. These blended cements consisted primarily of CaO (50–58%), SiO_2 (23–29%) and Al_2O_3 (6–9%). The minority components included Fe_2O_3 (3.0–3.7%), SO_3 (3.0–3.3%), MgO (2.0–2.2%) and K_2O (1.1–1.5%) and traces (<0.4 wt.%)of MnO, Na_2O, TiO_2 and P_2O_5. Loss on ignition (LOI) values varied from 1.97% to 2.72%, with the highest values observed for the blended cements made with ACW3 due to the presence of calcite (12%). The 10% or 20% ACW blended cements had higher silica and alumina contents and a lower lime content than the OPC. This can be attributed to the silico-aluminous nature of the ACW and the predominance of silica–calcium in OPC. These findings were similar to the results for other types of pozzolans analyzed in SiMn blended cements [7].

Table 4 compares the sulfate and chloride contents in the OPC and blended cements analyzed to the chemical requirements laid down in the existing European standard for Type II/A cements [18]. All the cements containing 10% or 20% ACW proved to be standard-compliant.

Table 4
Chemical requirements for ACW blended cements.

Cement EN standard requirement	SO_3 (%) ⩽4.0	Cl^- (%) ⩽0.10
10% ACW1	3.28	<0.02
20% ACW1	2.99	<0.02
10% ACW2	3.23	<0.02
20% ACW2	2.88	<0.02
10% ACW3	3.26	<0.02
20% ACW3	2.96	<0.02
OPC	3.57	0.02

3.2. Fineness of blended cements

In light of the important role played by material fineness in the behavior of cement matrices, the fineness and particles sizes of ACW blended cements were determined with laser granulometry. Fig. 2 shows both the particle size distribution and the density curves. The particle size distribution curves (top) were similar for all the ACW matrices, and in fact concurred between 0.9 and 175 μm. According to these curves, all the particles in the blended cements passed through the 87-μm sieve, while 50% of the particles were smaller than 12–12.5 μm and 10–10.5 μm in the blended cements prepared with 10% and 20% ACW, respectively. With respect to the density curves, two maxima were observed in all cases: a primary peak at 15–35 μm, mainly attributed to the clinker particles, and a secondary peak at 5–7 μm consisting largely of ACW particles. The curves in the bottom half of Fig. 2 clearly show that the replacement ratio induced visible changes in density, which was greater for all the 20% ACW blended cements than for the 10% ACW materials.

Finally, the real density values and laser granulometry findings were used to specific surface of the cements given in Table 5. As the table shows, the values ranged from 4500 to 5600 cm^2/g.

3.3. Rheological properties of blended cements

The rheological studies focused on water content at normal consistency and the determination of setting times as per European standards [19]. The water content at normal consistency for all the activated coal waste pastes followed the same pattern despite the variable origin of the ACW used. In general, the addition of activated tailings raised the water demand with respect to the control. Moreover, the higher the replacement ratio, the higher was the demand (Table 6). Adding 10% ACW raised the water demand by 4.7%, while with a 20% addition, demand rose by 12.1%, except in the cement prepared with 20% ACW3, where the rise was 12.8%. These findings reflect the greater fineness of the ACW than the OPC material. That circumstance had a direct effect on the consistency of blended cement mortars (Table 7), for which a water/binder ratio of 0.5 was used, pursuant to the standard in effect [18]. The inclusion of ACW lowered consistency by 6–10% in 10% blended cement mortars and by 12.7–19.8% in the 20% materials.

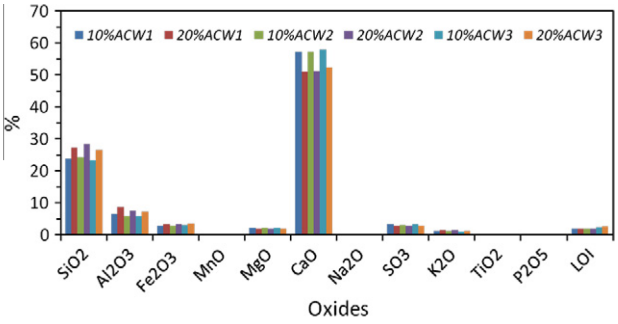


Fig. 1. XRF chemical composition of the blended cements.

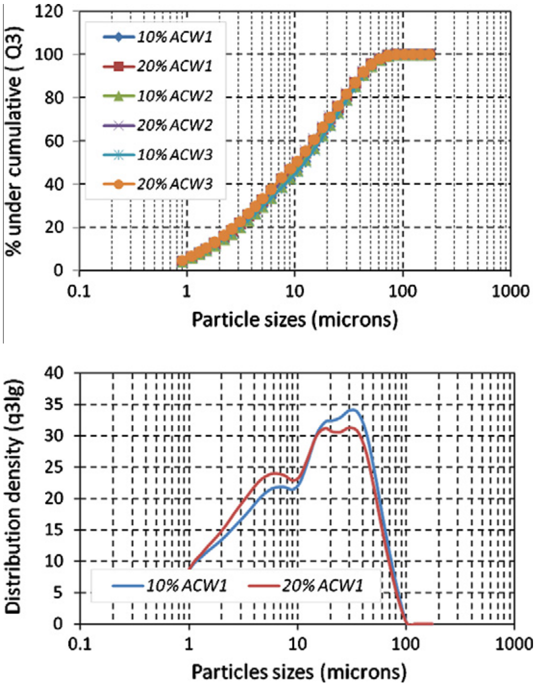


Fig. 2. Particle size distribution: cumulative (top) and density (bottom) curves.

Table 8 gives the initial and final setting times (±15 min) for the blended cement pastes studied, found as specified in the existing European standard [19]. The addition of ACW to the cement pastes clearly caused no material change in the initial and final setting times. The addition of 10% ACW to the cement paste had no effect whatsoever on the initial setting time; the minor differences between the values for the three blended cements can be attributed to testing error (±15 min). Raising the percentage of activated coal waste from 10% to 20% in the pozzolan blended cements delayed the initial setting time slightly, from 145 min for OPC to 170 min for ACW2 and ACW3. This delay might be related to the possible presence of low concentrations of heavy metals such as cadmium

Table 5
Specific surface and density values for blended cements.

Cements	10% ACW1	20% ACW1	10% ACW2	20% ACW2	10% ACW3	20% ACW3
S.S. (cm^2/g)	5058	5640	4496	4894	4515	5013
Density (g/cm)	2.69	2.52	3.02	2.91	2.99	2.94

Table 6
Relative water content (%) in blended cements.

Cement	10% ACW1	20% ACW1	10% ACW2	20% ACW2	10% ACW3	20% ACW3
W. content (%)	4.7	12.1	4.7	12.1	4.7	12.8

Table 7
Blended mortar consistency (mm).

Mortar	Control	10% ACW1	20% ACW1	10% ACW2	20% ACW2	10% ACW3	20% ACW3
Consistency	166	149	133	151	139	156	145

Table 8
Setting times (±15 min) for ACW blended cements.

Cement pastes	Initial set (min)	Final set (min)
OPC	145	260
10% ACW1	140	225
20% ACW1	155	245
10% ACW2	145	230
20% ACW2	170	260
10% ACW3	135	230
20% ACW3	170	260
EN standard requirement	⩾45, 60 and 75 min	Not specified

Table 9
Cement paste volume stability.

Cement pastes	Expansion (±0.5 mm)	Standard (mm)
OPC	0.5	⩽10
10% ACW1	0.5	
20% ACW1	0.5	
10% ACW2	0.5	
20% ACW2	0.5	
10% ACW3	0.5	
20% ACW3	0.5	

and nickel in coal ash [14]. According to the XRF analysis (Table 3), the ACW contained a number of minor elements, including chromium (190–308 ppm), nickel (43–57 ppm), lead (5–11 ppm) and zinc (27–46 ppm). Cadmium, which is known to raise the setting time in Portland cements [23], was not detected by XRF (value below the detection limit).

This behavior is contrary to the findings reported by Vegas et al. [24] for other cement pastes containing activated kaolinite-based wastes (10% activated paper sludge). Those authors reported a 23.5% decline in initial setting time in 10% activated paper sludge blended cements, which they attributed to the presence of calcite, a mineral known to accelerate setting by both physical and chemical mechanisms [1].

The final setting time for the blended cements followed the same trend as the initial setting time, although this parameter is not addressed in the standard.

3.4. Volume stability

The expansion test was conducted as specified in EN 196-3 [19]. The findings for the three blended cements (average of three measurements with a 0.5-mm test error) given in Table 9 show that the addition of ACW had no effect on cement paste volume stability.

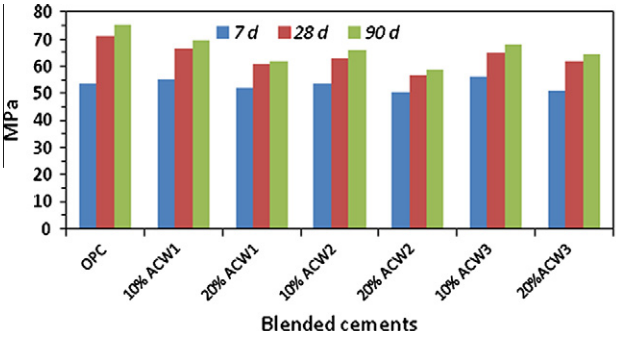
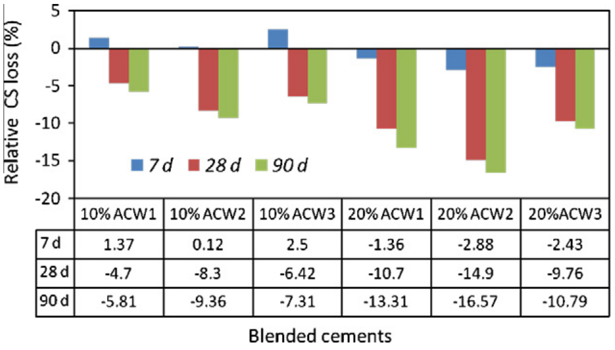


Fig. 3. Compressive strengths vs reaction time.



	10% ACW1	10% ACW2	10% ACW3	20% ACW1	20% ACW2	20%ACW3
7 d	1.37	0.12	2.5	-1.36	-2.88	-2.43
28 d	-4.7	-8.3	-6.42	-10.7	-14.9	-9.76
90 d	-5.81	-9.36	-7.31	-13.31	-16.57	-10.79

Fig. 4. Compressive strength loss.

3.5. Compressive strength

Fig. 3 shows compressive strength over time (average of six specimens). On the whole, the ACW blended cement mortars exhibited lower compressive strength than the OPC mortar. At early hydration ages (7 days), compressive strength was similar in all the mortars, while at longer reaction times (28 and 90 days) strength depended on the origin of the ACW and the replacement ratio.

The strength patterns are shown in greater detail in Fig. 4. The decline in compressive strength in blended cement mortars can be calculated from the OPC mortar values at different hydration times.

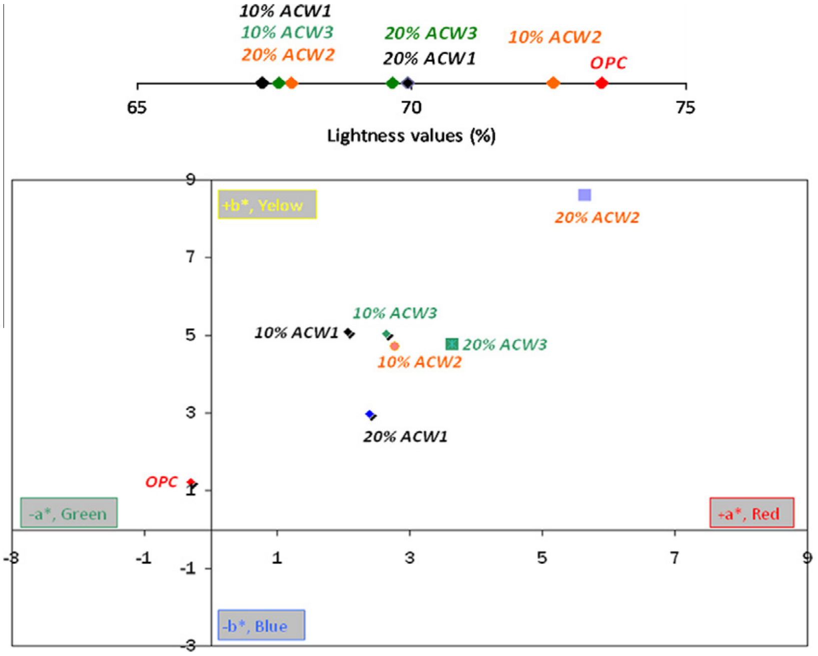


Fig. 5. L^* (top) and a^* and b^* (bottom) parameters in cements.

As Fig. 3 shows, 7-day strength rose slightly in the blended cement mortars containing 10% ACW, dipping in the 20% mortars, albeit by less than 3%. Thereafter, strength declined both with rising curing times and percentage of activated waste. ACW2 exhibited the poorest mechanical performance, with 90-day strength losses of 9.36% and 16.57%.

Strength loss in ACW blended cement with rising hydration time may be regarded as an exception among activated materials. Other such materials (fly ash, SiMn slag) exhibit lower compressive strength at early ages but 90-day values similar to the control mortar due to the ongoing progression of the pozzolanic reaction [1,7]. This behavior also differed substantially from other kaolinitic waste such as activated paper sludge, which shows early age strength gains [25].

No scientific explanation for this behavior can presently be put forward because of the novelty of the research and the absence of prior studies. Further to earlier research [23], the decline might be the result of the presence of heavy metals in either the coal tailing ash or the cement. That explanation is not consistent with the setting time findings, however. By contrast, in a previous paper, Frías et al. [17] reported high pozzolanic activity in these activated products in ACW/$Ca(OH)_2$ systems (80–90% of lime fixed between the 28th and 90th day) and identified CSH gels, C_4AH_{13} (Si/Al = 0.54), C_2ASH_8 (Si/Al = 0.83) and LDH compounds (hydrotalcite-like structures) (Si/Al = 1.15) as the main products of the pozzolanic reaction. Such activity was clearly not reflected in the mechanical behavior in the present study, although the strength losses in the 28-day blended cements came to about 50% of the replacement ratio, especially in ACW1 and ACW3. Consequently, further long-term research ($\geqslant$90 days) must be conducted to explain this mechanical behavior.

Despite the foregoing, all the ACW blended mortars had 28-day compressive strength values higher than recommended by the existing European standard ($\geqslant$52.5 MPa) for class 52.5 N and R cements.

3.6. Color of blended cement mortars

One factor to be taken into account in industrial waste recycling for use as active additions is the color of the resulting cement matrices, for these additions may alter the original gray tone of commercial cement.

Fig. 5 shows the lightness (L^*) (top) and chromaticity coordinate (a^* and b^*) (bottom) values. According to these findings, the addition of ACW to the cements lowered the OPC lightness (L^*) value slightly, by 8%. The a^* and b^* chromaticity values obtained for the ACW blended cement mortars (Fig. 5, bottom) were positioned toward yellow[1] and red, unlike the values for OPC. These characteristics of ACW blended cements could prove to be an advantage in stained cement and mortar manufacture, a sub-industry with a very promising future.

4. Conclusions

The conclusions drawn from the experimental results and patterns of behavior discussed above are as follows:

1. The silico-aluminous nature of activated coal mining waste led to higher silica (SiO_2) and alumina (Al_2O_3) contents in the blended cements containing 10% and 20% ACW than in the OPC, while the lime (CaO) content in the blended cements was lower than in the reference material.
2. The addition of ACW to the cement paste raised the water demand by 4.7% in pastes with a 10% addition and by 12.1–12.8% in the pastes containing 20% ACW.
3. Type II/A Portland cement pastes prepared with 10% and 20% ACW were European standard-compliant in terms of sulfate and chloride content.
4. The ACW blended cement pastes also met setting time and volume stability requirements.
5. Compressive strength in mortars with activated coal waste followed two trends: while up to 7 days, strength values were lightly higher than in OPC, they declined over time

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[1] For interpretation of color in Figs. 1–5, the reader is referred to the web version of this article.

and with rising ACW content. Nonetheless, all the blended cement mortars complied with the mechanical requirements laid down in the existing standards.
6. ACW blended mortars had lower L^* values than OPC and yellow–red hues not found in the reference material.

By way of summary, the use of activated coal waste as a pozzolanic material in blended cements is technically viable. The behavior of the three ACW pozzolans in blended cements was similar, despite their different origins. Further research is needed, however, before this knowledge can be transferred to the industry.

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