

USE OF COAL MINING WASTE AS POZZOLANIC MATERIAL IN NEW BLENDED CEMENT MATRIXES

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Abstract

Research and eco-innovation geared to obtain alternative sources of raw materials from waste constitute pathways for enhancing the competitiveness of resource-intensive industries. Cement and concrete manufacture calls for new sources of new, highly pozzolanic products to improve the mechanical properties and durability of the resulting matrices, while at the same time reducing production costs and environmental impact.

Spanish coal mining wastes generated in the extraction and washing steps from a mine in the Castilla-León region were investigated. Mineralogically, these wastes are composed by kaolinite (20-30%), illite (45-70%) and quartz (5-15). This composition is very interesting in order to activate, by controlled thermal activation, the present kaolinite that generates metakaolin, a highly pozzolanic product. Morphological, textural and microstructural changes affect the activity and reactivity of activated wastes.

These first studies open up a new research line, practically unknown to the international research community, and stand out the important economic and environmental benefits associated with the recycling of these wastes as supplementary cementing materials for future commercial blended cements.

1. Introduction

The Europe 2020 Strategy is a commitment to the future that will enable the continent to surmount the present circumstances and turn the EU into an intelligent, sustainable and integrated economy with higher levels of productivity, employment, eco-efficiency and social cohesion. One of the vehicles for research and innovation in this decade should be development and acknowledgement of the value of new processes, technologies and products with a reduced carbon footprint and a low energy input, to strengthen the competitive advantage of both large corporations and small and medium-sized enterprises

(SMEs). In that context, resource efficiency, including the valuation of the waste generated by productive activities in the form of materials or energy, stands as a priority option for action. Strategies that promote the rotation of large volumes of industrial waste and by-products in productive cycles can therefore exploit an attractive niche of economic opportunity. Construction plays a bilateral role in waste generation and valuation. It generates vast volumes of waste and has an obvious potential to recycle not only its own waste, but also waste and by-products from other industries. One consequence of the stockpiling of coal mining waste has been the study of eco-innovative solutions for its valuation [1] with a view to systematically recovering the embedded mineral and energy resources at the lowest possible environmental cost. Some of the co-authors of the present paper carried out the first studies on the characterization and pozzolanic properties of Spanish coal mining waste [2, 3]. The chemical composition of these coal wastes was as follows: SiO₂ (43-57%), Al₂O₃ (17-21%), Fe₂O₃ (5-8%). The percentage variations reflect the source of the two coal wastes: coal gangue waste and coal washing waste. The other oxides were below 4%. Its mineralogical phases were quartz and phyllosilicates such as kaolinite and micas. The conversion of these polluting coal mining waste into non-hazardous pozzolanic products activated coal mining waste for use in the manufacture of new eco-efficient cement matrices constitutes a priority.

2. Materials and methods

2.1. Materials

Coal gangue mining waste was recovered from a Spanish coal Group (Sociedad Anónima Hullera Vasco-Leonesa), located in the province of León (Santa Lucía): coal gangue waste from an open-cast mine, deposited in a landfill. The selected coal mining waste was activated at different temperatures of 500, 600, 700, 800 and 900°C for 2 hours in an electric laboratory furnace. All samples were ground to particle sizes less than 63 μm, which were then analyzed with laser granulometry, in an agate mortar and pestle [4].

2.2 Methods

The pozzolanic behavior in a pozzolan/calcium hydroxide system was studied using the solid residues after applying an accelerated chemical method elsewhere. After one, seven and twenty eight days of reaction, the residues obtained were washed with acetone and dried in an electric oven at 60°C for 24 hours, in order to stop the pozzolanic reaction. The content of fixed lime was calculated as the difference between the CaO concentration in the original saturated lime solution (17.68 mmol/l) and the content of this compound in the solution at the established time. The calcium hydroxide used was an extra pure Ph Eur, USP, BP chemical reagent.

Chemical characterization was carried out by X-ray fluorescence (XRF), using a Philips PW 1404 and X-ray tube of Sc-Mo. Fineness was analyzed by Laser Ray Diffraction (LRD), using a Sympatec Helos 12 KA spectrometer and isopropyl alcohol as a non-reactive liquid [5].

The mineralogical composition of the bulk samples was determined by random powder X-ray diffraction (XRD) and the <2 μm fraction by the oriented film method, in both cases on a Siemens D-5000 X ray diffractometer fitted with a Cu anode. Their operating conditions were 30 mA and 40 kV with a divergence slit=2 mm and a reception slit=0.6 mm,

respectively. The samples were scanned in (2 θ) 0.041 steps with a 3-s count time. The characterization and semiquantification of bulk samples was performed using the random power method operating from 3° to 65° 2 θ at a rate of 2°/min, and the capture of phyllosilicates was determined in the <2 μ m fraction using the oriented slides method, operating from 2° to 40° at scanning rate of 1°/min. SEM/EDX morphological observations and microanalysis of the samples were performed with an Inspect FEI Company Electron Microscopy, equipped with energy dispersive X-ray analyzer (W source, DX4i analyzer and Si/Li detector).

FTIR analyses were performed using a spectrometer Thermoscientific NICOLET 6700 with a DGTS CsI detector and 64 scans were recorded to register each sample. Specimens were prepared by mixing 1 mg of the sample in 300 mg of KBr. The spectral analysis was performed in the range 4000–400 cm⁻¹ with a spectral resolution of 4 cm⁻¹.

Dispersive Raman spectra at 633 nm were recorded with a Renishaw Raman Microscope System RM2000 equipped with a Leica microscope, an electrically refrigerated charge-coupled device camera (CCD), a 785 nm diode laser, and a 633 nm He–Ne Renishaw RL633 laser. The frequency was calibrated using the 520 cm⁻¹ line of silicon and the spectral resolution was set at 4 cm⁻¹. Spectra were recorded in triplicate, using an x50 objective lens, over wavenumber ranges 4000–100 cm⁻¹. The exposure time was 10 s, and each spectrum was accumulated 10 times.

3. Results and discussion

3.1. Characterization of starting coal mining waste

The chemical results for the coal-mining wastes obtained by XRF are formed by SiO₂ (49.8%), Al₂O₃ (21.8%), Fe₂O₃ (4.0%), CaO (3.8%) and K₂O (2.1%) as their main oxides. The loss on ignition value (LOI) was 26.47% of the total mass, mainly due to the different processes of decarbonation of calcite and dehydroxylation of kaolinite.

The mineralogical composition obtained by XRD of the waste shows the presence of phyllosilicates such as micas (25%) and kaolinite (14%), and quartz (37%), calcite (17%), dolomite (5%) and feldspars (2%). The phyllosilicates are the ones responsible for the pozzolanic activity, since it is known [6, 7] that thermal activation in air at 600°C–900°C of many clay minerals leads, by dehydroxylation, to breakdown or partial breakdown of the crystal lattice structure forming a transition phase with high reactivity. The clay is in its most reactive state when the activation temperature leads to loss of hydroxyls and results in a collapsed and disarranged clay structure. The calcining temperature of kaolinite that produces the active state of metakaolinite is within the range of 600°C–800°C [8]. The mica requires temperatures in excess of 930°C to activate and, even so, generally result in poor pozzolans.

3.2. Activated coal mining waste characterization

The study of XRD patterns for the activated products at different temperatures is shown in Figure 1. The spectra showed the power data for low quartz, the kaolinite disappeared at 600°C/2 hours of thermal activation, due to the transformation into metakaolinite. The treatments from 700°C to 900°C involved dehydroxylation and the formation of quasi-stable dehydroxylated mica. The dioctahedral micas give quasi-stable dehydroxylated

phases, but the trioctahedral micas tend to dehydroxylate and recrystallize more or less contemporaneously. The dehydroxylation of the 2:1 layers for the mica occurred at higher temperatures [9]. At 600°C/2 hours, a peak appeared at 2.69Å (33.30 2θ), which is attributed to the formation of hematite. On further heating from 700°C to 900°C, the hydrous oxides and the ferrous hydroxides, originally present on the coal mining waste, lost water to form well crystallized hematite. From 600 to 900°C, reflections at 2.43Å (36.98° 2θ) and 2.85Å (31.38° 2θ) indicating the presence of spinel-like phases [10].

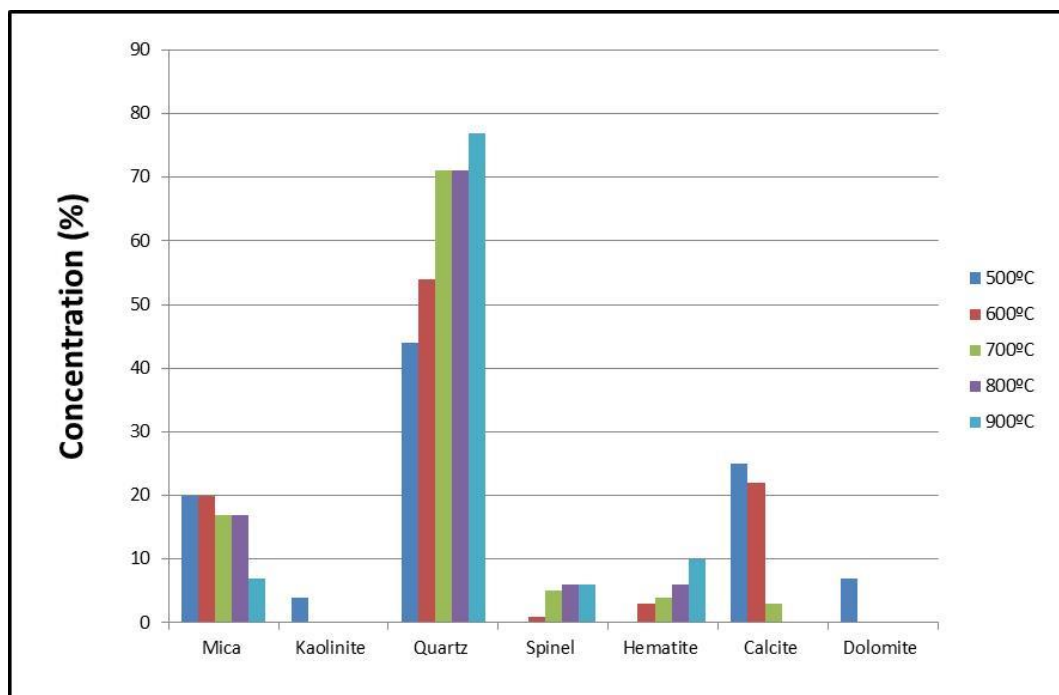


Figure 1. Mineralogical changes in the composition of activated waste at different temperatures.

FTIR results revealed the main mineralogical compounds identified from XRD analysis (Table 1).

Phase	Bands (cm ⁻¹)
kaolinite	3696, 3656, 3620, 1032, 1007, 912, 751, 798, 778, 694, 472, 535
mica	3628, 3545, 3423, 751
carbonate group	1426, 874
quartz	1090

Table 1. Principal wavenumbers by FTIR.

A Raman spectrum of coal waste showed two bands at 1597 and at 1346 cm⁻¹ corresponding to G (graphite peak) and D (disordered peak) bands, respectively, from carbon. A Raman spectrum differs from different carbon materials with Raman spectra of graphite monocrystal presenting only one band at 1575 cm⁻¹; a second line appears near to 1355 cm⁻¹ for all other graphitic materials such as activated charcoal, carbon black, and vitreous carbon. Raman spectra of the activated waste showed that intensity of the peaks decreases with increasing temperature. From 700°C, intensity of the bands is negligible. Moreover, the shape of the Raman carbon bands changed with the temperature, with a reduction in the intensity of both peaks. This reduction can be an indication of carbon combustion with CO and CO₂ emissions.

3.3. Pozzolanic activity of activated coal mining wastes

The formation of reactive metakaolinite at 600°C and the presence of mica with a low crystallinity, at 900°C is used to evaluate the pozzolanic activity of coal mining wastes calcined at 600°C and 900°C for 2 hours of retention. This observation reveals the influence of clayey minerals on both pozzolanic activity and the reaction kinetics.

The pozzolanic activity for the activated coal waste at 600°C and 900°C at 1, 7 and 28 days of reaction was evaluated. The results obtained under these conditions showed that the reaction rate was higher for the activated coal waste at 600°C than for the activated at 900°C, at short reaction times (1-7 days); both activated products showed a high pozzolanic activity in terms of the fixed lime results for the longer reaction times (28 days). Hence, 600°C/2 hours retention time is recommended as a suitable activation condition for coal waste from energetic and economic points of view, which were therefore the conditions selected for the research.

3.4. Identification and evolution of hydrated phases in activated coal waste/Ca(OH)₂ systems

Analysis of the activated coal waste by XRD (at 600°C and 900°C for 2 hours) up to 28 days of reaction (Figure 2) showed, in all cases, the crystalline hydrated phases during the pozzolanic reaction: a) tetracalcium aluminate hydrate; b) stratlingite; c) monosulfoaluminate hydrate and d) LDH compounds (phyllosilicate/carbonate). Their contents and evolution varied depending on the time and the activation conditions. Monosulfoaluminate hydrate was formed from one day of the reaction, as a consequence of the reaction between the reactive alumina of the pozzolan, tetracalcium aluminate hydrate was detected as traces at short reaction times; at 28 days of reaction, a slight increase of its content was observed in activated coal waste activated at 600°C/2 hours. However, the last one that was the predominant phase of the pozzolanic reaction in activated coal waste (at 900°C/2 hours) at 7 and 28 days. LDH compounds were formed from one day of the reaction in activated coal waste at 600°C/2 hours, passing to predominant phase from seven days of reaction.

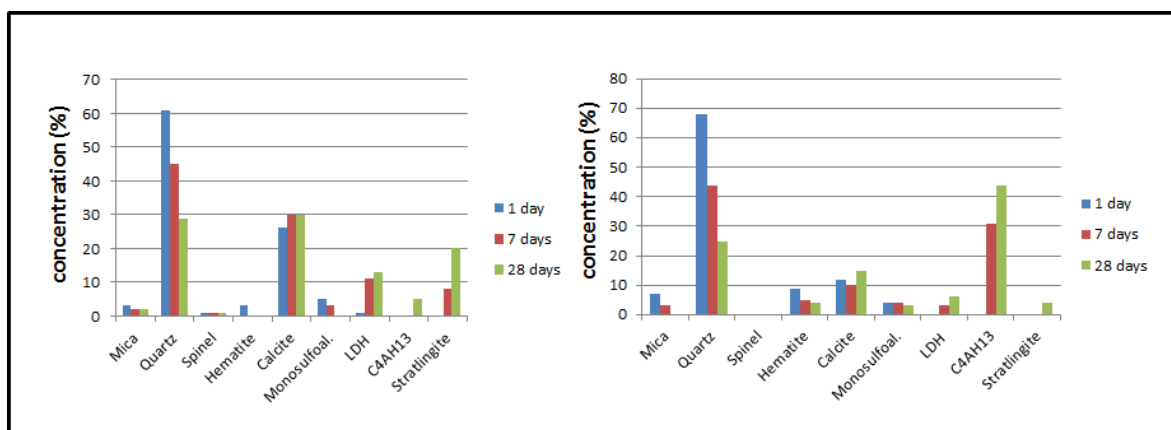


Figure 2. Evolution of hydrated phases in activated coal waste/Ca(OH)₂ systems, left: at 600°C/2 hours; right: at 900°C/2 hours.

Activation at 900°C reduced the formation of LDH compounds. The stratlingite was only formed at 28 days. The kinetic behavior of activated coal waste/Ca(OH)₂ system is

different to that observed in for the reaction between pure metakaolinite and calcium hydroxide: aluminum containing CSH gel, together with crystalline products, which include metastable phases such as calcium aluminate hydrates (C_4AH_{13}) and aluminate silicate hydrates (C_2ASH_8), and stable phases belonging to the hydrogarnet family (C_3AH_6 - C_3ASH_6) were identified [11-14].

At $pH > 10$, $Al(OH)_4^-$ is the dominant specie in solution, these ions start to combine with the readily available Ca^{2+} ions via metastable phases forming C_3AH_6 . The total dissolved silica concentration in equilibrium with quartz or amorphous silica will increase at high pH values. The total dissolved silica concentration will be the sum of the ionized and un-ionized species (H_4SiO_4 , $H_3SiO_4^-$ and $H_2SiO_4^{2-}$). If the total silica concentration in the solution becomes supersaturated with respect to amorphous silica, begins to form polymers which combine with the Ca^{2+} ions forming CSH gels and with $(CO_3)^{2-}$ ions via metastable phases forming LDH compounds [15].

These ions react with the previously formed C_3AH_6 to form C_2ASH_8 . High metakaolin contents were attributed, in part, to the formation of increased amounts of C_2ASH_8 and reduced amounts of C_4AH_{13} as the metakaolin content increased [16]. In this study, following the activation process of activated coal waste at $600^\circ C/2$ hours, the presence of high metakaolinite content and some form of alumina and silica sheet structures favored the formation of LDH compounds, forming stratlingite as the reaction proceeded, the latter being the predominant phase of the pozzolanic reaction at 28 days. The appearance of C_4AH_{13} is attributed to supersaturation of the aqueous phase with respect to calcium hydroxide and low metakaolinite contents.

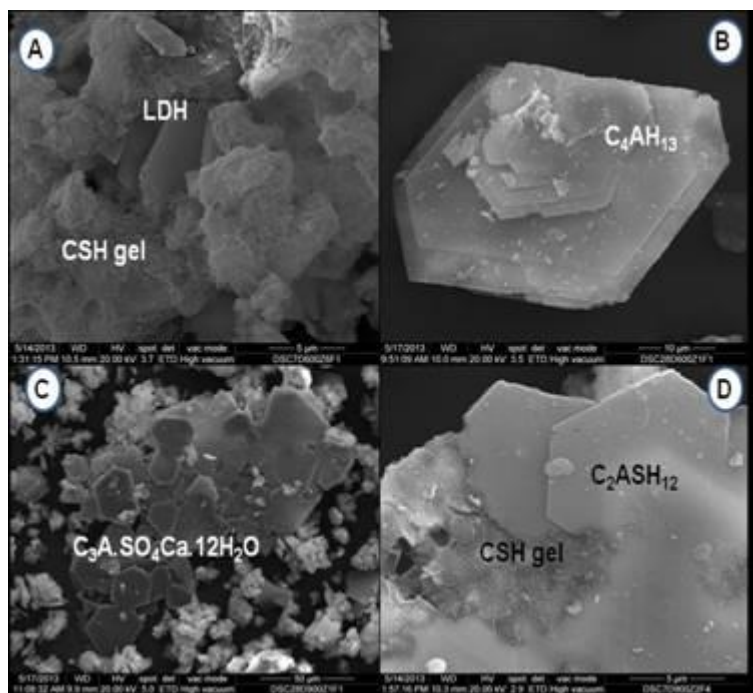


Figure 3. Morphological aspect of the CSH gel, C_4AH_{13} and LDH compounds at $600^\circ C/2$ hours (A and B). Morphological aspect of the CSH gel, $C_3A.SO_4Ca.12H_2O$ and C_2ASH_{12} at $900^\circ C/2$ hours (C and D).

SEM revealed the existence of laminar microaggregates of silica enriched composition, showing very porous surfaces upon the surface of which CSH gels were identified, more abundant in activated coal waste at $600^\circ C/2$ hours, with a spongy appearance in all cases.

The Ca/Si (CaO/SiO₂) ratio varied from 1.26 in activated coal waste 600°C/2 h to 1.73 in activated coal waste 900°C/2 hours. According to Taylor's classification [17], it would correspond to I-type gels in activated coal waste 600°C/2 hours and II-type gels in activated coal waste 900°C/2 hours. Laminar phase, interwoven with the gels, corresponded to LDH compounds, stratlingite, monosulfoaluminate hydrate and tetracalcium aluminate hydrate in a wide range of sizes (Figure 3).

4. Conclusions

The mineralogical composition of the starting wastes shows the presence, at different percentages, of phyllosilicates (micas and kaolinite), quartz, calcite, dolomite and feldspars.

Thermal treatment (500°C-900°C) involved dehydroxylation and the formation of quasi-stable dehydroxylated phases. Hematite and spinel-like phases are formed between 600°C and 900°C.

Raman spectroscopy is an adequate technique to study structural characterization of carbon. The Raman spectra of C present in the samples showed changes in both the intensity and the frequency of D (disordered structures) and G (graphite) carbon bands as the temperature increased. At temperatures higher than 600°C, combustion of amorphous carbon occurred.

The fixed lime results showed that the activated coal mining product obtained at 900°C/2 hours presented low activity over the first 7 days of the reaction period, while the products obtained from activated coal mining 600°C/2 hours revealed a high activity at one day (65% of fixed lime). At 28 days of curing, the fixed-lime contents showed greater similarity in both cases.

At 600°C/2 hours the abundance of metakaolinite and tetrahedral and octahedral layers from the dehydroxylation of mica favor the formation of LDH compounds and stratlingite as stable phases of the pozzolanic reaction. The appearance of C₄AH₁₃ as a stable phase at 900°C/2 hours is attributed to supersaturation of the aqueous phase with respect to calcium hydroxide and low metakaolinite, and tetrahedral and octahedral layers from the dehydroxylation of the mica content.

The results obtained from SEM/EDX techniques showed that the C-S-H gels are one of the main hydrated phases during the pozzolanic reaction in the activated coal mining/Ca(OH)₂ systems. The sulfur contained in the starting coal mining favoured the formation of monosulfoaluminate hydrate from the first day of the reaction period.

In summary, the research reported in the present study has stated the scientific viability of using coal mining waste as an active addition for the future manufacture of eco-efficient cements. According to their findings, the authors of the present work recommend 600°C/2 hours retention time as the best activation conditions to transform an inert material into a supplementary cementing material for future eco-efficient cements.

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