

Article

The Transformation of Coal-Mining Waste Minerals in the Pozzolanic Reactions of Cements

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Abstract: The cement industry has the potential to become a major consumer of recycled waste materials that are transformed and recycled in various forms as aggregates and pozzolanic materials. These recycled waste materials would otherwise have been dumped in landfill sites, leaving hazardous elements to break down and contaminate the environment. There are several approaches for the reuse of these waste products, especially in relation to clay minerals that can induce pozzolanic reactions of special interest in the cement industry. In the present paper, scientific aspects are discussed in relation to several inert coal-mining wastes and their recycling as alternative sources of future eco-efficient pozzolans, based on activated phyllosilicates. The presence of kaolinite in this waste indicates that thermal treatment at 600 °C for 2 h transformed these minerals into a highly reactive metakaolinite over the first seven days of the pozzolanic reaction. Moreover, high contents of metakaolinite, together with silica and alumina sheet structures, assisted the appearance of layered double hydroxides through metastable phases, forming stratlingite throughout the main phase of the pozzolanic reaction after 28 days (as recommended by the European Standard) as the reaction proceeded.

Keywords: metakaolinite; micas; coal-mining waste; LDH (layered double hydroxides); pozzolanic reaction

1. Introduction

A key vector of opportunity in the construction sector, in general, and for manufacturers of cement-based materials, in particular, is the efficient use of materials and energy resources, which moderates the carbon footprint of the final products. Our production of cements, mortars, and concretes, the most widely manufactured materials on the planet, involves energy-intensive exploitation of raw materials that remains a source of extremely high CO₂ emissions.

The research, validation, and enhancement of new mineral additives for cement should ensure their availability in sufficient quantities for profitable investments, thereby reducing the environmental impacts of Portland-cement-clinker production, the overall volume of waste products, and the energy consumption of the final product. These additives also assist reactivity that densifies the hydration products.

The coal industry, more than any other sector, has one of the most negative effects on the environment. Coal waste (in abundant amounts from various extraction processes) is disposed

of in landfills or is incinerated [1]. The use of coal waste to prevent environmental impacts has been explored in China [2] and elsewhere [3], especially in relation to building [4].

Coal-mining waste from the extraction and washing of debris from mines contains kaolinite, illite, and quartz of varying composition according to geological conditions and methods of extraction and purification. Above all, the composition of claystones generally consists of illite and kaolinite. Ferrous minerals, quartz, and carbonic matter may also be found in small amounts. All carboniferous rocks may also contain dolomitic veins, pyritic encrustations, and extensive quantities of plant detritus [4].

Pozzolans found in industrial waste have been linked to environmental and technological advantages that have driven research into their use. The incorporation of these industrial by-products and wastes together with natural materials in various production stages of blended cements was first prioritized in the cement industry. Experimentation with rice husk, fly ash, and palm oil has all been reported in the literature [5–8]. Materials with “pozzolanic” properties are linked to siliceous/aluminous materials. When added to water as fines, they can form cementitious properties in reaction with $\text{Ca}(\text{OH})_2$ [9]. Another class of pozzolans is from natural raw sources (volcanic material, limestone) or calcined materials (burnt shale, calcined kaolinite) with pozzolanic properties [10,11]. Blended with lime, their use in construction projects has been documented throughout history; natural pozzolans from magma deposits following volcanic activity have been added to mortars since classical antiquity. Natural pozzolans continue to be applied in many cement manufacturing processes to this day.

Calcined clays with pozzolanic activity draw structural water from the layers of crystalline clay, leaving amorphous or semi-amorphous materials with high surface areas and chemical reactivity.

Thermal activation of kaolinite at controlled temperatures produces metakaolinite, a product with highly pozzolanic properties. The investigation of thermal activation, within the ranges of between 650 and 750 °C with kaolinite-containing waste, resulted in products with a high latent pozzolanicity [12–18].

The works of Li et al. [19] and Beltramini et al. [20] pioneered the study of cement matrices containing activated coal-mining waste, providing useful results for future research. However, performance criteria at the percentages of coal-mining waste that they added and its activation conditions still require further research. Currently, studies in this investigative field are multiplying [21–23].

In this paper, the mineralogical transformations of coal waste are studied across a range of temperatures (500–900 °C) for the establishment of optimum calcination conditions that yield products with sufficient pozzolanic properties to be used as additives in the manufacture of cements and related materials.

2. Materials and Methods

2.1. Materials

Mining generates high volumes of waste that are currently dumped in slag heaps of no apparent utility. Our study concerns coal-mining waste supplied by a coal-mining company (Sociedad Anónima Hullera Vasco-Leonesa) in Santa Lucía (Province of León, Spain). The mine supplies coal to the power plant in the region of La Robla, and the mine waste employed in this study is used in a cement factory in the same region.

The geological materials from La Robla vary greatly. They are separated by easily identifiable irregularities and contain a variety of rocks: metamorphic shales and sedimentary limestone and dolomite with *Facies Utrillas* (detrital deposit formed in a sedimentary environment of river systems). Igneous activity is very low and only found in small porphyry dikes [24].

The waste products from that area are reasonably uniform and contain white quartzite with highly recrystallized micro-conglomerates, feldspar mixed with sandstone, foliated slate (containing

phyllite with mica and quartz, sericite, chlorite, zircon, pyrite, monazite, apatite, and tourmaline). The structure of dolomite changes in contact with St Lucia limestones and develops reddish hues.

There are grey limestones, found in marine environments, interbedded in massive reefs, with fauna in the form of bryozoans, crinoids, and brachiopods.

The mining waste material under study (coal, ore, and gangue with charcoal remains) was heat treated at different temperatures for activation, converting the kaolinite into metakaoline, among others chemical reactions.

Following its thermal activation at temperatures of 500, 600, 700, 800 and 900 °C for 2 h in an electric laboratory furnace, the best activation conditions were selected for use as a pozzolan in the manufacture of cement. The activated samples were placed in an agate mortar and pestle and crushed to particle sizes of less than 63 µm.

2.2. Methods

Chemical characterization was performed with a Philips PW 1404 X-ray Fluorescence (XRF) Spectrometer (Philips, Eindhoven, The Netherlands), Loss on ignition (LOI) was calculated in accordance with the method specified in the European standard (at 950 °C/1 h). Bulk sample mineralogical compositions were analyzed by random powder X-ray diffraction (XRD), using the oriented film method for the <2 µm fraction, employing a Cu anode and a Siemens D-5000, X-ray diffractometer (Siemens, Madrid, Spain) in both instances. The operating conditions were, respectively, 30 mA and 40 kV, with a divergence slit of 2 mm and a receiving slit of 0.6 mm. Each sample was scanned (2θ) at steps of 0.041 and a count time of 3-s. Bulk sample characterization and semi-quantification used the random-powder method, between 3° to 65° 2θ at a rate of 2°/min. Determination of phyllosilicates in the <2 µm fraction employed the oriented-slides method, operating from 2° to 40° at a scan rate of 1°/min. The Rietveld method was used for quantitative determination of the mineralogical composition.

A Thermo Scientific NICOLET 6700 spectrometer fitted with a DGTS CsI detector (Thermo Fisher, Waltham, MA, USA) performed the FTIR (Fourier Transform Infrared Spectroscopy) analyses, recording 64 scans on the samples. Specimen preparation was done by mixing 1 mg of the sample in 300 mg of KBr. Spectral analyses within the range of 4000–400 cm^{−1} was performed at a spectral resolution of 4 cm^{−1}.

A Renishaw Raman RM2000 Microscope System (Renishaw, Wotton-under-Edge, UK) fitted with a Leica microscope (Leica, Wetzlar, Germany), an electrically refrigerated charge-coupled device camera (CCD), a 785 nm diode laser, and a 633 nm He–Ne Renishaw RL633 laser (Renishaw) were used to record dispersive Raman spectra at 633 nm. Frequency calibration used a 520 cm^{−1} silicon line with a spectral resolution at 4 cm^{−1}. A 50× lens was used for triplicate spectra recordings over wave ranges of 4000–100 cm^{−1} at 10 s exposure times with 10 accumulations for each spectrum.

An Inspect FEI Company Electron Microscopy (Hillsboro, OR, USA) fitted with an energy dispersive X-ray analyzer (W source, DX4i analyzer and Si/Li detector) performed SEM/EDX (Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy) a morphological observation and microanalysis for each sample. The average chemical composition of each sample was based on ten analyses.

An accelerated chemical method was applied to solid waste in order to study the pozzolanic behavior of a pozzolan/calcium hydroxide (lime) system. The test involves leaving the material (1 g) in a lime-saturated solution (75 mL) and analyzing the CaO concentrations at 1, 7, and 28 days into the reaction time. The difference between its concentration in the lime-saturated control solution (17.69 mmol/L) and the CaO content of the solution in contact with the sample gave the combined CaO (mmol/L) content. The hydrated solid sample was then filtered, washed in ethanol, and heated at 60 °C for 24 h until the hydration reaction ended [25].

3. Discussion and Results

3.1. Raw-Carbon Wastes

The XRF results in relation to the carbon waste (initial sample without treatment) showed that the main oxides were SiO₂ (57%), Al₂O₃ (25%), Fe₂O₃ (5%), CaO (4%), and K₂O (3%), with some SO₃ (0.29%) as well. Loss on ignition (LOI) was 15% for initial waste and 3% for material that had been calcined at 500 °C; this change is related to the dehydroxylation processes of kaolinite and organic matter (carbon). Minor elements or traces were also present, such as chromium (120 ppm), vanadium (139 ppm), nickel (53 ppm), and cobalt (21 ppm).

XRD analysis showed the mineralogical composition of the carbon waste (room temperature), revealing the existence of mica (25%) and kaolinite (14%), quartz (37%), calcite (17%), dolomite (5%), and feldspars (2%) (Figures 1 and 2). Both mica and kaolinite contribute to pozzolanic activity, as it is well established that atmospheric thermal activation of a variety of clay minerals at 600 °C/900 °C following dehydroxylation causes the (partial) destruction of the crystal lattice structure, leading to a transitional and highly reactive phase. Mica requires temperatures over 930 °C for its activation and, as a result, it usually results in a weak pozzolan; tending to dissipate at temperatures over 900 °C.

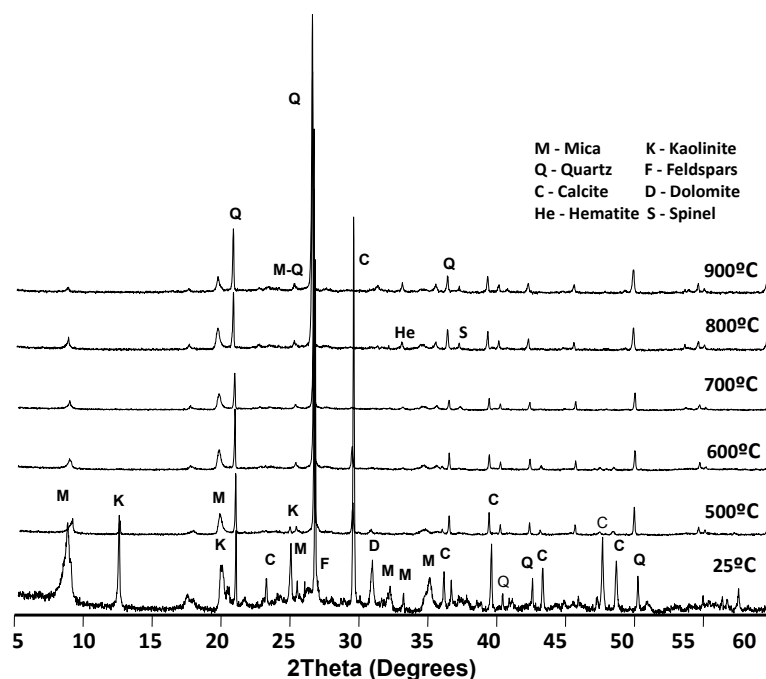


Figure 1. Mineralogical composition by X-ray diffraction (XRD) for the coal mining waste and the coal mining activated waste.

The XRD analysis also showed the formation of anorthite, the presence of which might be due to metakaolinite (from clay dehydration) reacting with calcium carbonate. The formation of mullite that the clay would otherwise generate during firing can be reduced by metakaolinite in reaction with calcium carbonate [26].

In comparison to the samples of coal-mining waste used in this study, in general terms, coal contains aluminum-bearing minerals that include kaolinite, illite, montmorillonite, chlorite, sanidine, albite, plagioclase, biotite, hornblende, and muscovite [27–30]. South African coal samples, for instance, contain quartz, kaolinite, illite I/S, calcite, dolomite, siderite, pyrite, analcite, basanite, bohemite, anatase, diaspore, and jarosite [31].

Even though it was not identified in the unheated sample in this study, the prevalent clay mineral in most South African coals is kaolinite [32–34] and would therefore be found in the raw coal. However,

anhydrite and hematite, identified in the ash produced at 350 °C, have not been observed in South African coals. Their presence in the heated samples used in the present study might suggest an alternative origin.

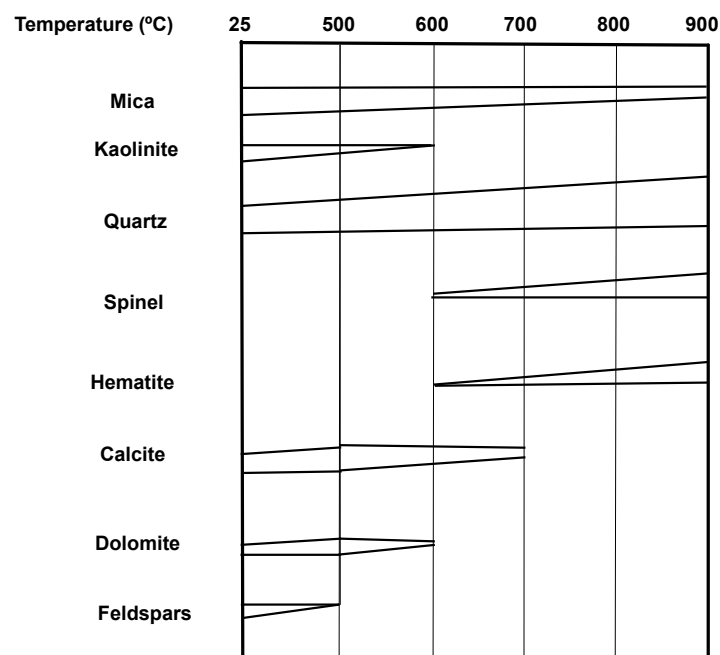


Figure 2. Mineralogical evolution by XRD for the coal mining waste and the coal mining activated waste.

In contrast, the main compounds reported in Australian coals are quartz, kaolinite, illite/smectite, calcite, dolomite, albite, siderite, pyrite, albite, apatite, gypsum, hematite, and anatase [35].

Calcite is the main carbonate mineral in Taoshuping coals with an average content of 9%, and lower amounts of siderite, anchorite, and dolomite [36].

3.2. Activated Coal-Mining Waste

After analyzing the samples of coal waste, they were then thermally activated by calcination at between 500 and 900 °C. In Figures 1 and 2, the XRD patterns of the activated products at different temperatures are shown. The spectra reflects low levels of quartz and kaolinite dissipated at 600 °C/2 h of thermal activation, due to their transformation into metakaolinite. Detrital quartz can also be cell-, cleat-, and fracture-fillings that are epigenetic in nature or syngenetic, such as aluminosilicates in coal [33,34,37].

The temperature at which kaolinite is calcinated to produce metakaolinite in the active state lies within the range of 600–800 °C. The activation of mica requires temperatures over 930 °C, although it usually produces poor pozzolans. Temperature tests (at 500, 600, 700, 800 and 900 °C) determined both phyllosilicate dehydroxylation and new phase-formation temperatures. Further studies were conducted after this test at 600 and at 900 °C, showing that 600 °C was the total dehydroxylation temperature of kaolinite and its neoformation into spinel-like phases took place at 900 °C.

Quasi-stable dehydroxylated mica was formed following dehydroxylation after thermal treatment between 700 and 900 °C. The quasi-stable dehydroxylated phases of these dioctahedral micas were unlike the trioctahedral mica phases, which tended to dehydroxylate and recrystallize more or less simultaneously. Dehydroxylation of the 2:1 mica layers needed higher temperatures. At 600 °C/2 h, a new characteristic peak appeared, explained by the appearance of hematite. As the heating increased from 700 to 900 °C, both hydrous oxides and ferrous hydroxides in the coal-mining

waste crystallized in the form of hematite as they lost water. The presence of hematite in all likelihood reflects pyritic oxidation of the coal. Calcite, habitually found in the four coal cleaning residues, is easily differentiated from other calcium carbonates, due to its Raman spectrum, which showed bands of 1085, 711 and 280 cm^{-1} [30] in similar studies of a range of American coal samples. As observed in Brazilian materials, the Fe-oxide mineral hematite is commonly found in most coals and coal-cleaning residues.

XRD analysis between 600 and 900 °C showed reflections at 2.43 Å ($36.98^\circ 2\theta$) and 2.85 Å ($31.38^\circ 2\theta$), revealing spinel-like phases, resulting from the heating of aluminous clay minerals. Hematite was present as a pyritic product in minor concentrations in the original coal waste and its presence increased at higher temperatures. At temperatures of 700, 800 and 900 °C, well crystallized hematite appeared following loss of water in the hydrous oxides and the ferrous hydroxides of the original coal waste. Finally, dolomite dissipated at 600 °C and subsequently, calcite at 700 °C.

As oxidation continued, ferric sulfate was formed, eventually producing sodium, calcium, magnesium, and potassium sulfate.

The principal mineralogical compounds identified from the XRD data were subjected to FTIR analysis. Kaolinite was identified in the (O–H) bands at 3696, 3656 and 3620 cm^{-1} , mica at 3628 and 3545 cm^{-1} (both overlapping with kaolinite and water), and at 3423 cm^{-1} . Standard carbonate group bands were detected at 1426 and 874 cm^{-1} . With regard to silicates, Si–O vibrations revealed the presence of kaolinite at 1032 and 1007 cm^{-1} and quartz at 1090 cm^{-1} at tetrahedral sites. At lower frequencies ($<1000 \text{ cm}^{-1}$), the Al–O–H vibration, mainly associated with kaolinite (also at 751 cm^{-1}) and mica, was detected at 912 cm^{-1} . Vibrations of the Si–O quartz bond were identified at bands of 798, 778 (doublet), 694, and 472 cm^{-1} . OH absorption of mica is suggested by the presence of absorption bands in the OH-stretching region at 3432 cm^{-1} . The original coal residues revealed a further absorption band at 3656 cm^{-1} , also explained by OH group stretching frequencies, which disappeared in the thermally activated waste. This observation points to the appearance of impure, low crystalline mica, and further isomorphous substitution in the crystalline structure.

Characterization of all tectosilicates, feldspars, and quartz was within the absorption band ranges of 950 to 1200 cm^{-1} , reflecting stretching vibrations of Si–O–Si, and between 400 and 550 cm^{-1} , reflecting O–Si–O bending vibrations. Two hematite bands were observed at 535 and 469 cm^{-1} , both overlapping the main band of mica. IR spectra (465 and 614 cm^{-1}) of the thermally activated waste revealed AB_2O_4 spinel.

A Raman spectrum in the thermally activated coal waste revealed two bands at 1597 and 1346 cm^{-1} , corresponding to graphite and disordered peak bands, respectively, from carbon. The Raman spectrum of calcite, which is commonly found in all four coal-waste composites, may easily be differentiated from other calcium carbonates by its bands at 1085, 711 and 280 cm^{-1} .

3.3. Pozzolanitic Reactivity of Activated Coal-Mining Wastes

The removal of structural water from the crystalline clay layers of calcined clay waste is a consequence of its pozzolanitic reactivity, leaving semi-amorphous products with high surface areas and chemical reactivity. The calcining temperature that is required is dependent upon the nature of the clay mineral and the thermal energy required for dehydroxylation of the clays. The calcining temperature required to produce this active state is usually in the range 600–1000 °C [9,12,38]. Crystallization occurs above this temperature and activity declines. Even higher firing temperatures lead to the formation of a liquid phase that cools into a solid amorphous glass phase, also showing pozzolanitic activity. Reactive metakaolinite is formed at 600 °C and hematite and spinel is formed between 600 and 900 °C that contains mica with a low crystallinity, at 900 °C; all of which contribute to the pozzolanitic activity of the coal-mining wastes calcined to 600 and 900 °C (Figure 3). Clay minerals were shown to have pozzolanitic activity that influenced the reaction kinetics.

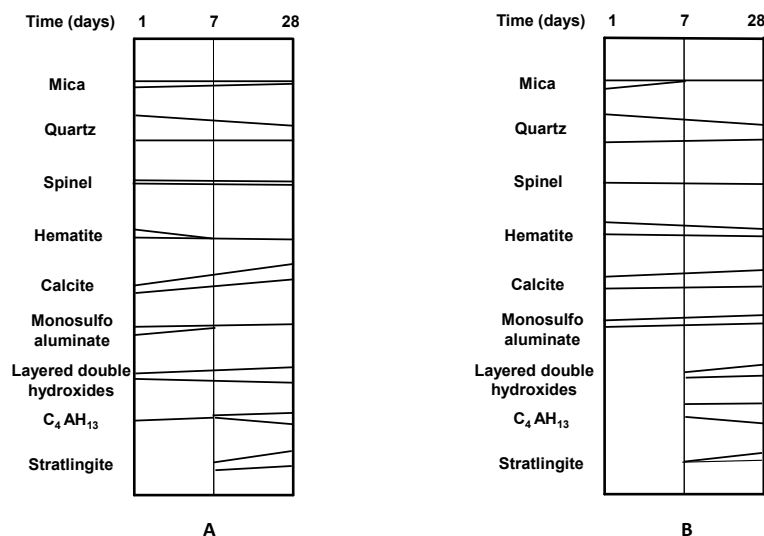


Figure 3. Mineralogical evolution of coal mining waste by XRD; (A) activated at 600 °C/2 h; (B) activated at 900 °C/2 h.

The pozzolanic activity of the coal-mining waste that was activated at 600 °C and 900 °C/2 h had values, at one day, of 65.2%, at 600 °C, and 3.0%, at 900 °C; at seven days, these values were 67.2%, at 600 °C, and 33.1%, at 900 °C, and at 28 days into the reaction reached 72.4%, at 600 °C, and 65.8%, at 900 °C. These percentile results reflect a higher reaction rate at 600 °C than at 900 °C, over short reaction times (one to seven days); both activated products showed a high pozzolanic activity in terms of the fixed lime results over longer reaction times (28 days).

Recommended activation conditions from both an energetic and an economic point of view were therefore set at 600 °C/2 h retention time for the research.

3.4. Evolution of Hydrated Phases in Activated Coal Waste/Lime Systems

Characterization of the hydrated phases by XRD and SEM-EDX in both cases confirmed evidence of a pozzolanic reaction between the metakaolinate (from the coal waste) and the lime.

XRD analysis of the activated coal waste at 600 °C and 900 °C-2 h/ $\text{Ca}(\text{OH})_2$ at one, seven, and 28 days into the reaction revealed the following crystalline hydrated phases: stratlingite (C_2ASH_8), tetracalcium aluminate hydrate (C_4AH_{13}), monosulfoaluminate hydrate ($\text{C}_3\text{A} \cdot \text{SO}_4\text{Ca} \cdot 12\text{H}_2\text{O}$), and layered double hydroxides. All the crystalline phases in the XRD analysis with their evolution and reaction times are shown in Figure 2. The formation of monosulfoaluminate hydrate ($\text{C}_3\text{A} \cdot \text{SO}_4\text{Ca} \cdot 12\text{H}_2\text{O}$) in the thermically activated coal was evident at day one, as a consequence of the reaction between the reactive alumina of pozzolan, sulfate ions, and portlandite. Traces of tetracalcium aluminate hydrate (C_4AH_{13}) were identified at short reaction times; slight increases in its content were observed in the coal waste activated at 600 °C/2 h at day 28 of the reaction. Activation at 900 °C was joined by the formation of layer double hydroxides; stratlingite C_2ASH_8 was formed after seven days of reaction at 600 °C/2 h. Calcination at 900 °C prevented any further formation of stratlingite.

Alkaline solutions of these samples had pH values of ≈ 12 . The most prevalent were Al^{3+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$, without other ligands. The most prevalent species in the solution at high pH (pH > 10) was $\text{Al}(\text{OH})_4^-$. These ions combined with readily available Ca^{2+} ions through metastable phases yielding C_3AH_6 . At high pH values (pH > 10), total dissolved silica concentrations in equilibrium with quartz and amorphous silica increased. At pH values of ≈ 12 , the sum of the ionized and un-ionized species (H_4SiO_4 , H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{2-}$) was equal to the total concentration of dissolved silica. If supersaturation of the total silica concentration in the solution with respect to amorphous silica occurs, polymers form that combine with the Ca^{2+} ions to form CSH

(Calcium silicate hydrate) gels and with $(\text{CO}_3)^{2-}$ ions via metastable phases to form LDH (Layered double hydroxides) [39].

The appearance of C_4AH_{13} is explained by supersaturation of calcium hydroxide and low metakaolinite contents in the aqueous phase. Increased temperatures of coal waste at $900^\circ\text{C}/2\text{ h}$ reduced the presence of alumina and metakaolinite and silica sheet structures, assisting the formation of the main hydration product, C_4AH_{13} .

Traces of portlandite and tetracalcium aluminate hydrate were identified at short reaction times [40,41]. However, tetracalcium aluminate hydrate was the prevalent phase in the pozzolanic reaction of coal waste at 900°C at seven and 28 days; layered double hydroxides formed at day one of the reaction in coal waste at 600°C to become the prevalent phase at day seven of the pozzolanic reaction. Stratlingite was evident at day seven of the reaction in the activated wastes and was the prevalent phase in the pozzolanic reaction after 28 days.

Following SEM analysis (Figure 4), an enriched composition of laminar microaggregates of silica were observed, with very porous surfaces covered with CSH gels, more abundantly at $600^\circ\text{C}/2\text{ h}$, having in all cases a spongy appearance. The Ca/Si (CaO/SiO_2) ratio varied between 1.26 at 600°C over 2 h (I-type gels) [10] and at all times was 1.73 in $900^\circ\text{C}/2\text{ h}$ (II-type gels) [10]. A laminar phase, interlaced with the gels, consisted of layered double hydroxide, stratlingite C_2ASH_8 , monosulfoaluminate hydrate ($\text{C}_3\text{A} \cdot \text{SO}_4\text{Ca} \cdot 12\text{H}_2\text{O}$), and tetracalcium aluminate hydrate (C_4AH_{13}) of widely varying sizes. SEM imagery showed a gradual layered double hydroxide with stratlingite crystallization throughout the hydrothermal treatment and an increase in crystal size that depended on the duration of the temperature. Both the SEM and the XRD analyses yielded similar results.

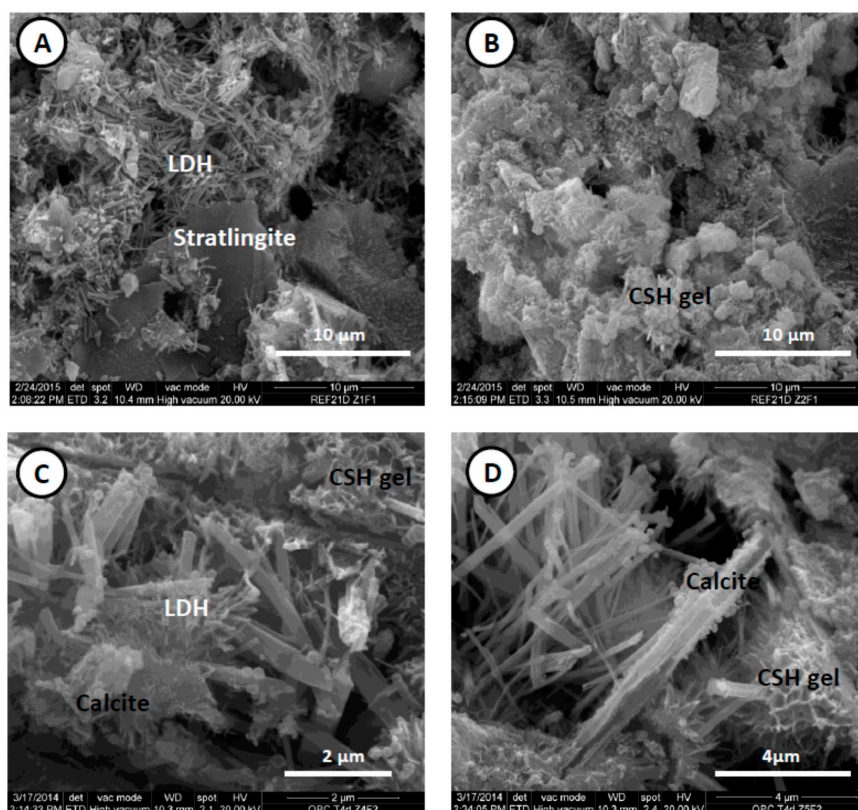


Figure 4. Morphological aspect of the CSH (Calcium silicate hydrate) gel, $\text{C}_4\text{ASH}_{12}$, and C_2ASH_8 phases at $600^\circ\text{C}/2\text{ h}$ (A and B). Morphological aspect of the CSH gel, C_4AH_{13} and LDH (Layered double hydroxide) structures at $900^\circ\text{C}/2\text{ h}$ (C and D). (A) Layered double hydroxides with stratlingite; (B) Calcium silicate hydrate with spongy appearance; (C) Calcite crystal with typical morphology; (D) Calcite fibbers and layered double hydroxides.

4. Conclusions

The coal waste that has been studied had a mineralogical composition of kaolinite, micas, quartz, calcite, dolomite, and feldspars.

The presence of kaolinite indicated that thermal treatment at 600 °C/2 h transformed kaolinite in metakaolinite, a highly reactive component of the pozzolanic reaction.

Unlike hydrated phases obtained from a natural kaolinite (CSH gels, C_4AH_{13} , and C_2ASH_8), metakaolinite from thermal activation of the coal-mining waste in the stable phase of the pozzolanic reaction assisted the appearance of metastable layered double hydroxide compounds and stratlingite. All these compounds indicate that the products resulting from thermal activation at 600 °C/2 h from coal-mining waste contain highly pozzolanic properties over the first seven days into the reaction.

Following the activation of the coal-mining waste at 900 °C/2 h, C_4AH_{13} was the stable phase in the pozzolanic reaction, following supersaturation of the aqueous phase in the presence of calcium hydroxide and low metakaolinite and tetrahedral and octahedral layers resulting from the dehydroxylation of the mica content. SEM/EDX analysis pointed to CSH gels among the main hydrated phases of the pozzolanic reaction in activated/lime systems during.

The use of this waste generates benefits and limits environmental damage such as (1) land occupation, and both soil and groundwater contamination, are reduced; (2) less exploitation of natural resources (kaolin deposits) and reduced emissions of greenhouse gases per unit of cement produced (CO_2 in the clinker production process); (3) coal waste containing residues of fossil carbon give the starting material a heating value which can be used in the alignment process (heating to the required temperature).

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Author Contributions: Moisés Frías and Raquel Vigil de la Villa Mencía conceived and designed the experiments; Virginia Rubio performed the experiments; Moisés Frías, Raquel Vigil de la Villa Mencía and Rosario García-Giménez analyzed the data; Virginia Rubio contributed materials and analysis tools; Rosario García-Giménez wrote the paper.

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References

1. Zhao, Y.; Zhang, J.; Zheng, C.G. Transformation of aluminum-rich minerals during combustion of a bauxite-bearing Chinese coal. *Int. J. Coal Geol.* **2012**, *94*, 182–190. [[CrossRef](#)]
2. Liu, H.; Liu, Z. Recycling utilization patterns of coal mining waste in China. *Res. Cons. Recycl.* **2010**, *54*, 1331–1340.
3. Bian, Z.; Dong, J. The impact of disposal and treatment of coal mining wastes on environment and farmland. *Environ. Geol.* **2009**, *58*, 625–634. [[CrossRef](#)]
4. Skarzynska, K. Reuse of coal mining wastes in civil engineering—Part 2: Utilization of minestone. *Waste Manag.* **1995**, *15*, 83–126. [[CrossRef](#)]
5. Nehdi, M.; Duquette, J.; El Damatty, A. Performance of rice husk ash produced using a new technology as a mineral admixture in concrete. *Cem. Concr. Res.* **2003**, *33*, 1203–1210. [[CrossRef](#)]
6. Chindaprasirt, P.; Homwuttiwong, S.; Jaturapitakkul, C. Strength and water permeability of concrete containing palm oil fuel ash and rice husk–bark ash. *Constr. Build. Mater.* **2007**, *21*, 1492–1499. [[CrossRef](#)]
7. García Giménez, R.; Vigil de la Villa, R.; Goñi, S.; Frías, M. Fly ash/paper sludge as constituents of cements: Hydration phases. *J. Environ. Eng. Sci.* **2015**, *10*, 46–52. [[CrossRef](#)]
8. Frías, M.; Villar-Cociña, E.; Savastano, H. Brazilian sugar bagasse ashes from the cogeneration industry as active pozzolans for cement manufacture. *Cem. Concr. Comp.* **2011**, *33*, 490–496. [[CrossRef](#)]
9. Sabir, B.B.; Wild, S.; Bai, J. Metakaolin and calcined clays as pozzolans for concrete: A review. *Cem. Concr. Comp.* **2001**, *23*, 441–454. [[CrossRef](#)]
10. Taylor, H.F.W. *Cement Chemistry*, 1997; Thomas Telford Services Ltd.: London, UK, 1997.

11. Siddique, R.; Klaus, J. Influence of metakaolin on the properties of mortar and Concrete: A review. *Appl. Clay Sci.* **2009**, *43*, 392–400. [[CrossRef](#)]
12. Ambroise, J.; Murat, M.; Pera, J. Hydration reaction and hardening of calcined clays and related minerals: V. Extension of the research and general conclusions. *Cem. Concr. Res.* **1985**, *15*, 261–268. [[CrossRef](#)]
13. De la Vigil Villa, R.; Frías, M.; Sánchez de Rojas, M.I.; Vegas, I.; García, R. Mineralogical and morphological changes of calcined paper sludge at different temperatures and retention in furnace. *Appl. Clay Sci.* **2007**, *36*, 279–286. [[CrossRef](#)]
14. Frías, M.; García, R.; Vigil, R.; Ferreiro, S. Calcination of art paper sludge waste for the use as a supplementary cementing material. *Appl. Clay Sci.* **2008**, *42*, 189–193. [[CrossRef](#)]
15. Banfill, P.F.G.; Rodríguez, O.; Sánchez de Rojas, M.I.; Frías, M. Effect of activation conditions of a kaolinite based waste on rheology of blended cement pastes. *Cem. Concr. Res.* **2009**, *39*, 843–848. [[CrossRef](#)]
16. Rodríguez Largo, O.; de la Vigil Villa, R.; de Sánchez Rojas, M.I.; Frías, M. Novel use of kaolin wastes in blended cements. *J. Am. Ceram. Soc.* **2009**, *92*, 2443–2446. [[CrossRef](#)]
17. Vegas, I.; Urreta, J.; Frías, M.; García, R. Freeze-thaw resistance of blended cements containing calcined paper sludge. *Constr. Build. Mater.* **2009**, *23*, 2862–2868. [[CrossRef](#)]
18. Frías, M.; Rodríguez, O.; Nebreda, B.; García, R.; Villar-Cocina, E. Influence of activation temperature of kaolinite based clay wastes on pozzolanic activity and kinetic parameters. *Adv. Cem. Res.* **2010**, *22*, 135–142. [[CrossRef](#)]
19. Li, D.; Song, X.; Gong, C.; Pan, Z. Research on cementitious behaviour and mechanism of pozzolanic cement with coal gangue. *Cem. Concr. Res.* **2006**, *36*, 1752–1759. [[CrossRef](#)]
20. Beltramini, L.B.; Suárez, M.L.; Guillarducci, A.; Carrasco, M.F.; Grether, R.O. Aprovechamiento de residuos de la depuración del carbón mineral: Obtención de adiciones puzolánicas para el cemento Portland. *Revista Técnica de Ciencias. Universidad Tecnológica Nacional de Argentina* **2010**, *3*, 7–18. (In Spanish)
21. Frías, M.; de Sánchez Rojas, M.I.; García, R.; Juan, A.; Medina, C. Effect of activated coal mining wastes on the properties of blended cement. *Cem. Concr. Comp.* **2012**, *34*, 678–683. [[CrossRef](#)]
22. Vigil de la Villa, R.; Frías, M.; García-Giménez, R.; Martínez-Ramírez, S.; Fernández-Carrasco, L. Chemical and mineral transformations that occur in mine waste and washery rejects during pre-utilization calcination. *Int. J. Coal Geol.* **2014**, *132*, 123–130. [[CrossRef](#)]
23. García, R.; Vigil de la Villa, R.; Frías, M.; Rodríguez, O.; Martínez-Ramírez, S.; Fernández-Carrasco, L.; de Soto, I.S.; Villar-Cociña, E. Mineralogical study of calcined coal waste in a pozzolan/Ca(OH)₂ system. *Appl. Clay Sci.* **2015**, *108*, 45–54. [[CrossRef](#)]
24. Leyva, F.; Matas, J.; Rodríguez Fernández, L.R. *Memoria y Hoja del Mapa Geológico de España, Escala 1:50.000, No. 129 La Robla, 2ª Serie Magna*; IGME: Madrid, Spain, 1984. (In Spanish)
25. Frías, M.; Vigil de la Villa, R.; García, R.; Sánchez de Rojas, M.I.; Balboa, T.A. Mineralogical evolution of kaolin-based drinking water treatment waste for use as pozzolanic material. The effect of activation temperature. *J. Am. Ceram. Soc.* **2012**, *96*, 3188–3195. [[CrossRef](#)]
26. Zimmer, A.; Bergmann, C.P. Fly ash of mineral coal as ceramic tiles raw material. *Waste Manag.* **2007**, *27*, 59–68. [[CrossRef](#)] [[PubMed](#)]
27. Dai, S.; Ren, D.; Chou, C.L.; Li, S.; Jiang, Y. Mineralogy and geochemistry of the No. 6 Coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China. *Int. J. Coal Geol.* **2006**, *66*, 253–270. [[CrossRef](#)]
28. Vassilev, S.V.; Vassileva, C.G. Mineralogy of combustion wastes from coal-fired power stations. *Fuel Process. Technol.* **1996**, *47*, 261–280. [[CrossRef](#)]
29. Vassilev, S.V.; Vassileva, C.G. A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour. *Fuel* **2007**, *86*, 1490–1512. [[CrossRef](#)]
30. Ward, C.R.; Bocking, M.A.; Ruan, C. Mineralogical analysis of coals as an aid to seam correlation in the Gloucester Basin, New South Wales, Australia. *Int. J. Coal Geol.* **2001**, *47*, 31–49. [[CrossRef](#)]
31. Pinetown, K.L.; Ward, C.R.; van der Westhuizen, W.A. Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage. *Int. J. Coal Geol.* **2007**, *70*, 166–183. [[CrossRef](#)]
32. Gaigher, J.L. The Mineral Matter in Some South African coals. Master Thesis, University of Pretoria, Pretoria, South Africa, 1980.
33. Ward, C.R. Analysis and significance of mineral matter in coal seams. *Int. J. Coal Geol.* **2002**, *50*, 135–168. [[CrossRef](#)]

34. Dai, S.; Tian, L.; Chou, C.L.; Zhou, Y.; Zhang, M.; Zhao, L.; Wang, J.; Yang, Z.; Cao, H.; Ren, D. Mineralogical and compositional characteristics of Late Permian coals from an area of high lung cancer rate in Xuan Wei, Yunnan, China: Occurrence and origin of quartz and chamosite. *Int. J. Coal Geol.* **2008**, *76*, 318–327. [[CrossRef](#)]
35. Ruan, C.-D.; Ward, C.R. Quantitative X-ray powder diffraction analysis of clay minerals in Australian coals using Rietveld methods. *Appl. Clay Sci.* **2002**, *21*, 227–240. [[CrossRef](#)]
36. Wang, X.; Dai, X.; Chou, C.; Zhang, M.; Wang, J.; Song, X.; Wang, W.; Jiang, Y.; Zhou, Y.; Ren, D. Mineralogy and geochemistry of Late Permian coals from the Taoshuping Mine, Yunnan Province, China: Evidences for the sources of minerals. *Int. J. Coal Geol.* **2012**, *96*, 49–59. [[CrossRef](#)]
37. Tian, L.; Dai, S.; Wang, J.; Huang, Y.; Ho, S.C.; Zhou, Y.; Lucas, D.; Koshland, C.P. Nanoquartz in Late Permian C1 coal and the high incidence of female lung cancer in the Pearl River Origin area: A retrospective cohort study. *BMC Public Health* **2008**, *8*, 398. [[CrossRef](#)] [[PubMed](#)]
38. Ambroise, J.; Martín Calle, S.; Pera, J. Pozzolanic behavior of thermally activated kaolin. In Proceedings of the Fourth CANMET/ACI International Conference on Fly Ash, SF, Slag and Natural Pozzolans in Concrete, Istanbul, Turkey, 3–8 May 1992; Malhotra, V.M., Ed.; Volume 1, pp. 731–741.
39. De Wintd, L.; Deneele, D.; Maubec, N. Kinetic of lime/bentonite pozzolanic reaction at 20 and 50 °C: Batch tests and modeling. *Cem. Concr. Res.* **2014**, *59*, 34–42. [[CrossRef](#)]
40. Kaminskas, R.; Cesnauskas, V.; Kulibiute, R. Influence of different artificial additives on Portland cement hydration and hardening. *Constr. Build. Mater.* **2015**, *95*, 537–544. [[CrossRef](#)]
41. De Azeredo, A.F.N.; Azeredo, G.; Carneiro, A.M.P. Performance of lime-metakaolin pastes and mortars in two curing conditions containing kaolin wastes. *Key Eng. Mater.* **2016**, *668*, 419–432. [[CrossRef](#)]



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