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Research paper

Influence of ZnO on the activation of kaolinite-based coal waste: Pozzolan activity and mineralogy in the pozzolan/lime system

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ABSTRACT

One inconvenience presented by the thermal activation of kaolinite-based wastes is their low content of metakaolinite, a highly pozzolanic product listed in current standards for the manufacture of commercial cements. The addition of a chemical activator during the thermal activation process is a priority line of research to increase the reactivity of the recycled metakaolinite. In this paper, an additional chemical activator, ZnO, is studied and its effect on both pozzolanic properties and the evolution of mineralogical phases in the thermal activation of coal waste with a reaction time of up to 90 days in the pozzolan/lime system. To do so, activation temperatures of between 550 °C/650 °C were selected and additions of chemical activator (ZnO) in percentages of between 0.0% and 3.0% by weight of coal waste, because it is an activator with a positive effect on a 100% natural kaolinite. The results showed that the incorporation of ZnO inhibited the reactivity of the recycled metakaolinite and in consequence, the capacity of the metakaolinite to react with the surrounding lime; even more so when the content of added chemical activator was raised, albeit with some exceptions, in the samples activated at 550 °C and 650 °C with 0.5% of chemical activator. In none of the cases under analysis was the chemical activator able to improve the properties of the metakaolinite in comparison with the properties of the reference sample activated only with temperature. The hydrated phases that appeared in the pozzolanic reaction were tetracalcium aluminat hydrate, stratlingite, monosulfoaluminate hydrate and LDH (phyllosilicate/carbonat).

1. Introduction

The cement industry, because of its characteristics, is one of the principal sectors contributing to the increase of greenhouse gases (methane, nitrous oxide, sulfur hexafluoride, hydro/perfluorocarbons and carbon dioxide). Hence, the efforts made to reduce those emissions, above all those of atmospheric CO₂, during the manufacture of Portland cement. The use of pozzolanic materials in the manufacture of commercial cements is a viable solution from an energetic, economic, and environmental point of view. As a priority policy of the Circular Economy, studies over the last decade have centered on by-products and industrial waste for use as secondary cement materials.

Recently, various studies have centered on metakaolin (MK), a calcinated product that is obtained from the dehydroxylation of kaolinite (K) under controlled conditions and that presents highly pozzolanic properties (Cassagnabere et al., 2009; Alujas et al., 2015). The use of

this pozzolan is accepted in current international norms for the manufacture of commercial cements (UNE EN 197-1, 2011).

The cement industry was one of the first to recycle and to value industrial sub-products and wastes, as well as natural materials, incorporating them into different production stages in the manufacture of cement mixes (Taylor et al., 1985; Lilkov and Stoitchkov, 1996). Investigations with palm oil, rice husks, and fly ash waste have been described in the literature (Chindaprasirt and Rukzon, 2008; Tironi et al., 2014). The term “pozzolan” is associated with materials of a siliceous nature and silica-aluminum that in the presence of water reacts chemically with Ca(OH)₂ to form compounds with cementitious properties (Sabir et al., 2001). One of these standard pozzolans is obtained from the thermal activation of natural kaolinite to obtain MK (Snelson et al., 2008; Siddique and Klaus, 2009; García Giménez et al., 2012; Yuan et al., 2013). However over recent times, the research has centered on obtaining this pozzolan from different industrial wastes, such

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as paper sludge, sewage sludge, and coal waste, among others (Vigil et al., 2007; Frias et al., 2008; Vigil de la Villa et al., 2014; Modarres and Nosoudy, 2015). The objective is reduced the environmental footprint of the cement industries (Tobón et al., 2012).

There have been numerous studies along these lines, both on the optimum conditions for activation processes in which inert materials taken from coal mining waste is transformed into a material with pozzolanic properties and on its behavior in binary cements (Alujas et al., 2015; Liu et al., 2017).

Recently, Taylor-Lange et al. (2012) proposed the use of zinc oxide to increase the reactivity of MK from a 100% natural kaolinite, obtaining good results in pure metakaolin-cement systems. However, a vast area of investigation is at present unfolding on the behavior of this chemical activator in kaolinite-based industrial waste, where the presence of other materials can influence the reactivity of the recycled MK.

The objective of the present paper is to analyze the combined effect of the activation of a K-based coal waste on pozzolanic reactivity and on the evolution of mineralogical phases in a metakaolin/lime (MK/CaO) system cured at 1, 7, 28, and 90 days reaction time. To do so, activation temperatures between 550 °C and 650 °C were analyzed as well as percentages of ZnO between 0.5% and 3.0% by weight of sample.

2. Materials and characterization methods

2.1. Materials

A kaolinite-based coal-mining waste was selected for the study, extracted from an open-cast coal mine, the property of the company “Sociedad Anónima Hullera Vasco Leonesa”, located in the area of Santa Lucía (León, Spain). The mineralogically sterile coal is formed of phyllosilicates (kaolinite 14% and mica 25%), quartz 25%, calcite 22%, dolomite 2%, and feldspars 2%.

Subsequently, the waste was subjected to a combined high-temperature activation process (at 550, 600 and 650 °C) with ZnO as a chemical activator (0.0; 0.5; 1.0; 1.5 and 3.0% by weight of coal waste). Once calcinated, the products (Activated Coal Waste or ACW) were crushed in an agate mortar and pestle to a size of less than 90 µm for subsequent analysis.

2.2. Methodology

2.2.1. Pozzolanic activity method

The pozzolanic activity of the calcinated products was evaluated by means of an accelerated chemical method (Frías, 2006) in the pozzolan/lime (Ca(OH)₂) system at 1, 7, 28, and 90 days of reaction. It was then filtered, where the solid wastes were introduced in acetone to inhibit the hydration reaction (24 h), subsequently they were dried in an electric oven at 60 °C for 24 h and, finally maintained in a desiccator until characterization by means of different instrumental techniques. In the liquids, the lime reacting with the pozzolan was determined at each fixed hydration time. The content of fixed lime was calculated as the difference between the CaO concentration (mmol/L) in the original saturated lime solution (17.68 mmol/L) and the content of this compound in the solution at the established time. An extra pure PhEur, USP, BP chemical reagent of calcium hydroxide was used (Frías, 2006).

2.3. Characterization techniques

Different techniques were used for the material characterizations in the current study, as well as for following the evolution of the hydrated phases formed during the pozzolanic reaction and for their identification.

The mineralogical composition of the bulk samples was determined by random powder X-ray diffraction (XRD) on a Siemens D-5000 (Munich, Germany) X-ray diffractometer fitted with a Cu anode. Its

Fig. 1. Evolution of fixed lime throughout the reaction time in joint thermal and chemical activation systems.

operating conditions were set at 30 mA and 40 kV, at divergences of 2.0 and 0.6 mm with reception slits, respectively. The samples were scanned in (2θ) 0.041 steps with a 3-s count time. The characterization of the bulk samples was performed with the Rietveld method (Rietveld, 1969; De Ruan and Ward, 2002). Rutile was used as an internal reference patron at a concentration of around 5% in all cases. Quantification accuracy via Rietveld method is typically presented using the constants R and χ^2 . While, R exclusively compares peak intensities from the calculated spectra of the material and the one obtained experimentally, χ^2 also considers phase weight. Ideally, both constants should be equal to 1; however, due to the discrepancy between observed and calculated data, which increases greatly for materials containing over three phases, values under $R = 20$ and $\chi^2 = 10$ are commonly accepted to be adequate enough for valid results.

Morphological observation and microanalyses of the samples were carried out by SEM/EDX, using an Inspect FEI Company Electron Microscopy (Hillsboro, OR), equipped with an energy dispersive X-ray analyzer (W source, DX4i analyzer and Si/Li detector). The chemical composition was obtained by an average value of ten analyzes for each sample in this case the value was the mean standard deviation. The results are expressed in oxides (wt%), adjusted to 100%.

A confocal Renishaw Invia Raman microscope equipped with a

Table 1

Percentage of presents phases with the activation temperature and with no chemical activator.

Temperature (°C)	Calcite (%)	Kaolinite (%)	Quartz (%)	Mica (%)	Amorphous material (%)	R	Global chi ²
550	5	4	33	20	38	12.62	5.44
600	6	n.d.	30	1	50	15.37	6.72
650	4	n.d.	33	23	40	13.65	6.11

n.d. = not detected.

Fig. 2. XRD patterns of CW550 and ZnO at 1 day of reaction time.**Table 2**

Present phases in the pozzolanic reaction at 550 °C with different additions and days of duration from the pozzolanic reaction (Ca = calcite; K = kaolinite; Q = quartz; M = mica; L = LDH phyllosilicate/carbonate; Mo = monosulphoaluminate hydrate; St = stratlingite; A = tricalcium aluminate hydrate; Am = amorphous material).

DSC (days)	ZnO addition (%)	Ca (%)	K (%)	Q (%)	M (%)	L (%)	Mo (%)	St (%)	A (%)	Am (%)	R	Global chi ²
1	0.0	6	4	32	25	n.d.	6	n.d.	n.d.	27	14.12	6.45
1	0.5	5	4	33	25	n.d.	3	n.d.	n.d.	30	13.25	5.08
7	0.0	7	4	32	17	3	3	3	n.d.	32	13.52	2.55
7	0.5	4	4	26	20	5	9	3	n.d.	32	16.37	5.39
28	0.0	4	4	43	14	traces	traces	3	n.d.	32	17.21	7.36
28	0.5	7	3	32	14	3	3	7	n.d.	31	10.15	8.93
28	1.0	5	4	30	27	4	n.d.	n.d.	n.d.	30	11.63	5.29
90	0.0	4	4	42	15	traces	traces	3	n.d.	32	14.28	6.15
90	0.5	7	4	5	18	4	2	7	n.d.	32	15.33	6.22
90	1.0	7	4	22	15	4	2	7	9	30	16.43	5.12

n.d. = not detected.

Leica microscope and an electrically refrigerated CCD camera was used for sample analysis. Laser excitation was from a Renishaw Nd YAG laser (532 nm) with a laser beam power of 5 mW. Typical spectra from 100 to 4000 cm⁻¹ were recorded with a resolution of 4 cm⁻¹. The time acquisition was 10 s and 5 scans were recorded to improve the signal-to-noise ratio. Correct calibration of the instrument was verified by checking the position of the Si band at ± 520.6 cm⁻¹.

The FTIR analyses employed the KBr pellet method (300 mg KBr/1.2 mg of sample). The equipment used was a Bruker-brand Alpha

model that determined the spectra in the range of compressed frequencies of between 4000 and 400 cm⁻¹, with a definition of 2 cm⁻¹.

3. Results and discussion

3.1. Pozzolanic activity

Fig. 1 covers the results of fixed lime for each one of the thermal activation and combined thermal activation conditions (thermal +

Fig. 3. SEM/EDX analysis for the ACW550: a) Superficial aspect; b) ZnO deposits; c) layers of monosulfaluminate in 0.5ACW550; layers of stratlingite with LDH and CSH gels in 0.5ACW550; e) compact aggregates and fibers in 3.0ACW550 at 7 days; f) aggregates with CSH gels and mica at 90 days in 1.0ACW550.

ZnO) up until 90 days of pozzolanic reaction. It is clearly appreciated that the addition of the chemical agent, ZnO, in the activation process produces an effect that inhibits the pozzolanic reactivity of the recycled MK from the coal waste.

The three activation temperatures (550 °C/2 h, 600 °C/2 h and 650 °C/2 h) presented very high fixed lime values in the short and medium term of the reaction, reaching values of between 40/50% within the first 24 h of the reaction and over 80% of available lime as from 28 days (Frías et al., 2016). However, combined with ZnO in the thermal activation of the coal waste, the fixed lime values were very low in all cases under analysis, with the exception of the waste activated at 550 + 0.5% ZnO, where the reactivity was quite similar to the sample without ZnO as from 7 days of reaction time.

At 90 days into the reaction, samples 550 + 1.0% ZnO and 650 + 0.5% also had values close to the reference sample (without ZnO). It is evident in all cases under analysis, with and without

pozzolanic activity, that the addition of the chemical agent, ZnO, presented no benefit in terms of activated coal waste reactivity. Very different from the behavior observed by Taylor-Lange et al. (2012), which mentioned the good behavior of this chemical activator agent in the mechanical properties of natural MK blended cement mortars.

3.2. Mineralogical evolution of the hydrated phases identified in the pozzolanic reaction

The reaction products obtained at 1, 7, 28, and 90 days of pozzolanic reaction in the recycled MK/lime system, calcinated at various temperatures and percentages of ZnO, were analyzed, in order to investigate the influence of the chemical activator on the evolution of the hydrated phases. The results obtained in the samples solely activated with temperature (550, 600 and 650 °C, with no chemical activator) are presented in Table 1.

The mineralogically activated products were similar at all temperatures (rutile was introduced as a standard reference) with minimum variations in the quantity of calcite and quartz. The presence of K traces at 550 °C (practically total dehydroxylation), the reduction of mica and the increase of amorphous material were evident at 600 °C. At 650 °C, the values were very similar to the coal waste activated at 550 °C. In the SEM observation, compact aggregates of scaled surfaces, a sign of the start of phyllosilicate dehydroxylation, were detected.

Successive additions of ZnO appear to favor the surface descaling process, recognizable through SEM following the appearance of porous aggregates. In the case of a 3.0% addition, the ZnO particles were even deposited on the aggregate surface and edges.

As an example of the results obtained by XRD under the different test conditions, only those diffractograms of coal waste activated at 550 °C (ACW) are shown in Fig. 2 with the different contents of ZnO at day 1 of the reaction.

The hydrated phases that appeared in the pozzolanic reaction were: a) tricalcium aluminate hydrate (C_4AH_{13}) (A) with reflections at 7.9 Å (11.18 20), 2.88 Å (31.02 20), 2.86 Å (31.24 20) and 2.45 Å (36.64 20); b) stratlingite (C_2ASH_8) (St) at 12.61 Å (7.0 20), 6.28 Å (14.08 20), 4.15 Å (21.38 20) and 2.87 Å (31.14 20); c) monosulfoaluminate hydrate ($C_3A \cdot SO_4Ca \cdot 12H_2O$) (Mo) characterized by reflections at 8.92 Å (9.91° 20) and 2.87 Å (31.16° 20) and d) LDH (phyllosilicate/carbonate) (L) at 7.60 Å (11.64 20), 7.41 Å (11.94 20), and 3.78 Å (23.52 20) (Santos Silva et al., 2014).

The presence and evolution of the hydrated mineralogical phases depended on the reaction time and the percentage of added ZnO. Considering only the existence of reactivity between the MK and the Ca (OH)₂, quantification of the mineralogical phases was performed with the Rietveld method (Renaudin et al., 2009), the values of which are shown in Table 2. Thus, LDH (L) appeared as a mineralogical phase as from day 7 of the reaction time, reaching its maximum concentration at 28 days, as the only crystalline phase that was formed. In turn, Mo was complementary to LDH at that same age. At the other ages, LDG, Mo, and St coexisted, this last phase being, in general terms, the predominant against the other two, principally at 90 days. In all cases, the amorphous material has stabilized at a constant value, which has increased slightly since the youngest age (1 day). The rest of ages and

proportions, only keep the products of departure.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) techniques can detect the existence of C-S-H gels on the surface of the aggregated layers generated during calcination that are rich in silica and with porous surfaces (Fig. 3a). These gels have a spongy appearance and little thickness, and therefore, the analysis, corresponds to the gels and to the substrate on which they develop (Fig. 3b).

The compounds of laminar morphology are formed at the expense of the C-S-H gels that act as a substrate for crystallization, finding themselves interspersed with them and forming aggregates (Fig. 3a and Table 3).

In the analysis of these phases in Table 3, the composition of the substrate on which they nucleate is detected, yielding values for composition that are at some distance from those corresponding to their stoichiometries.

The addition of 0.5% ZnO to the coal waste maintained the reaction products formed at the time of analysis and the results were not modified when that chemical activator was not added. At 7 days into the reaction, it only favored the formation of Mo and, at all the ages, the appearance of a very fine C-S-H gels coating that is the substrate for laminar growth (Fig. 3c and d).

The increased concentration of chemical activator from 1.0% to 3.0% prevented the formation of all crystalline phases after 1, 7, and 28 days of reaction time. Moreover, the non-appearance of spongy gels, which act as a crystallization substrate for laminar growth, meant that the clayey aggregates became more compact (Fig. 3e), and elongated fibers developed from them, at ages of up to 28 days.

After 90 days of reaction time had elapsed, the addition of 1.0% of ZnO, in addition, generated the formation of tetracalcium aluminate hydrate (C_4AH_{13}) (A) (Table 2) and a thin layer of gels with a spongy appearance started to form that served as a substrate upon which the products of the reaction crystallized in laminar forms (Fig. 3f). The compositions of the clayey aggregates at times presented deposits of zinc, while the sulfur and the calcium were concentrated in the fibbers.

When the concentrations of ZnO additive were increased to 1.5% and 3.0%, the formation of all crystalline products of the reaction were inhibited. Through SEM, the formation of compact aggregates may be seen where small laminas form; the lengthier fibers are very abundant

Table 3
Chemical analysis by EDX of hydrated phases in CW550 at different times.

Oxides (%)	CSH gels 7 days	Monosulfoaluminate 7 days	C ₂ ASH ₈ 90 days	LDH 90 days
Na ₂ O	0.36 ± 0.11	n.d.	n.d.	n.d.-
MgO	0.86 ± 0.31	n.d.	n.d.	n.d.
Al ₂ O ₃	25.17 ± 0.59	31.64 ± 1.19	31.43 ± 1.18	32.70 ± 2.16
SiO ₂	55.77 ± 3.16	3.42 ± 0.46	20.84 ± 0.86	35.29 ± 2.42
SO ₃	n.d.	12.45 ± 1.77	2.25 ± 0.74	1.63 ± 0.39
K ₂ O	2.41 ± 0.62	n.d.	0.73 ± 0.39	1.16 ± 0.13
CaO	14.07 ± 1.27	52.48 ± 3.18	43.03 ± 1.79	28.04 ± 1.67
Fe ₂ O ₃	1.36 ± 0.77	n.d.	1.71 ± 0.29	1.14 ± 0.69

n.d. = not detected.

Table 4
Chemical analysis by EDX of hydrated phases in 0.5ACW550 at different times.

Oxides (%)	Substrate Fe 7 days	Substrate Zn 7 days	C ₂ ASH ₈ 7 days	Monosulfoaluminate 7 days	CSH gels-Zn 90 days	LDH-Zn 90 days
MgO	3.34	n.d.	n.d.	n.d.	0.53	n.d.
Al ₂ O ₃	20.41	26.38	31.64 ± 1.28	27.75 ± 2.14	25.13	26.74 ± 0.62
SiO ₂	35.21	49.22	23.77 ± 1.43	2.96 ± 0.84	49.02	48.58 ± 1.27
SO ₃	2.50	n.d.	10.08 ± 0.69	21.95 ± 2.47	n.d.	n.d.
K ₂ O	2.10	3.15	1.53 ± 0.72	n.d.	2.58	2.04 ± 0.41
CaO	9.32	11.10	32.98 ± 1.87	47.34 ± 1.75	10.65	19.14 ± 2.16
Fe ₂ O ₃	26.37	1.92	n.d.	n.d.	1.63	2.86 ± 0.59
ZnO	0.75	8.22	n.d.	n.d.	10.45	0.64 ± 0.27

n.d. = not detected.

Fig. 4. FTIR analysis in the studied samples: A and B: ACW550; C and D: ACW600; E and F: ACW650.

with variable compositions with regard to Si and Al. The excess ZnO was deposited on the surfaces or on the fibers in an oriented way.

The composition of the gels is very heterogeneous depending on the material that they coat; no average measurement that would be

significant can be obtained, because scattered deposits are observed of ions such as Fe, Zn, Ca and S (Table 4).

The high fluorescence of ACW550 samples does not allow information to be obtained on the phases formed in the pozzolanic

Table 5

Present phases in the pozzolanic reaction at 600 °C with different additions and days of duration from the pozzolanic reaction (Ca = calcite; Q = quartz; M = mica; L = LDH phyllosilicate/carbonate; Mo = monosulphoaluminate hydrate; St = stratlingite; A = tricalcium aluminate hydrate; Am = amorphous material).

DSC (days)	ZnO addition (%)	Ca (%)	Q (%)	M (%)	L (%)	Mo (%)	St (%)	A (%)	Am (%)	R	Global chi ²
1	0.0	6	29	40	4	n.d.	n.d.	3	18	16.14	8.62
7	0.0	6	30	27	3	4	7	3	20	15.32	7.25
7	0.5	5	34	21	n.d.	3	n.d.	n.d.	37	17.54	6.13
28	0.0	9	36	23	n.d.	n.d.	10	3	19	18.66	7.07
28	0.5	3	33	27	4	n.d.	n.d.	n.d.	33	15.14	8.52
90	0.0	5	37	23	4	n.d.	7	n.d.	24	11.78	7.19
90	0.5	33	44	20	4	n.d.	7	n.d.	22	14.16	7.98

n.d. = not detected.

Fig. 5. SEM/EDX analysis: a) LDH and CSH gels, b) Stratlingite and CSH gels in 0.5ACW600 at 7 days; c) Aggregates in 3.0ACW600 at 7 days; d) Aggregates in 3.0ACW600 at 28 days.

Table 6

Present phases in the pozzolanic reaction at 650 °C with different additions and days of duration from the pozzolanic reaction (Ca = calcite; K = kaolinite; Q = quartz; M = mica; L = LDH phyllosilicate/carbonate; Mo = monosulphoaluminate hydrate; St = stratlingite; A = tricalcium aluminate hydrate; Am = amorphous material).

DSC (days)	ZnO addition (%)	Ca (%)	Q (%)	M (%)	L (%)	Mo (%)	St (%)	A (%)	Am (%)	R	Global chi ²
7	0.0	6	36	21	3	3	7	3	21	16.24	6.23
28	0.0	4	33	24	3	3	9	3	20	15.36	7.12
90	0.0	3	26	22	3	3	10	n.d.	33	16.70	5.19
90	0.5	3	24	20	9	6	n.d.	3	35	17.20	6.87

n.d. = not detected.

reaction of the waste through Raman spectroscopy.

The results obtained from the analysis of the FTIR spectra of the samples, indicated a clear effect on the development of reaction products, in the comparison prepared for the different temperatures, due to the presence of ZnO. This effect is turned into a diminishment in the intensity of some absorption bands and especially in those that appear in the region between 4000 and 3000 cm⁻¹ due to the absorption of the

bonds of the H₂O groups of the C-S-H gels and the OH groups of some hydrated species. When increasing the proportion of ZnO in the mixtures, a progressive diminishment of the aforementioned bands was noted, both in the samples at 550 °C, 600 °C and 650 °C.

The spectra in Fig. 4A represent the samples treated at 550 °C at 7 and 90 days with ZnO contents of 0.0, 0.5, and 3.0%. At 7 days, they all presented absorption bands, due to ν(O-H) from Mo at around

Fig. 6. XRD patterns de ACW650 at 90 days of reaction time.

Fig. 7. a) CSH gels under aggregates at 28 days; b) CSH gels under aggregates at 90 days; c) layers under CSH gels at 90 days; d) general aspect at 90 days. All samples were made in 0.5ACW650.

3647 cm^{-1} , and another band at around 3623 cm^{-1} , also of $\nu(\text{O}-\text{H})$, revealing $\text{Al}-\text{OH}$ –both are more intense in the samples with ZnO content ranging between 1.0%–3.0%. The last band is difficult to assign, although it could be due to the compound C_4AH_{13} (A), and it could also represent aluminum hydroxide, as both present an absorption band in that zone. Band $\nu_3\text{-H}_2\text{O}$ of C-S-H gel was observed at around

3434 cm^{-1} , clearly of a higher intensity in the sample with no ZnO (0.0% ZnO). This assumption would support the results found with other techniques that refer to lower reactivity, due to the presence of ZnO . At 90 days (Fig. 4B), the position of the absorption bands had not changed (Fig. 4B), but an increase was noted in the bands, due to the C-S-H gel, especially in the sample with an addition of 0.5%, which is

Table 7

Evolution of weight losses (90 °C/300 °C) of the TG curves with the temperature and the addition of ZnO.

TG loss (%)	ZnO (%)	7 days	28 days	90 days
550 °C	0.0	2.62	3.31	3.70
	0.5	2.34	2.98	3.68
	3.0	0.93	1.13	1.21
600 °C	0.0	2.71	3.35	3.63
	0.5	1.00	1.20	2.68
	3.0	0.99	1.11	1.17
650 °C	0.0	2.99	3.35	4.10
	0.5	1.01	1.24	3.43
	3.0	1.07	1.13	1.15

practically identical to the one without any addition (0.0% ZnO); the bands of the samples with 1% ZnO clearly increased. There would be a practically identical increase in the pozzolanic reaction at these ages in the samples without (0.0%) and with 0.5% of ZnO.

When the activation of the coal waste was complete at 600 °C/2 h with the different additions of chemical activator, it yielded the material phases as shown in Table 5.

In a similar way, to thermal activation at 550 °C/2 h in the ACW600 samples, the chemical additions of 0.5% ZnO were only significant and of course the thermal activations with no addition (0.0% de ZnO) and the same hydrated phases were recognized: LDH, Mo and St. The LDH phase appears at 1 and 7 days (with no chemical additions) and at 28 days with 0.5% of addition. St predominated at 7 and 28 days with no addition and at 90 days without addition and with 0.5%.

Mo appeared at only 7 days of activation, the only single phase having an addition of 0.5% of ZnO. It is also important to stress the identification of the hydrated A phase at 1, 7 and 28 days. At this calcination temperature, the process of total deshydroxylation of K and partial deshydroxylation of mica was conspicuous. When adding zinc oxide, the process of surface descaling was favored giving rise to the formation of porous aggregates, with deposits of zinc on surfaces and edges. C-S-H gels of a spongy appearance were detected on the aggregate surfaces. Laminar compounds were formed to the detriment of C-S-H gels that acted as a crystallization substrate and were found interspersed with them forming aggregates (Fig. 5a and b).

The presence of ZnO inhibited the formation of spongy gels on the clayey aggregates; the appearance of the aggregates became compacted as the time of the pozzolanic reaction increased (Fig. 5c).

The absence of these spongy gels forces a change in the appearance of the reaction products; the formation of elongated fibers, both isolated and in groups, of variable sizes for the times under analysis were observed in most places and for all the conditions under consideration. Variations in their compositions may be found, principally with regard to Si, Al, S and Ca. Zn was deposited on fiber edges and the surfaces in

Fig. 9. Raman spectrum of ACW650 samples with 0%, 0.5% and 1% ZnO and 90 days in a saturated solution of lime.

an oriented direction and appeared to contribute to the growth in fiber thickness (Fig. 5d). The aforementioned fibers were also observed with Raman microscopy.

Fig. 4 C and D presents the samples activated at 600 °C/2 h where an inhibition of the reactivity of the ZnO may be appreciated for any proportion at the age of 7 days; nevertheless, the absorption bands were presented in the same positions. At 90 days, there was no increase in the reactivity of these samples.

The highest and the final activation temperature under consideration, 650 °C/2 h, to which the coal waste is subject with the foreseen additions of ZnO shown in Table 6 and Fig. 6.

At this temperature, the joint activation temperature + chemical additive was only notable at 90 days of pozzolanic reaction and with 0.5% ZnO; in addition, under these conditions, all the hydrated phases, identified up until that point had formed, with the exception of St, which were mainly LDH and Mo.

The presence of ZnO at the preset quantities inhibited the formation of all the crystalline products of the reaction at early ages, 1 and 7 days, an effect appreciated later on, at 28 and 90 days, at concentrations of 1.0%, 1.5% and 3.0%.

The ZnO concentration at 0.5% had a selective behavior with regard to the inhibition at 90 days of reaction, given that neither St nor A compounds appeared (the absence of spongy gels prevents the formation of laminar products, observing only the formation of fibers), while Mo and L formed.

Fig. 8. DTG curves of ACW550 and ACW650 with 0.0, 0.5 and 3.0% ZnO additions.

At 90 days, the concentration of 0.5% ZnO strengthened the formation of all the reaction products. The gels were maintained at 90 days and were responsible for the formation of all the laminar products in the reaction (Fig. 7a, b, c and d).

The spectra corresponding to 650 °C/2 h of thermal activation (Fig. 4E and F) once again reproduced the situation described earlier: the sample with no addition was the one that presented the highest formation of CSH gels, followed by the sample with an addition of 0.5% ZnO.

No high variations in other regions of the spectrum were observed. Bands due to Si–O vibrations in tetrahedral sites appeared at 1032 cm⁻¹ and 1010 cm⁻¹ for kaolinite; at 1023 cm⁻¹ for illite; and, at 1080 cm⁻¹ for quartz. In the lower frequency region, bands at 797, 781 (doublet), 698 and 472 cm⁻¹ correspond to the vibrations of the Si–O quartz bond. Finally, the characteristic frequencies at 533 and 472 cm⁻¹ correspond to Si–O–Al and Si–O for kaolinite and illite, respectively.

The thermogravimetric studies (TG/DTG) confirmed that the results for the saturated lime solution with regard to the addition of ZnO in the majority of cases inhibited a pozzolanic reaction, which implies the non-formation of the typical hydrated phases in the ACW-lime system (García et al., 2015). These hydrated phases, under thermal effects, experienced weight loss within the interval of 100 °C/300 °C, due to a process of dehydroxylation, principally hydrates of C-S-H gels, carboaluminates, calcium and silicoaluminates, which are phases identified in the pozzolan/lime system, in accordance with the nature of the pozzolan.

Table 7 shows TG loss of the three calcination temperatures with additions of only 0.5% and 3.0% ZnO, because they represent the extreme values under analysis, while the additions of 1.0 and 1.5% of the chemical agent in no way modified the reactivity of MK at any temperature. These values are totally in accordance with those obtained for the fixed lime: at 550 °C; with the addition of only 0.5% of the chemical agent. The losses were similar to the losses in the reference sample (550 °C + 0.0%ZnO) and a slight increase in the losses of the waste at 600 °C and 650 °C with 0.5% ZnO at 90 days into the reaction.

Fig. 8 shows, as an example of all the products obtained. The DTG curves at 7 days (Fig. 8a) and 90 days (Fig. 8b) of the pozzolanic reaction for the samples activated at 550 °C and 650 °C with 0.5% and 3.0% ZnO, because these conditions are the extreme conditions for activation under analysis and in which some modification of the reactivity of recycled MK was detected with regard to the samples without ZnO (0.0%).

Two dehydroxylation bands were detected, located at 148 °C and 199 °C, in both cases clearly within the temperature interval between 100 °C/300 °C. In turn, temperature bands at 100 °C in this pozzolan/lime system would correspond to the humidity loss that the samples underwent during storage and testing and to water absorption due to the clayey minerals themselves. The band at 148 °C is typical of C-S-H gels, as a result of the reaction between the reactive silica of the pozzolan and Ca (OH)₂ of the solution, increasing in intensity over the reaction time (90 days without ZnO). The second band, at 199 °C, was located in the typical dehydroxylation zone of the hexagonal phases C₄AH₁₃, with calcium monosulfoaluminate and carboaluminates and LDH structures, identified by XRD. At 90 days of reaction time, a band appeared at 160 °C, overlapping the principal one of the C-S-H gels, which would correspond to the dehydroxylation of the stratlingite (C₂ASH₈).

At higher activation temperatures, a small broad band appeared between 300 °C and 500 °C, under the activation conditions, which corresponds to the presence of traces of K of very low crystallinity (Table 7). With the increased activation temperature, the band at 689 °C was due to the decarbonation of the calcite, both from the original sample and from possible carbonation of the saturated lime solution.

Through Raman spectroscopy, the formation of hydrated phases was observed in the case of the samples ACW650 at 90 days into the

reaction and with low concentrations of ZnO. In Fig. 9, the Raman spectrum is shown, in the interval 1200–900 cm⁻¹, for the samples in saturated lime solution over 90 days, with 0.5 and 1.0% ZnO, as well as the reference sample (0.0% ZnO).

In the reference sample (0.0% ZnO), characteristic signs of CaCO₃ in the form of calcite may be observed; when increasing the ZnO content up to 0.5%. The presence of a small signal at 1068 cm⁻¹ was also observed, characteristic of the presence of carboaluminate in the sample, which indicates that the pozzolanic reaction in the sample between the waste and Ca(OH)₂ did indeed take place.

Likewise, a small shoulder was observed at 980 cm⁻¹ that could indicate the formation of AFm-type-compounds. In the interval 3800–3600 cm⁻¹, the spectrum presented a broad band that could indicate vibrations of OH groups of the C₄AH₁₃ phases and stratlingite (Torrens-Martín et al., 2013).

Finally, it was observed that the Raman spectrum showed no signal within the interval 1200–900 cm⁻¹, which might indicate the lack of a reaction in the waste.

4. Conclusions

The hydrated phases that appeared in the pozzolanic reaction were: a) tetracalcium aluminate hydrate (C₄AH₁₃) (A); b) stratlingite (C₂ASH₈) (St); c) monosulfoaluminate hydrate (C₃A.SO₄Ca.12H₂O) (Mo) and d) LDH (phyllosilicate/carbonate) (L).

Thermal activation at different activation temperatures (550 °C, 600 °C and 650 °C) without the addition of ZnO, maintained a very similar mineralogy, with the exception of K.

At 550 °C/2 h, the addition of chemical activator from 1.0% to 3.0% inhibited the formation of all mineralogical phases of the pozzolanic reaction at 1, 7 and 28 days of treatment, as well as the non-appearance of spongy gels that act as a crystallization substrate for lamina growth.

At 650 °C/2 h, the same pozzolanic reaction products were formed and the inhibitory effect of the ZnO was observed at all the preset times and at concentrations of over 0.5%, on the presence of spongy gels, which are precursors to the formation of laminar products in the reaction, observing only the formation of fibbers in all cases.

The laminar morphological compounds were formed to the detriment of the C-S-H gels that acted as a substrate for crystallization and were found interspersed with them, forming aggregates.

In view of the results obtained in the present research, it has been highlighted that the addition of the chemical activator during the thermal activation of the coal waste has an inhibitory effect on the pozzolanic reaction between the recycled MK and the portlandite. In some cases, with small additions of ZnO 0.5%/1.0%, its effect is null or delays the reaction. In none of the cases under investigation, did the ZnO present properties to increase the reactivity of the MK in the coal waste, a different behavior when investigated in a 100% natural kaolinite.

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References

- Alujas, A., Fernández, R., Quintana, R., Scrivener, K.L., Martirena, F., 2015. Pozzolanic reactivity of low-grade kaolinitic clays: influence of calcination temperature and impact of calcination products on OPC hydration. *Appl. Clay Sci.* 108, 94–101.
- Cassagnabere, F., Escadeillas, G., Mouret, M., 2009. Study of the reactivity of cement/MK binders at early age for specific use in steam cured precast concrete. *Constr. Build. Mater.* 23, 775–784.

- Chindaprasirt, P., Rukzon, S., 2008. Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk and fly ash mortar. *Constr. Build. Mater.* 22 (8), 1601–1606.
- Frías, M., 2006. The effect of MK on the reaction products and microporosity in blended cement pastes submitted to long hydration time and high curing temperature. *Adv. Cem. Res.* 18, 1–6.
- Frías, M., García, R., Vigil, R., Ferreira, S., 2008. Calcination of art paper sludge waste for the use as a supplementary cementing materia. *Appl. Clay Sci.* 42, 189–193.
- Frías, M., García, R., Vigil de la Villa, R., Martínez-Ramírez, S., 2016. Coal mining waste as a future eco-efficient supplementary cementing material: scientific aspects. *Theatr. Rec.* 1, 232–241.
- García Giménez, R., Rodríguez, O., Vigil de la Villa, R., Frías, M., 2012. Changes to the triaxial, composition of the hydrated phases in the MK/lime system. *J. Am. Ceram. Soc.* 95 (3), 1118–1122.
- García, R., Vigil de la Villa, R., Frías, M., Rodríguez, O., Martínez-Ramírez, S., Fernández-Carrasco, L., de Soto, I.S., Villar-Cociña, E., 2015. Mineralogical study of calcined coal waste in a pozzolan/Ca(OH)₂ system. *Appl. Clay Sci.* 108, 45–54.
- Lilkov, V., Stoitchkov, V., 1996. Effect of the pozzolanic active mineral admixture on the properties of cement mortars and concrete. Part 2. Pozzolanic activity. *Cem. Concr. Res.* 26 (7), 1073–1084.
- Liu, Y., Lei, S., Lin, M., Li, Y., Ye, Z., Fan, Y., 2017. Assessment of pozzolanic activity of calcined coal-series kaolin. *Appl. Clay Sci.* 143, 159–167.
- Modarres, A., Nosoudy, Y.M., 2015. Clay stabilization using coal waste and lime — technical and environmental impacts. *Appl. Clay Sci.* 116–117, 281–288.
- Renaudin, G., Russias, J., Leroux, F., Frizon, F., 2009. Structural characterization of C–S–H and C–A–S–H samples—part I: long-range order investigated by Rietveld analyses. *J. Solid State Chem.* 182, 3312–3319.
- Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* 2, 65–71.
- Ruan, C.D., Ward, C.R., 2002. Quantitative X-ray powder diffraction analysis of clay minerals in Australian coals using Rietveld methods. *Appl. Clay Sci.* 21, 227–240.
- Sabir, B.B., Wild, S., Bai, J., 2001. Metakaolin and calcined clays as pozzolans for concrete: a review. *Cem. Concr. Compos.* 23, 441–454.
- Santos Silva, A., Gameiro, A., Grillo, J., Veiga, R., Velosa, A., 2014. Long-term behaviour of lime-metakaolin pastes at ambient temperature and humid curing condition. *Appl. Clay Sci.* 88–89, 49–55.
- Siddique, R., Klaus, J., 2009. Influence of metakaolin on the properties of mortar and concrete: a review. *Appl. Clay Sci.* 43, 392–400.
- Snelson, D., Wild, S., O'Farrell, M., 2008. Heat of hydration of Portland cement-MK-FA blends. *Cem. Concr. Res.* 38 (6), 832–840.
- Taylor, H.F.W., Mohan, K., Moir, H., 1985. Analytical study of pure and extended Portland cement pastes. I. Pure Portland cement pastes. *J. Am. Ceram. Soc.* 68 (12), 680–685.
- Taylor-Lange, S., Riding, K., Juenger, M., 2012. Increasing the reactivity of MK cement blends using zinc oxide. *Cem. Concr. Compos.* 34, 835–847.
- Tironi, A., Trezza, M.A., Scian, A.N., Irassar, E.F., 2014. Potential use of Argentina kaolinitic clays as pozzolanic material. *Appl. Clay Sci.* 101, 468–476.
- Tobón, J., Payá, J.J., Borrachero, M.V., Restrepo, O.J., 2012. Mineralogical evolution of Portland cement blended with silica nanoparticles and its effect on mechanical strength. *Constr. Build. Mater.* 36, 736–742.
- Torrens-Martín, D., Fernández-Carrasco, L., Martínez-Ramírez, S., Ibáñez, J., Artus, L., Matschei, T., 2013. Raman spectroscopy of anhydrous and hydrated calcium aluminates and sulfoaluminates. *J. Am. Ceram. Soc.* 96 (11), 3589–3595.
- UNE EN 197-1, 2011. Standards, Cement-Part-1: Composition, Specifications and Conformity Criteria for Common Cements.
- Vigil de la Villa, R., Frías, M., García Giménez, R., Martínez Ramírez, S., Fernández-Carrasco, L., 2014. Chemical and mineral transformations that occur in mine waste and washery rejects during pre-utilization calcination. *Int. J. Coal Geol.* 132, 123–130.
- Vigil, R., Frías, M., Sánchez de Rojas, M.I., Vegas, I., García, R., 2007. Mineralogical and morphological changes of calcined paper sludge at different temperatures and retention in furnace. *Appl. Clay Sci.* 36, 279–286.
- Yuan, P., Tan, D., Annabi-Bergaya, F., Yan, W., Liu, D., Liu, Z., 2013. From platy kaolinite to aluminosilicate nanoroll via one-step delamination of kaolinite: effect of the temperature of intercalation. *Appl. Clay Sci.* 83–84, 68–76.