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1   **Influence of ZnO on the activation of Kaolinite-based coal waste: pozzolanic activity and**

2   **mineralogy in the pozzolan/lime system**

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11

12   **Abstract**

13   One inconvenience presented by the thermal activation of kaolinite-based wastes is their low

14   content of metakaolinite, a highly pozzolanic product listed in current standards for the

15   manufacture of commercial cements. The addition of a chemical activator during the thermal

16   activation process is a priority line of research to increase the reactivity of the recycled

17   metakaolinite. In this paper, an additional chemical activator, ZnO, is studied and its effect on

18   both pozzolanic properties and the evolution of mineralogical phases in the thermal activation of

19   coal waste with a reaction time of up to 90 days in the pozzolan/lime system. To do so,

20   activation temperatures of between 550ºC/650ºC were selected and additions of chemical

21   activator (ZnO) in percentages of between 0.0% and 3.0% by weight of coal waste, because it is

22   an activator with a positive effect on a 100% natural kaolinite. The results showed that the

23   incorporation of ZnO inhibited the reactivity of the recycled metakaolinite and in consequence,

24   the capacity of the metakaolinite to react with the surrounding lime; even more so when the

25   content of added chemical activator was raised, albeit with some exceptions, in the samples

26   activated at 550ºC and 650ºC with 0.5% of chemical activator. In none of the cases under

27   analysis was the chemical activator able to improve the properties of the metakaolinite in

28   comparison with the properties of the reference sample activated only with temperature. The

29   hydrated phases that appeared in the pozzolanic reaction were tetracalcium aluminate hydrate,

30   stratlingite, monosulfoaluminate hydrate and LDH (phyllosilicate/carbonate).

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 CO_2, 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 al., 2013). However over recent times, the research has centered on obtaining this pozzolan from different industrial wastes, such as paper sludge, sewage sludge, and coal waste, among others (Vigil et

60　al., 2007; Frías et al., 2008, Vigil de la Villa et al., 2014; Modarres and Nosoudy, 2015), The

61　objective is reduced the environmental footprint of the cement industries (Tobón et al., 2012).

62　There have been numerous studies along these lines, both on the optimum conditions for

63　activation processes in which inert materials taken from coal mining waste is transformed into a

64　material with pozzolanic properties and on its behavior in binary cements (Alujas et al., 2015;

65　Liu et al., 2017).

66　Recently, Taylor-Lange et al. (2012) proposed the use of zinc oxide to increase the reactivity of

67　MK from a 100% natural kaolinite, obtaining good results in pure metakaolin-cement systems.

68　However, a vast area of investigation is at present unfolding on the behavior of this chemical

69　activator in kaolinite-based industrial waste, where the presence of other materials can

70　influence the reactivity of the recycled MK.

71　The objective of the present paper is to analyze the combined effect of the activation of a K-

72　based coal waste on pozzolanic reactivity and on the evolution of mineralogical phases in a

73　metakaolinite/lime (MK/CaO) system cured at 1, 7, 28, and 90 days reaction time. To do so,

74　activation temperatures between 550ºC and 650ºC were analyzed as well as percentages of

75　ZnO between 0.5% and 3.0% by weight of sample.

76　**2. Materials and Characterization methods.**

77　　*2.1. Materials.*

78　A kaolinite-based coal-mining waste was selected for the study, extracted from an open-cast

79　coal mine, the property of the company "Sociedad Anónima Hullera Vasco Leonesa", located in

80　the area of Santa Lucía (León, Spain). The mineralogically sterile coal is formed of

81　phyllosilicates (kaolinite 14% and mica 25%), quartz 25%, calcite 22%, dolomite 2%, and

82　feldspars 2%.

83　Subsequently, the waste was subjected to a combined high-temperature activation process (at

84　550, 600 and 650ºC) with ZnO as a chemical activator (0.0; 0.5; 1.0; 1.5 and 3.0 % by weight of

85　coal waste). Once calcinated, the products (Activated Coal Waste or ACW) were crushed in an

86　agate mortar and pestle to a size of less than 90 microns for subsequent analysis.

87　***2.2. Methodology.***

88　*2.2.1. Pozzolanic activity Method.*

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89   The pozzolanic activity of the calcinated products was evaluated by means of an accelerated

90   chemical method (Frías et al., 2006) in the pozzolan/lime ($Ca(OH)_2$) system at 1, 7, 28, and 90

91   days of reaction. It was then filtered, where the solid wastes were introduced in acetone to

92   inhibit the hydration reaction (24 hours), subsequently they were dried in an electric oven at

93   60ºC for 24 hours and, finally maintained in a desiccator until characterization by means of

94   different instrumental techniques. In the liquids, the lime reacting with the pozzolan was

95   determined at each fixed hydration time. The content of fixed lime was calculated as the

96   difference between the CaO concentration (mmol/L) in the original saturated lime solution

97   (17.68 mmol/L) and the content of this compound in the solution at the established time. An

98   extra pure PhEur, USP, BP chemical reagent of calcium hydroxide was used (Frías, 2006).

99   *2.3. Characterization Techniques.*

100 Different techniques were used for the material characterizations in the current study, as well as

101 for following the evolution of the hydrated phases formed during the pozzolanic reaction and for

102 their identification.

103 The mineralogical composition of the bulk samples was determined by random powder X-ray

104 diffraction (XRD) on a Siemens D-5000 (Munich, Germany) X-ray diffractometer fitted with a Cu

105 anode. Its operating conditions were set at 30 mA and 40 kV, at divergences of 2.0 and 0.6 mm

106 with reception slits, respectively. The samples were scanned in (2θ) 0.041 steps with a 3-s

107 count time. The characterization of the bulk samples was performed with the Rietveld method

108 (Rietveld 1969; De Ruan and Ward, 2002). Rutile was used as an internal reference patron at a

109 concentration of around 5% in all cases. Quantification accuracy via Rietveld method is typically

110 presented using the constants R and Chi². While, R exclusively compares peak intensities from

111 the calculated spectra of the material and the one obtained experimentally, Chi² also considers

112 phase weight. Ideally, both constants should be equal to 1; however, due to the discrepancy

113 between observed and calculated data, which increases greatly for materials containing over

114 three phases, values under R=20 and Chi²=10 are commonly accepted to be adequate enough

115 for valid results.

116 Morphological observation and microanalyses of the samples were carried out by SEM/EDX,

117 using an Inspect FEI Company Electron Microscopy (Hillsboro, OR), equipped with an energy

118 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 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 + 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 (550ºC/2h, 600ºC/2h and 650ºC/2h) 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 hours 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

148 al. (2012), which mentioned the good behavior of this chemical activator agent in the

149 mechanical properties of natural MK blended cement mortars.

150 *3.2. Mineralogical evolution of the hydrated phases identified in the pozzolanic reaction.*

151 The reaction products obtained at 1, 7, 28, and 90 days of pozzolanic reaction in the recycled

152 MK/lime system, calcinated at various temperatures and percentages of ZnO, were analyzed, in

153 order to investigate the influence of the chemical activator on the evolution of the hydrated

154 phases. The results obtained in the samples solely activated with temperature (550, 600 and

155 650ºC, with no chemical activator) are presented in Table 1.

156 The mineralogically activated products were similar at all temperatures (rutile was introduced as

157 a standard reference) with minimum variations in the quantity of calcite and quartz. The

158 presence of K traces at 550ºC (practically total dehydroxylation), the reduction of mica and the

159 increase of amorphous material were evident at 600ºC. At 650ºC, the values were very similar

160 to the coal waste activated at 550ºC. In the SEM observation, compact aggregates of scaled

161 surfaces, a sign of the start of phyllosilicate dehydroxylation, were detected.

162 Successive additions of ZnO appear to favor the surface descaling process, recognizable

163 through SEM following the appearance of porous aggregates. In the case of a 3.0% addition,

164 the ZnO particles were even deposited on the aggregate surface and edges.

165 As an example of the results obtained by XRD under the different test conditions, only those

166 diffractograms of coal waste activated at 550ºC (ACW) are shown in Fig. 2 with the different

167 contents of ZnO at day 1 of the reaction.

168 The hydrated phases that appeared in the pozzolanic reaction were: a) tricalcium aluminate

169 hydrate (C_4AH_{13}) (A) with reflections at 7.9Å (11.18^0 2θ), 2.88Å (31.02^0 2θ), 2.86Å (31.24^0 2θ)

170 and 2.45Å (36.64^0 2θ); b) stratlingite (C_2ASH_8) (St) at 12.61Å (7.0^0 2θ), 6.28Å (14.08^0 2θ),

171 4.15Å (21.38^0 2θ) and 2.87Å (31.14^0 2θ); c) monosulfoaluminate hydrate ($C_3A.SO_4Ca.12H_2O$)

172 (Mo) characterized by reflections at 8.92Å (9.91º 2θ) and 2.87Å (31.16º 2θ) and d) LDH

173 (phyllosilicate/carbonate) (L) at 7.60Å (11.64^0 2θ), 7.41Å (11.94^0 2θ), and 3,78Å (23.52^0 2θ)

174 (Santos Silva et al., 2014).

175 The presence and evolution of the hydrated mineralogical phases depended on the reaction

176 time and the percentage of added ZnO. Considering only the existence of reactivity between the

177 MK and the $Ca(OH)_2$, quantification of the mineralogical phases was performed with the

178   Rietveld method (Renaudin et al., 2009), the values of which are shown in Table 2. Thus, LDH

179   (L) appeared as a mineralogical phase as from day 7 of the reaction time, reaching its maximum

180   concentration at 28 days, as the only crystalline phase that was formed. In turn, Mo was

181   complementary to LDH at that same age. At the other ages, LDG, Mo, and St coexisted, this

182   last phase being, in general terms, the predominant against the other two, principally at 90

183   days. In all cases, the amorphous material has stabilized at a constant value, which has

184   increased slightly since the youngest age (1 day). The rest of ages and proportions, only keep

185   the products of departure.

186   Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) techniques can

187   detect the existence of C-S-H gels on the surface of the aggregated layers generated during

188   calcination that are rich in silica and with porous surfaces (Fig. 3a). These gels have a spongy

189   appearance and little thickness, and therefore, the analysis, corresponds to the gels and to the

190   substrate on which they develop (Fig. 3b).

191   The compounds of laminar morphology are formed at the expense of the C-S-H gels that act as

192   a substrate for crystallization, finding themselves interspersed with them and forming

193   aggregates (Fig. 3a and Table 3).

194   In the analysis of these phases in table 3, the composition of the substrate on which they

195   nucleate is detected, yielding values for composition that are at some distance from those

196   corresponding to their stoichiometries.

197   The addition of 0.5% ZnO to the coal waste maintained the reaction products formed at the time

198   of analysis and the results were not modified when that chemical activator was not added. At 7

199   days into the reaction, it only favored the formation of Mo and, at all the ages, the appearance

200   of a very fine C-S-H gels coating that is the substrate for laminar growth (Fig. 3c and d).

201   The increased concentration of chemical activator from 1.0% to 3.0% prevented the formation of

202   all crystalline phases after 1, 7, and 28 days of reaction time. Moreover, the non-appearance of

203   spongy gels, which act as a crystallization substrate for laminar growth, meant that the clayey

204   aggregates became more compact (Fig. 3e), and elongated fibers developed from them, at

205   ages of up to 28 days.

206   After 90 days of reaction time had elapsed, the addition of 1.0% of ZnO, in addition, generated

207   the formation of tetracalcium aluminate hydrate (C_4AH_{13}) (A) (Table 2) and a thin layer of gels

208 with a spongy appearance started to form that served as a substrate upon which the products of

209 the reaction crystallized in laminar forms (Fig. 3f). The compositions of the clayey aggregates at

210 times presented deposits of zinc, while the sulfur and the calcium were concentrated in the

211 fibbers.

212 When the concentrations of ZnO additive were increased to 1.5% and 3.0%, the formation of all

213 crystalline products of the reaction were inhibited. Through SEM, the formation of compact

214 aggregates may be seen where small laminas form; the lengthier fibers are very abundant with

215 variable compositions with regard to Si and Al. The excess ZnO was deposited on the surfaces

216 or on the fibers in an oriented way.

217 The composition of the gels is very heterogeneous depending on the material that they coat; no

218 average measurement that would be significant can be obtained, because scattered deposits

219 are observed of ions such as Fe, Zn, Ca and S (Table 4).

220 The high fluorescence of ACW550 samples does not allow information to be obtained on the

221 phases formed in the pozzolanic reaction of the waste through Raman spectroscopy.

222 The results obtained from the analysis of the FTIR spectra of the samples, indicated a clear

223 effect on the development of reaction products, in the comparison prepared for the different

224 temperatures, due to the presence of ZnO. This effect is turned into a diminishment in the

225 intensity of some absorption bands and especially in those that appear in the region between

226 4000-3000 cm^{-1} due to the absorption of the bonds of the H_2O groups of the C-S-H gels and the

227 OH groups of some hydrated species. When increasing the proportion of ZnO in the mixtures, a

228 progressive diminishment of the aforementioned bands was noted, both in the samples at

229 550ºC, 600ºC and 650ºC.

230 The spectra in Fig. 4A represent the samples treated at 550ºC at 7 and 90 days with ZnO

231 contents of 0.0, 0.5, and 3.0%. At 7 days, they all presented absorption bands, due to ν(O-H)

232 from Mo at around 3647 cm^{-1}, and another band at around 3623 cm^{-1}, also of ν(O-H), revealing

233 Al-OH –both are more intense in the samples with ZnO content ranging between 1.0%-3.0%.

234 The last band is difficult to assign, although it could be due to the compound C_4AH_{13} (A), and it

235 could also represent aluminum hydroxide, as both present an absorption band in that zone.

236 Band ν3-H_2O of C-S-H gel was observed at around 3434 cm^{-1}, clearly of a higher intensity in the

237 sample with no ZnO (0.0% ZnO). This assumption would support the results found with other

238 techniques that refer to lower reactivity, due to the presence of ZnO. At 90 days (Fig. 4B), the

239 position of the absorption bands had not changed (Fig. 4B), but an increase was noted in the

240 bands, due to the C-S-H gel, especially in the sample with an addition of 0.5%, which is

241 practically identical to the one without any addition (0.0% ZnO); the bands of the samples with

242 1% ZnO clearly increased. There would be a practically identical increase in the pozzolanic

243 reaction at these ages in the samples without (0.0%) and with 0.5% of ZnO.

244 When the activation of the coal waste was complete at 600ºC/2 hours with the different

245 additions of chemical activator, it yielded the material phases as shown in Table 5.

246 In a similar way, to thermal activation at 550ºC/2 hours in the ACW600 samples, the chemical

247 additions of 0.5% ZnO were only significant and of course the thermal activations with no

248 addition (0.0% de ZnO) and the same hydrated phases were recognized: LDH, Mo and St. The

249 LDH phase appears at 1 and 7 days (with no chemical additions) and at 28 days with 0.5% of

250 addition. St predominated at 7 and 28 days with no addition and at 90 days without addition and

251 with 0.5%.

252 Mo appeared at only 7 days of activation, the only single phase having an addition of 0.5% of

253 ZnO. It is also important to stress the identification of the hydrated A phase at 1, 7 and 28 days.

254 At this calcination temperature, the process of total deshydroxylation of K and partial

255 deshydroxylation of mica was conspicuous. When adding zinc oxide, the process of surface

256 descaling was favored giving rise to the formation of porous aggregates, with deposits of zinc

257 on surfaces and edges. C-S-H gels of a spongy appearance were detected on the aggregate

258 surfaces. Laminar compounds were formed to the detriment of C-S-H gels that acted as a

259 crystallization substrate and were found interspersed with them forming aggregates (Fig. 5a and

260 b).

261 The presence of ZnO inhibited the formation of spongy gels on the clayey aggregates; the

262 appearance of the aggregates became compacted as the time of the pozzolanic reaction

263 increased (Fig. 5c).

264 The absence of these spongy gels forces a change in the appearance of the reaction products;

265 the formation of elongated fibers, both isolated and in groups, of variable sizes for the times

266 under analysis were observed in most places and for all the conditions under consideration.

267 Variations in their compositions may be found, principally with regard to Si, Al, S and Ca. Zn

268   was deposited on fibber edges and the surfaces in an oriented direction and appeared to

269   contribute to the growth in fiber thickness (Fig. 5d). The aforementioned fibers were also

270   observed with Raman microscopy.

271   Fig. 4 C and D presents the samples activated at 600ºC/2 hours where an inhibition of the

272   reactivity of the ZnO may be appreciated for any proportion at the age of 7 days; nevertheless,

273   the absorption bands were presented in the same positions. At 90 days, there was no increase

274   in the reactivity of these samples.

275   The highest and the final activation temperature under consideration, 650ºC/2 hours, to which

276   the coal waste is subject with the foreseen additions of ZnO shown in Table 6 and Fig. 6.

277   At this temperature, the joint activation temperature + chemical additive was only notable at 90

278   days of pozzolanic reaction and with 0.5% ZnO; in addition, under these conditions, all the

279   hydrated phases, identified up until that point had formed, with the exception of St, which were

280   mainly LDH and Mo.

281   The presence of ZnO at the preset quantities inhibited the formation of all the crystalline

282   products of the reaction at early ages, 1 and 7 days, an effect appreciated later on, at 28 and 90

283   days, at concentrations of 1.0%, 1.5% and 3.0%.

284   The ZnO concentration at 0.5% had a selective behavior with regard to the inhibition at 90 days

285   of reaction, given that neither St nor A compounds appeared (the absence of spongy gels

286   prevents the formation of laminar products, observing only the formation of fibbers), while Mo

287   and L formed.

288   At 90 days, the concentration of 0.5% ZnO strengthened the formation of all the reaction

289   products. The gels were maintained at 90 days and were responsible for the formation of all the

290   laminar products in the reaction (Fig. 7 a, b, c and d).

291   The spectra corresponding to 650ºC/2hours of thermal activation (Fig. 4 E and F) once again

292   reproduced the situation described earlier: the sample with no addition was the one that

293   presented the highest formation of CSH gels, followed by the sample with an addition of 0.5%

294   ZnO.

295   No high variations in other regions of the spectrum were observed. Bands due to Si-O vibrations

296   in tetrahedral sites appeared at 1032 cm^{-1} and 1010 cm^{-1} for kaolinite; at 1023 cm^{-1} for illite;

297   and, at 1080 cm^{-1} for quartz. In the lower frequency region, bands at 797, 781 (doublet), 698

298 and 472 cm^{-1} correspond to the vibrations of the Si–O quartz bond. Finally, the characteristic

299 frequencies at 533 and 472 cm^{-1} correspond to Si–O–Al and Si–O for kaolinite and illite,

300 respectively.

301 The thermogravimetric studies (TG/DTG) confirmed that the results for the saturated lime

302 solution with regard to the addition of ZnO in the majority of cases inhibited a pozzolanic

303 reaction, which implies the non-formation of the typical hydrated phases in the ACW-lime

304 system (García et al., 2016). These hydrated phases, under thermal effects, experienced weight

305 loss within the interval of 100ºC/300ºC, due to a process of dehydroxylation, principally hydrates

306 of C-S-H gels, carboaluminates, calcium and silicoaluminates, which are phases identified in the

307 pozzolan/lime system, in accordance with the nature of the pozzolan.

308 Table 7 shows TG loss of the three calcination temperatures with additions of only 0.5% and

309 3.0% ZnO, because they represent the extreme values under analysis, while the additions of

310 1.0 and 1.5% of the chemical agent in no way modified the reactivity of MK at any temperature.

311 These values are totally in accordance with those obtained for the fixed lime: at 550ºC; with the

312 addition of only 0.5% of the chemical agent. The losses were similar to the losses in the

313 reference sample (550ºC + 0.0%ZnO) and a slight increase in the losses of the waste at 600ºC

314 and 650ºC with 0.5% ZnO at 90 days into the reaction.

315 Fig. 8 shows, as an example of all the products obtained. The DTG curves at 7days (Fig. 8a)

316 and 90 days (Fig. 8b) of the pozzolanic reaction for the samples activated at 550Cº and 650ºC

317 with 0.5% and 3.0% ZnO, because these conditions are the extreme conditions for activation

318 under analysis and in which some modification of the reactivity of recycled MK was detected

319 with regard to the samples without ZnO (0.0%).

320 Two dehydroxylation bands were detected, located at 148ºC and 199ºC, in both cases clearly

321 within the temperature interval between 100ºC/300ºC. In turn, temperature bands at 100ºC in

322 this pozzolan/lime system would correspond to the humidity loss that the samples underwent

323 during storage and testing and to water absorption due to the clayey minerals themselves. The

324 band at 148ºC is typical of C-S-H gels, as a result of the reaction between the reactive silica of

325 the pozzolan and Ca (OH)$_2$ of the solution, increasing in intensity over the reaction time (90

326 days without ZnO). The second band, at 199ºC, was located in the typical dehydroxylation zone

327 of the hexagonal phases C_4AH_{13}, with calcium monosulfoaluminate and carboaluminates and

328 LDH structures, identified by XRD. At 90 days of reaction time, a band appeared at 160ºC,

329 overlapping the principal one of the C-S-H gels, which would correspond to the dehydroxylation

330 of the stratlingite (C_2ASH_8).

331 At higher activation temperatures, a small broad band appeared between 300ºC and 500ºC,

332 under the activation conditions, which corresponds to the presence of traces of K of very low

333 crystallinity (Table 7). With the increased activation temperature, the band at 689ºC was due to

334 the decarbonation of the calcite, both from the original sample and from possible carbonation of

335 the saturated lime solution.

336 Through Raman spectroscopy, the formation of hydrated phases was observed in the case of

337 the samples ACW650 at 90 days into the reaction and with low concentrations of ZnO. In Fig. 9,

338 the Raman spectrum is shown, in the interval 1200-900 cm^{-1}, for the samples in saturated lime

339 solution over 90 days, with 0.5 and 1.0% ZnO, as well as the reference sample (0.0% ZnO).

340 In the reference sample (0.0% ZnO), characteristic signs of $CaCO_3$ in the form of calcite may be

341 observed; when increasing the ZnO content up to 0.5%. The presence of a small signal at 1068

342 cm^{-1} was also observed, characteristic of the presence of carboaluminate in the sample, which

343 indicates that the pozzolanic reaction in the sample between the waste and $Ca(OH)_2$ did indeed

344 take place.

345 Likewise, a small shoulder was observed at 980 cm^{-1} that could indicate the formation of AFm-

346 type-compounds. In the interval 3800-3600 cm^{-1}, the spectrum presented a broad band that

347 could indicate vibrations of OH groups of the C_4AH_{13} phases and stratlingite (Torrens-Martín et

348 al., 2013).

349 Finally, it was observed that the Raman spectrum showed no signal within the interval 1200-900

350 cm^{-1}, which might indicate the lack of a reaction in the waste.

351 **4. Conclusions**

352 The hydrated phases that appeared in the pozzolanic reaction were: a) tetracalcium aluminate

353 hydrate (C_4AH_{13}) (A); b) stratlingite (C_2ASH_8) (St); c) monosulfoaluminate hydrate

354 ($C_3A.SO_4Ca.12H_2O$) (Mo) and d) LDH (phyllosilicate/carbonate) (L).

355 Thermal activation at different activation temperatures (550ºC, 600ºC and 650ºC) without the

356 addition of ZnO, maintained a very similar mineralogy, with the exception of K.

357   At 550ºC/2 hours, the addition of chemical activator from 1.0% to 3.0% inhibited the formation of

358   all mineralogical phases of the pozzolanic reaction at 1, 7 and 28 days of treatment, as well as

359   the non-appearance of spongy gels that act as a crystallization substrate for lamina growth.

360   At 650ºC/2 hours, the same pozzolanic reaction products were formed and the inhibitory effect

361   of the ZnO was observed at all the preset times and at concentrations of over 0.5%, on the

362   presence of spongy gels, which are precursors to the formation of laminar products in the

363   reaction, observing only the formation of fibbers in all cases.

364   The laminar morphological compounds were formed to the detriment of the C-S-H gels that

365   acted as a substrate for crystallization and were found interspersed with them, forming

366   aggregates.

367   In view of the results obtained in the present research, it has been highlighted that the addition

368   of the chemical activator during the thermal activation of the coal waste has an inhibitory effect

369   on the pozzolanic reaction between the recycled MK and the portlandite. In some cases, with

370   small additions of ZnO 0.5%/1.0%, its effect is null or delays the reaction. In none of the cases

371   under investigation, did the ZnO present properties to increase the reactivity of the MK in the

372   coal waste, a different behavior when investigated in a 100% natural kaolinite.

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447
448   **Caption of Figures and Tables**
449

450
451   **Tables**

452   Table 1. Percentage of presents phases with the activation temperature and with no chemical

453   activator.

454   Table 2. Present phases in the pozzolanic reaction at 550ºC with different additions and days of

455   duration from the pozzolanic reaction (Ca = calcite; K = kaolinite; Q = quartz; M = mica; L = LDH

456   phyllosilicate/carbonate; Mo = monosulphoaluminate hydrate; St = stratlingite; A = tricalcium

457   aluminate hydrate; Am = amorphous material)

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

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

460   Table 5. Present phases in the pozzolanic reaction at 600ºC with different additions and days of

461   duration from the pozzolanic reaction (Ca = calcite; Q = quartz; M = mica; L = LDH

462   phyllosilicate/carbonate; Mo = monosulphoaluminate hydrate; St = stratlingite; A = tricalcium

463   aluminate hydrate; Am = amorphous material)

464   Table 6. Present phases in the pozzolanic reaction at 650ºC with different additions and days of

465   duration from the pozzolanic reaction (Ca = calcite; K = kaolinite; Q = quartz; M = mica; L = LDH

466   phyllosilicate/carbonate; Mo = monosulphoaluminate hydrate; St = stratlingite; A = tricalcium

467   aluminate hydrate; Am = amorphous material)

468   Table 7. Evolution of weight losses (90ºC/300ºC) of the TG curves with the temperature and the

469   addition of ZnO.

470

471   **Figures**

472

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

474   activation systems.

475   Fig. 2: XRD patterns of CW550 and ZnO at 1 day of reaction time.

476   Fig. 3: SEM/EDX analysis for the ACW550: a) Superficial aspect; b) ZnO deposits; c) layers of

477   monosulfoaluminate   in 0.5ACW550; layers of stratlingite with LDH and CSH gels in

478   0.5ACW550; e) compact aggregates and fibbers in 3.0ACW550 at 7 days; f) aggregates with

479   CSH gels and mica at 90 days in 1.0ACW550.

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

481   ACW650.

482   Fig.5: SEM/EDX analysis: a) LDH and CSH gels, b) Stratlingite and CSH gels in 0.5ACW600 at

483   7 days; c) Aggregates in 3.0ACW600 at 7 days; d) Aggregates in 3.0ACW600 at 28 days.

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

485   Fig. 7: a) CSH gels under aggregates at 28 days; b) CSH gels under aggregates at 90 days; c)

486   layers under CSH gels at 90 days; d) general aspect at 90 days. All samples were made in

487   0.5ACW650.

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

489   Fig. 9:- Raman spectrum of ACW650 samples with 0%, 0.5% and 1% ZnO and 90 days in a

490   saturated solution of lime.

491

492

Table 1. Percentage of presents phases with the activation temperature and with no chemical activator.

Temperature (ºC)	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

Table 2. Present phases in the pozzolanic reaction at 550ºC 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

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

Oxides (%)	CSH gels 7 days	Monosulfoaluminate 7 days	C_2ASH_8 90 days	LDH 90 days
Na_2O	0.36 ± 0.11	n.d.	n.d.	n.d.-
MgO	0.86 ± 0.31	n.d.	n.d.	n.d.
Al_2O_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_2O	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_2O_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.

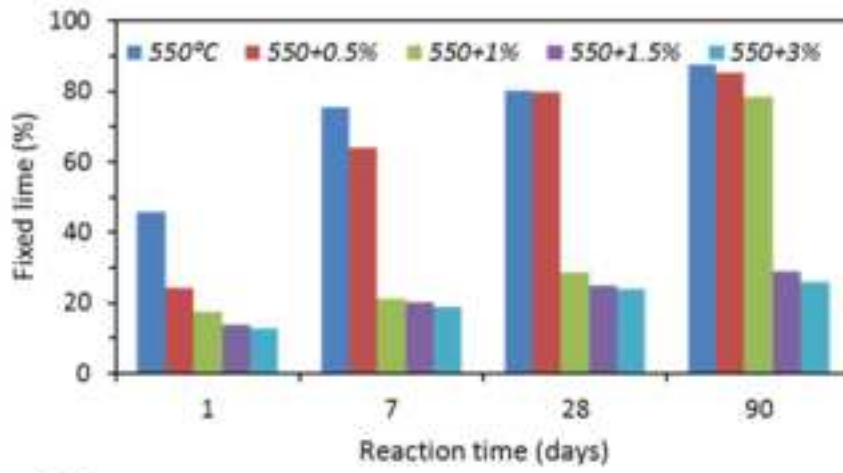| Oxides (%)	Substrate Fe 7 days	Substrate Zn 7days	C_2ASH_8 7 days	Monosulfoaluminate 7 days	CSH gels-Zn 90 days	LDH-Zn 90 days
MgO	3.34	n.d.	n.d.	n.d.	0.53	n.d.
Al_2O_3	20.41	26.38	31.64 ± 1.28	27.75 ± 2.14	25.13	26.74 ± 0.62
SiO_2	35.21	49.22	23.77 ± 1.43	2.96 ± 0.84	49.02	48.58 ± 1.27
SO_3	2.50	n.d.	10.08 ± 0.69	21.95 ± 2.47	n.d.	n.d.
K_2O	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_2O_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

Table 5. Present phases in the pozzolanic reaction at 600ºC 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)
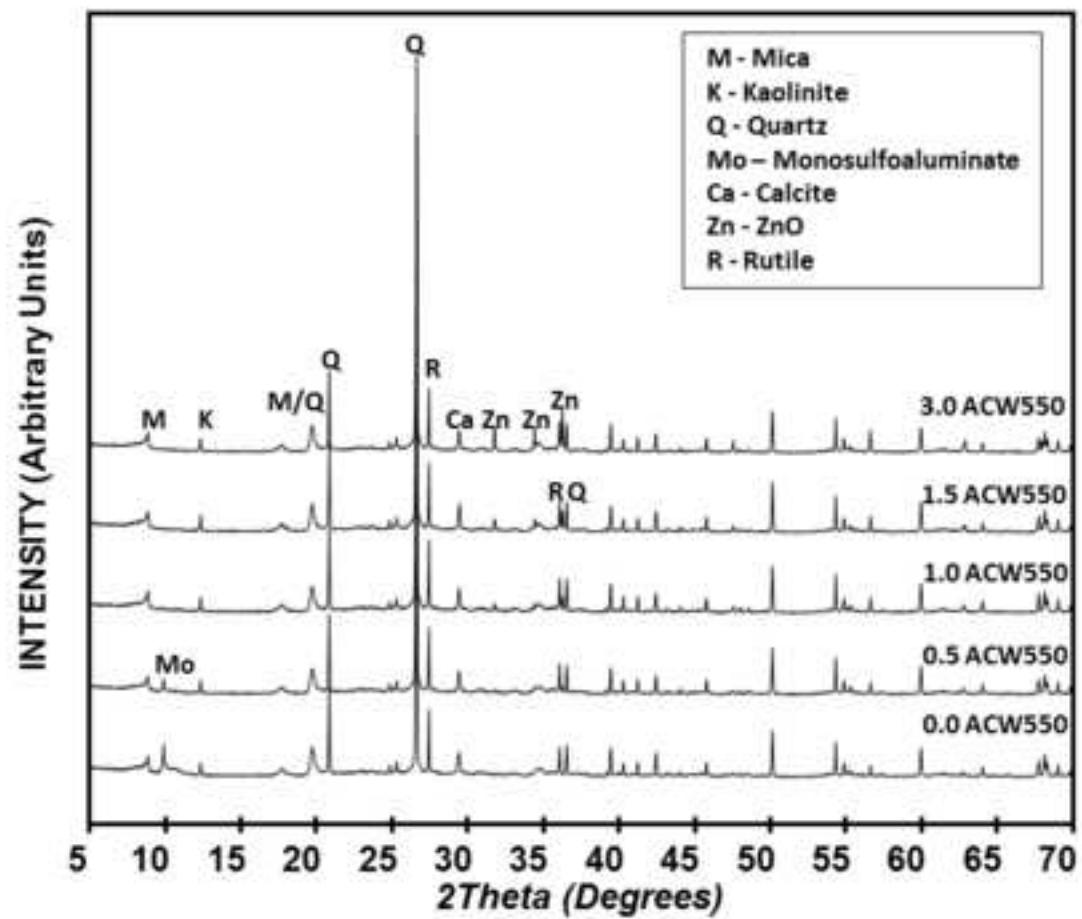
DSC (days)	ZnO addition (%)	Ca (%)	Q (%)	M (%)	L (%)	Mo (%)	St (%)	A (%)	Am (%)	R	Global chi^2
1	0.0	6	29	40	4	n.d.	n.d.	3	18	16.14	8.62
7	0.0	6	30	27	3	4	7	3	20	15.32	7.25
7	0.5	5	34	21	n.d.	3	n.d.	n.d.	37	17.54	6.13
28	0.0	9	36	23	n.d.	n.d.	10	3	19	18.66	7.07
28	0.5	3	33	27	4	n.d.	n.d.	n.d.	33	15.14	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

Table 6. Present phases in the pozzolanic reaction at 650ºC 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)

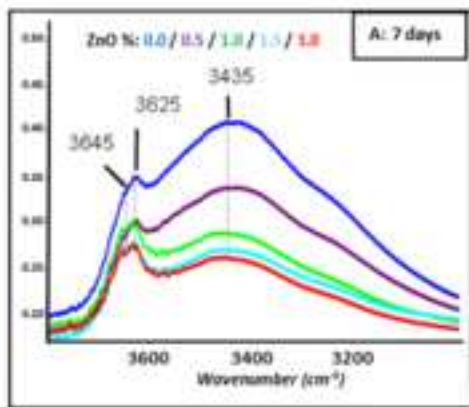| DSC (days)	ZnO addition (%)	Ca (%)	Q (%)	M (%	L (%)	Mo (%)	St (%)	A (%)	Am (%)	R	Global chi^2
7	0.0	6	36	21	3	3	7	3	21	16.24	6.23
28	0.0	4	33	24	3	3	9	3	20	15.36	7.12
90	0.0	3	26	22	3	3	10	n.d.	33	16.70	5.19
90	0.5	3	24	20	9	6	n.d.	3	35	17.20	6.87

n.d. = not detected

Table 7. Evolution of weight losses (90⁰C/300⁰C) of the TG curves with the temperature and the addition of ZnO.

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

(a)

5 µm

(b)

Zn deposits

10 µm

(c)

Mo

5 µm

(d)

St

LDH

CSH gels

St

10 µm

(e)

Fibers

Aggregate

20 µm

(f)

CSH gels

M

5 µm

ZnO %: 0.0 / 0.5 / 1.0 / 1.5 / 2.0

(a) ... L ... CSH gel ... 10 μm

(b) ... St ... CSH gel ... 2 μm

(c) ... Fibbers ... 2 μm

(d) ... 2 μm

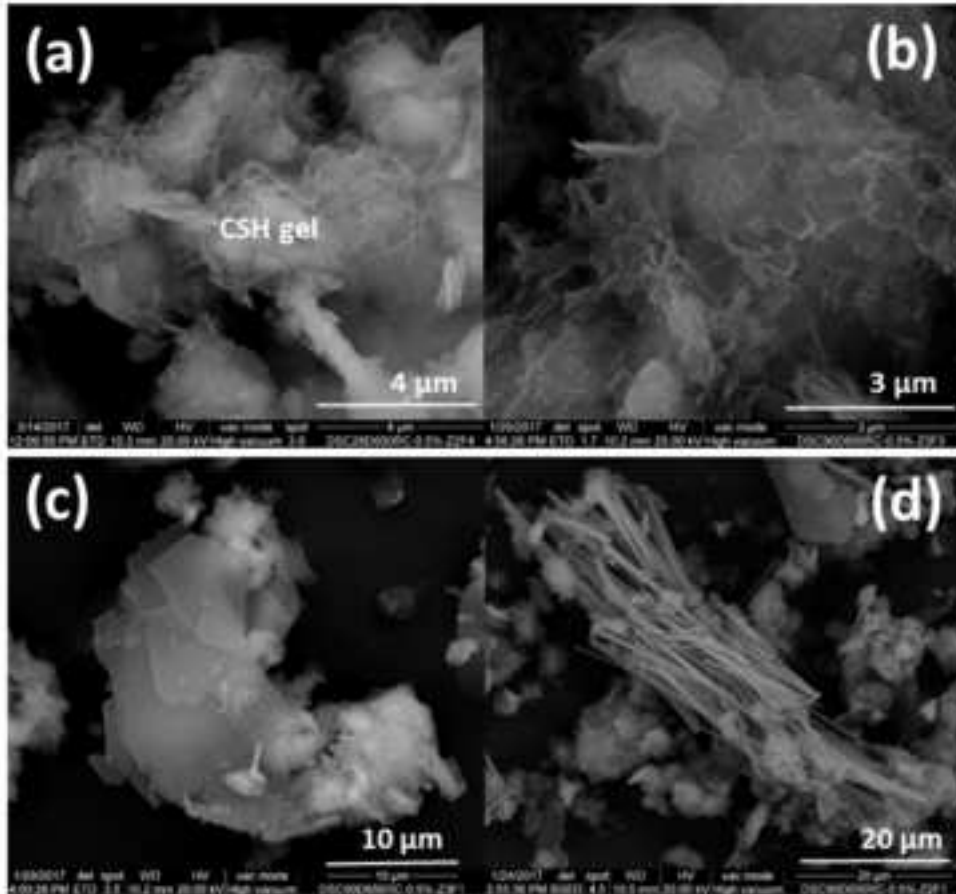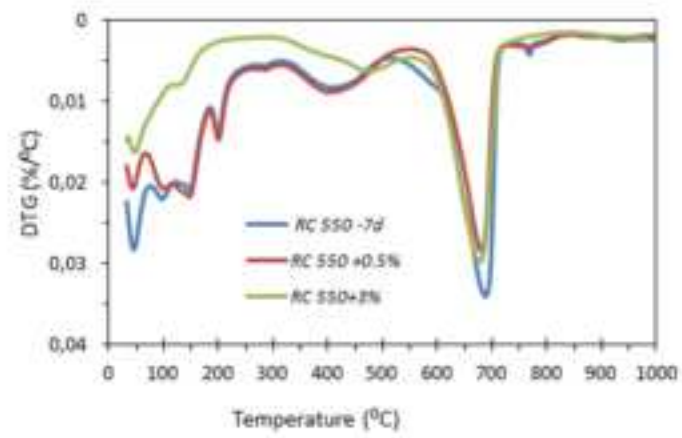DTG (%/ °C)
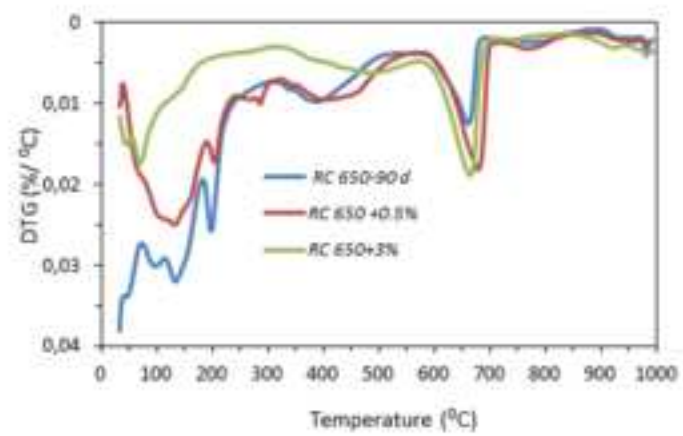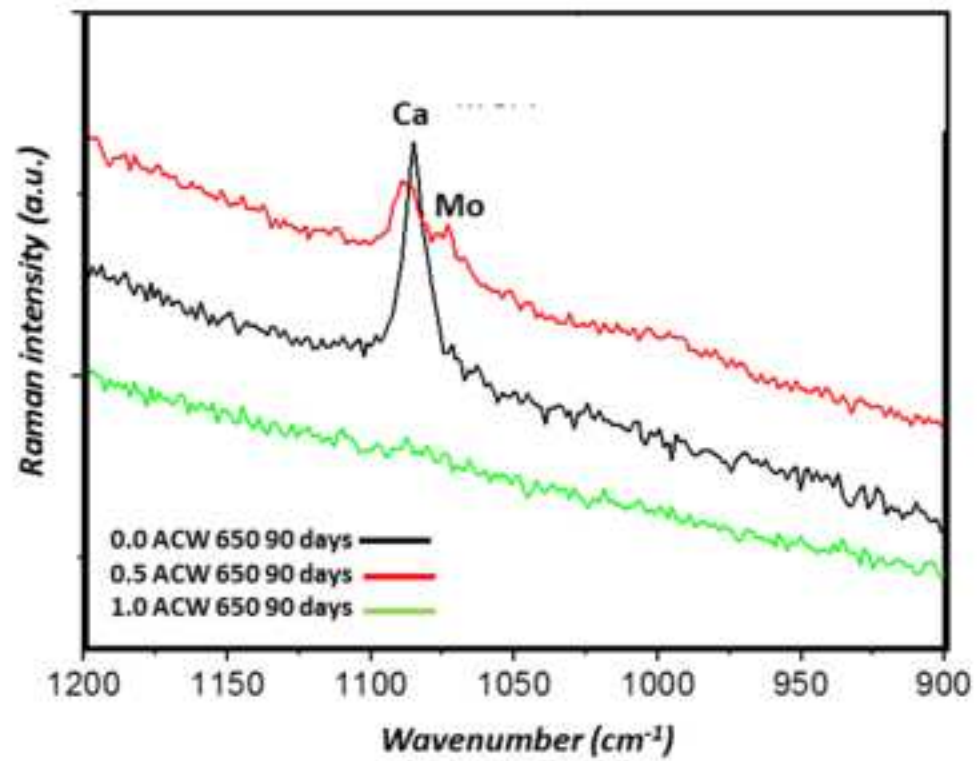
Temperature (⁰C)

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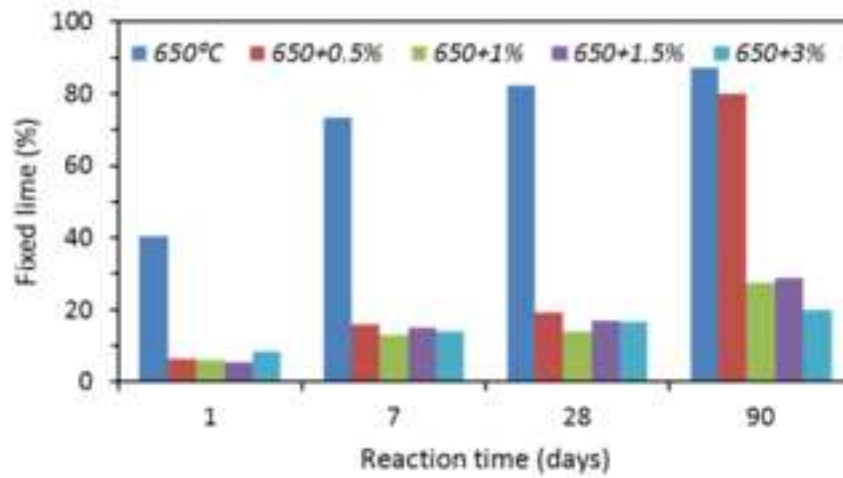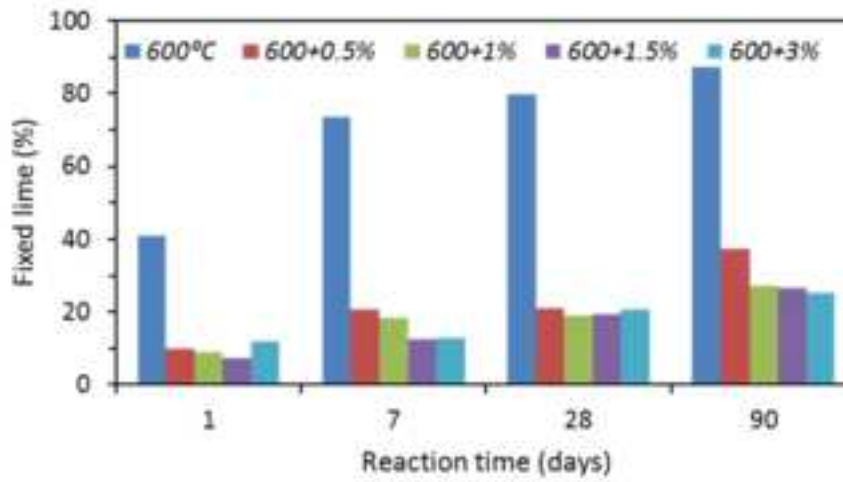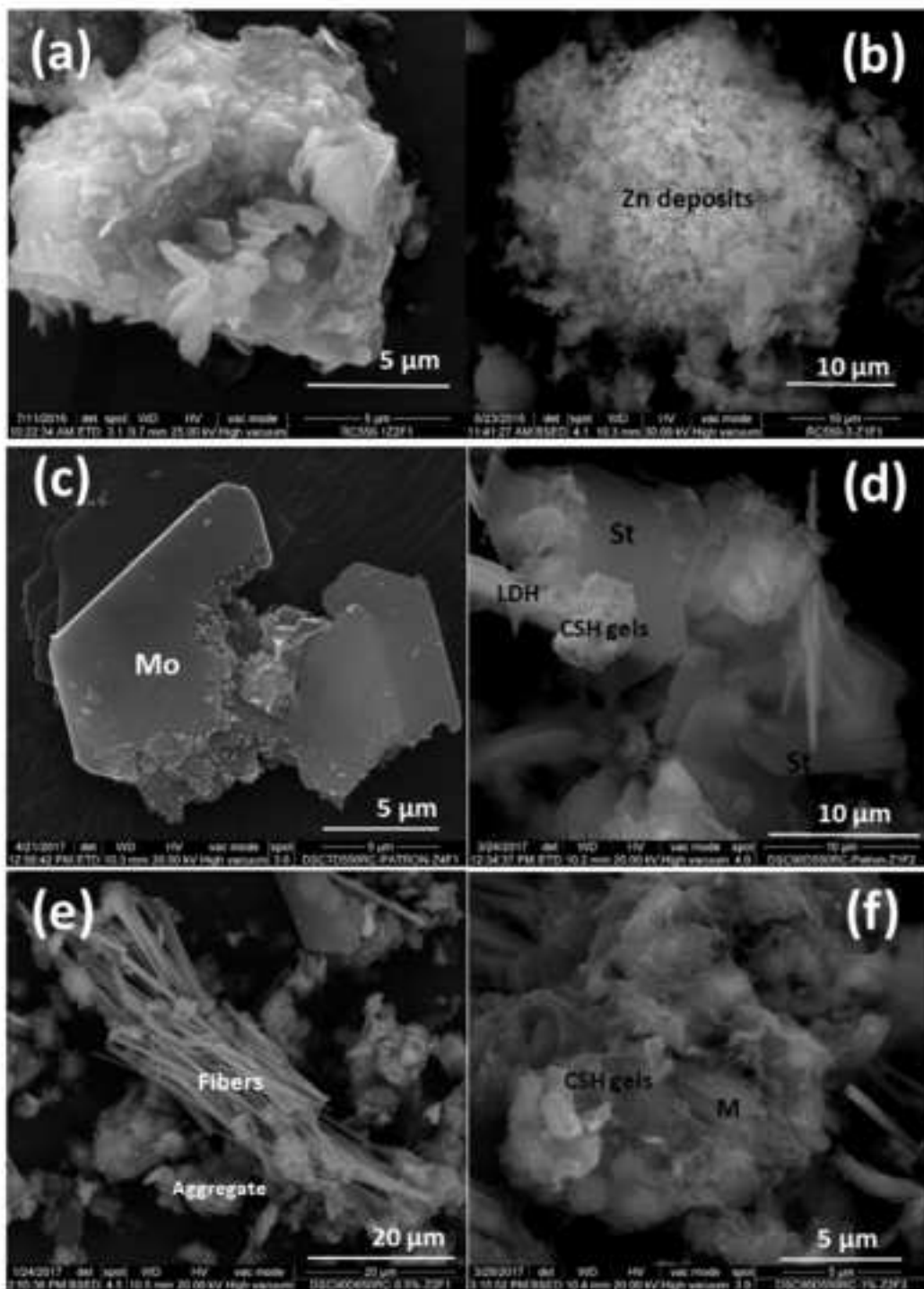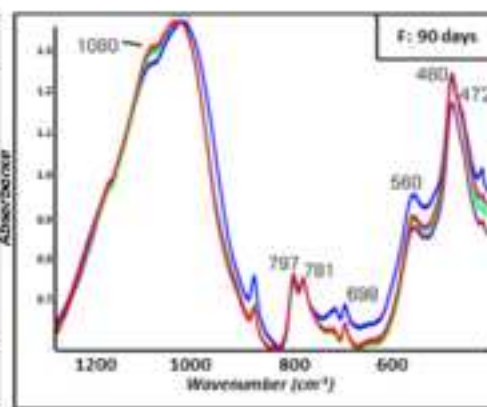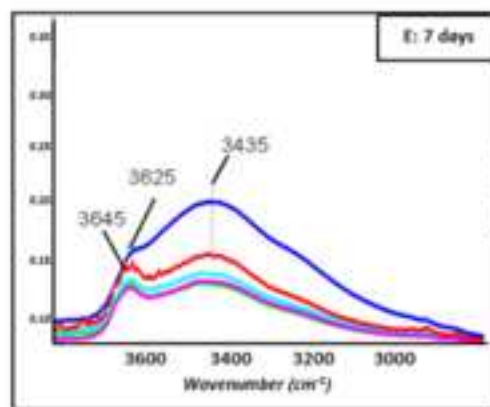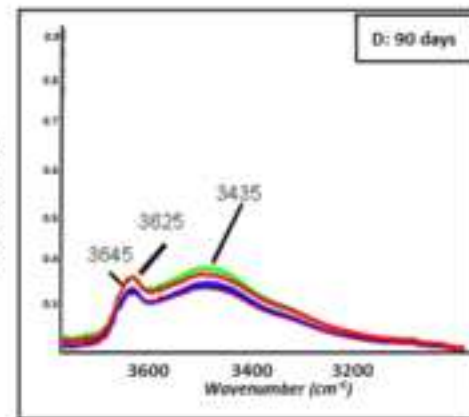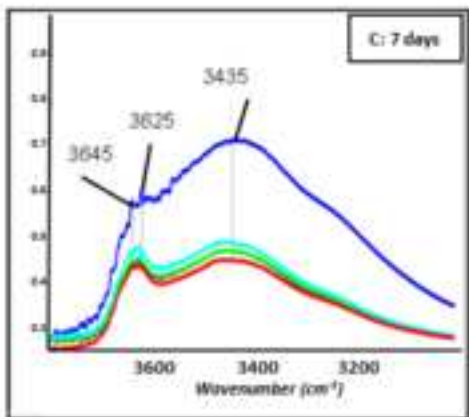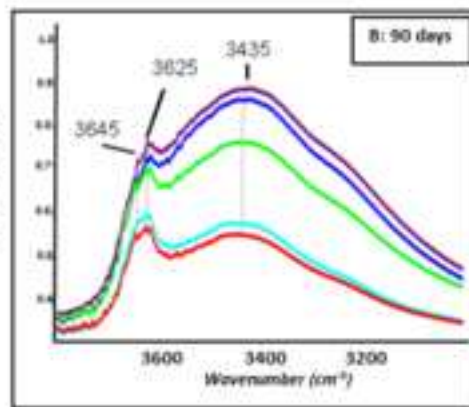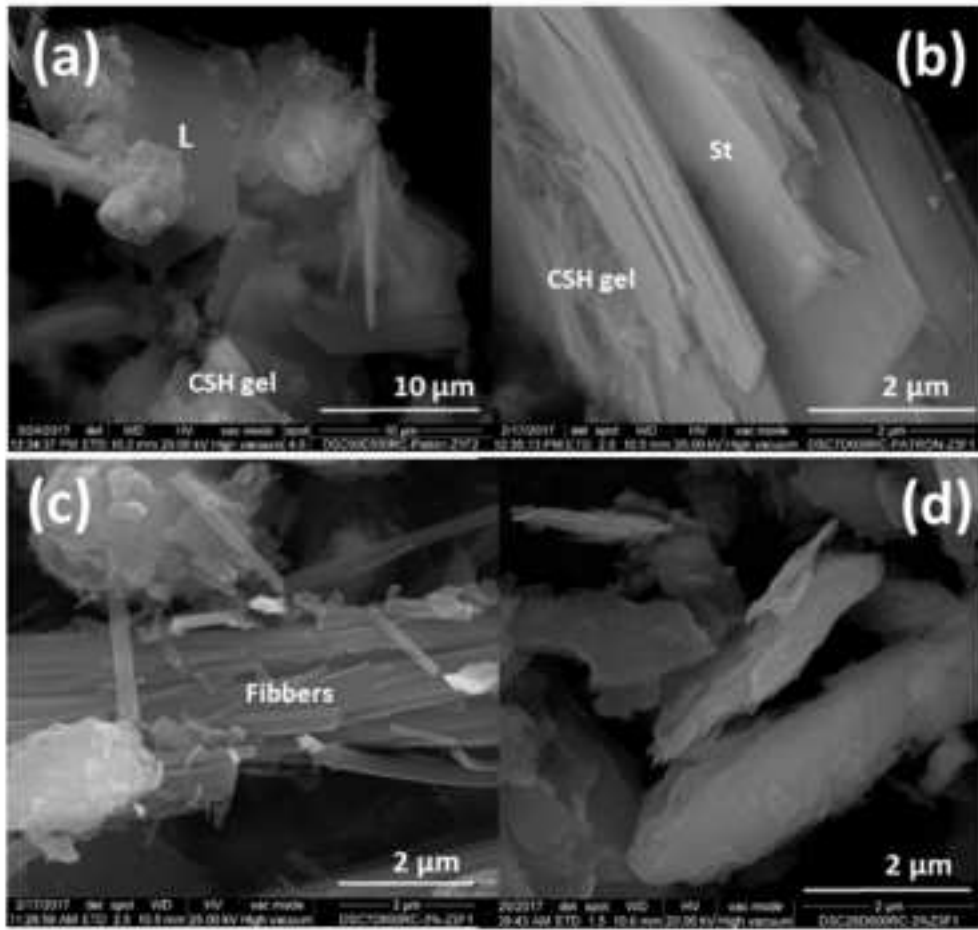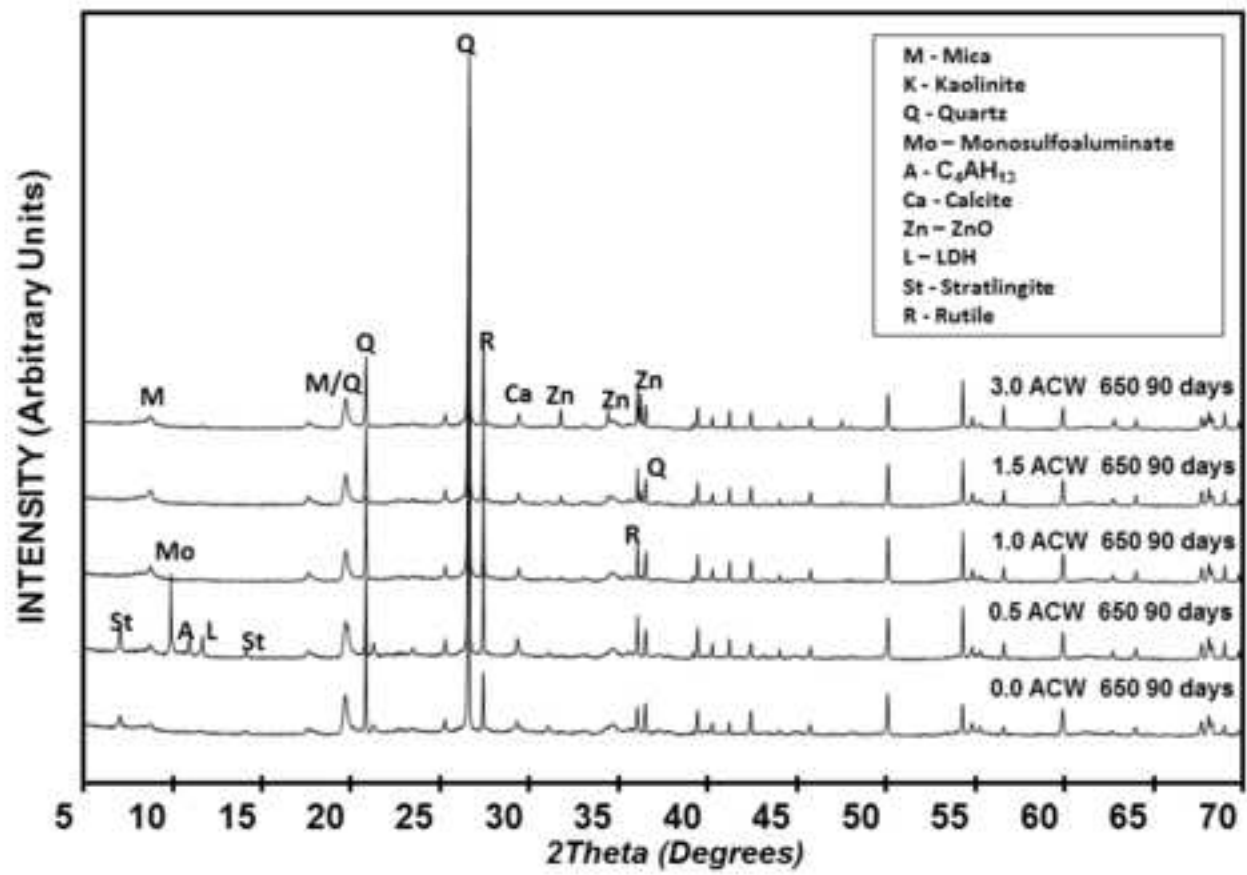
Abstract

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 550ºC/650ºC 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 550ºC and 650ºC 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 aluminate hydrate, stratlingite, monosulfoaluminate hydrate and LDH (phyllosilicate/carbonate).