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Lime/pozzolan/geopolymer systems: performance in pastes and mortars.

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Abstract

Use of lime as construction material is limited mainly by low initial strength. These properties can be improved by adding pozzolanic materials, but the evolution of the reaction usually needs older ages than 7 days. Alkali-activated materials, or geopolymers, are good-performance materials that can be produced with residual waste. The combination of traditional and new materials can lead to new uses of lime mortars. This paper studies a lime/pozzolan and geopolymer mixture. The chosen pozzolan is fluid catalytic cracking catalyst residue (FCC), a material employed as a precursor in alkali-activated material. FCC is activated by two activators: a mixture of NaOH and waterglass; a mixture of NaOH and rice husk ash (RHA). The new materials were studied in microstructure and mechanical behaviour terms. The results demonstrated that lime/pozzolan/geopolymer obtained superior compressive strengths after 1 curing day to that obtained for the corresponding lime/pozzolan mortar after 90 days. An improvement in compressive strength of around 145% was achieved for the mortar with 40% geopolymer compared to the mortar with only lime/pozzolan at 28 curing days.

Keywords: lime, pozzolan, geopolymer, waste material, fluid catalytic cracking catalyst residue

1 Introduction

Lime mortar is an ancient construction material that has been used in different places and periods of history [1,2]. The Romans are certainly responsible for the main technological contribution to lime mortars: addition of volcanic ash or calcined clay significantly improved mechanical properties, and allowed it to set and harden under water. The durability of lime mortars is demonstrated by today's good conditions from the architectural heritage of Roman times [3].

After the discovery of Portland cement, the use of lime mortar drastically reduced due to the new binder's excellent mechanical and durability properties: fast setting, excellent strength development, etc. Nevertheless, current Portland cement (PC) mortars do not meet some sustainability criteria designated by the international community (sustainability development goals) [4]. PC production generates large amounts of CO_2 emissions to the atmosphere, and is responsible for about 5-8% of CO_2 emissions worldwide [5]. Thus a good option is to use alternative binders (lime/pozzolan, geopolymer systems, magnesium oxide cements, etc.) that are often associated with a lower environmental impact [6].

Studies about lime/pozzolan binders report good mechanical strength and durability aspects, depending on the type of used pozzolan [1,7–10]. However, in most cases, the mechanical strength for early curing times (< 28 days) is reduced due to the slow setting and hardening process of lime/pozzolan systems.

Palomo et al. studied the similarity between the ancient lime/pozzolan mortars of historic Roman marine concrete and hybrid-Portland alkaline cement [11]. More specifically, these researchers found similar products of reaction by comparing ancient concrete in marine structures and hybrid alkaline materials (a combination of Portland cement and alkali-activated fly ash). The particularity of seawater concretes in Roman times was studied in depth in the last few years by paying attention to the formation of the so-called "Al-tobermorite" [12,13]. The stability of Al-tobermorite can be a starting point in an attempt to synthesise similar products.

Alkali-activated materials (AAM) are relatively new construction materials, and geopolymer is often used as an additional terminology. Research into these systems is growing and they are expected to be used in many applications in the construction domain. These materials are basically a mixture of an aluminosilicate source and an

alkaline-activating solution [14]. The most typically used precursors are metakaolin (MK), fly ash (FA), ground granulated blast furnace (BFS), etc. Alkaline solutions are normally a mixture of sodium hydroxide and sodium silicate (or potassium as a cation), although other activators can be used: sodium carbonate, sodium sulphate, etc.[15,16].

The new geopolymer technology goal is to use residual materials to prepare alkaline solutions. The carbon footprint related to alkali hydroxides is smaller than that for alkali silicates. Many research groups are investigating the use of alternative silica sources to obtain a commercial silicate or waterglass alternative. These silica sources are mainly rice husk ash (RHA), diatomaceous earth residue, glass waste, sugar cane straw ash and silica fume, among others [17–22].

In some studies on geopolymeric systems, the addition of calcium compounds enhances the activation reaction to result in improved compressive strength [23,24]. Moreover, the use of materials that include calcium in their composition can improve the reactivity of waste, but an excess of calcium has negative effects on compressive strength [25].

The combination of these two binder types (lime/pozzolan and geopolymer) would reduce environmental issues caused by CO_2 emissions, increase waste valorisation and improve the mechanical properties at curing ages lasting less than 28 days.

Allali et al. studied the influence of calcium content on geopolymeric matrices for their use in restoration mortars [26]. They substituted metakaolin (MK) for calcium hydroxide in mortars with potassium and sodium salts as an alkaline solution. When they employed calcium hydroxide in both sodium or potassium solution, $Ca(OH)_2$ totally or partially dissolved. They observed fast setting and compressive strength was lower than for the mortar with only MK (42 MPa for the mortar without hydrated lime and 10 MPa for the mortars with 41% replacement of MK with hydrated lime at 7 curing days).

Recently, glass powder in different systems has been used. In mixtures with PC, it reacted as pozzolanic material. In geopolymeric systems, it was blended with slag, fly ash and lime [27]. With the glass powder and lime mixtures, which were activated by a 4M NaOH solution, a compressive strength of 31MPa was achieved in systems cured at 60ºC for 28 days. The formation of a similar calcium silicate hydrate to tobermorite was suggested for the SEM/EDS study.

Several authors have studied the alkaline activation of MK with calcium hydroxide [28,29]. They followed different analytical techniques to characterise the products formed in this mixture, and concluded that reaction products differed depending on the OH^- concentration in the aqueous medium. When the activator concentration was high (> 10M of NaOH), the formed alkaline aluminosilicate gel was the principal product, while hydrated calcium silicate was the secondary product. However, when the activator concentration was low (< 5M of NaOH), dissolved aluminates were insufficient to produce aluminosilicate gel and pozzolanic products predominated.

Boonjaeng et al. studied the system of lime and calcined clay materials with different alkaline solutions of sodium hydroxide (NaOH). When comparing several molarities (0.1M -10M), they concluded that the reaction of the mixture was dominated by the NaOH concentration [30]. At low concentrations (<1M), the pozzolanic reaction was dominant, while the zeolite-formation reaction predominated at medium NaOH molarities (1M<NaOH<5M). Finally, at a high NaOH molarity (>5M), the principal reaction was the geopolymerization process.

Fluid catalytic cracking catalyst residue (FCC) has been employed as a precursor in geopolymeric mixtures in some reported studies. Tashima et al. made samples with different SiO_2/Na_2O molar ratios [31]. These authors obtained mortars with a compressive strength of 68 MPa after 3 curing days at 65ºC. Trochez et al. obtained similar compressive strength in pastes after curing at ambient temperature for 7 days [32].

The use of RHA has been studied by different research groups as an alternative activator (source of silica). Mejía et al. employed two types of RHA and sodium silicate (as a control mix) to activate mixtures with FA and BFS as precursors[17]. The samples with sodium silicate displayed better mechanical strength than the mortars with RHA, but the results of these mixtures gave a compressive strength close to 42 MPa. Bouzón et al. employed RHA in systems with FCC as a precursor [18]. These authors obtained mortars with very similar compressive strengths to the mortar with sodium silicate (40 MPa). Another research work has reported poor results when RHA was compared to commercial reagents. Luukkonen et al. compared the use of RHA and microsilica with that of sodium silicate [33]. The compressive strength of mortars with an alternative activator was lower than the commercial one, but proved sufficient for certain uses, and performed well with freeze-thawing cycles. Villaquirán-Caicedo and Mejía de Gutiérrez [34] studied MK-based geopolymers using mixtures of RHA or silica fume with KOH as activators. They

achieved a 47% reduction in the warming potential emissions for this system compared to the corresponding commercial potassium silicate-activated system.

The present research studies the development of binary mixtures where the lime/pozzolan binder was partially replaced with a geopolymeric mortar.

Lime mortars were made with a residual pozzolan, namely FCC. The geopolymeric material was a mixture of FCC activated in two different ways: i) a solution of sodium silicate (waterglass) and sodium hydroxide; ii) a suspension prepared as a mixture of sodium hydroxide and RHA.

2 Materials and Methods

A commercial hydrated lime supplied by Cales Pascual (Paterna, Spain) was used. This material is designed as CL90-S according to Spanish standard UNE-EN 459-1 [35]. The FCC residue was supplied by BP Oil España, S.A.U (Grao de Castellón, Spain). RHA was supplied by Dacsa S.A (Tabernes Blanques, Spain).

FCC was employed as both the mineral admixture in the lime/pozzolan system and a precursor in the geopolymer formulation.

The geopolymer was activated by two activators:

- A conventional alkaline solution prepared with a mix of waterglass (Na_2SiO_3, commercial sodium silicate) (Merck, 28% SiO_2; 8% Na_2O and 64% H_2O) and sodium hydroxide (Panreac-SA, 98% purity).
- An environmental-friendly alkaline solution where RHA was employed as an alternative source of "sodium silicate". RHA was mixed with water and sodium hydroxide in a thermal bottle [22].

The chemical composition of FCC and RHA was analysed by X-Ray fluorescence (XRF) equipment (Magic Pro Spectrometer-Philips). The results are summarised in Table 1.

Table 1. Chemical composition of the used materials: fluid catalytic cracking catalyst residue (FCC) and rice husk ash (RHA)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	Others	*LOI
FCC	47.76	49.26	0.60	0.11	0.17	0.02	0.02	0.31	0.03	1.20	0.54
RHA	85.58	0.25	0.21	1.83	0.50	0.26	3.39	-	0.67	0.32	6.99

*LOI: loss on ignition

The mean particle diameter of the supplied FCC was 21 μm. RHA was milled in an industrial mill and its mean particle diameter was 20 μm. All the granulometric measurements were taken in a Malvern Mastersizer 2000 in aqueous medium.

The amorphous content of RHA was 31.5%, calculated by an extractive method using HCl and KOH [36].

Lime/pozzolan mortars and pastes were prepared at the following ratios: lime/FCC =1/1; water/binder = 0.8; sand/binder = 3. The lime/pozzolan ratio was chosen based on the research group's previous research [37]. The employed sand was siliceous in nature with a fineness modulus of 4.3. Mortars were moulded in cubic 40*40*40 mm^3 casts and stored at 25ºC and RH 73% for 24 h. Specimens were wrapped in film until tested. Pastes were moulded in sealed polyethylene phials and stored at 25ºC.

For the geopolymeric binder, the formulation of the alkaline activator solution was selected according to a previous work [18]. The solution had a SiO_2/Na_2O molar ratio of 1.17, a sodium molality of 7.5 and a water/binder ratio of 0.6.

The replacements of lime/pozzolan binder mass with geopolymeric binder were 0% (control sample), 10%, 20%, 30% and 40%.

Table 2 summarises the quantity (expressed as grams) of the materials employed in mortars. The control mortar was the mixture with only lime and pozzolan (CON). The geopolymeric mortar (GEOP) was the mixture of FCC with the activator of NaOH and Na_2SiO_3. The lime/pozzolan/GEOP mixtures were named CCx or CAx, where: i) CC is the geopolymer activated by the conventional solution (waterglass and sodium hydroxide) and CA is the geopolymer when RHA was employed as a silica source in alkaline activator (RHA + water + sodium hydroxide); ii) x is the lime/pozzolan replacement percentage with FCC geopolymer. For example, mortar CA10 contained 10% geopolymer (FCC and an alkaline activator composed of a mixture of RHA, NaOH and water).

The abbreviation FCC^P represents the quantity of FCC in the lime/pozzolan binder, while the abbreviation FCC^G denotes the quantity of FCC in the geopolymeric binder. H_2O^P was the water content in the lime/pozzolan system. The water used to prepare the geopolymeric binder is indicated in the activator as H_2O^G.

Table 2. Composition of lime/pozzolan mortar, lime/pozzolan/GEOP mortars and GEOP mortar (weight in grams).

	Lime/pozzolan binder		GEOP binder						Sand
					Activator				
	Lime	FCC^P	H_2O^P	FCC^G	H_2O^G	NaOH	Na_2SiO_3	RHA	
CON	262.5	262.5	420.0	-	-	-	-	-	1575.0
CC10	236.3	236.3	378.0	52.5	12.6	6.4	29.5	-	1575.0
CA10	236.3	236.3	378.0	52.5	31.5	9.4		9.2	1575.0
CC20	210.0	210.0	336.0	105.0	25.2	12.8	59.1	-	1575.0
CA20	210.0	210.0	336.0	105.0	63.0	18.9	-	18.4	1575.0
CC30	183.8	183.8	294.0	157.5	37.8	.2	88.6	-	1575.0
CA30	183.8	183.8	294.0	157.5	94.	28.4	-	27.6	1575.0
CC40	157.5	157.5	252.0	210.0	50.4	25.6	118.3	-	1575.0
CA40	157.5	157.5	252.0	210.0	126.0	37.8	-	36.7	1575.0
GEOP	-	-	-	525.0	126.0	64.0	295.3	_	1575.0

Pastes lime/pozzolan, lime/pozzolan/GEOP and GEOP had the same proportions of materials as the corresponding mortars, but without sand. An additional paste containing 80% GEOP and 20% hydrated lime was fabricated and called GEOP-CH.

Compressive strength was measured in an INSTRON 3282 machine for the ages of 1, 2, 3, 7, 28 and 90 days, and was the average of four individual tests.

The microstructural analysis of pastes was carried out by a thermogravimetric analysis (TG/DTG), powder X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM).

The TG analysis was done using a TGA 850 Mettler-Toledo thermobalance. The TG experiments were performed from 50ºC to 600ºC at a heating rate of $10ºC.min^{-1}$. Aluminium-sealed crucibles (70 µL volume) were used with a pinholed lid and a nitrogen atmosphere (flow gas rate of $75\ mL.min^{-1}$). The XRD analyses were carried out in a Bruker AXS D8 Advance device from 10º to 70º 2θ (2s accumulation time in a 0.02 angle step). The FTIR analyses were run in a Bruker Tensor 27 and analysed within the 400-4000 cm^{-1} range. The FESEM micrographs were taken in a Zeiss ULTRA 55. Pastes were carbon-coated and images were taken at 2kV. For the EDS analysis (X-ray energy dispersive spectroscopy), data were taken at 15kV.

3 Results and Discussion

3.1 Compressive strength development

In the first stage, the study of incorporating the geopolymer fabricated with commercial reagents (sodium silicate as a silica source) was analysed. The substitution percentages went from 10% to 40%, and the selected curing ages were 1, 2, 3, 7, 28 and 90 days. The results are represented in Figure 1. For all the curing ages, the mortars with geopolymer obtained higher compressive strengths than that for the mortar with only FCC and lime (the control mortar: CON). After 1 curing day, mortar CC40 (14.9 MPa) had the same compressive strength as CON (14.3 MPa) after 90 curing days.

It is highlighted the compressive strength gain at early ages with the incorporation of the geopolymer into the lime/pozzolan systems. With the 10% substitution (sample CC10), compressive strength was 45% greater than the strength for CON after 1 curing day and was 152% greater after 7 curing days.

Figure 1 illustrates how the CON mortars had a low compressive strength (< 2 MPa) until 7 days. Compressive strength evolution was 190% from 7 days to 28 days, with 37% evolution from 28 days to 90 curing days. Mixture CC40 yielded fast evolution between 1 and 7 days (65%), when its evolution was asymptotic until 90 days with compressive strength at around 25 MPa.

The evolution of mortar CC10 was remarkable. The sample began with only 2.08 MPa at 1 curing day, but reached 21.09 MPa at 90 curing days (913% evolution). This compressive strength was only slightly lower than that found for the mortar with the highest geopolymer content (CC40). The effect of a small amount of geopolymer on the lime/pozzolan system was marked. The incorporation of geopolymer enhanced the formation of the new reaction products, which improved the strength of the mortars. The new aluminosilicate gel type C(N)ASH was probably formed in the lime/pozzolan/geopolymer systems. García-Lodeiro et al.[38] reported the formation of this product type in hybrid alkaline cements using FA and Portland cement. Sodium ions replaced calcium ions as charge balancers.

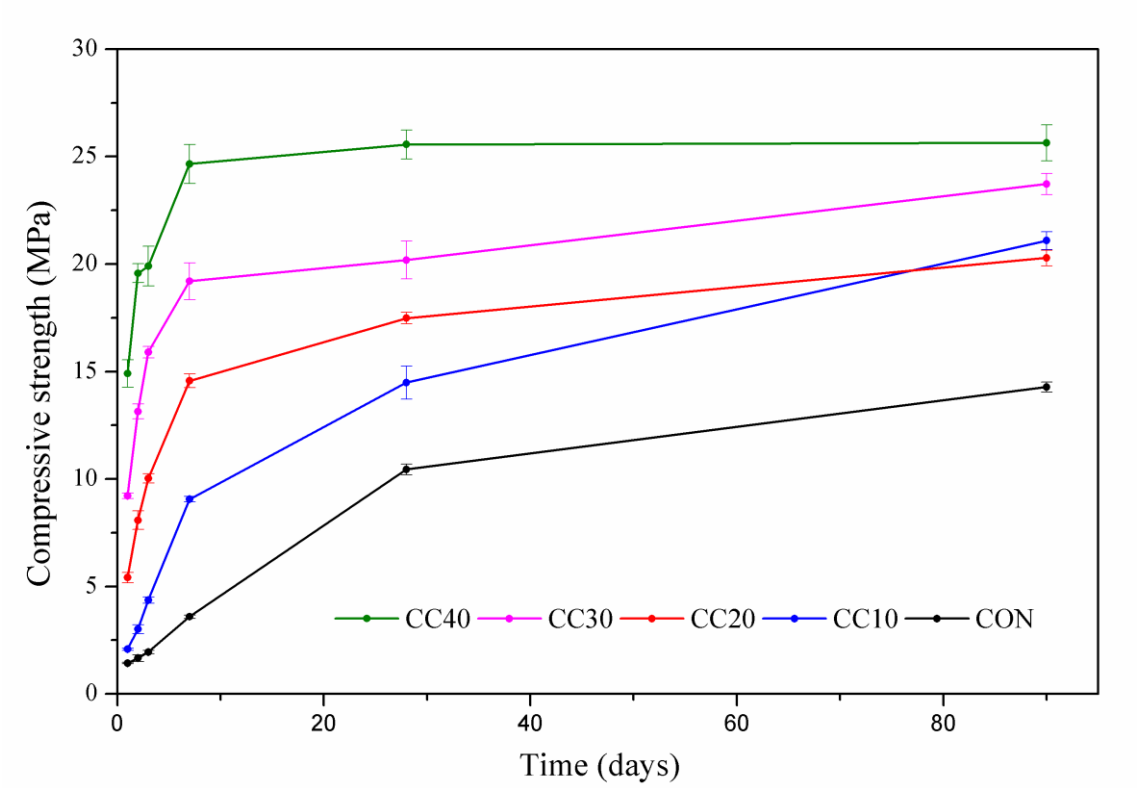


Fig 1. Evolution of the compressive strength of mortars CON and CC at 1, 2, 3, 7, 28 and 90 curing days.

For this above-discussed first stage, the obtained results contrasted those obtained by other researchers. Boonjaeng et al, used MK and lime systems, and indicated that geopolymeric gel was not as strong as CASH and CSH gel [30]. In the present work, the alkaline activator dose was used only for FCC as a precursor, and the other part of mortar (lime-pozzolan) was mixed only with water. Conversely in the research by Boonjaeng et al, the lime/MK mixture was considered the binder and was activated with NaOH [30].

The geopolymeric mortar without lime (pure geopolymer, GEOP) was analysed for the same curing ages. The compressive strength of this sample was generally very high, especially at early curing ages, between 1 and 7 curing days. After the first curing day the GEOP mortars yielded 13.38 MPa and the compressive strength increases until 53.90 MPa at 7 curing days. No CCx system had a compressive strength greater than 25 MPa. The nature of the gel in these mortars was the NASH type [39].

A comparison of the strength values at early (1-7 days) and long-term (28-90 days) ages can be made to analyse strength development in the different mortars CC. Theoretical strength (R_{th}) can be calculated by taking into account the contribution of the lime/pozzolan and geopolymer fractions as follows (Equation 1):

$$R_{th}=R_{lp}*X_{lp}+R_g*X_g \quad (1)$$

Where R_{lp} and R_g are the strength of the mortar lime-pozzolan (CON) and the mortar pure geopolymer (GEOP), respectively; X_{lp} and X_g are the mass fractions of both mortars in the CC mixtures (0.9-0.6 for X_{lp}; 0.1-0.4 for X_g).

Table 3 compares the theoretical values (R_{th}) to the experimental values (R_{ex}), and the difference in strength (D) is summarised for the mortars cured within the curing time range of 1-90 days. The D values for CC20, CC30 and CC40 were positive at early curing ages (1-3 days), which suggests that the role of calcium from lime is crucial for developing a strong cementing gel. In this case, gels CASH or C(N)ASH formed. For longer curing times, the opposite trend was seen, and the D values were negative after 28 and 90 curing days. This behaviour suggests that the contribution of the NASH gel to strength became less relevant when the binary system was fabricated. It was noteworthy that for 1-3 curing days, the presence of calcium in the mixture enhanced the gel's strength properties, which confirmed the positive effect by mixing both types of cementing systems.

Table 3. Difference (D, in MPa) in mortar strengths, calculated as experimental strength (R_{ex}) minus theoretical strength (R_{th}).

	Curing days					
System	**1**	**2**	**3**	**7**	**28**	**90**
CC10	-0.55	-1.10	-0.83	0.44	-0.34	2.54
CC20	1.59	1.52	1.59	0.91	-1.71	-2.55
CC30	4.19	4.12	4.21	0.52	-3.39	-3.40
CC40	8.69	8.11	4.97	0.94	-2.39	-5.76

In the second stage, the use of an alternative alkaline activator was explored. Resorting to RHA as a silica source was investigated as a sodium silicate substitute. The RHA and NaOH mixture in a thermal bottle was used as an activator at the same proportions as the commercial reagents. A strength variation percentage (VR) was calculated for the alternative mixtures (CA) using Equation 2:

$$VR = 100*(R_{CAx}-R_{CCx}/R_{CCx}) \quad (2)$$

Where R_{CAx} is the compressive strength for a given percentage of geopolymer (x) in a mortar with RHA (CA); R_{CCx} is the compressive strength for the same percentage (x) in a mortar with sodium silicate (CC).

Figure 2 represents the VR evolution for all the replacement percentages and curing ages. The samples with values over the red line yielded a compressive strength that was more than 2-fold higher than the values yielded by mortars CC.

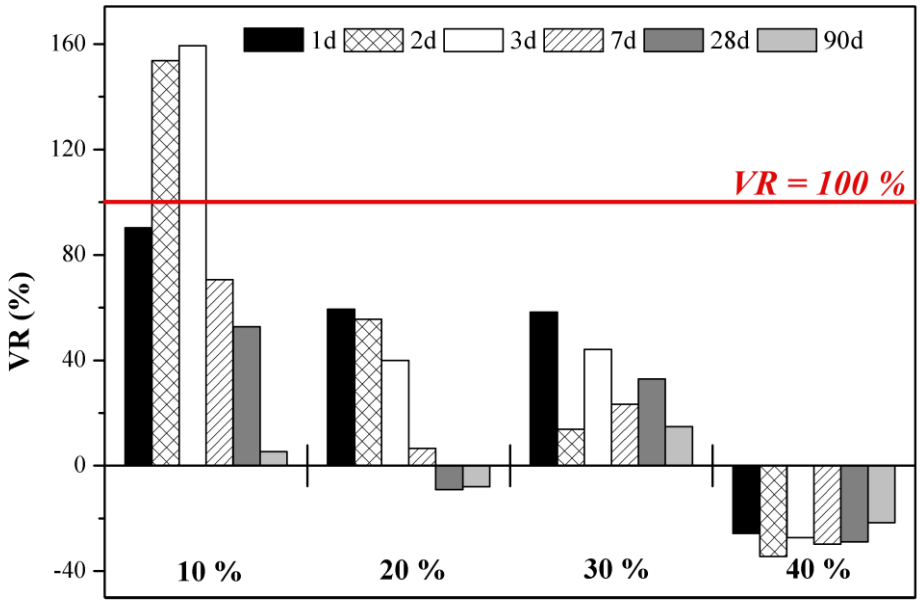


Figure 2. Strength variation (VR) percentages for the mortars with alternative silicate (CA samples).

Higher VR values were obtained for the 10% substitution percentage. For 2 and 3 curing days, these values were higher than 100% (153.7% and 159.3%, respectively) and the minimum value was obtained at 90 curing days (5.34%). The systems with 20% and 30% geopolymers were less effective. With 20% (CA20 samples), mortars had low negative VR values (-9.1% and -7.92%, respectively), even at 28 and 90 days. The samples with the 40% substitution yielded negative VR values for all the curing ages. These negative values can be attributed to the poor workability of the RHA-containing mortars, whereas the mixtures with the commercial reagent were easily compacted.

The good behaviour of RHA as silica source may be the result of a more enhanced connectivity in microstructure of the samples activated with this material as said Villaquirán- Caicedo in the paper published in 2019 [40]. The results were very interesting from a practical viewpoint because mixtures can be obtained with good compressive strength without using commercial sodium silicate, which is a synthetic chemical reagent with a large carbon footprint, as previously reported [41]. The replacement of commercial sodium silicate with RHA led to very good mortar performance in terms of early-age compressive strength, which makes the small geopolymer dose in the lime/pozzolan system more appealing.

3.2 Thermogravimetric studies

The lime-pozzolan (CON), lime-pozzolan/geopolymer (CC and CA samples) and geopolymer (GEOP) pastes had the same proportions as the mortars, but without sand. To simplify the study, it represented only the pastes with the 10% and 40% substitution percentages, CON and GEOP. The selected curing ages were 3, 28 and 90 days. Figure 3 depicts the DTG curves.

Three principal zones of mass loss were observed in the CON paste, but a continuous mass loss fell within the 100-600ºC range. Zone 1 (100-180ºC) was attributed to the dehydration of CSH; zone 2 (180-300ºC) was related to the dehydration of CASH and CAH; zone 3 was assigned to the dehydroxylation of $Ca(OH)_2$ [42]. The GEOP paste had only one peak centred at about 150ºC, attributed to the dehydration of the NASH gel [43]. In the pastes with lime-pozzolan/geopolymer, peaks differed in accordance with the substitution percentage. Pastes CC10 and CA10 with the 10% substitution looked a lot like the CON paste, while pastes CC40 and CA40 with the 40% substitution had a similar profile to the geopolymeric paste (GEOP).

The main peak in pastes CON, CC10 and CA10 at 3 and 7 curing days was centred in zone 2, and was attributed to the dehydration of CASH and CAH. At 90 days, a well-defined peak was seen for CSH dehydration on the DTG curves. The presence of hydrated lime was observed until 28 days for the control pastes, and in paste CC10 at 3 curing days. Hence, the reaction of hydrated lime to FCC was much faster when the geopolymer was present.

The principal peak in GEOP, CC40 and CA40 at all the curing ages was centred at about 150ºC. This peak was attributed to the NASH gel for GEOP and a mixture of NASH and C(N)ASH gels for CC40 and CA40. The peak in paste GEOP was much wider than that in pastes CC40 and CA40. The NASH gel probably had a higher temperature decomposition range than the C(N)ASH gel.

The mass losses within the different temperature ranges were analysed to understand the evolution of the geopolymeric and pozzolanic reactions. The chosen mass loss zones were: 50ºC to 180 ºC (ML_1); 80ºC to 300ºC (ML_2); total mass loss went from 35ºC to 600ºC (ML_T). Table 4 summarises the results.

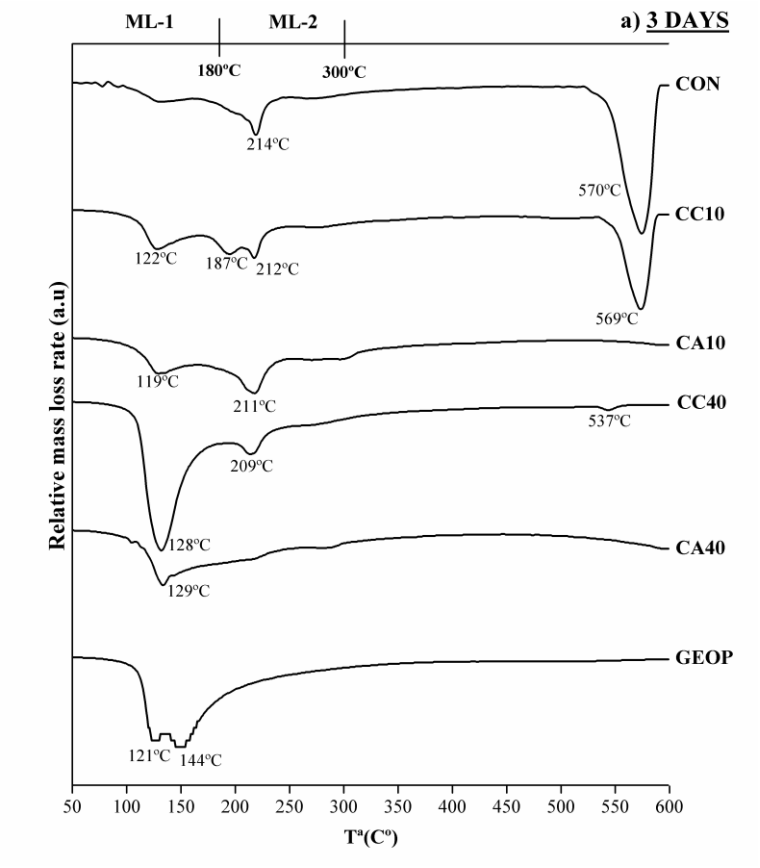
Table 4. Mass loss (TG analysis) of pastes for 3, 28 and 90 curing days.

	ML_1 (50-180ºC)	**ML_2 (180-300ºC)**	**ML_T (35-600ºC)**
CON 3d	2.14	4.21	15.88
CON 28d	4.44	8.61	20.61
CON 90d	5.69	8.36	18.67
CC10 3d	3.49	4.87	15.43
CC10 28d	4.70	7.07	16.75
CC10 90d	5.43	8.09	18.05
CA10 3d	3.68	5.97	12.00
CA10 28d	4.28	10.17	18.59
CA10 90d	4.88	6.63	15.12
CC40 3d	6.12	3.79	14.67
CC40 28d	6.57	4.86	16.04
CC40 90d	6.92	4.13	15.27
CA40 3d	5.24	3.83	13.04
CA40 28d	5.32	3.78	13.51
CA40 90d	6.48	4.10	14.66
GEOP 3d	7.96	3.94	14.07
GEOP 28d	9.23	4.25	15.49
GEOP 90d	9.38	3.69	15.19

For the pastes in which the geopolymer reaction was the principal reaction and the gel C(N)ASH or NASH were the main products, the mass loss within the ML_1 range was greater than within the ML_2 range. The mass loss within interval ML_2 was, in this case,

attributed to the same product as the decomposition peak was wide. The geopolymer reaction was the predominant reaction in pastes GEOP, CC40 and CA40 as the activator concentration was higher than that in the samples with only the 10% substitution. This conclusion falls in line with previously reported papers [28, 29, 44], which studied lime/MK mixtures at different sodium hydroxide concentrations. When the activator concentration was low, the principal reaction product was CSH; when the concentration was high, the main product was the C(N)ASH gel and CSH formed as a secondary reaction product.

In the paper published in 2013 by García-Lodeiro et al.[38] the authors explained the conversion of NASH gel into C(N)ASH gel. The presence of a solution enriched with $Al(OH)_4^-$ and $Si(OH)_4$ species, in addition to the presence of sodium ions, induced this type of NASH gel. Depending on the calcium concentration in the medium, total conversion into CASH gel can take place.


a) 3 DAYS
ML-1
ML-2
180ºC
300ºC
CON
214ºC
570ºC
CC10
122ºC
187ºC
212ºC
569ºC
CA10
119ºC
211ºC
CC40
537ºC
209ºC
128ºC
CA40
129ºC
GEOP
121ºC
144ºC
Relative mass loss rate (a.u)
50 100 150 200 250 300 350 400 450 500 550 600
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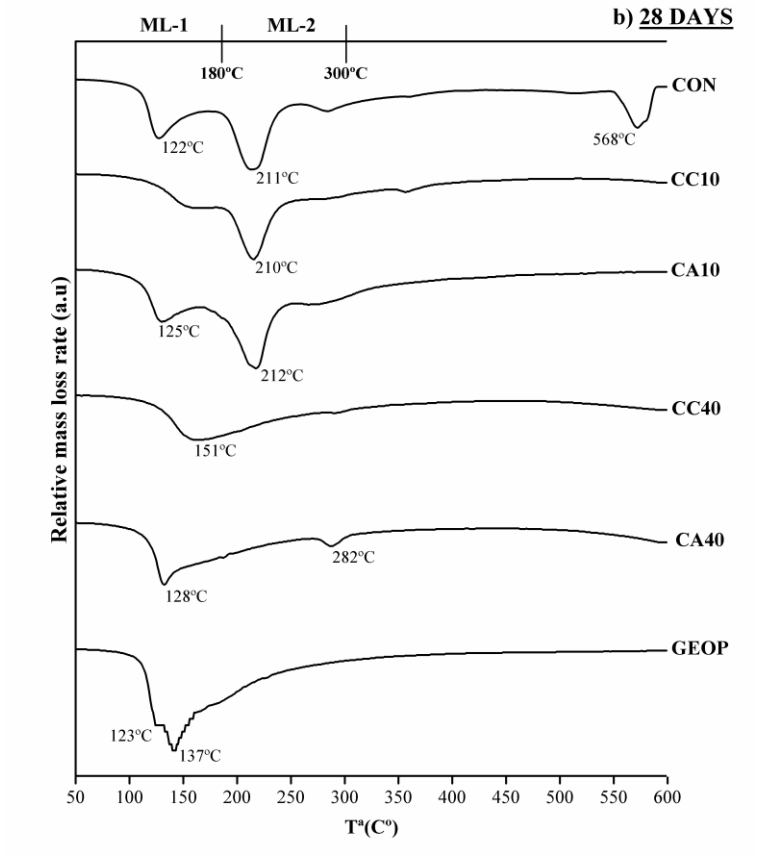

b) 28 DAYS
ML-1
ML-2
180ºC
300ºC
CON
122ºC
211ºC
568ºC
CC10
210ºC
CA10
125ºC
212ºC
CC40
151ºC
CA40
282ºC
128ºC
GEOP
123ºC
137ºC
Relative mass loss rate (a.u)
50 100 150 200 250 300 350 400 450 500 550 600
Tª(Cº)

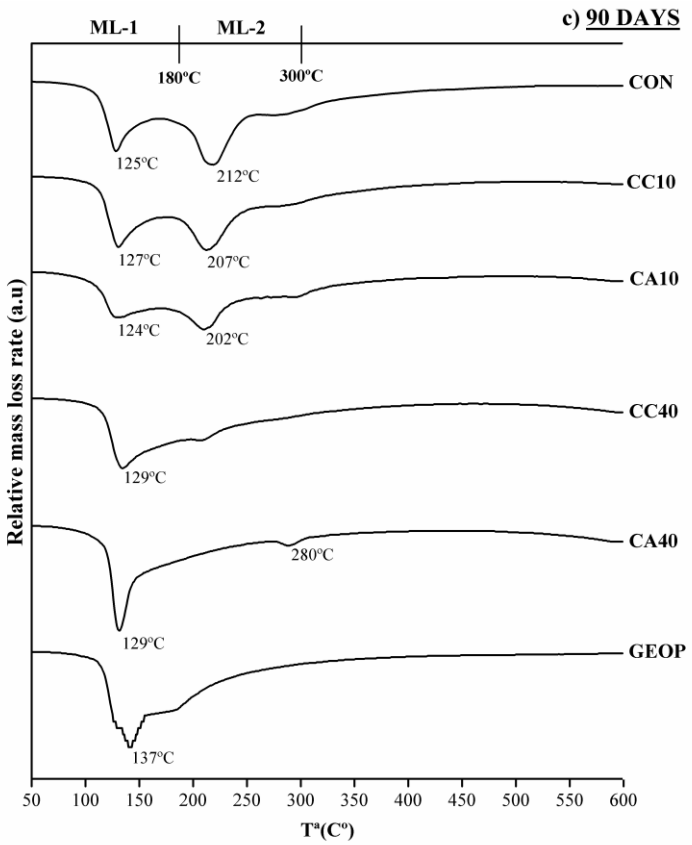


Figure 3. DTG curves for the pastes cured at: a) 3; b) 28; and c) 90 curing days.

To analyse the role of calcium in a geopolymeric paste, a paste (GEOP-CH) was fabricated by mixing 80% GEOP paste (FCC with NaOH and Na_2SiO_3 as an alkaline activator) and 20% hydrated lime. The first problem was that this paste (GEOP-CH) needed water, which was added because it was impossible to prepare paste at the 0.6 water/FCC ratio (lack of workability), and the new water/FCC ratio was increased to 1.1. The paste was analysed after 7 curing days. Figure 4 represents the DTG curves for pastes GEOP and GEOP-CH. GEOP-CH did not present a peak for the dehydroxylation of hydrated lime within the 500-600ºC range. The calcium from the hydrated lime was incorporated into the aluminosilicate gel. Its decomposition peak fell within the same decomposition temperature range observed for the paste without hydrated lime.

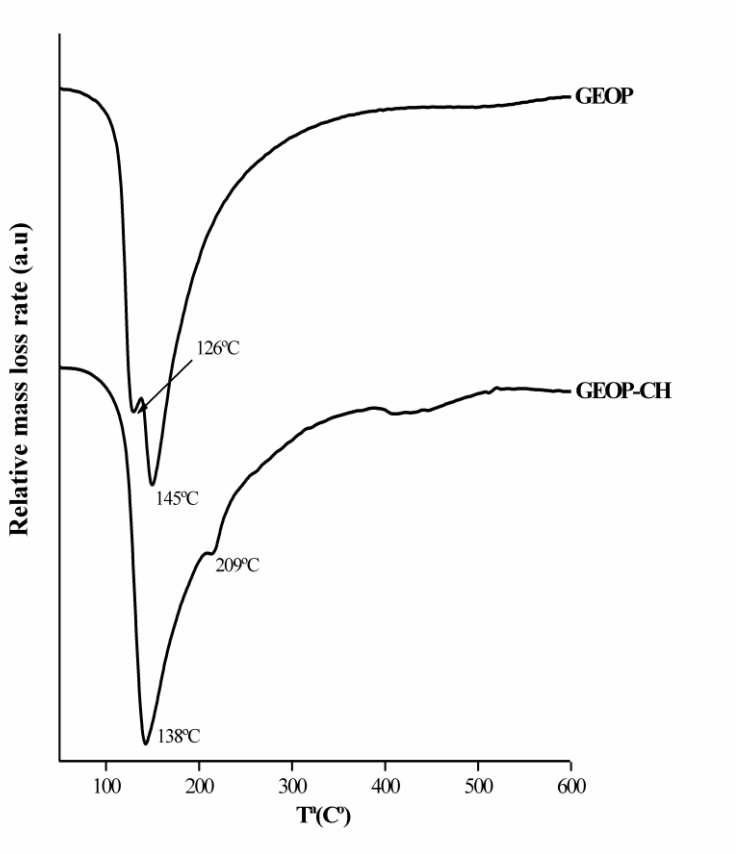


Figure 4. DTG curves for pastes GEOP and GEOP-CH after 7 curing days.

3.3 FTIR studies

Figure 5 illustrates the evolution of the reaction process for pastes CON, CC10, CA10, CC40, CA40 and GEOP at 3, 28 and 90 curing days by the FTIR technique.

The evolution of lime/pozzolan paste is represented in Figure 5.a, and the principal peaks were: i) presence of carbonates and carboaluminates (bands at 1,700, 1,435 and 875 cm^{-1}). The asymmetric stretching vibrations of the C-O group were represented at a wave number of around 1,435 cm^{-1} and the band at 875 cm^{-1} corresponded to the bending mode of the carbonate ion [40, 45]; ii) the bands of CSH caused by the bending of SiO_4 tetrahedral units fell within an approximate range of 400-500 cm^{-1} and the asymmetric Si-O stretching vibration of the CSH within the 1,100-960 cm^{-1} interval [42,46]; iii) the presence of the signals attributed to vibrations Si-O-Si, Si-O-Al and Al-O at 528 and 709 cm^{-1} as a result of the presence of CASH and CAH [42,47,48]. The presence of carbonates could be due to a number of factors: presence of calcite in the hydrated lime; formation of carboaluminate by a reaction of carbonate and the alumina of FCC; carbonation of reaction products. The band of the asymmetric Si-O stretching vibration

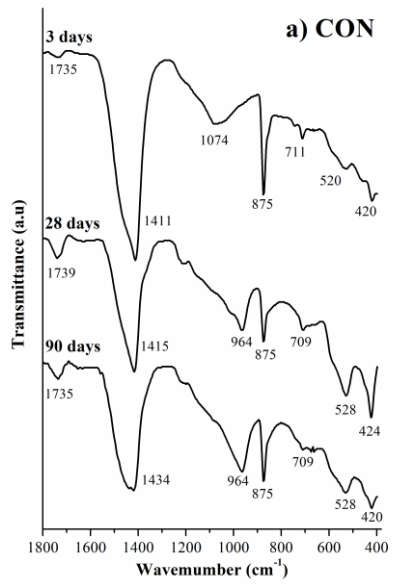
of CSH for the samples cured for 3 days was located at a higher wave number than for the pastes cured for 28 and 90 days.

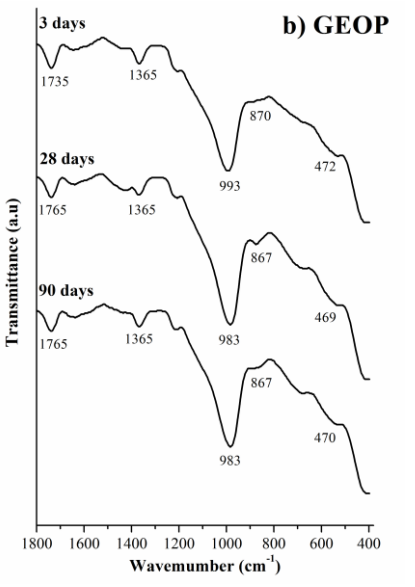
The geopolymeric paste is represented in Figure 5.b. The observed principal peak was due to the presence of the NASH gel, with a band at 983-993 cm^{-1} for the geopolymeric binder. A high-intensity broad band of between 1,200-900 cm^{-1} was identified, which corresponded to the asymmetrical stretching of Si-O-T (T = Si or Al bonds [40]). In particular, the SiQ^2 unit showed infrared absorption at around 950 cm^{-1}. The bands at 1,735 and 1,365 cm^{-1} were attributed to the presence of carbonate [47,48]. The bands with lesser intensity, around 867 cm^{-1}, were identified as Si-O stretching and OH bending (Si-OH). The peak was attributed to bending bands (Si-O-Si and O-Si-O) with those at around 470 cm^{-1}[49].

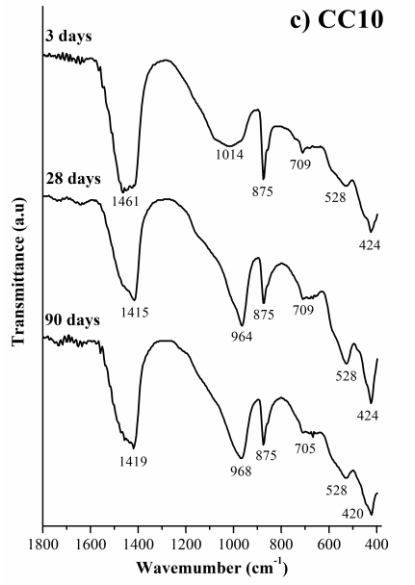
The pastes containing 10% geopolymer showed similar peaks to the lime-pozzolan paste. These peaks were located at around 1,460-1,420, 1,014-950, 875 and 435-420 cm^{-1}. Allali et al.[26] established that when the MK geopolymer included calcium in the system, the Si-O-Si band was displaced from 985 cm^{-1} to an Si-O-Ca band at 930 cm^{-1}. In the present research, this displacement was especially observed for the CA sample at 90 curing days. The corresponding band was found at 950 cm^{-1}, and significantly differed from that for the CC sample (968 cm^{-1}). This meant that the presence of a different source of silica in the geopolymer changed the final geopolymeric gel structure.

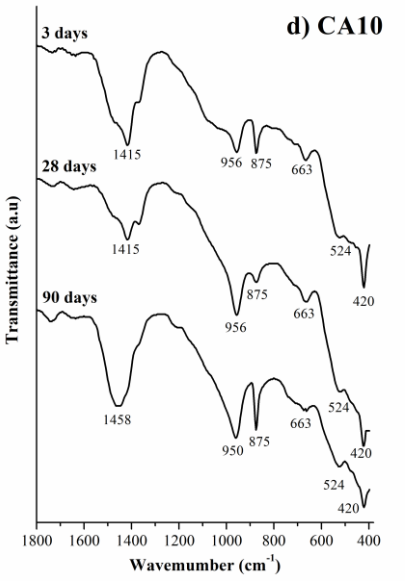
For the CC40 paste, the signal attributed to the gel (NASH) was found at 968 cm^{-1} (after 90 curing days). For the CA40 paste, the corresponding signal was displaced at a lower wave number (950 cm^{-1}). Once again, the different source of silica modified the gel's nature.

García Lodeiro et al. established that adding Ca to the NASH gel would change the orientation of the structure, but this change was not easily observed by FTIR [50].


a) CON
3 days
1735
1411
1074
875
711
520
420
28 days
1739
1415
964
875
709
528
424
90 days
1735
1434
964
875
709
528
420
Transmittance (a.u)
1800 1600 1400 1200 1000 800 600 400
Wavemumber (cm-1)


b) GEOP
3 days
1735
1365
870
993
472
28 days
1765
1365
867
983
469
90 days
1765
1365
867
983
470
Transmittance (a.u)
1800 1600 1400 1200 1000 800 600 400
Wavemumber (cm-1)


c) CC10
3 days
1461
1014
875
709
528
424
28 days
1415
964
875
709
528
424
90 days
1419
968
875
705
528
420
Transmittance (a.u)
1800 1600 1400 1200 1000 800 600 400
Wavemumber (cm-1)


d) CA10
3 days
1415
956
875
663
28 days
1415
524
420
875
956
663
90 days
1458
524
950
875
663
420
524
420
Transmittance (a.u)
1800 1600 1400 1200 1000 800 600 400
Wavemumber (cm-1)

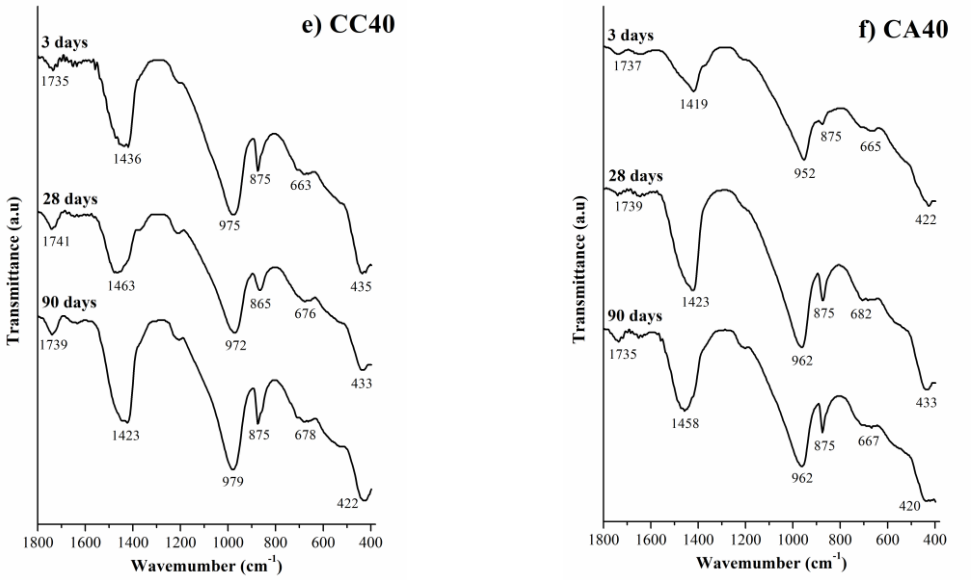


Figure 5. FTIR curves for the pastes cured at 3, 28 and 90 days

Paste GEOP-CH was also studied by FTIR. Figure 6 represents pastes GEOP-CH and GEOP at 7 curing days. A displacement of the band (995 cm^{-1} vs. 948 cm^{-1}) related to the NASH gel took place in the paste with lime (GEOP-CH). This spectrum confirmed the incorporation of Ca into the aluminosilicate gel's structure.

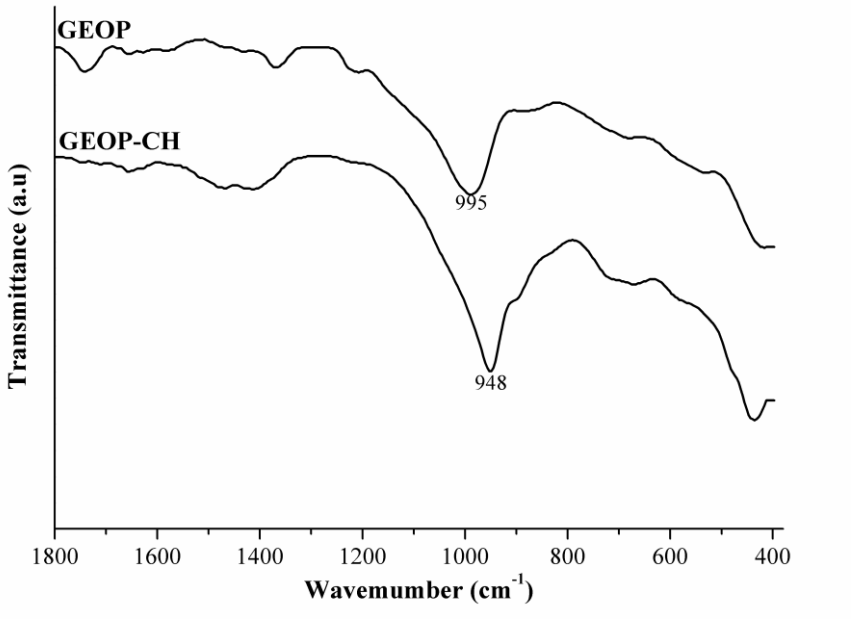


Figure 6. FTIR curves for GEOP and pastes GEOP-CH after 7 curing days.

3.4 XRD studies

The X-ray diffraction patterns are depicted in Figures 7-10. Pastes CON, CC10, CC40, CA10 and CA40 were studied by comparing 3, 28 and 90 curing days, and pastes GEOP and GEOP-CH were also compared. In general, a baseline deviation within the $2\Theta=20^{o} – 40^{o}$ range in all the studied pastes suggested the presence of an amorphous phase. With the progress made in curing time, the baseline deviation was more evident given the progress made in the geopolymerization reaction. Table 5 summarises the employed key, name of phases, chemical formula and PDF Card for the mineral phases found in the pastes.

Table 5. PDF Card of the phases and chemical formula of phases present in pastes.

Key	Phase	Chemical formula	PDF Card
P	Portlandite	$Ca(OH)_2$	#040733
S	Strätlingite	$Ca_2Al_2SiO_7.8H_2O$	#290285
Q	Quartz	SiO_2	#331161
A	Albite	$NaAlSi_3O_8$	#191184
M	Mullite	$Al_6Si_2O_{13}$	#150776
C	Calcite	$CaCO_3$	#050586
L	Carboaluminate	$Ca_4Al_2O_6CO_3.11H_2O$	#410210
B	Carboaluminate	$Ca_8Al_4O_{14}CO_2.24H_2O$	#360129
Z	Zeolite A	$Na_2Al_2Si_{3.3}O_{10.6}.7H_2O$	#120228
T	Trona	$Na_3H(CO_3)_2.2H_2O$	#291447
W	Wollastonite	$CaSiO_3$	#100489
V	Vaterite	$CaCO_3$	#240030
X	Zeolite X type	$Na_2Al_2Si_{2.4}O_{8.8}.6.7H_2O$	#120246
Za	Zeolite ZK5	$2.85Na_2O.1.89Al_2O_3.7.92SiO_2.12.2H_2O$	#370360
Cr	Cristobalite	SiO_2	#391425
F	Faujasite	$Na_2Al_2Si_4O_{12}.8H_2O$	#391380

Figure 7 shows the XRD patterns of paste CON (lime-pozzolan) after 3, 28 and 90 curing days. The peaks of the non-reacted portlandite (P) were observed after 3 curing days. Characteristic peaks of albite (A) and traces of faujasite were also found. It was noteworthy that calcite was not present in the CON paste at an early age and carbonate was combined with aluminium as carboaluminates (characteristic L and B peaks). Other authors have made these observations in lime-pozzolan samples [51,52]. After 28 curing days, less intense portlandite peaks were detected as the FCC reaction progressed, and no faujasite peaks appeared in the XRD pattern. Traces of quartz (Q), A and mullite (M) were also observed. Characteristic strätlingite (S) peaks were noted in the CON paste at this age, which confirmed the peak observed on the DTG curves within the 210-280ºC temperature range. This compound is typical in lime-pozzolan materials with a high aluminium content [52,53], as for FCC (Al_2O_3 = 49.26 %; see Table 1). After 90 curing days, the diffractogram of paste CON was similar to that for 28 curing days. To a large extent, the P peaks had mitigated and the main S peak appeared more intensely, which

suggests high pozzolanic reactivity with curing time. A broad peak was seen within the 28.5º-29.5º 2Θ range, which suggests the presence of the CSH/CASH gel, especially after 90 curing days.

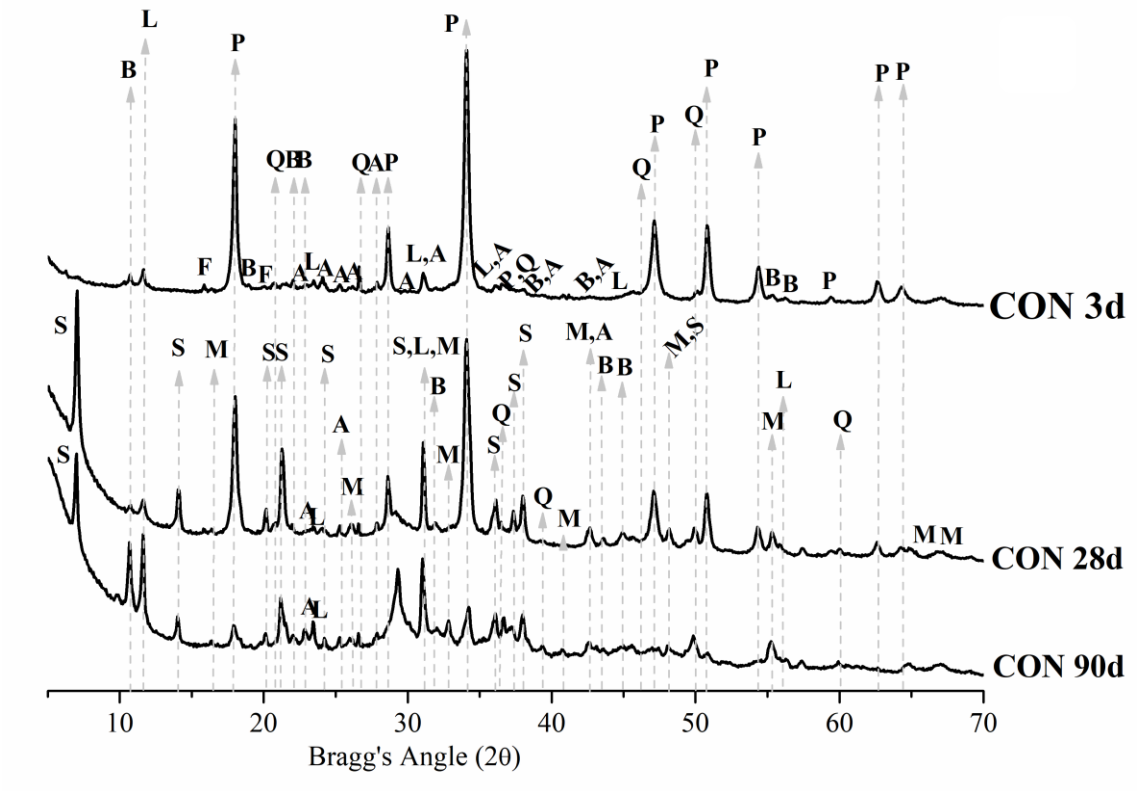


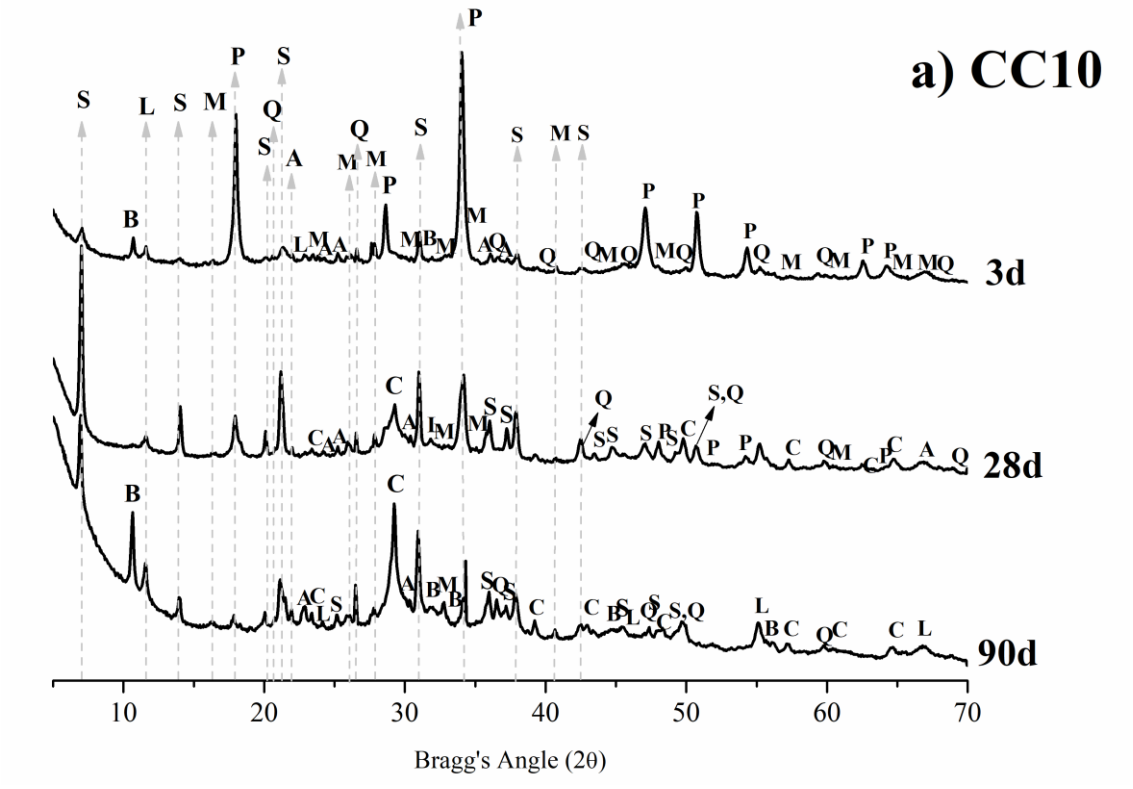
Figure 7. XRD patterns of the CON paste after 3, 28 and 90 days

Figures 8-9 show the XRD patterns of the lime-pozzolan/geopolymer activated with the alkali solution prepared by using commercial sodium silicate and RHA, respectively. The pastes with 10% geopolymer (CC10 or CA10) and with 40% geopolymer (CC40 or CA40) were tested and analysed after 3, 28 and 90 curing days.

In paste CC10 (Figure 8a), the main characteristics peaks were P and S at 28 at 90 curing day. Strätlingite (S) was attributed to the pozzolanic reaction. As with the CON paste, the intensity of the peaks corresponding to P and S diminished and increased, respectively, with curing time. Minority peaks (Q and A) were present at the three analysed curing times. Carboaluminate peaks (L and B) were found, whose intensity increased with time. Calcite (C) peaks were also found after 28 and 90 curing days. In this case, the broad peak related to CSH/CASH, together with the main C peak whose

intensity was significant after 28 days, which was earlier than for CON and suggests a faster reaction rate for this gel type to form.

When the 40% geopolymer was employed (CC40), the portlandite peaks were low in intensity (especially for 90 curing days) and the peak of the CSH/CASH gel was strong in this XRD pattern. A new crystalline phase Z (Zeolite A) was also detected, mainly at 90 curing days. The formation of Zeolite A and Zeolite X has been reported in other papers in which geopolymers were prepared with the activation of MK/RHA [54]. As the CC10 paste pattern shows, traces of Q and A and B/L carboaluminate peaks were present throughout the three analysed ages for paste CC40. No S was detected in this paste, which suggests that its formation by the pozzolanic reaction was not favourable, and gels NASH or C(N)ASH should be preferably produced, as corroborated by the large broad peak shown (28.5º-29.5º 2Θ,) after 3 curing days.



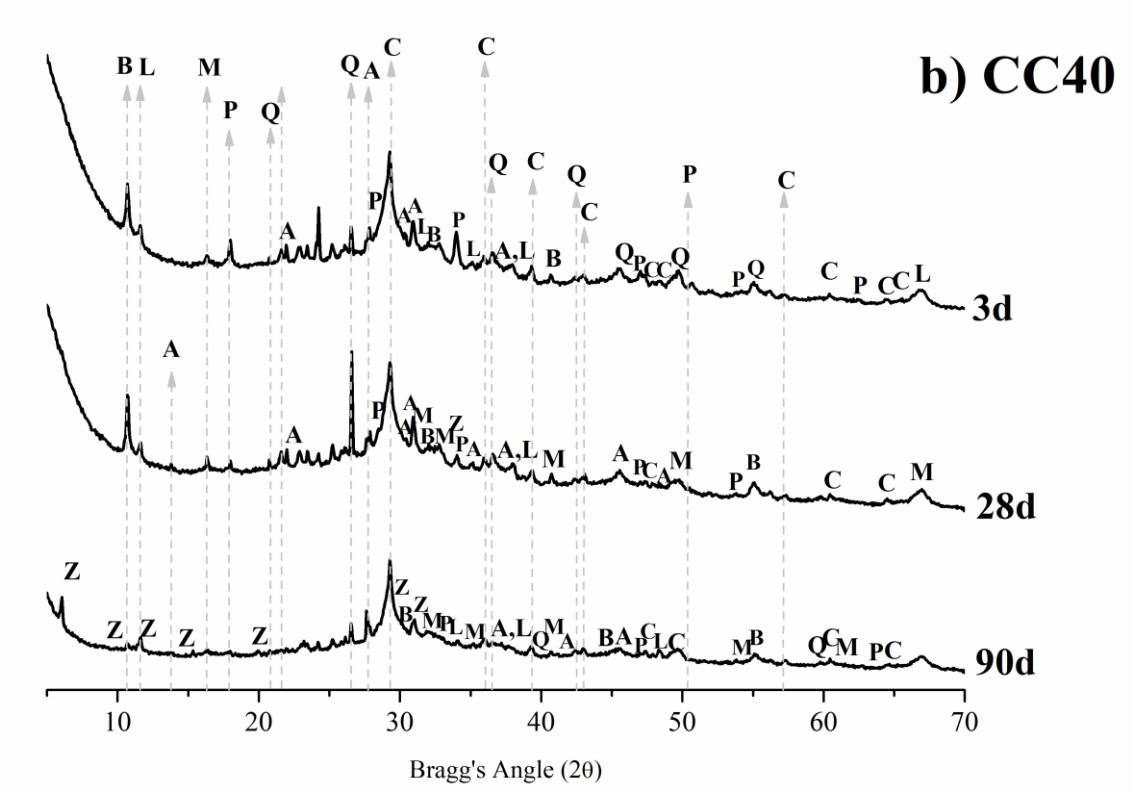
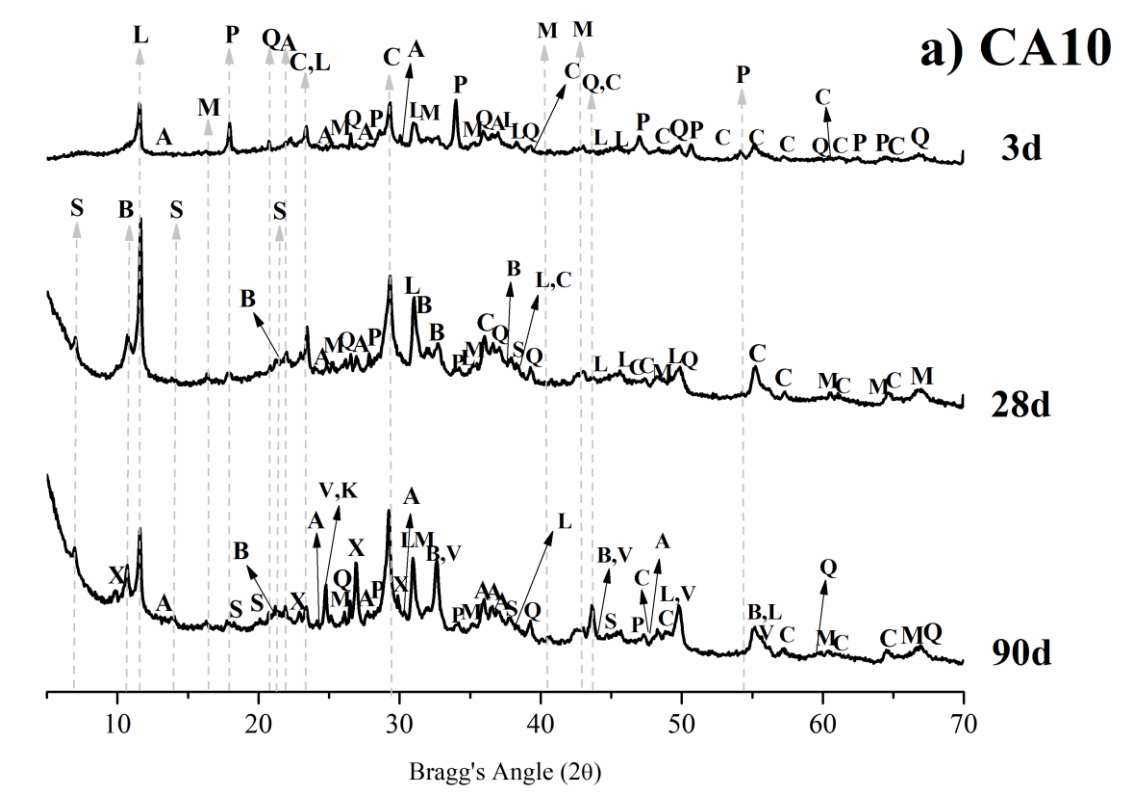


Figure 8. XRD patterns of the lime-pozzolan/geopolymer pastes activated with the alkali solution prepared using commercial sodium silicate (CC) after 3, 28 and 90 days: a) paste CC10; b) paste CC40.

When RHA was employed as the silica source in the alkali activator for the lime-pozzolan/geopolymer systems, changes were evidenced in the XRD patterns. Figures 9a and 9b show the patterns for paste CA10 and paste CA40, respectively. We can see that the signals corresponding to P for the 10% geopolymer paste were not intense after 28 curing days, unlike CC10, which suggests that the presence of RHA favoured the pozzolanic reaction rate. The signals for S were also slightly intense after 28 and 90 days, which indicates that S formation was not favoured. Probably due to the presence of amorphous SiO_2 in RHA, the pozzolanic reaction was activated and more CSH was formed. The main signal for this gel was considerably intense in the XRD pattern in CA10. The broad peak related to the presence of gel was intense after 3 curing days. Some traces of zeolite X (X) were identified after 90 curing days. For paste CA40, the intensity of the P signals in the XRD pattern were very low at the early curing age and a baseline deviation appeared within the 28-32º 2Θ range in relation to the formed gels (NASH, C(N)ASH, CSH). Some zeolitic structures (Z) appeared after 90 curing days.



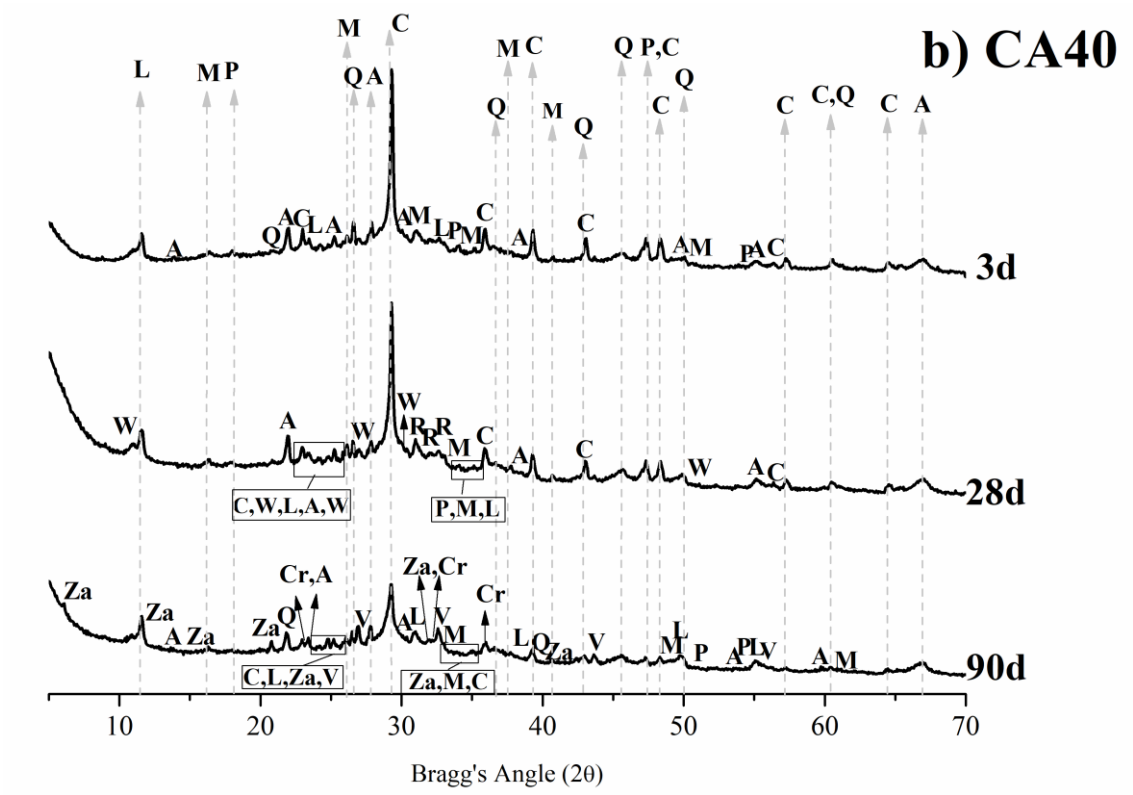


Figure 9. XRD patterns of the lime-pozzolan/geopolymer pastes activated with the alkali solution prepared by using RHA (CA pastes) after 3, 28 and 90 days: a) paste CA10; b) paste CA40.

The XRD patterns (Figure 10) of GEOP and GEOP-CH at 28 days displayed major changes. A baseline deviation was observed in GEOP and GEOP-CH, with a relative high intensity of peaks Q, M and A due to the crystalline phases from FCC. The F peaks disappeared in these two pastes, which indicated that the zeolitic fraction of FCC was highly reactive. Excess sodium ions favoured the formation of trona (T) in paste GEOP. In this case, the nature of the gel, mainly NASH, was shown as a baseline deviation within the 20-32º range. Due to calcium addition, carboaluminate peaks (L and B) were identified in the GEOP-CH pattern. In this case, the baseline deviation was strong and the broadness within the 25-32º range indicates CASH/C(N)ASH formation. This means that if a large amount of calcium is present, CASH/C(N)ASH gels form. They are easily observed in the XRD patterns for CC10, CC40, CA10 and CA40. It was more difficult to identify the presence of NASH because this gel showed less intensity and a more broadly shaped diffraction signal.

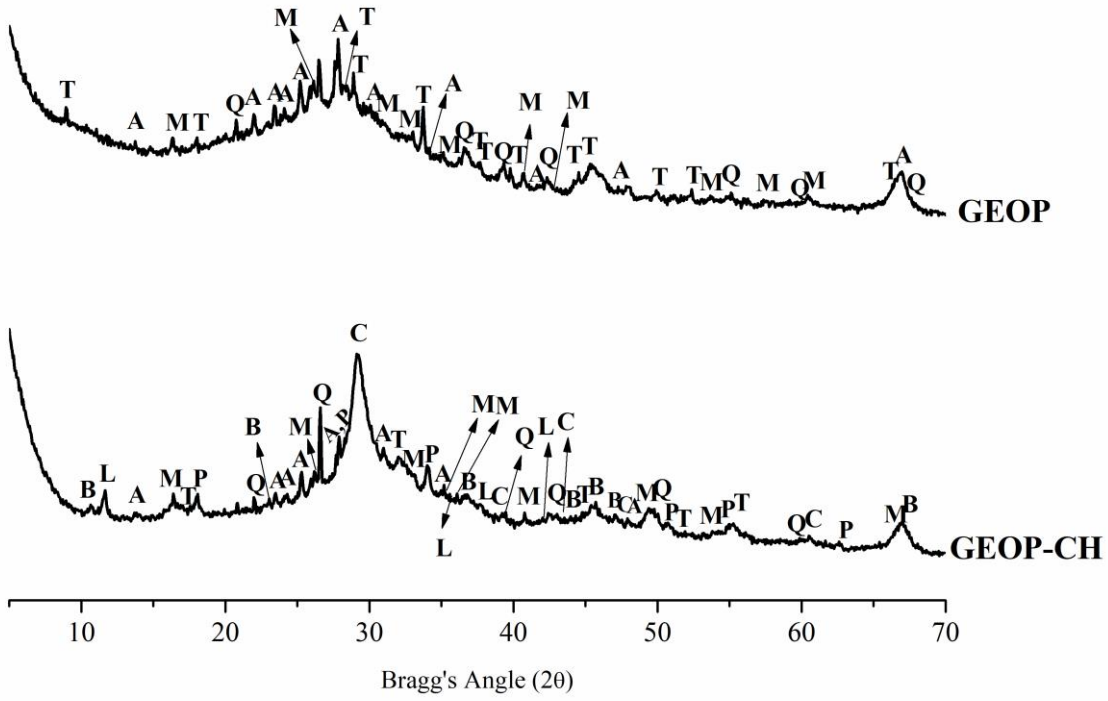
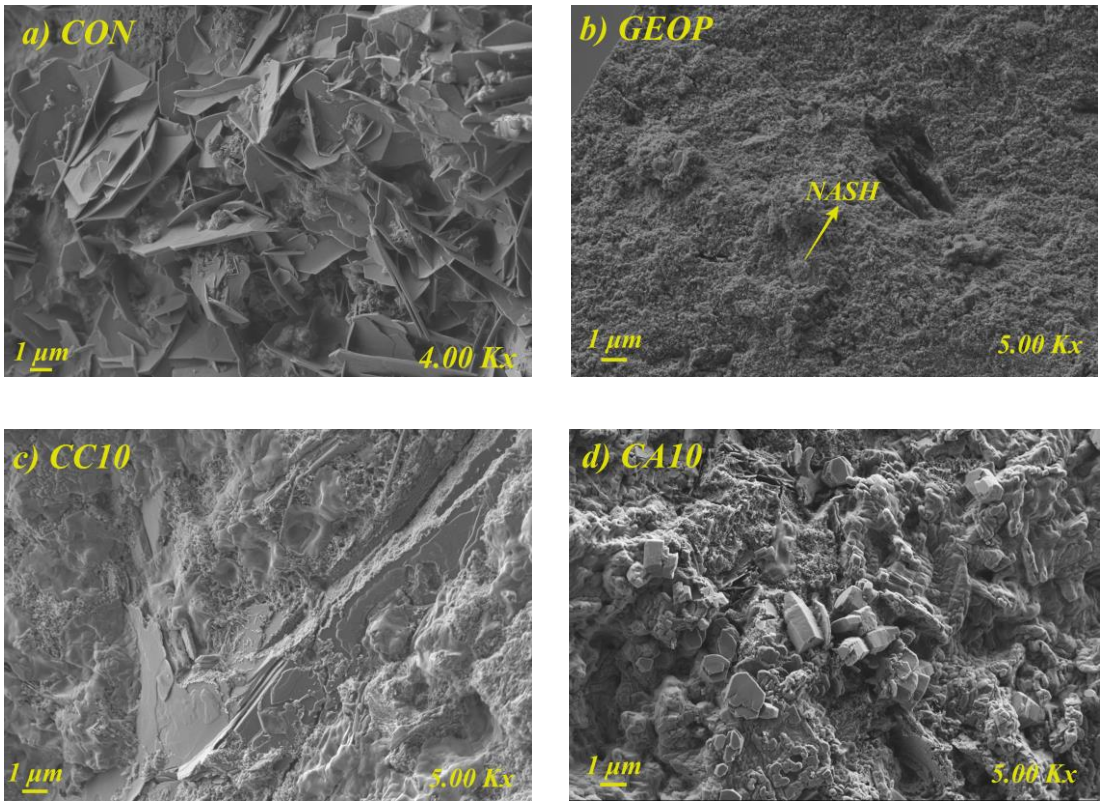


Figure 10. XRD patterns for pastes GEOP and GEOP-CH after 28 curing days.

3.5 FESEM studies

The FESEM images for all the pastes cured for 28 days are depicted in Figure 11. In the lime-pozzolan paste (CON), the typical reaction product from the pozzolanic process was observed (Figure 11.a) (strätlingite) [53] Figure 11.b represents the GEOP paste, where the paste's microstructure was denser and the principal formed product was the NASH gel [55, 56].

In pastes CC10 and CA10 (Figures 11.c and 11.d), products were observed with a different appearance to those for pastes CON and GEOP. In these pastes, pozzolanic and geopolymeric products probably coexisted. Finally, in pastes CC40 and CA40 (Figures 11.e and 11.f), the principal reaction product was C(N)ASH gel, although some NASH gel was probably present. Duramae et al reported C(N)ASH formation as a result of partial NASH substitution in the system [57]. In the CA40 paste, the formation of little cubic-shape particles took place, which may be attributed to the presence of zeolite A [58].



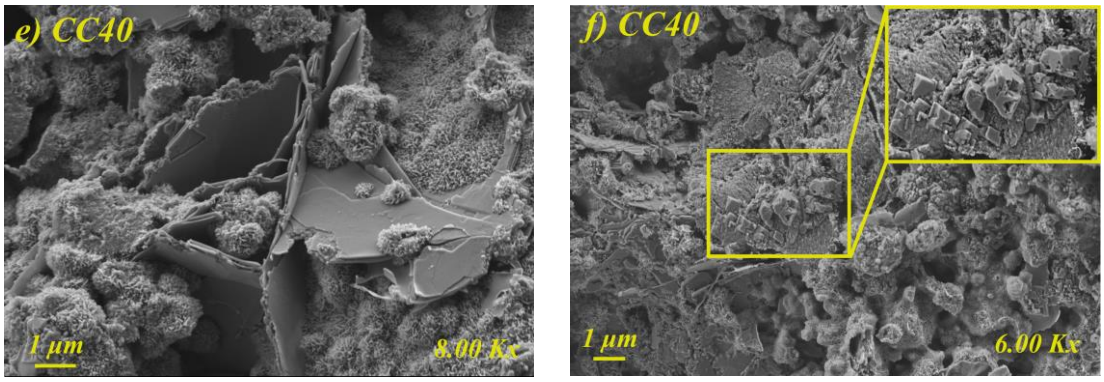


Figure 11. FESEM micrographs for pastes after 28 curing days: a) CON; b) GEOP; c) CC10; d) CA10; e) CC40; f) CA40.

4 CONCLUSIONS

The mechanical behaviour and microstructure of lime-pozzolan/geopolymer mixtures were analysed, in which pozzolan and the precursor were the same aluminosilicate waste (spent FCC catalyst).

The changes in the lime-pozzolan system made by adding the geopolymeric binder were highly positive in compressive strength development terms for mortars:

- It is highlighted the strength improvement at short times thus, the mortars with a 10-40% replacement of lime-pozzolan binder with geopolymer, prepared with the NaOH/waterglass solution, yielded strength values within the 9-25 MPa range at 7 curing days *versus* 3.59 MPa for the lime-pozzolan mortar.
- For the long curing time (90 days), the 10% geopolymer mortar was 50% higher than the lime-pozzolan one, and the 40% geopolymer mortar was almost double.

The contribution of RHA as a silica source in the alternative alkali activator was remarkably positive compared to the commercial chemical reagent (waterglass), especially at early curing ages (1-3 days) for the smallest geopolymer addition (10%). Apparently, the reason for the different nature of the binding gel formed when RHA was present was responsible for the achieved higher strength.

The addition of a geopolymer to a lime-pozzolan system brings about significant changes in the nature of hydration products:

- The hydration of lime-pozzolan systems produces typical products: CSH/CASH gel, calcium carboaluminate hydrates and S, as well as unreacted portlandite at early (3 days) and mid-term (28 days) curing ages.
- The addition of 10% geopolymer slightly modified the nature of hydration products. However, the reaction rate rose and portlandite consumption was significantly higher.
- The addition of 40% geopolymer led to a more marked modification in the nature of hydration products: a NASH/C(N)ASH gel was formed, and no presence of S and portlandite was detected.

In summary, adding geopolymer to a lime-pozzolan system is a good proposal for improving the early- and long-term strength performance of mortars. Using RHA as an alternative silica source for replacing waterglass has a very high potential to avoid or to reduce employing synthetic chemical reagents that have a significant carbon footprint.

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December 1, 2020

Professor Michael C Forde, PhD, FREng, FRSE, Hon.ACI
Editor-in-Chief
Construction & Building Materials

Re: REVISED Manuscript submission

Revision notes of the manuscript: "**Lime/pozzolan/geopolymer systems: performance in pastes and mortars**"

Paper number: CONBUILDMAT-D-20-09089 (First submission)

Authors: Ariel R. Villca, Lourdes Soriano, Alba Font, Mauro M. Tashima, José Monzó, María Victoria Borrachero, Jordi Payá.

Dear professor,

The authors would like to express their appreciation to the editor and the reviewers for their precious time in the revision of the paper. We have carefully addressed all the comments proposed by the two reviewers, and the refinements made in the revised paper are summarized in our response below to improve the quality of the manuscript for its publication in *Construction & Building Materials*.

First of all, we wish to apologize for the confusion in the numbering of the bibliography throughout the text. Apparently, in the latest version of the manuscript there was an unintended change from the database we are working with.

Reviewer #1 comments are in red

Reviewer #3 comments are in green

Author comments are in black.

Note: Line numbers and references in this letter correspond to those in the new manuscript.

Reviewer #1:

Comments to the authors:

It is an interesting paper with many results; however, the presentation of the results and the discussion should be improved because the interaction between lime/pozzolan/geopolymer for example in mechanical strength is not clear, there is absence of data compressive strength for geopolymer. The reaction and the formation of a mixture of gels (N-A-S-H and N, C-A-S-H) is not well supported. The authors could support their results with a greater comparison with literature.

1) Introduction - in part where the lime / pozzolan systems are indicated, article to be referenced below

The effect of type and concentration of activators on flowability and compressive strength of natural. Pages 337-347.

Thanks for your suggestion, it is a really attractive article but this did not work on lime / pozzolan systems that were partially replaced by a geopolymer, but on a study of the effect of different parameters in the alkaline solution on the slag-based geopolymer to which a pozzolana was added. natural.

This article must be used to analyze the results of mechanical resistance:

Studying different silica sources for preparation of alternative waterglass used in preparation of binary geopolymer binders from metakaolin/boiler slag. Construction and Building Materials 227 (2019) 116621.

This paper was included in the discussion to explain the good results of mortars with RHA as silica source:

"The good behaviour of RHA as silica source may be the result of a more enhanced connectivity in microstructure of the samples activated with this material as said Villaquirán- Caicedo in the paper published in 2019 [40]." (L: #288-290).

2) Materials and Method- Please, correct Table 1, the sum of the percentages does not give 100% and the Al2O3 content is missing.

There was some mistake in the last version of the submitted manuscript with the Table 1 format. In the new manuscript it has been modified as follows:

(L: #150)

Table 1. Chemical composition of the used materials: fluid catalytic cracking catalyst residue (FCC) and rice husk ash (RHA)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	Others	*LOI
FCC	47.76	49.26	0.60	0.11	0.17	0.02	0.02	0.31	0.03	1.20	0.54
RHA	85.58	0.25	0.21	1.83	0.50	0.26	3.39	-	0.67	0.32	6.99

*LOI: loss on ignition

3) Materials and Method- line 13- the author indicates the sand/binder ratio is 3, if there is, the fluidity of samples is high. According to Table 2 is binder:sand ratio = 3, Please check and correct.

The correct form is SAND/BINDER RATIO = 3 (L: #159). With the data from Table 2 (L: #183):

Binder = 525.0 g >>>>> sand/binder = 3; Sand = 3 * 525 = 1575 g

4) Materials and Method- line 13- the author indicates "The lime/pozzolan ratio was chosen based on the research group's previous research [33]" but the reference [33] is T. Luukkonen, Z. Abdollahnejad, J. Yliniemi, P. Kinnunen, M. Illikainen, Comparison of alkali and silica sources in one-part alkali-activated

blast furnace slag mortar, Journal of Cleaner Production. 187 (2018) 171-179. doi:10.1016/j.jclepro.2018.03.202 from University of Oulu in Finland. Please check and correct.

All references in the new manuscript have been reviewed and actualized in order to correct its correlationship with the text references.

The reference in this case is [37] (L: #160) related with:

[37] J.G. Martí, M. V. Borrachero, J. Payá, J. Monzó, D. Alveiro, A. Salas. Reutiliización de ceniza de cascarilla de arroz y residuo de catalizador de craqueo catalítico en conglomerantes cal-puzolana para concretos de bajo coste económico y medioambiental, Proceedings of the 6th Amazon & Pacifics Green Materials Congress and Sustainable Construction Materials Lat-RILEM Conference, Cali, Colombia, 2016, 623–636

5) Results and Discussion section- compressive strength… "The geopolymeric mortar without lime (pure geopolymer, GEOP) was analysed for the same curing ages. The compressive strength of this sample was generally very high, especially at early curing ages". What were the compressive strength reached by the geopolymer? I don't see the results for geopolymer only.

This paragraph has been completed with the mechanical results of the GEOP mortar as follow:

"The geopolymeric mortar without lime (pure geopolymer, GEOP) was analysed for the same curing ages. The compressive strength of this sample was very high, especially at early curing ages, between 1 and 7 curing days. After the first curing day the GEOP mortar yielded 13.38 MPa and the compressive strength increases until 53.90 MPa at 7 curing days. No CCx system had a compressive strength greater than 25 MPa." (L: #239 – 244)

6) Results and Discussion section- compressive strength… "Conversely in the research by Boonjaeng et al, the lime/MK mixture was considered the binder and was activated with NaOH [28]." The reference doesn't correspond to Boonjaeng, please check and confirm the references. The [28] is:

[28] S. Alonso, A. Palomo, Alkaline activation of metakaolin and calcium hydroxide mixtures: Influence of temperature, activator concentration and solids ratio, Materials Letters. 47 (2001) 55-62. doi:10.1016/S0167-577X(00)00212-3.

In the re-submitted manuscript this mistake has been corrected as follows:

"Conversely in the research by Boonjaeng et al, the lime/MK mixture was considered the binder and was activated with NaOH [30]." (L: #237 - 238).

Then in the bibliography section:

[30] S. Boonjaeng, P. Chindaprasirt, K. Pimraksa, Lime-calcined clay materials with alkaline activation: Phase development and reaction transition zone, Applied Clay Science. 95 (2014) 357–364. doi:10.1016/j.clay.2014.05.002.

7) Results and Discussion section- compressive strength… the author saying "The nature of the gel in these mortars was the NASH type [34]" and reviewing this reference corresponds to a study where Na+ was not used. K+ was used as the alkali ion. So, the speculative explanation of formed gels does not correspond. please check and confirm the references. Rewrite this paragraph and make use of bibliographic references, also rely on the results of FITR.

[34] M.A. Villaquirán-Caicedo, R.M. de Gutiérrez, Synthesis of ceramic materials from ecofriendly geopolymer precursors, Materials Letters. 230 (2018) 300-304.

In the re-submitted manuscript this mistake has been corrected as follows:

"The nature of the gel in these mortars was the NASH type [39]." (L: #244)

Then in the bibliography section:

[39] A. Font, M.V. Borrachero, L. Soriano, J. Monzó, A. Mellado, J. Payá, New eco-cellular concretes: Sustainable and energy-efficient materials, Green Chemistry. 20 (2018) 14684. doi:10.1039/c8gc02066c.

8) Results and Discussion section- Please improve resolution for curved DTGs, they look blurry.
The all figures in the re-submitted manuscript have been improved and now are attached in tiff format and 300dpi.

9) Results and Discussion section- FTIR-line 58 "When the activator concentration was low, the principal reaction product was CSH; when the concentration was high, the main product was the C(N)ASH gel and CSH formed as a secondary reaction product".
According with previous explanations, I think the author want to say C(N)ASH gel and NASH. Please revising sentence.

This sentence (L: #335 – 338) is related with the thermogravimetric analysis but not with the FTIR. The authors checked this affirmation and is correct. When the concentration of the activator was high the main product formed was C(N)ASH. The CSH is also formed but in a lesser degree (as a secondary product). Please take advice the referenced papers for this affirmation [28,29,44].

10) Results and Discussion section- FTIR- In Figure 5b, numbers corresponding to <993 cm-1 wavenumber are missing.
"The bands with lesser intensity, around 867 cm-1, were identified as Si-O stretching and OH bending (Si-OH). The peak was attributed to bending bands (Si-O-Si and O-Si-O) with those at around 470 cm-1[49]." Please identified in fig 5b.

These peaks are now identified in the Figure 5b. (L: #394)

11) Results and Discussion section- FTIR- "For the CC40 paste, the signal attributed to the gel was found at 968 cm-1 (after 90 curing days)." Please explaining which gel, NASH, N(C)ASH?

To clarify this the sentence has been modified as follow:

"For the CC40 paste, the signal attributed to the gel (NASH) was found at 968 cm^{-1} (after 90 curing days)." (L: 389 – 390)

12) Results and Discussion section- Please improve resolution for curved XRD, they look blurry.
As are above mentioned, the all figures in the re-submitted manuscript have been improved and now are attached in tiff format and 300dpi.

13) The unit for X axis in XRD figures is angle …. 2θ (angle) or 2θ (°)
As is indicated in the figures the angle is the "Bragg's Angle (2 theta)" this is the commonly referenced to the 2θ (angle).

Theta is the name of this Greek letter. To improve the understanding in the re-submitted manuscript the unit for X-axis in XRD figures are drawn as: "Bragg's Angle (2θ)".

14) Results and Discussion section- XRD -Why the XRD patterns for CC40 look different of CA40, if, is silica source from RHA is amorphous? in CC40 there is a peak for Q but in CA40 there is not. then one would expect the reaction products formed to be similar between the two binders. Please explaining.
In the CA40 XRD pattern there is the presence of Q peak, the same that for the CC40 paste, but with lower intensity. In some cases, depending on the preparation of the sample for XRD test (preferential orientation of particles) and depending on the intensity of the peaks from other crystalline phases and the baseline deviation (attributed to the amorphous content), it is usual to have apparently different composition. Quartz is not a reaction product, this SiO2 crystalline phase is present in the FCC (yo can take advice on the following reference: Erich D. Rodríguez, Susan A. Bernal, John L. Provis, John D. Gehman, José M. Monzó, Jordi Payá, M. Victoria Borrachero, Geopolymers based on spent catalyst residue from a fluid catalytic cracking (FCC) process, Fuel, Volume 109, 2013, Pages 493-502, https://doi.org/10.1016/j.fuel.2013.02.053.)

Reviewer #3:

1) The pozzolan used is not in the name of the article, nor at least in the name of the geopolymer. I think it is worth replacing the "pozzolan" by FCC.
Thanks for your consideration, but at least the authors decided to conserve the title: "**Lime/pozzolan/geopolymer systems: performance in pastes and mortars.**"

The aim of the present paper is the study of development of binary mixtures where the lime/pozzolan binder was partially replaced with a geopolymeric mortar.

The FCC was employed as both the mineral admixture in the lime/pozzolan system and the precursor in the geopolymer formulation.

2) Abstract: The abstract must be written in a single paragraph containing: introduction, methodology, results and conclusions.
The abstract has been modified and in the re-submitted manuscript it is a single paragraph containing introduction, methodology, results and conclusions.

3) Keywords: the pozzolan chosen was FCC, why not put FCC as the keyword instead of "pozzolan"?
The "fluid catalytic cracking catalyst residue" has been added as a new keyword.

4) Item 3.1 Compressive strength development: I think it is worth highlighting in this item that as the geopolymer replacement is increased, little variation in resistance gain is observed after 10 days. It is worth remembering that geopolymers are famous for presenting a marked resistance gain in the first days, and this was proved by the CC30 samples and, mainly by the CC40, which had little variation after 10 days of cure.
This reflection about the gain of strength by the geopolymer addition into the lime/pozzolan system has been added in the following paragraph:

"It is highlighted the compressive strength gain at early ages with the incorporation of the geopolymer into the lime/pozzolan systems. With the 10% substitution (sample CC10), compressive strength was 45% greater than the strength for CON after 1 curing day and was 152% greater after 7 curing days." (L: #212 – 215).

5) Page 19, Line 28: You say "In our case ...". All text must be written in third person.
"In our case…" has been replaced by "In the present research…." (L: #385)

6) At least three articles have been published by some of the authors of this article on geopolymer based on fluid catalytic cracking catalyst residue and no comparison has been made with the results of this new geopolymer.
As you mentioned the previous works were about the geopolymer mortars based on FCC, but not about the incorporation into lime/pozzolan systems, thus the behavior of the geopolymer was not the aim in the present research. In the present research the influence of the combination of both systems in the resulted materials properties was discussed.

The previous works that you refer might be used to help the understanding and compare the chemical stoichiometry, the resulted reaction products and microestructural behavior of the new combined systems, but not to compare the mechanical behavior thus the nature of the mixes was completely different:

a) This paper aims to study the geopolymers based in FCC activated by silica from the RHA:

[18] N. Bouzón, J. Payá, M. V. Borrachero, L. Soriano, M.M. Tashima, J. Monzó, Refluxed rice husk ash/NaOH suspension for preparing alkali activated binders, Materials Letters. 115 (2014) 72–74. doi:10.1016/j.matlet.2013.10.001.

This investigation was employed in the present work:

"For the geopolymeric binder, the formulation of the alkaline activator solution was selected according to a previous work [18]" (L:#164 – 165).

b) This paper aims to study the geopolymers based in FCC activated by silica from the residual diatomaceous earth:

[19] A. Font, L. Soriano, L. Reig, M.M. Tashima, M. V. Borrachero, J. Monzó, J. Payá, Use of residual diatomaceous earth as a silica source in geopolymer production, Materials Letters. 223 (2018) 10–13. doi:10.1016/j.matlet.2018.04.010.

c) The last one, studied the influence of the activators into the conventional geopolymer based on FCC:

[31] M.M. Tashima, J.L. Akasaki, J.L.P. Melges, L. Soriano, J. Monzó, J. Payá, M. V Borrachero, Alkali activated materials based on fluid catalytic cracking catalyst residue (FCC): Influence of SiO_2/Na_2O and H_2O/FCC ratio on mechanical strength and microstructure, 108 (2013) 833–839.

These three previous works provide a scientific basis in the introduction about the use of FCC as a precursor in the geopolymers preparation.

Based on both, the aim of the present investigation and the obtained results, there are previous related investigations from other authors which allow a logical discussion and reflection about the behavior of the new lime / pozzolan / geopolymer systems presented.

7) Conclusions: write results in topics more succinctly.
The sentences in the conclusions section have been reorganized as the order that those appear in the results and discussion section. Furthermore, the conclusions have been rewritten and synthetized.

8) What criteria are being used to number citations? It is not in order that it appears in the text or in alphabetical order. Please review and choose a criterion. Citations [32] and [33] appear after [34] in the text. The quotations [35], [36] and [37] appear after [38] in the text. Following after [38] is [44]. So it is repeated, without a logical criterion.
References not cited in the text: [39], [43], [55] and [56]. Remove from the list of references or insert in the text.
Sorry, there was a mistake in the citations. The all references in re-submitted manuscript have been revised and actualized in order to correct its correlation with the text references.

Highlights

- Fluid catalytic cracking residue (FCC) was used as pozzolan and a precursor
- Rice husk ash (RHA) was used as an alternative source of silica
- Geopolymeric binders in classic pozzolan/lime mortars gave high strength gain
- Strength gain was obtained for short curing times

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Term	Ariel Villca	Alba Font	Lourdes Soriano	Mauro M. Tashima	José Monzó	M. Victoria Borrachero	Jordi Payá
Conceptualization			X		X	X	
Methodology		X		X		X	X
Formal analysis	X	X		X	X		
Investigation	X	X	X		X	X	X
Resources			X			X	X
Writing - Original Draft		X	X				
Writing - Review & Editing	X	X	X	X	X	X	X
Visualization		X		X			
Supervision			X		X	X	
Project administration					X	X	
Funding acquisition			X		X	X	

Title page

Lime/pozzolan/geopolymer systems: performance in pastes and mortars.

Lime/pozzolan/geopolymer systems: performance in pastes and mortars.

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Abstract

Use of lime as construction material is limited mainly by low initial strength. These properties can be improved by adding pozzolanic materials, but the evolution of the reaction usually needs older ages than 7 days. Alkali-activated materials, or geopolymers, are good-performance materials that can be produced with residual waste. The combination of traditional and new materials can lead to new uses of lime mortars. This paper studies a lime/pozzolan and geopolymer mixture. The chosen pozzolan is fluid catalytic cracking catalyst residue (FCC), a material employed as a precursor in alkali-activated material. FCC is activated by two activators: a mixture of NaOH and waterglass; a mixture of NaOH and rice husk ash (RHA). The new materials were studied in microstructure and mechanical behaviour terms. The results demonstrated that lime/pozzolan/geopolymer obtained superior compressive strengths after 1 curing day to that obtained for the corresponding lime/pozzolan mortar after 90 days. An improvement in compressive strength of around 145% was achieved for the mortar with 40% geopolymer compared to the mortar with only lime/pozzolan at 28 curing days.

Keywords: lime, pozzolan, geopolymer, waste material, fluid catalytic cracking catalyst residue

1 Introduction

Lime mortar is an ancient construction material that has been used in different places and periods of history [1,2]. The Romans are certainly responsible for the main technological contribution to lime mortars: addition of volcanic ash or calcined clay significantly improved mechanical properties, and allowed it to set and harden under water. The durability of lime mortars is demonstrated by today's good conditions from the architectural heritage of Roman times [3].

After the discovery of Portland cement, the use of lime mortar drastically reduced due to the new binder's excellent mechanical and durability properties: fast setting, excellent strength development, etc. Nevertheless, current Portland cement (PC) mortars do not meet some sustainability criteria designated by the international community (sustainability development goals) [4]. PC production generates large amounts of CO_2 emissions to the atmosphere, and is responsible for about 5-8% of CO_2 emissions worldwide [5]. Thus a good option is to use alternative binders (lime/pozzolan, geopolymer systems, magnesium oxide cements, etc.) that are often associated with a lower environmental impact [6].

Studies about lime/pozzolan binders report good mechanical strength and durability aspects, depending on the type of used pozzolan [1,7–10]. However, in most cases, the mechanical strength for early curing times (< 28 days) is reduced due to the slow setting and hardening process of lime/pozzolan systems.

Palomo et al. studied the similarity between the ancient lime/pozzolan mortars of historic Roman marine concrete and hybrid-Portland alkaline cement [11]. More specifically, these researchers found similar products of reaction by comparing ancient concrete in marine structures and hybrid alkaline materials (a combination of Portland cement and alkali-activated fly ash). The particularity of seawater concretes in Roman times was studied in depth in the last few years by paying attention to the formation of the so-called "Al-tobermorite" [12,13]. The stability of Al-tobermorite can be a starting point in an attempt to synthesise similar products.

Alkali-activated materials (AAM) are relatively new construction materials, and geopolymer is often used as an additional terminology. Research into these systems is growing and they are expected to be used in many applications in the construction domain. These materials are basically a mixture of an aluminosilicate source and an

alkaline-activating solution [14]. The most typically used precursors are metakaolin (MK), fly ash (FA), ground granulated blast furnace (BFS), etc. Alkaline solutions are normally a mixture of sodium hydroxide and sodium silicate (or potassium as a cation), although other activators can be used: sodium carbonate, sodium sulphate, etc.[15,16].

The new geopolymer technology goal is to use residual materials to prepare alkaline solutions. The carbon footprint related to alkali hydroxides is smaller than that for alkali silicates. Many research groups are investigating the use of alternative silica sources to obtain a commercial silicate or waterglass alternative. These silica sources are mainly rice husk ash (RHA), diatomaceous earth residue, glass waste, sugar cane straw ash and silica fume, among others [17–22].

In some studies on geopolymeric systems, the addition of calcium compounds enhances the activation reaction to result in improved compressive strength [23,24]. Moreover, the use of materials that include calcium in their composition can improve the reactivity of waste, but an excess of calcium has negative effects on compressive strength [25].

The combination of these two binder types (lime/pozzolan and geopolymer) would reduce environmental issues caused by CO_2 emissions, increase waste valorisation and improve the mechanical properties at curing ages lasting less than 28 days.

Allali et al. studied the influence of calcium content on geopolymeric matrices for their use in restoration mortars [26]. They substituted metakaolin (MK) for calcium hydroxide in mortars with potassium and sodium salts as an alkaline solution. When they employed calcium hydroxide in both sodium or potassium solution, $Ca(OH)_2$ totally or partially dissolved. They observed fast setting and compressive strength was lower than for the mortar with only MK (42 MPa for the mortar without hydrated lime and 10 MPa for the mortars with 41% replacement of MK with hydrated lime at 7 curing days).

Recently, glass powder in different systems has been used. In mixtures with PC, it reacted as pozzolanic material. In geopolymeric systems, it was blended with slag, fly ash and lime [27]. With the glass powder and lime mixtures, which were activated by a 4M NaOH solution, a compressive strength of 31MPa was achieved in systems cured at 60ºC for 28 days. The formation of a similar calcium silicate hydrate to tobermorite was suggested for the SEM/EDS study.

Several authors have studied the alkaline activation of MK with calcium hydroxide [28,29]. They followed different analytical techniques to characterise the products formed in this mixture, and concluded that reaction products differed depending on the OH^- concentration in the aqueous medium. When the activator concentration was high (> 10M of NaOH), the formed alkaline aluminosilicate gel was the principal product, while hydrated calcium silicate was the secondary product. However, when the activator concentration was low (< 5M of NaOH), dissolved aluminates were insufficient to produce aluminosilicate gel and pozzolanic products predominated.

Boonjaeng et al. studied the system of lime and calcined clay materials with different alkaline solutions of sodium hydroxide (NaOH). When comparing several molarities (0.1M -10M), they concluded that the reaction of the mixture was dominated by the NaOH concentration [30]. At low concentrations (<1M), the pozzolanic reaction was dominant, while the zeolite-formation reaction predominated at medium NaOH molarities (1M<NaOH<5M). Finally, at a high NaOH molarity (>5M), the principal reaction was the geopolymerization process.

Fluid catalytic cracking catalyst residue (FCC) has been employed as a precursor in geopolymeric mixtures in some reported studies. Tashima et al. made samples with different SiO_2/Na_2O molar ratios [31]. These authors obtained mortars with a compressive strength of 68 MPa after 3 curing days at 65ºC. Trochez et al. obtained similar compressive strength in pastes after curing at ambient temperature for 7 days [32].

The use of RHA has been studied by different research groups as an alternative activator (source of silica). Mejía et al. employed two types of RHA and sodium silicate (as a control mix) to activate mixtures with FA and BFS as precursors[17]. The samples with sodium silicate displayed better mechanical strength than the mortars with RHA, but the results of these mixtures gave a compressive strength close to 42 MPa. Bouzón et al. employed RHA in systems with FCC as a precursor [18]. These authors obtained mortars with very similar compressive strengths to the mortar with sodium silicate (40 MPa). Another research work has reported poor results when RHA was compared to commercial reagents. Luukkonen et al. compared the use of RHA and microsilica with that of sodium silicate [33]. The compressive strength of mortars with an alternative activator was lower than the commercial one, but proved sufficient for certain uses, and performed well with freeze-thawing cycles. Villaquirán-Caicedo and Mejía de Gutiérrez [34] studied MK-based geopolymers using mixtures of RHA or silica fume with KOH as activators. They

achieved a 47% reduction in the warming potential emissions for this system compared to the corresponding commercial potassium silicate-activated system.

The present research studies the development of binary mixtures where the lime/pozzolan binder was partially replaced with a geopolymeric mortar.

Lime mortars were made with a residual pozzolan, namely FCC. The geopolymeric material was a mixture of FCC activated in two different ways: i) a solution of sodium silicate (waterglass) and sodium hydroxide; ii) a suspension prepared as a mixture of sodium hydroxide and RHA.

2 Materials and Methods

A commercial hydrated lime supplied by Cales Pascual (Paterna, Spain) was used. This material is designed as CL90-S according to Spanish standard UNE-EN 459-1 [35]. The FCC residue was supplied by BP Oil España, S.A.U (Grao de Castellón, Spain). RHA was supplied by Dacsa S.A (Tabernes Blanques, Spain).

FCC was employed as both the mineral admixture in the lime/pozzolan system and a precursor in the geopolymer formulation.

The geopolymer was activated by two activators:

- A conventional alkaline solution prepared with a mix of waterglass (Na_2SiO_3, commercial sodium silicate) (Merck, 28% SiO_2; 8% Na_2O and 64% H_2O) and sodium hydroxide (Panreac-SA, 98% purity).
- An environmental-friendly alkaline solution where RHA was employed as an alternative source of "sodium silicate". RHA was mixed with water and sodium hydroxide in a thermal bottle [22].

The chemical composition of FCC and RHA was analysed by X-Ray fluorescence (XRF) equipment (Magic Pro Spectrometer-Philips). The results are summarised in Table 1.

Table 1. Chemical composition of the used materials: fluid catalytic cracking catalyst residue (FCC) and rice husk ash (RHA)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	Others	*LOI
FCC	47.76	49.26	0.60	0.11	0.17	0.02	0.02	0.31	0.03	1.20	0.54
RHA	85.58	0.25	0.21	1.83	0.50	0.26	3.39	-	0.67	0.32	6.99

*LOI: loss on ignition

The mean particle diameter of the supplied FCC was 21 µm. RHA was milled in an industrial mill and its mean particle diameter was 20 µm. All the granulometric measurements were taken in a Malvern Mastersizer 2000 in aqueous medium.

The amorphous content of RHA was 31.5%, calculated by an extractive method using HCl and KOH [36].

Lime/pozzolan mortars and pastes were prepared at the following ratios: lime/FCC =1/1; water/binder = 0.8; sand/binder = 3. The lime/pozzolan ratio was chosen based on the research group's previous research [37]. The employed sand was siliceous in nature with a fineness modulus of 4.3. Mortars were moulded in cubic 40*40*40 mm^3 casts and stored at 25ºC and RH 73% for 24 h. Specimens were wrapped in film until tested. Pastes were moulded in sealed polyethylene phials and stored at 25ºC.

For the geopolymeric binder, the formulation of the alkaline activator solution was selected according to a previous work [18]. The solution had a SiO_2/Na_2O molar ratio of 1.17, a sodium molality of 7.5 and a water/binder ratio of 0.6.

The replacements of lime/pozzolan binder mass with geopolymeric binder were 0% (control sample), 10%, 20%, 30% and 40%.

Table 2 summarises the quantity (expressed as grams) of the materials employed in mortars. The control mortar was the mixture with only lime and pozzolan (CON). The geopolymeric mortar (GEOP) was the mixture of FCC with the activator of NaOH and Na_2SiO_3. The lime/pozzolan/GEOP mixtures were named CCx or CAx, where: i) CC is the geopolymer activated by the conventional solution (waterglass and sodium hydroxide) and CA is the geopolymer when RHA was employed as a silica source in alkaline activator (RHA + water + sodium hydroxide); ii) x is the lime/pozzolan replacement percentage with FCC geopolymer. For example, mortar CA10 contained 10% geopolymer (FCC and an alkaline activator composed of a mixture of RHA, NaOH and water).

The abbreviation FCC^P represents the quantity of FCC in the lime/pozzolan binder, while the abbreviation FCC^G denotes the quantity of FCC in the geopolymeric binder. H_2O^P was the water content in the lime/pozzolan system. The water used to prepare the geopolymeric binder is indicated in the activator as H_2O^G.

Table 2. Composition of lime/pozzolan mortar, lime/pozzolan/GEOP mortars and GEOP mortar (weight in grams).

	Lime/pozzolan binder		GEOP binder						Sand
					Activator				
	Lime	FCC^P	H_2O^P	FCC^G	H_2O^G	NaOH	Na_2SiO_3	RHA	
CON	262.5	262.5	420.0	-	-	-	-	-	1575.0
CC10	236.3	236.3	378.0	52.5	12.6	6.4	29.5	-	1575.0
CA10	236.3	236.3	378.0	52.5	31.5	9.4		9.2	1575.0
CC20	210.0	210.0	336.0	105.0	25.2	12.8	59.1	-	1575.0
CA20	210.0	210.0	336.0	105.0	63.0	18.9	-	18.4	1575.0
CC30	183.8	183.8	294.0	157.5	37.8	.2	88.6	-	1575.0
CA30	183.8	183.8	294.0	157.5	94.	28.4	-	27.6	1575.0
CC40	157.5	157.5	252.0	210.0	50.4	25.6	118.3	-	1575.0
CA40	157.5	157.5	252.0	210.0	126.0	37.8	-	36.7	1575.0
GEOP	-	-	-	525.0	126.0	64.0	295.3	_	1575.0

Pastes lime/pozzolan, lime/pozzolan/GEOP and GEOP had the same proportions of materials as the corresponding mortars, but without sand. An additional paste containing 80% GEOP and 20% hydrated lime was fabricated and called GEOP-CH.

Compressive strength was measured in an INSTRON 3282 machine for the ages of 1, 2, 3, 7, 28 and 90 days, and was the average of four individual tests.

The microstructural analysis of pastes was carried out by a thermogravimetric analysis (TG/DTG), powder X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM).

The TG analysis was done using a TGA 850 Mettler-Toledo thermobalance. The TG experiments were performed from 50ºC to 600ºC at a heating rate of $10ºC.min^{-1}$. Aluminium-sealed crucibles (70 µL volume) were used with a pinholed lid and a nitrogen atmosphere (flow gas rate of 75 $mL.min^{-1}$). The XRD analyses were carried out in a Bruker AXS D8 Advance device from 10º to 70º 2θ (2s accumulation time in a 0.02 angle step). The FTIR analyses were run in a Bruker Tensor 27 and analysed within the 400-4000 cm^{-1} range. The FESEM micrographs were taken in a Zeiss ULTRA 55. Pastes were carbon-coated and images were taken at 2kV. For the EDS analysis (X-ray energy dispersive spectroscopy), data were taken at 15kV.

3 Results and Discussion

3.1 Compressive strength development

In the first stage, the study of incorporating the geopolymer fabricated with commercial reagents (sodium silicate as a silica source) was analysed. The substitution percentages went from 10% to 40%, and the selected curing ages were 1, 2, 3, 7, 28 and 90 days. The results are represented in Figure 1. For all the curing ages, the mortars with geopolymer obtained higher compressive strengths than that for the mortar with only FCC and lime (the control mortar: CON). After 1 curing day, mortar CC40 (14.9 MPa) had the same compressive strength as CON (14.3 MPa) after 90 curing days.

It is highlighted the compressive strength gain at early ages with the incorporation of the geopolymer into the lime/pozzolan systems. With the 10% substitution (sample CC10), compressive strength was 45% greater than the strength for CON after 1 curing day and was 152% greater after 7 curing days.

Figure 1 illustrates how the CON mortars had a low compressive strength (< 2 MPa) until 7 days. Compressive strength evolution was 190% from 7 days to 28 days, with 37% evolution from 28 days to 90 curing days. Mixture CC40 yielded fast evolution between 1 and 7 days (65%), when its evolution was asymptotic until 90 days with compressive strength at around 25 MPa.

The evolution of mortar CC10 was remarkable. The sample began with only 2.08 MPa at 1 curing day, but reached 21.09 MPa at 90 curing days (913% evolution). This compressive strength was only slightly lower than that found for the mortar with the highest geopolymer content (CC40). The effect of a small amount of geopolymer on the lime/pozzolan system was marked. The incorporation of geopolymer enhanced the formation of the new reaction products, which improved the strength of the mortars. The new aluminosilicate gel type C(N)ASH was probably formed in the lime/pozzolan/geopolymer systems. García-Lodeiro et al.[38] reported the formation of this product type in hybrid alkaline cements using FA and Portland cement. Sodium ions replaced calcium ions as charge balancers.

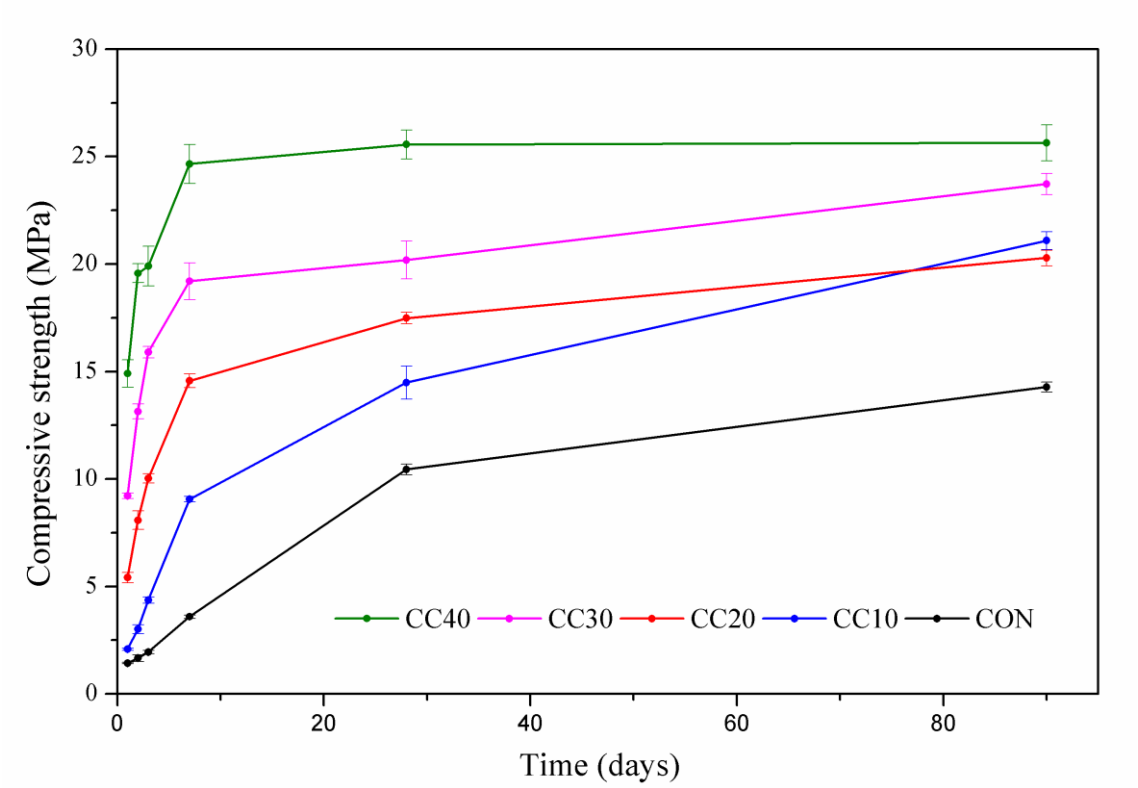


Fig 1. Evolution of the compressive strength of mortars CON and CC at 1, 2, 3, 7, 28 and 90 curing days.

For this above-discussed first stage, the obtained results contrasted those obtained by other researchers. Boonjaeng et al, used MK and lime systems, and indicated that geopolymeric gel was not as strong as CASH and CSH gel [30]. In the present work, the alkaline activator dose was used only for FCC as a precursor, and the other part of mortar (lime-pozzolan) was mixed only with water. Conversely in the research by Boonjaeng et al, the lime/MK mixture was considered the binder and was activated with NaOH [30].

The geopolymeric mortar without lime (pure geopolymer, GEOP) was analysed for the same curing ages. The compressive strength of this sample was generally very high, especially at early curing ages, between 1 and 7 curing days. After the first curing day the GEOP mortars yielded 13.38 MPa and the compressive strength increases until 53.90 MPa at 7 curing days. No CCx system had a compressive strength greater than 25 MPa. The nature of the gel in these mortars was the NASH type [39].

A comparison of the strength values at early (1-7 days) and long-term (28-90 days) ages can be made to analyse strength development in the different mortars CC. Theoretical strength (R_{th}) can be calculated by taking into account the contribution of the lime/pozzolan and geopolymer fractions as follows (Equation 1):

$$R_{th}=R_{lp}*X_{lp}+R_g*X_g \quad (1)$$

Where R_{lp} and R_g are the strength of the mortar lime-pozzolan (CON) and the mortar pure geopolymer (GEOP), respectively; X_{lp} and X_g are the mass fractions of both mortars in the CC mixtures (0.9-0.6 for X_{lp}; 0.1-0.4 for X_g).

Table 3 compares the theoretical values (R_{th}) to the experimental values (R_{ex}), and the difference in strength (D) is summarised for the mortars cured within the curing time range of 1-90 days. The D values for CC20, CC30 and CC40 were positive at early curing ages (1-3 days), which suggests that the role of calcium from lime is crucial for developing a strong cementing gel. In this case, gels CASH or C(N)ASH formed. For longer curing times, the opposite trend was seen, and the D values were negative after 28 and 90 curing days. This behaviour suggests that the contribution of the NASH gel to strength became less relevant when the binary system was fabricated. It was noteworthy that for 1-3 curing days, the presence of calcium in the mixture enhanced the gel's strength properties, which confirmed the positive effect by mixing both types of cementing systems.

Table 3. Difference (D, in MPa) in mortar strengths, calculated as experimental strength (R_{ex}) minus theoretical strength (R_{th}).

	Curing days					
System	**1**	**2**	**3**	**7**	**28**	**90**
CC10	-0.55	-1.10	-0.83	0.44	-0.34	2.54
CC20	1.59	1.52	1.59	0.91	-1.71	-2.55
CC30	4.19	4.12	4.21	0.52	-3.39	-3.40
CC40	8.69	8.11	4.97	0.94	-2.39	-5.76

In the second stage, the use of an alternative alkaline activator was explored. Resorting to RHA as a silica source was investigated as a sodium silicate substitute. The RHA and NaOH mixture in a thermal bottle was used as an activator at the same proportions as the commercial reagents. A strength variation percentage (VR) was calculated for the alternative mixtures (CA) using Equation 2:

$$VR = 100*(R_{CAx}-R_{CCx}/R_{CCx}) \quad (2)$$

Where R_{CAx} is the compressive strength for a given percentage of geopolymer (x) in a mortar with RHA (CA); R_{CCx} is the compressive strength for the same percentage (x) in a mortar with sodium silicate (CC).

Figure 2 represents the VR evolution for all the replacement percentages and curing ages. The samples with values over the red line yielded a compressive strength that was more than 2-fold higher than the values yielded by mortars CC.

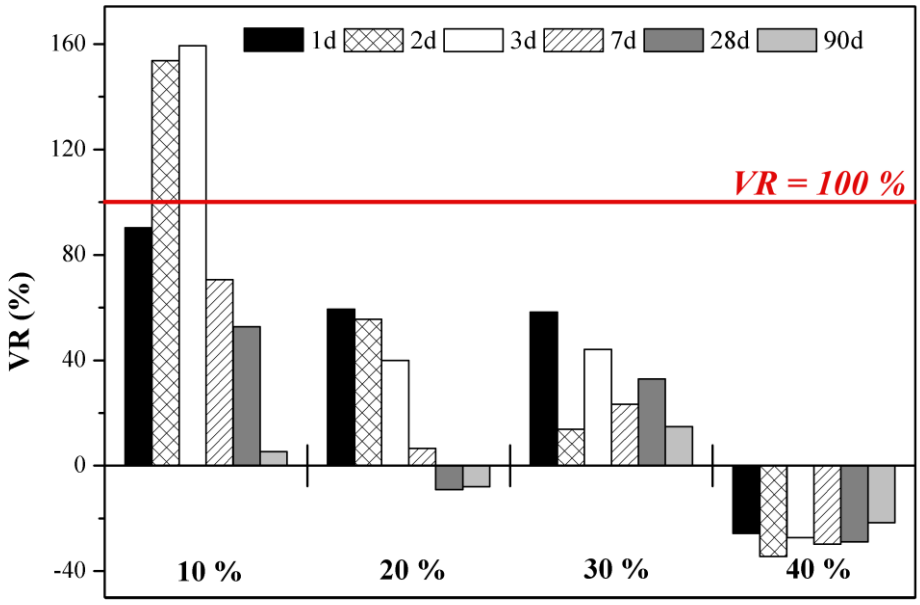


Figure 2. Strength variation (VR) percentages for the mortars with alternative silicate (CA samples).

Higher VR values were obtained for the 10% substitution percentage. For 2 and 3 curing days, these values were higher than 100% (153.7% and 159.3%, respectively) and the minimum value was obtained at 90 curing days (5.34%). The systems with 20% and 30% geopolymers were less effective. With 20% (CA20 samples), mortars had low negative VR values (-9.1% and -7.92%, respectively), even at 28 and 90 days. The samples with the 40% substitution yielded negative VR values for all the curing ages. These negative values can be attributed to the poor workability of the RHA-containing mortars, whereas the mixtures with the commercial reagent were easily compacted.

The good behaviour of RHA as silica source may be the result of a more enhanced connectivity in microstructure of the samples activated with this material as said Villaquirán- Caicedo in the paper published in 2019 [40]. The results were very interesting from a practical viewpoint because mixtures can be obtained with good compressive strength without using commercial sodium silicate, which is a synthetic chemical reagent with a large carbon footprint, as previously reported [41]. The replacement of commercial sodium silicate with RHA led to very good mortar performance in terms of early-age compressive strength, which makes the small geopolymer dose in the lime/pozzolan system more appealing.

3.2 Thermogravimetric studies

The lime-pozzolan (CON), lime-pozzolan/geopolymer (CC and CA samples) and geopolymer (GEOP) pastes had the same proportions as the mortars, but without sand. To simplify the study, it represented only the pastes with the 10% and 40% substitution percentages, CON and GEOP. The selected curing ages were 3, 28 and 90 days. Figure 3 depicts the DTG curves.

Three principal zones of mass loss were observed in the CON paste, but a continuous mass loss fell within the 100-600ºC range. Zone 1 (100-180ºC) was attributed to the dehydration of CSH; zone 2 (180-300ºC) was related to the dehydration of CASH and CAH; zone 3 was assigned to the dehydroxylation of $Ca(OH)_2$ [42]. The GEOP paste had only one peak centred at about 150ºC, attributed to the dehydration of the NASH gel [43]. In the pastes with lime-pozzolan/geopolymer, peaks differed in accordance with the substitution percentage. Pastes CC10 and CA10 with the 10% substitution looked a lot like the CON paste, while pastes CC40 and CA40 with the 40% substitution had a similar profile to the geopolymeric paste (GEOP).

The main peak in pastes CON, CC10 and CA10 at 3 and 7 curing days was centred in zone 2, and was attributed to the dehydration of CASH and CAH. At 90 days, a well-defined peak was seen for CSH dehydration on the DTG curves. The presence of hydrated lime was observed until 28 days for the control pastes, and in paste CC10 at 3 curing days. Hence, the reaction of hydrated lime to FCC was much faster when the geopolymer was present.

The principal peak in GEOP, CC40 and CA40 at all the curing ages was centred at about 150ºC. This peak was attributed to the NASH gel for GEOP and a mixture of NASH and C(N)ASH gels for CC40 and CA40. The peak in paste GEOP was much wider than that in pastes CC40 and CA40. The NASH gel probably had a higher temperature decomposition range than the C(N)ASH gel.

The mass losses within the different temperature ranges were analysed to understand the evolution of the geopolymeric and pozzolanic reactions. The chosen mass loss zones were: 50ºC to 180 ºC (ML_1); 80ºC to 300ºC (ML_2); total mass loss went from 35ºC to 600ºC (ML_T). Table 4 summarises the results.

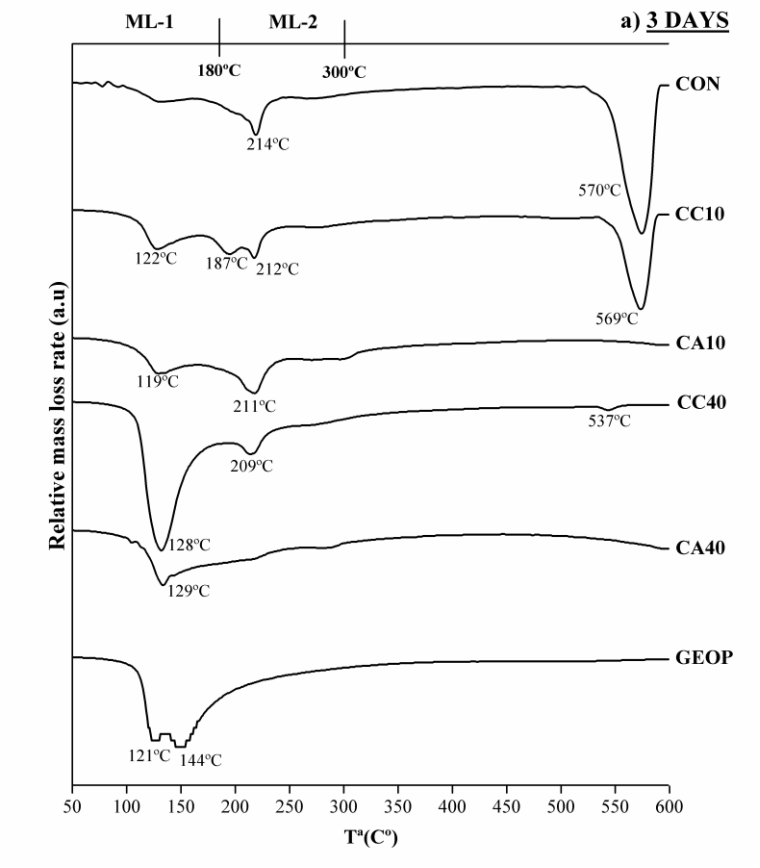
Table 4. Mass loss (TG analysis) of pastes for 3, 28 and 90 curing days.

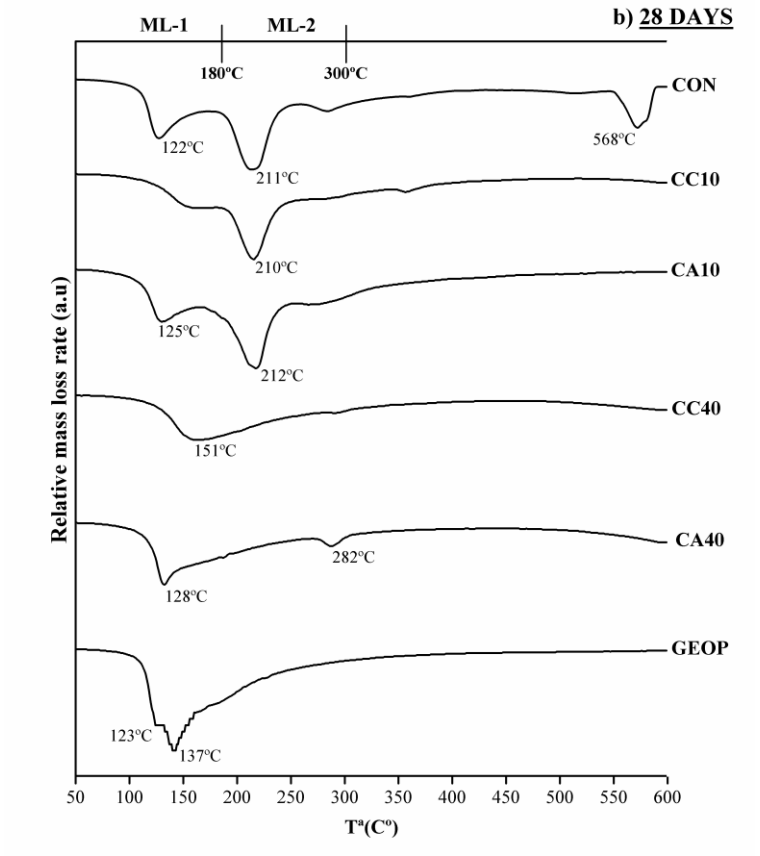
	ML_1 (50-180ºC)	**ML_2 (180-300ºC)**	**ML_T (35-600ºC)**
CON 3d	2.14	4.21	15.88
CON 28d	4.44	8.61	20.61
CON 90d	5.69	8.36	18.67
CC10 3d	3.49	4.87	15.43
CC10 28d	4.70	7.07	16.75
CC10 90d	5.43	8.09	18.05
CA10 3d	3.68	5.97	12.00
CA10 28d	4.28	10.17	18.59
CA10 90d	4.88	6.63	15.12
CC40 3d	6.12	3.79	14.67
CC40 28d	6.57	4.86	16.04
CC40 90d	6.92	4.13	15.27
CA40 3d	5.24	3.83	13.04
CA40 28d	5.32	3.78	13.51
CA40 90d	6.48	4.10	14.66
GEOP 3d	7.96	3.94	14.07
GEOP 28d	9.23	4.25	15.49
GEOP 90d	9.38	3.69	15.19

For the pastes in which the geopolymer reaction was the principal reaction and the gel C(N)ASH or NASH were the main products, the mass loss within the ML_1 range was greater than within the ML_2 range. The mass loss within interval ML_2 was, in this case,

attributed to the same product as the decomposition peak was wide. The geopolymer reaction was the predominant reaction in pastes GEOP, CC40 and CA40 as the activator concentration was higher than that in the samples with only the 10% substitution. This conclusion falls in line with previously reported papers [28, 29, 44], which studied lime/MK mixtures at different sodium hydroxide concentrations. When the activator concentration was low, the principal reaction product was CSH; when the concentration was high, the main product was the C(N)ASH gel and CSH formed as a secondary reaction product.

In the paper published in 2013 by García-Lodeiro et al.[38] the authors explained the conversion of NASH gel into C(N)ASH gel. The presence of a solution enriched with $Al(OH)_4^-$ and $Si(OH)_4$ species, in addition to the presence of sodium ions, induced this type of NASH gel. Depending on the calcium concentration in the medium, total conversion into CASH gel can take place.


a) 3 DAYS
ML-1
ML-2
180ºC
300ºC
CON
214ºC
570ºC
CC10
122ºC
187ºC
212ºC
569ºC
CA10
119ºC
211ºC
CC40
537ºC
209ºC
128ºC
CA40
129ºC
GEOP
121ºC
144ºC
Relative mass loss rate (a.u)
50 100 150 200 250 300 350 400 450 500 550 600
Tª(Cº)


b) 28 DAYS
ML-1
ML-2
180ºC
300ºC
CON
122ºC
211ºC
568ºC
CC10
210ºC
CA10
125ºC
212ºC
CC40
151ºC
CA40
282ºC
128ºC
GEOP
123ºC
137ºC
Relative mass loss rate (a.u)
50 100 150 200 250 300 350 400 450 500 550 600
Tª(Cº)

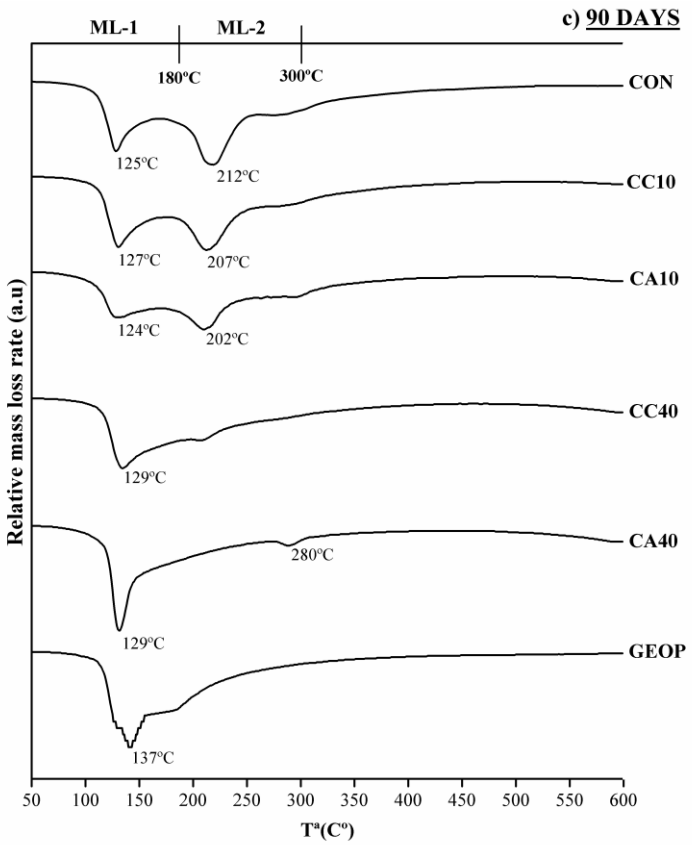


Figure 3. DTG curves for the pastes cured at: a) 3; b) 28; and c) 90 curing days.

To analyse the role of calcium in a geopolymeric paste, a paste (GEOP-CH) was fabricated by mixing 80% GEOP paste (FCC with NaOH and Na_2SiO_3 as an alkaline activator) and 20% hydrated lime. The first problem was that this paste (GEOP-CH) needed water, which was added because it was impossible to prepare paste at the 0.6 water/FCC ratio (lack of workability), and the new water/FCC ratio was increased to 1.1. The paste was analysed after 7 curing days. Figure 4 represents the DTG curves for pastes GEOP and GEOP-CH. GEOP-CH did not present a peak for the dehydroxylation of hydrated lime within the 500-600ºC range. The calcium from the hydrated lime was incorporated into the aluminosilicate gel. Its decomposition peak fell within the same decomposition temperature range observed for the paste without hydrated lime.

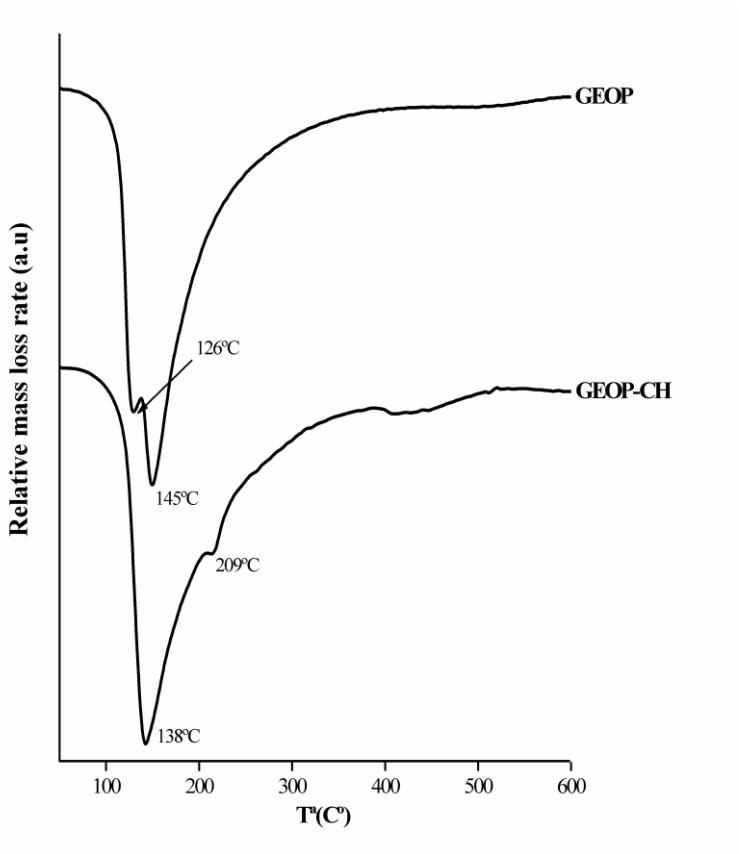


Figure 4. DTG curves for pastes GEOP and GEOP-CH after 7 curing days.

3.3 FTIR studies

Figure 5 illustrates the evolution of the reaction process for pastes CON, CC10, CA10, CC40, CA40 and GEOP at 3, 28 and 90 curing days by the FTIR technique.

The evolution of lime/pozzolan paste is represented in Figure 5.a, and the principal peaks were: i) presence of carbonates and carboaluminates (bands at 1,700, 1,435 and 875 cm^{-1}). The asymmetric stretching vibrations of the C-O group were represented at a wave number of around 1,435 cm^{-1} and the band at 875 cm^{-1} corresponded to the bending mode of the carbonate ion [40, 45]; ii) the bands of CSH caused by the bending of SiO_4 tetrahedral units fell within an approximate range of 400-500 cm^{-1} and the asymmetric Si-O stretching vibration of the CSH within the 1,100-960 cm^{-1} interval [42,46]; iii) the presence of the signals attributed to vibrations Si-O-Si, Si-O-Al and Al-O at 528 and 709 cm^{-1} as a result of the presence of CASH and CAH [42,47,48]. The presence of carbonates could be due to a number of factors: presence of calcite in the hydrated lime; formation of carboaluminate by a reaction of carbonate and the alumina of FCC; carbonation of reaction products. The band of the asymmetric Si-O stretching vibration

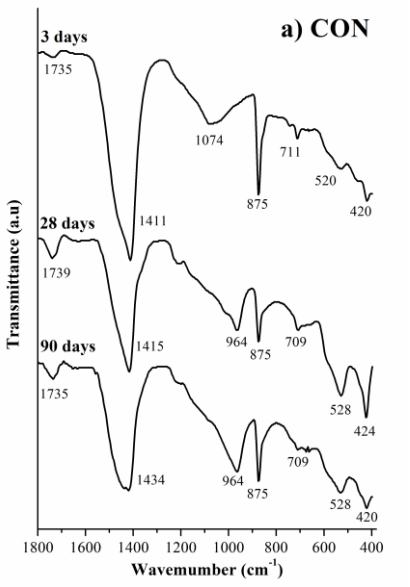
of CSH for the samples cured for 3 days was located at a higher wave number than for the pastes cured for 28 and 90 days.

The geopolymeric paste is represented in Figure 5.b. The observed principal peak was due to the presence of the NASH gel, with a band at 983-993 cm^{-1} for the geopolymeric binder. A high-intensity broad band of between 1,200-900 cm^{-1} was identified, which corresponded to the asymmetrical stretching of Si-O-T (T = Si or Al bonds [40]). In particular, the SiQ^2 unit showed infrared absorption at around 950 cm^{-1}. The bands at 1,735 and 1,365 cm^{-1} were attributed to the presence of carbonate [47,48]. The bands with lesser intensity, around 867 cm^{-1}, were identified as Si-O stretching and OH bending (Si-OH). The peak was attributed to bending bands (Si-O-Si and O-Si-O) with those at around 470 cm^{-1}[49].

The pastes containing 10% geopolymer showed similar peaks to the lime-pozzolan paste. These peaks were located at around 1,460-1,420, 1,014-950, 875 and 435-420 cm^{-1}. Allali et al.[26] established that when the MK geopolymer included calcium in the system, the Si-O-Si band was displaced from 985 cm^{-1} to an Si-O-Ca band at 930 cm^{-1}. In the present research, this displacement was especially observed for the CA sample at 90 curing days. The corresponding band was found at 950 cm^{-1}, and significantly differed from that for the CC sample (968 cm^{-1}). This meant that the presence of a different source of silica in the geopolymer changed the final geopolymeric gel structure.

For the CC40 paste, the signal attributed to the gel (NASH) was found at 968 cm^{-1} (after 90 curing days). For the CA40 paste, the corresponding signal was displaced at a lower wave number (950 cm^{-1}). Once again, the different source of silica modified the gel's nature.

García Lodeiro et al. established that adding Ca to the NASH gel would change the orientation of the structure, but this change was not easily observed by FTIR [50].



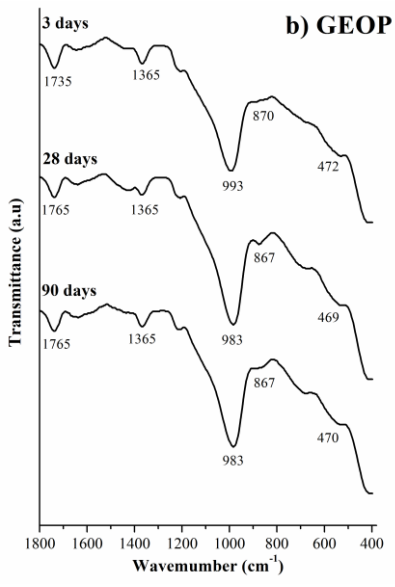
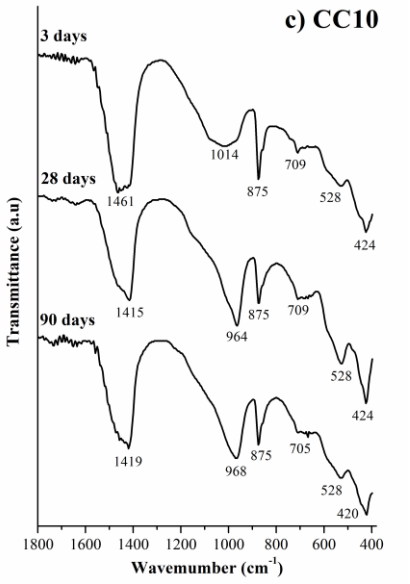
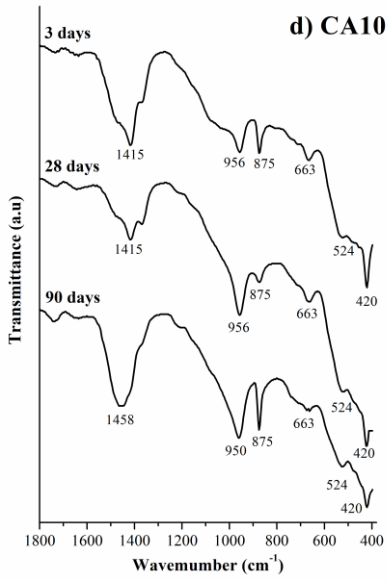


figure modified





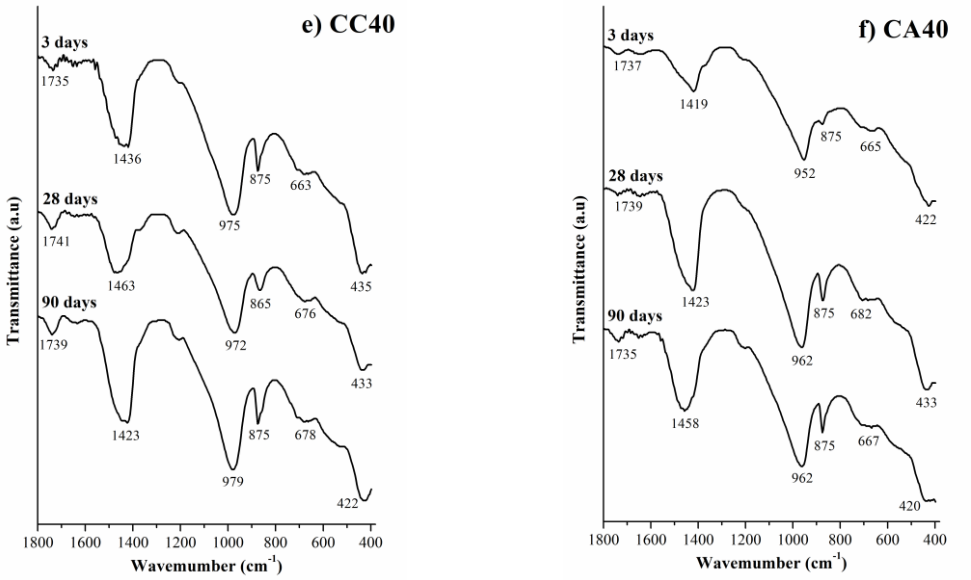


Figure 5. FTIR curves for the pastes cured at 3, 28 and 90 days

Paste GEOP-CH was also studied by FTIR. Figure 6 represents pastes GEOP-CH and GEOP at 7 curing days. A displacement of the band (995 cm^{-1} vs. 948 cm^{-1}) related to the NASH gel took place in the paste with lime (GEOP-CH). This spectrum confirmed the incorporation of Ca into the aluminosilicate gel's structure.

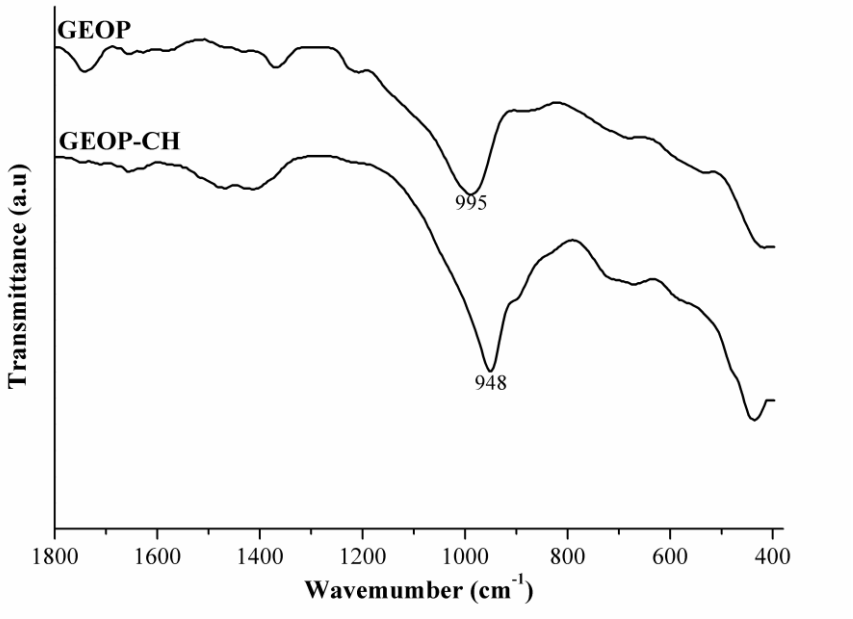


Figure 6. FTIR curves for GEOP and pastes GEOP-CH after 7 curing days.

3.4 XRD studies

The X-ray diffraction patterns are depicted in Figures 7-10. Pastes CON, CC10, CC40, CA10 and CA40 were studied by comparing 3, 28 and 90 curing days, and pastes GEOP and GEOP-CH were also compared. In general, a baseline deviation within the $2\Theta=20^{o} – 40^{o}$ range in all the studied pastes suggested the presence of an amorphous phase. With the progress made in curing time, the baseline deviation was more evident given the progress made in the geopolymerization reaction. Table 5 summarises the employed key, name of phases, chemical formula and PDF Card for the mineral phases found in the pastes.

Table 5. PDF Card of the phases and chemical formula of phases present in pastes.

Key	Phase	Chemical formula	PDF Card
P	Portlandite	$Ca(OH)_2$	#040733
S	Strätlingite	$Ca_2Al_2SiO_7.8H_2O$	#290285
Q	Quartz	SiO_2	#331161
A	Albite	$NaAlSi_3O_8$	#191184
M	Mullite	$Al_6Si_2O_{13}$	#150776
C	Calcite	$CaCO_3$	#050586
L	Carboaluminate	$Ca_4Al_2O_6CO_3.11H_2O$	#410210
B	Carboaluminate	$Ca_8Al_4O_{14}CO_2.24H_2O$	#360129
Z	Zeolite A	$Na_2Al_2Si_{3.3}O_{10.6}.7H_2O$	#120228
T	Trona	$Na_3H(CO_3)_2.2H_2O$	#291447
W	Wollastonite	$CaSiO_3$	#100489
V	Vaterite	$CaCO_3$	#240030
X	Zeolite X type	$Na_2Al_2Si_{2.4}O_{8.8}.6.7H_2O$	#120246
Za	Zeolite ZK5	$2.85Na_2O.1.89Al_2O_3.7.92SiO_2.12.2H_2O$	#370360
Cr	Cristobalite	SiO_2	#391425
F	Faujasite	$Na_2Al_2Si_4O_{12}.8H_2O$	#391380

Figure 7 shows the XRD patterns of paste CON (lime-pozzolan) after 3, 28 and 90 curing days. The peaks of the non-reacted portlandite (P) were observed after 3 curing days. Characteristic peaks of albite (A) and traces of faujasite were also found. It was noteworthy that calcite was not present in the CON paste at an early age and carbonate was combined with aluminium as carboaluminates (characteristic L and B peaks). Other authors have made these observations in lime-pozzolan samples [51,52]. After 28 curing days, less intense portlandite peaks were detected as the FCC reaction progressed, and no faujasite peaks appeared in the XRD pattern. Traces of quartz (Q), A and mullite (M) were also observed. Characteristic strätlingite (S) peaks were noted in the CON paste at this age, which confirmed the peak observed on the DTG curves within the 210-280ºC temperature range. This compound is typical in lime-pozzolan materials with a high aluminium content [52,53], as for FCC (Al_2O_3 = 49.26 %; see Table 1). After 90 curing days, the diffractogram of paste CON was similar to that for 28 curing days. To a large extent, the P peaks had mitigated and the main S peak appeared more intensely, which

suggests high pozzolanic reactivity with curing time. A broad peak was seen within the 28.5º-29.5º 2Θ range, which suggests the presence of the CSH/CASH gel, especially after 90 curing days.

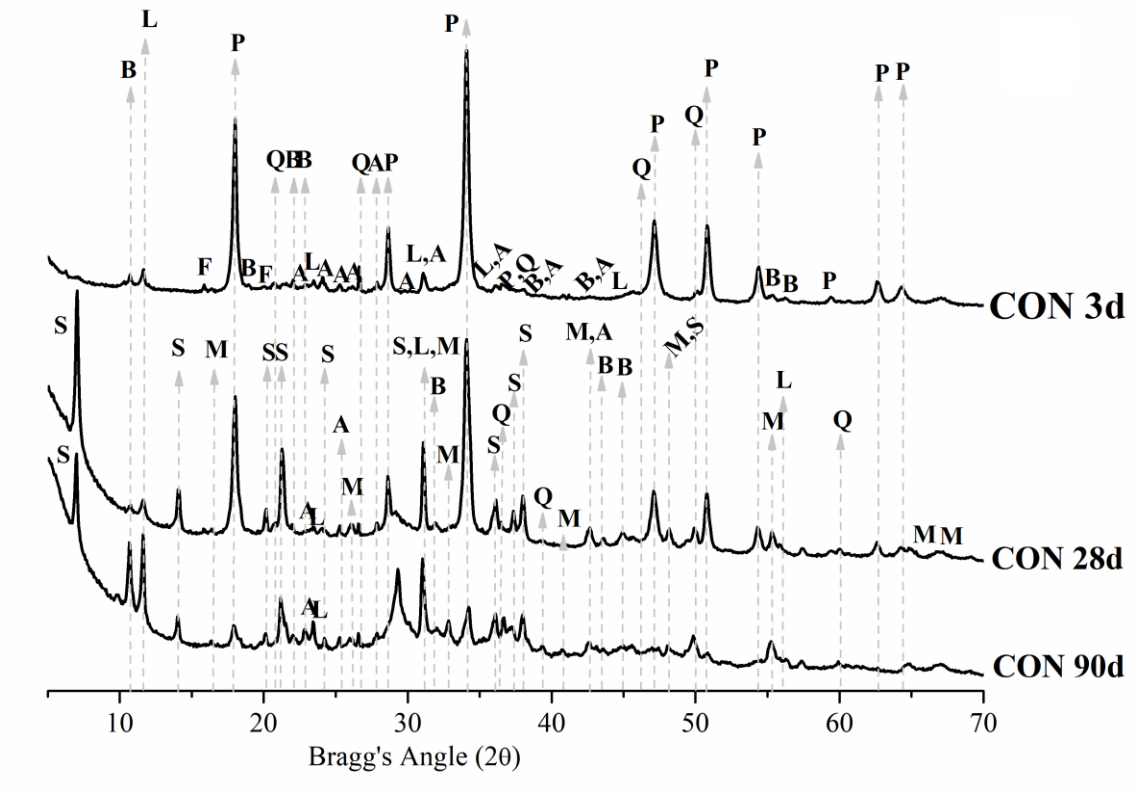


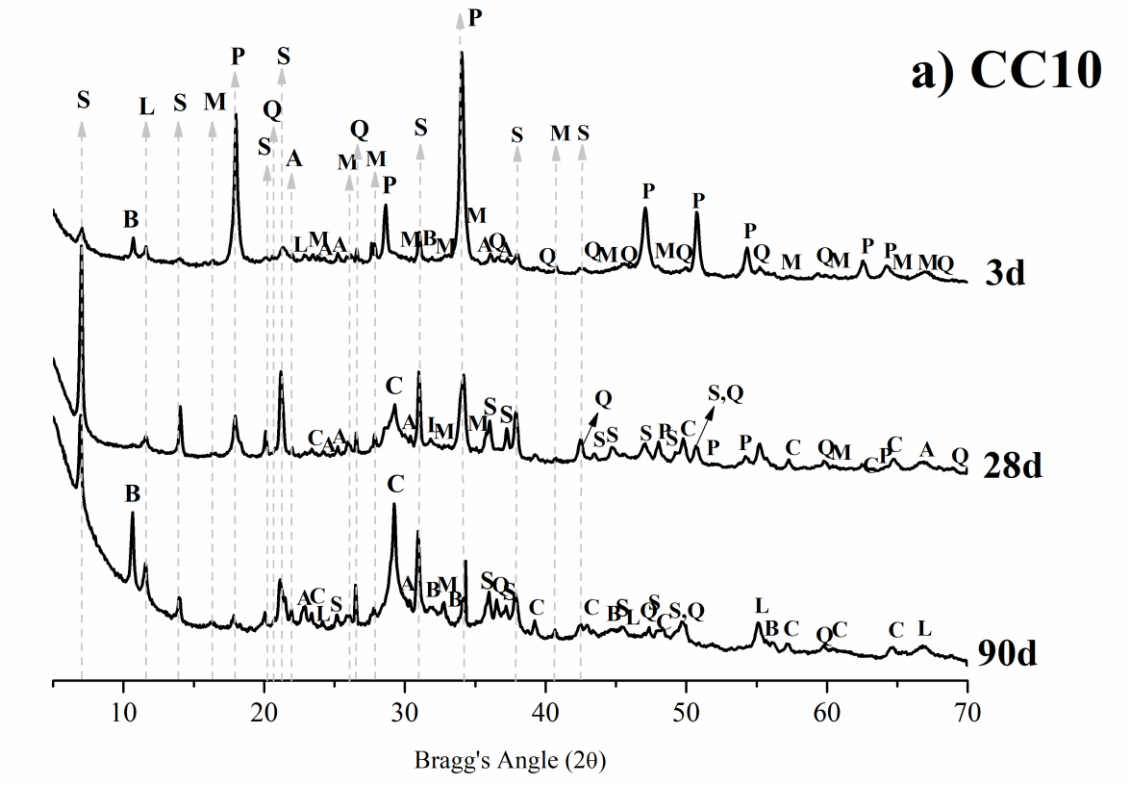
Figure 7. XRD patterns of the CON paste after 3, 28 and 90 days

Figures 8-9 show the XRD patterns of the lime-pozzolan/geopolymer activated with the alkali solution prepared by using commercial sodium silicate and RHA, respectively. The pastes with 10% geopolymer (CC10 or CA10) and with 40% geopolymer (CC40 or CA40) were tested and analysed after 3, 28 and 90 curing days.

In paste CC10 (Figure 8a), the main characteristics peaks were P and S at 28 at 90 curing day. Strätlingite (S) was attributed to the pozzolanic reaction. As with the CON paste, the intensity of the peaks corresponding to P and S diminished and increased, respectively, with curing time. Minority peaks (Q and A) were present at the three analysed curing times. Carboaluminate peaks (L and B) were found, whose intensity increased with time. Calcite (C) peaks were also found after 28 and 90 curing days. In this case, the broad peak related to CSH/CASH, together with the main C peak whose

intensity was significant after 28 days, which was earlier than for CON and suggests a faster reaction rate for this gel type to form.

When the 40% geopolymer was employed (CC40), the portlandite peaks were low in intensity (especially for 90 curing days) and the peak of the CSH/CASH gel was strong in this XRD pattern. A new crystalline phase Z (Zeolite A) was also detected, mainly at 90 curing days. The formation of Zeolite A and Zeolite X has been reported in other papers in which geopolymers were prepared with the activation of MK/RHA [54]. As the CC10 paste pattern shows, traces of Q and A and B/L carboaluminate peaks were present throughout the three analysed ages for paste CC40. No S was detected in this paste, which suggests that its formation by the pozzolanic reaction was not favourable, and gels NASH or C(N)ASH should be preferably produced, as corroborated by the large broad peak shown (28.5º-29.5º 2Θ,) after 3 curing days.



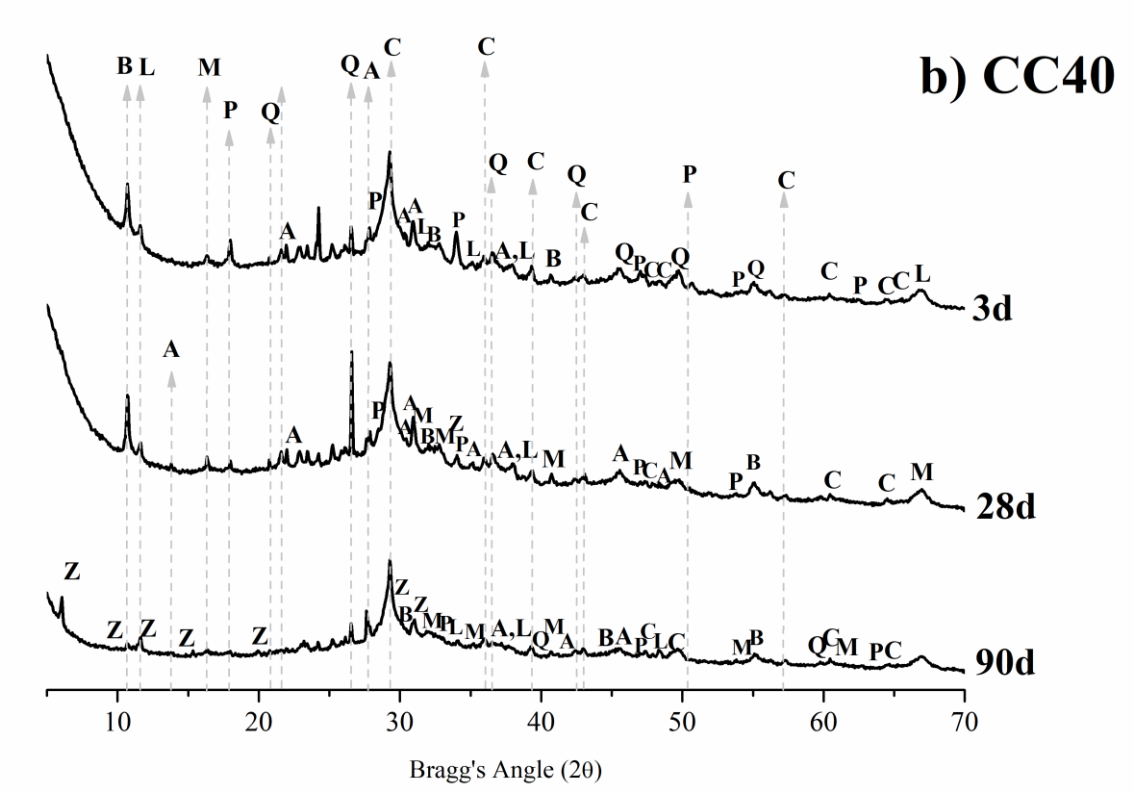
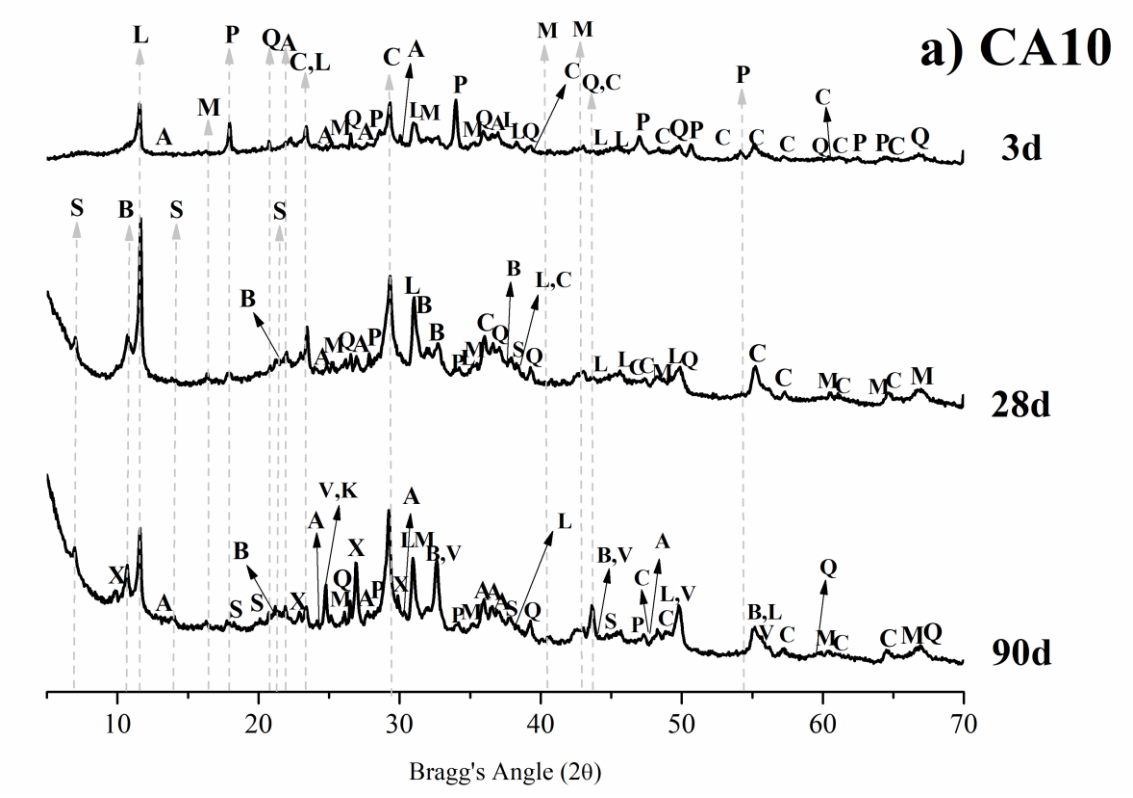


Figure 8. XRD patterns of the lime-pozzolan/geopolymer pastes activated with the alkali solution prepared using commercial sodium silicate (CC) after 3, 28 and 90 days: a) paste CC10; b) paste CC40.

When RHA was employed as the silica source in the alkali activator for the lime-pozzolan/geopolymer systems, changes were evidenced in the XRD patterns. Figures 9a and 9b show the patterns for paste CA10 and paste CA40, respectively. We can see that the signals corresponding to P for the 10% geopolymer paste were not intense after 28 curing days, unlike CC10, which suggests that the presence of RHA favoured the pozzolanic reaction rate. The signals for S were also slightly intense after 28 and 90 days, which indicates that S formation was not favoured. Probably due to the presence of amorphous SiO_2 in RHA, the pozzolanic reaction was activated and more CSH was formed. The main signal for this gel was considerably intense in the XRD pattern in CA10. The broad peak related to the presence of gel was intense after 3 curing days. Some traces of zeolite X (X) were identified after 90 curing days. For paste CA40, the intensity of the P signals in the XRD pattern were very low at the early curing age and a baseline deviation appeared within the 28-32º 2Θ range in relation to the formed gels (NASH, C(N)ASH, CSH). Some zeolitic structures (Z) appeared after 90 curing days.



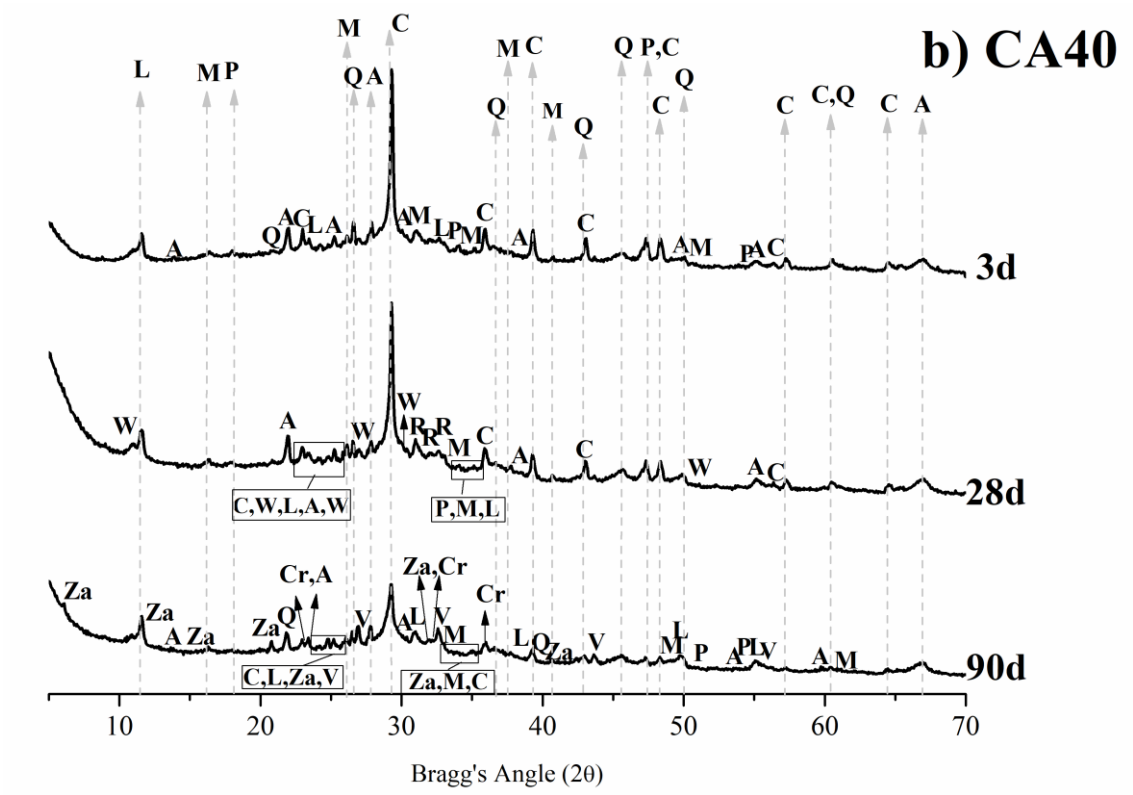


Figure 9. XRD patterns of the lime-pozzolan/geopolymer pastes activated with the alkali solution prepared by using RHA (CA pastes) after 3, 28 and 90 days: a) paste CA10; b) paste CA40.

The XRD patterns (Figure 10) of GEOP and GEOP-CH at 28 days displayed major changes. A baseline deviation was observed in GEOP and GEOP-CH, with a relative high intensity of peaks Q, M and A due to the crystalline phases from FCC. The F peaks disappeared in these two pastes, which indicated that the zeolitic fraction of FCC was highly reactive. Excess sodium ions favoured the formation of trona (T) in paste GEOP. In this case, the nature of the gel, mainly NASH, was shown as a baseline deviation within the 20-32º range. Due to calcium addition, carboaluminate peaks (L and B) were identified in the GEOP-CH pattern. In this case, the baseline deviation was strong and the broadness within the 25-32º range indicates CASH/C(N)ASH formation. This means that if a large amount of calcium is present, CASH/C(N)ASH gels form. They are easily observed in the XRD patterns for CC10, CC40, CA10 and CA40. It was more difficult to identify the presence of NASH because this gel showed less intensity and a more broadly shaped diffraction signal.

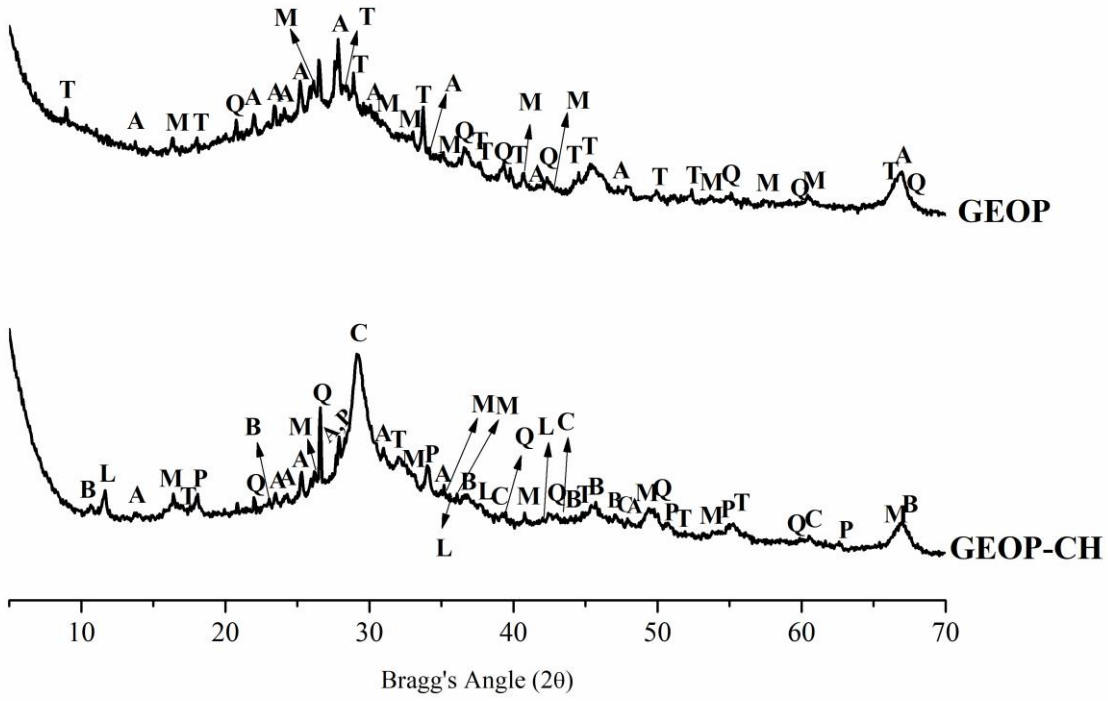
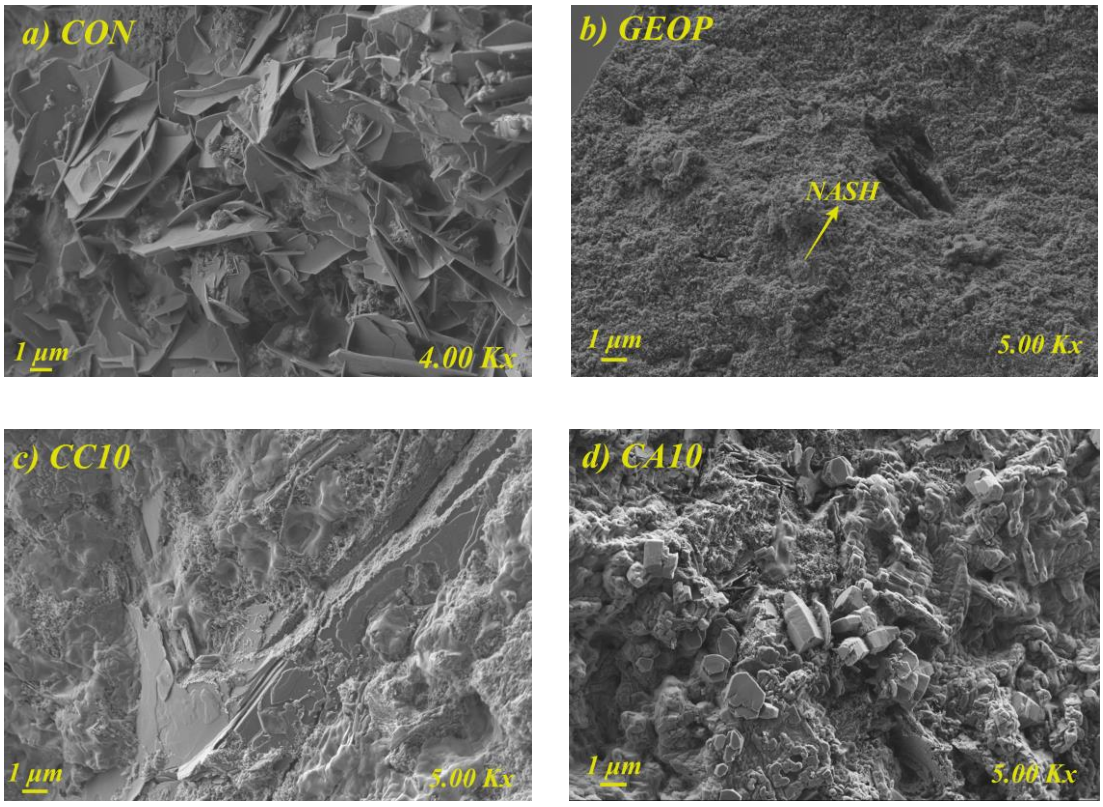


Figure 10. XRD patterns for pastes GEOP and GEOP-CH after 28 curing days.

3.5 FESEM studies

The FESEM images for all the pastes cured for 28 days are depicted in Figure 11. In the lime-pozzolan paste (CON), the typical reaction product from the pozzolanic process was observed (Figure 11.a) (strätlingite) [53] Figure 11.b represents the GEOP paste, where the paste's microstructure was denser and the principal formed product was the NASH gel [55, 56].

In pastes CC10 and CA10 (Figures 11.c and 11.d), products were observed with a different appearance to those for pastes CON and GEOP. In these pastes, pozzolanic and geopolymeric products probably coexisted. Finally, in pastes CC40 and CA40 (Figures 11.e and 11.f), the principal reaction product was C(N)ASH gel, although some NASH gel was probably present. Duramae et al reported C(N)ASH formation as a result of partial NASH substitution in the system [57]. In the CA40 paste, the formation of little cubic-shape particles took place, which may be attributed to the presence of zeolite A [58].



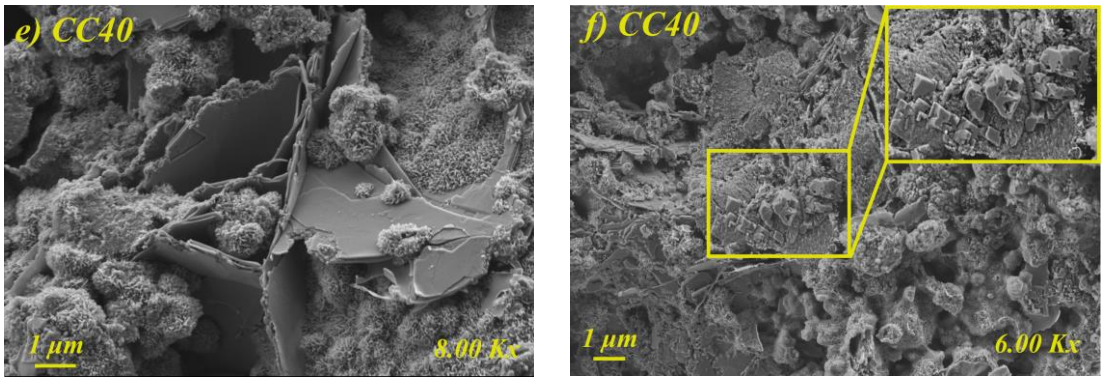


Figure 11. FESEM micrographs for pastes after 28 curing days: a) CON; b) GEOP; c) CC10; d) CA10; e) CC40; f) CA40.

4 CONCLUSIONS

The mechanical behaviour and microstructure of lime-pozzolan/geopolymer mixtures were analysed, in which pozzolan and the precursor were the same aluminosilicate waste (spent FCC catalyst).

The changes in the lime-pozzolan system made by adding the geopolymeric binder were highly positive in compressive strength development terms for mortars:

- It is highlighted the strength improvement at short times thus, the mortars with a 10-40% replacement of lime-pozzolan binder with geopolymer, prepared with the NaOH/waterglass solution, yielded strength values within the 9-25 MPa range at 7 curing days *versus* 3.59 MPa for the lime-pozzolan mortar.
- For the long curing time (90 days), the 10% geopolymer mortar was 50% higher than the lime-pozzolan one, and the 40% geopolymer mortar was almost double.

The contribution of RHA as a silica source in the alternative alkali activator was remarkably positive compared to the commercial chemical reagent (waterglass), especially at early curing ages (1-3 days) for the smallest geopolymer addition (10%). Apparently, the reason for the different nature of the binding gel formed when RHA was present was responsible for the achieved higher strength.

The addition of a geopolymer to a lime-pozzolan system brings about significant changes in the nature of hydration products:

- The hydration of lime-pozzolan systems produces typical products: CSH/CASH gel, calcium carboaluminate hydrates and S, as well as unreacted portlandite at early (3 days) and mid-term (28 days) curing ages.
- The addition of 10% geopolymer slightly modified the nature of hydration products. However, the reaction rate rose and portlandite consumption was significantly higher.
- The addition of 40% geopolymer led to a more marked modification in the nature of hydration products: a NASH/C(N)ASH gel was formed, and no presence of S and portlandite was detected.

In summary, adding geopolymer to a lime-pozzolan system is a good proposal for improving the early- and long-term strength performance of mortars. Using RHA as an alternative silica source for replacing waterglass has a very high potential to avoid or to reduce employing synthetic chemical reagents that have a significant carbon footprint.

Acknowledgements

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