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Use of industrial waste-based zeolites in the fabrication of cementitious materials

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ABSTRACT: Two types of zeolites, coming from the total conversion of hazardous aluminum waste, have been considered in this study: NaP-type zeolite and LTA-type zeolite. Both zeolites are proposed to be used in cementitious mortars by substituting cement content in 5, 10 and 15%. The microstructure of both zeolites was characterized and they have certain interesting characteristics to be used as supplementary cementitious materials. The main fresh state characteristics and the mechanical performance of the fabricated mortars were also evaluated. The lower particle size of LTA-type zeolite promotes a filler effect that increases the fluidity of the mortar mixes and they also acts as nucleation sites for the cement hydrates, thus accelerating the cement hydration reactions. This acceleration of the cement hydration promotes the increase of the initial compressive strength of the mortars fabricated with this zeolite type. The higher silica content of NaP-type zeolite promotes pozzolanic reactions that significantly increase the long-term compressive strength of the fabricated mortars.

KEY WORDS: Waste-based zeolite; Cementitious material; Characterization; Mechanical performance; Sustainability.

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RESUMEN: *Empleo de zeolitas fabricadas a partir de residuos industriales en la preparación de materiales de base cemento.* En este estudio se han considerado dos tipos de zeolitas, procedentes de la conversión total de residuos peligrosos de aluminio: la zeolita tipo NaP y la zeolita tipo LTA. Ambas zeolitas se proponen para ser utilizadas en morteros de cemento sustituyendo el contenido de cemento en un 5, 10 y 15%. Al caracterizar la microestructura de ambas zeolitas se detectaron ciertas características interesantes para ser utilizadas como adiciones en materiales de base cemento. También se evaluaron las principales características en estado fresco y el comportamiento mecánico de los morteros fabricados. El menor tamaño de partícula de las zeolitas tipo LTA promueve un efecto filler que aumenta la fluidez de las mezclas de mortero y también actúan como sitios de nucleación de los hidratos del cemento, acelerando así las reacciones de hidratación del cemento. Esta aceleración de la hidratación del cemento genera un aumento de la resistencia a la compresión inicial de los morteros fabricados con este tipo de zeolita. Por otro lado, el mayor contenido de sílice de la zeolita tipo NaP genera reacciones puzolánicas que aumentan significativamente la resistencia a la compresión a largo plazo de los morteros fabricados con este segundo tipo de zeolita.

PALABRAS CLAVE: Zeolitas procedentes de residuos; Material de base cemento; Caracterización; Propiedades mecánicas; Sostenibilidad.

1. INTRODUCTION

The International Zeolite Association (1) defines zeolite as a structure linked with tetrahedrons that contain cavities occupied by water molecules and cations. Zeolites are natural or synthetic crystalline aluminosilicates characterized by a three-dimensional network of AlO_4 and SiO_4 tetrahedra interconnected through shared oxygen atoms. Usually, zeolites synthetized from pure chemical reagent are highly pure with uniform crystal size and useful for particular industrial applications, whereas natural zeolites contain other phases such as quartz, silicates, etc., resulting in non-uniform crystal size. These materials exhibit regular and uniform porous structures, forming voids such as channels, cages or cavities (2-5). The presence of these voids enables zeolites to demonstrate unique properties, facilitating the sorption and diffusion of ions and molecules. For this reason, in various industrial sectors including catalysis, agriculture, environmental protection, and water/gas purification, zeolites find extensive applications (6-11).

Natural zeolites are also being used in construction with different objectives, but mainly for the fabrication of concretes. For example, due to their lower density compared to natural aggregates, they are used as lightweight aggregates in the development of lightweight concretes (12). Anyway, their main application in construction is as supplementary cementitious materials because, even they are crystalline, they exhibit certain pozzolanic reactivity (13). In fact, in some cases, this reaction was detected to be higher than in fly ash (14). In this respect, the substitution of cement by natural zeolites has yielded increases in compression strength with negligible effect on the concrete workability provided that the replacement of zeolite does not exceed 10% (15-19). Moreover, not only the mechanical properties have been reported to be enhanced due to the presence of natural zeolites, but also some durability properties for concrete such as the resistance against alkali-silica reaction, sulfate attack or freeze-thaw cycles (20-22), and even the reduction of the drying shrinkage (23). However, considering the increase in the sustainability expected in the construction market, the production of synthetic zeolites from waste is emerging as a very interesting approach.

Within the framework of the circular economy, the European Commission recently launched two policy initiatives: the European Green Deal (24), which is a roadmap for a sustainable EU economy, and the Circular Economy Action Plan (25), which aims to transform the economy into a green, low-carbon economy in the future. In this context, the construction and renovation of buildings requires considerable amounts of energy and mineral resources (sand, gravel, clay, water, etc.). At the same time, the increase in hazardous waste generation, associated with rapid global industrialization, has become a relevant environmental problem (26). For this reason, the development of more sustainable construction materials processes is necessary and the construction materials are one of the most suitable options for the reuse of waste.

There are many recent studies where the reutilization of wastes in construction materials has been reported, mainly as raw materials for the fabrication of concretes, for example as aggregates, fibers and as cement substitution (27-30). This use of waste is generating cementitious materials with special or different properties with respect to the conventional ones. In fact, the reuse of waste in construction materials will be facilitated as long as they improve their properties or give them new ones. Considering the specific case of the present manuscript, hazardous wastes are less-common raw materials for the preparation of valuable materials due to they usually require expensive or complicated pretreatments before they can be used (31).

One of the most hazardous wastes is generated in the aluminum industry. According to the US Geological Survey, the world aluminum output increased slightly in 2022, coming in at 69 million metric tons (MT) compared to 67.5 million MT the previous year (32). This metal is obtained from bauxite in the primary industry and from materials that have reached the end of their life (scraps) in the secondary industry (33). Both industries generate slags which are recycled by the tertiary industry by means of shredding, milling, and sieving processes, followed by granulometric classification (34-37). Thus, the present study promotes the use of waste from the aluminum industry for the manufacture of zeolites that will be used in the preparation of cement-based materials.

In previous studies, different wastes or byproducts have been studied as raw materials for the production of zeolites (38, 39). In most of these studies, the synthesis of zeolite-like materials has been accomplished by using fly ash due to its similar chemical structure (40-43). However, this can lead to some disadvantages increasing the cost of the synthesis processes. Regarding this issue, some of the current authors of the present article have already demonstrated the total conversion of hazardous aluminum waste into two types of zeolites, NaP (44) and LTA (45). These zeolites were synthetized by a conventional hydrothermal method, in a one step, under mild operating conditions. The process was carried out in an autoclave reactor, where the reagents, namely aluminium waste, NaOH, and Na_2SiO_3, were added in the necessary amounts to maintain the stoichiometric ratio for zeolite formation. The mixture was kept under constant stirring, at autogenous pressure, and under the specific temperature and time conditions required for the synthesis of each zeolite: 80°C for 12 hours for LTA zeolite, and 120°C for 6 hours for NaP zeolite. After the reaction time was completed, the solution was filtered and the zeolitic material was dried for subsequent use.

In the present paper, a characterization of both types of zeolite focused on their use in cementitious materials is carried out as well as the evaluation of their influence when they are used in the fabrication of cementitious mortars. Different percentages of cement substitution have been considered, up to 15%, and the modifications promoted both in the fresh state and in the mechanical properties of the mortars have been analyzed.

2. MATERIALS AND METHODS

2.1. Zeolites used in the study

Two different zeolites synthetized from a hazardous aluminum waste were used as admixtures in the manufacture of cementitious materials: a NaP-type zeolite synthesized at bench scale by Sánchez-Hernández et al. (44), and a Linde Type-A (LTA) zeolite synthesized at pilot scale by López-Delgado et al. (45). Although most of the characteristics of both zeolites, such as morphology, structure and thermal stability were reported in the referred papers, some other ones of special relevance to understand the final characteristics of the obtained cementitious materials have been determined in this work.

The mineralogical composition of the zeolites was determined by XRD. A Bruker D8 Advance Diffractometer with CuKα radiation was used for X-ray diffraction analysis (XRD). The semi-quantification of the amorphous phase of the zeolites was performed using Diffrac.Suite EVA software. The chemical composition of the zeolites used in this study was determined by X-ray fluorescence (XRF) using a pressed pellet of 10 g of the zeolite without additives in a wavelength dispersive X-ray fluorescence spectrometer (Bruker, S8 Tiger). The loss of ignition (LOI) was calculated by subjecting the samples to heating at 1000 ºC for 1 h. Samples density was determined in triplicate by using the Archimedean method. Textural characterization of the zeolites was conducted by determination of nitrogen adsorption/desorption isotherms at 77 K in an ASAP 2010 Micromeritics equipment. Before the measurements, the samples underwent outgassing at 50 ºC under vacuum for 24 h. The particle size distribution (parameters d_{10}, d_{16}, d_{50}, d_{84} and d_{90}) of the zeolites was determined by laser diffraction (Dispersion Analyser LUMISizer 610 Berlin, Germany).

2.2. Mortars fabricated in the study

Seven different mortar mixes were designed and characterized. CEM I 42.5R according to EN 197-1 and siliceous sand (0/2 mm) were used in all of them. The density of the cement used was 3.1 g/cm^3 with a mean particle size of 19.2 µm (particle size distribution: 10% < 1.9 µm, 50% < 14.4 µm and 90% < 44.5 µm). The two zeolites characterized in this study were considered: a NaP-type for the NaP mortars (M_{NaP}) and a LTA-type for the LTA mortars (M_{LTA}). Each zeolite was considered in mass percentages of 5%, 10% and 15% of cement content. Previous studies mentioned that above 10% the natural zeolites limited the performance of cementitious materials (15-19). Therefore, the authors aimed to evaluate if this percentage is similar when using synthetic zeolites from aluminum waste. An additional mortar without zeolite was produced as reference mix. Table 1 shows the composition of the mortars fabricated. Both the binder content and the water to binder ratio were maintained constant in all cases.

Table 1. Composition of the mortar mixes (g).

Zeolite substitution (%)	Mix name	Cement (g)	Water (g)	Sand (g)	NaP-type zeolite (g)	LTA-type zeolite (g)
0%	REF	450	225	1350	0	0
5%	M_{NaP}-5	427.5	225	1350	22.5	0
10%	M_{NaP}-10	405	225	1350	45	0
15%	M_{NaP}-15	382.5	225	1350	67.5	0
5%	M_{LTA}-5	427.5	225	1350	0	22.5
10%	M_{LTA}-10	405	225	1350	0	45
15%	M_{LTA}-15	382.5	225	1350	0	67.5

The consistency of the fresh mortar mixes was determined by the flow table test according to EN 1015-3 and the density content was determined according to EN 1015-6. The consistency was also measured after different times from the start of the mixing process in order to evaluate the maintenance of the consistency over the first 90 minutes. Regarding the mechanical properties. Two determinations of the density, the consistency and the maintenance of the consistency were made for each mortar mix. 12 square section prisms of 40 mm × 40 mm × 160 mm were cast for each mortar mix in order to evaluate the flexural and compressive strength after 2, 7, 28 and 90 days of moist curing (98% RH, 20±2ºC). The flexural and compressive strength of the hardened mortars were determined according to EN 196-1 standard. Every prism was firstly submitted to a three-point bending flexural strength test. The resultant halves of each prism were then subjected to a compressive strength test. The outcome is three flexural and six compressive strength measurements per mix and curing age. The measurement of these mechanical properties has allowed to evaluate the influence of the zeolite type and content on both parameters.

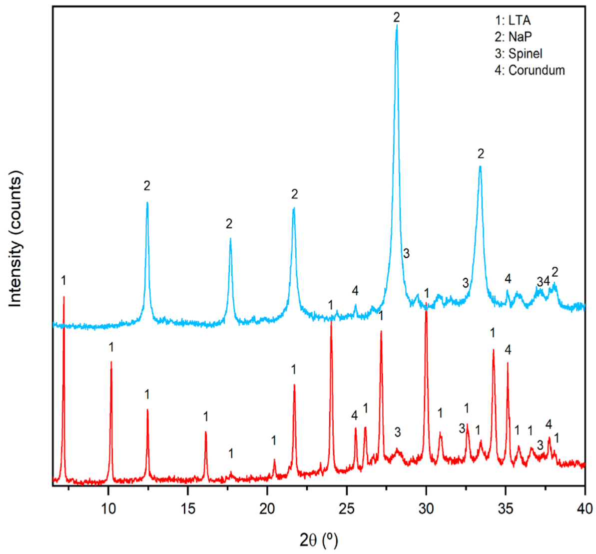

FIGURE 1. XRD of the zeolites used in the fabrication of the mortars.

3. RESULTS AND DISCUSSION

3.1. Microstructural characterization of the zeolites used in the study

Figure 1 shows the XRD patterns of the two zeolites used in this study and high crystallinity in both samples (NaP = blue, LTA = red) is detected. Apart from the diffraction peaks corresponding to both zeolites, peaks attributable to corundum and spinel phases are detected in both cases. Nevertheless, the background analysis of the corresponding profile by EVA software revealed an amorphous phase content of 26.5 % for zeolite NaP and of 30.6 % for zeolite LTA.

The chemical composition of both zeolites is collected in Table 2. They consist principally of SiO_2, Al_2O_3 and Na_2O, even though several compositional differences are observed. Thus, although both zeolites correspond to low Si/Al ratio zeolite type, the Si/Al ratio in zeolite LTA is 0.71, that is lower than the value 1.15 for zeolite NaP. It is worth noting the TiO_2 content in zeolite LTA (2.44 wt.%), could partially replace the SiO_4 tetrahedra in the crystal lattice. In this way, the (Si+Ti)/Al increases up to 0.79. Similarly, the K content is higher in zeolite LTA, this indicating a partial substitution of the Na^+ exchange cations. These two low Si/Al molar ratio zeolites have a high cation exchange capacity due to the saturation of the negative charge compensation cations introduced by Al (Na^+, K^+...), which are very easy to exchange, especially in aqueous media. Moreover, they are very hydrophilic due to dipolar interactions with the electrostatic fields located between the charge compensating cations and the negative charges in the lattice.

The physical and textural characteristics of both zeolites, such as density, particle size distribution, specific surface area (S_{BET}), external surface area (S_{ext}),

TABLE 2. Chemical composition of zeolites LTA and NaP (expressed as wt.%) determined by X-ray fluorescence (XRF).

Sample	SiO_2	Al_2O_3	Na_2O	Cl	MgO	CaO	SO_3	Fe_2O_3	TiO_2	ZnO	CuO
NaP	39.76	26.87	14.82	0.03	0.88	0.80	0.04	0.19	0.69	0.08	0.04
LTA	30.30	33.01	14.29	0.02	0.60	0.71	0.05	0.22	2.44	0.05	0.04
Sample	**K_2O**	**MnO**	**P_2O_5**	**BaO**	**ZrO_2**	**Cr_2O_3**	**SrO**	**NiO**	**Hg**	**LOI**	**Total**
NaP	0.48	0.02	0.03	0.33	0.05	0.01	0.01	0.01		14.84	100.00
LTA	1.44	0.01		0.11	0.41	0.01	0.01		0.06	16.21	100.00

and pore volume, are listed in the Table 3. The initial pH values are also included. The density and pH value of NaP are higher than those of LTA. Both zeolites exhibit a particle size distribution ranging from 0.1 to 60 µm, with slightly smaller particles observed for the LTA zeolite (see Figure 2). Analysis reveals that 50% of the particles are smaller than 18 µm for the NaP zeolite and 5 µm for the LTA zeolite, indicating a larger particle size for NaP compared to LTA. Considering the 16th to 84th percentiles, the particle size range for NaP zeolite is between 11.0 ± 0.8 µm and 30 ± 2 µm, while for LTA, it ranges from 1.92 ± 0.03 µm to 11 ± 3 µm. Accordingly, LTA zeolite exhibits a greater particle size dispersion than NaP zeolite. Furthermore, for NaP, 90% of the particles measure under 35 µm, twice the size observed for LTA at 12 µm. As for the specific surface area, even though the value is quite similar for both zeolites, the value of micropore volume is much higher for the LTA zeolite, i.e. this zeolite exhibits a higher microporosity.

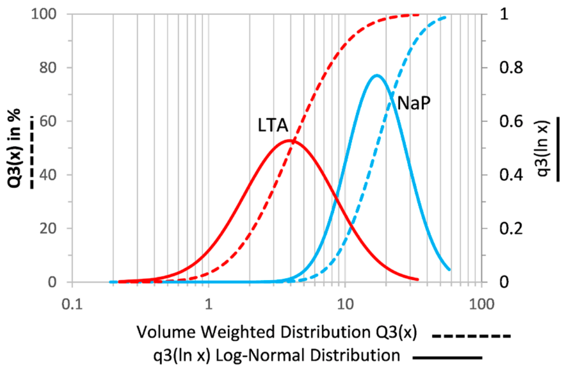

Figure 2. Particle size distribution and cumulative curves for LTA (red) and NaP (blue) zeolites.

3.2. Evaluation of the performance of the mortars with zeolites

The potential use of the fabricated zeolites in cementitious materials has been evaluated by characterizing the influence of their incorporation on the fresh and the hardened state of mortars. Regarding the fresh state, density, consistency and “open time” at 0, 15, 30, 60, 75 and 90 minutes have been measured. Open time refers to the time that the mortar mix maintains an acceptable consistency; this parameter is important in order to evaluate the incorporation of zeolites in concrete technology since a very low maintenance of the consistency over time could make difficult their scalability to the real market.

Figure 3 shows the density values measured in the fresh state of the fabricated mortars. The density values obtained are very similar in all cases but slightly higher in mortars with zeolites. Furthermore, as the zeolite content increases, the fresh density of the mortar slightly increases too. The observed performance differs from that observed in mortars with natural zeolites in previous studies (46). Nevertheless, Nagrockiene et al. (22) also observed increases in the fresh density of concretes with natural zeolites and the density of the concrete increased as the content of natural zeolite used increased. The reported increases were similar to those obtained in the LTA mortars but lower than the ones obtained in NaP mortars, even though the density of the natural zeolites used was little higher than the density of the zeolites used in the present paper. For example, in the mix with 10% of natural zeolite, the concrete density increased 1% with respect to the reference concrete while this increase is around 3% for the mortars with 10% of NaP-type zeolite and 1% for the LTA mortars with 10% of LTA-type zeolite with respect to the reference mortar. It is also remarkable that in the same works it was shown that at early ages porosity decreased, so it is possible that the synthetic zeolites used in

Table 3. Physical characteristics and initial pH value of zeolites LTA and NaP.

Property	LTA	NaP
Density (g ml^{-1})	1.83 ± 0.03	2.05 ± 0.01
Particle size distribution (µm):		
d_{10}	1.5 ± 0.1	9.5 ± 0.7
d_{16}	1.92 ± 0.03	11.0 ± 0.8
d_{50}	5 ± 1	18 ± 1
d_{84}	11 ± 3	30 ± 2
d_{90}	12 ± 4	35 ± 2
S_{BET} (m^2 g^{-1})	11.12 ± 0.09	9.28 ± 0.05
Micropore Volume (cm^3 g^{-1})	0.001478	0.000283
S_{ext} (m^2 g^{-1})	8.1127	8.7416
Initial pH	10.9	11.1

this study promotes a more compacted mixture. Actually, the present results agree with those observed by Girskas et al. (47) in the hardened density values of concretes with zeolites derived from the waste of aluminum fluoride production by low-temperature synthesis; they detected that 10% of zeolite increased 1.5% the density of the concrete at 28 days. However, these authors detected decreases in the fresh density of the same concretes when the same synthetic zeolite content was used in combination with air-entraining admixture while slowly increases were detected without this chemical additive. Thus, possibly the combination of zeolites, both natural and synthetic, with different chemical additives can explain the previously published contradictory results. In this regard, any chemical additive was used in the present study so only the effect of the synthetic zeolite used is taken into account. Furthermore, although the density of the zeolites used is lower than the density of the cement, higher compaction of the mixtures could occur due to the lower particle size of the zeolites with respect to the cement one, thus slightly increasing the density of the resulting fresh mortar mixes.

Figure 4 (A) shows the initial consistency measured in the mortars and its evolution over time while Figure 4 (B) shows the percentage of loss of consistency with respect to the initial value over time. Except for M_{LTA-5} mortar, the consistency of the mortars with zeolites is lower than the one of the reference mortar during all the test period. Moreover, the higher the zeolite content, the lower the initial consistency measured. This observation agrees with the higher absorption/adsorption of water by zeolites with respect to cement, due to their porosity. In fact, it is clearly detected that the addition of NaP-type zeolite decreases the consistency values in a greater extension than the addition of LTA zeolites. These results do not agree with the S_{BET} and micropore volume values given in Table 3, since NaP zeolites showed lower values. However, LTA zeolites have lower particle size (see Figure 2) and possibly they can have a filler effect that improve the fluidity of the fresh mortar mix, which agrees with the higher initial consistency measured in M_{LTA-5} mortar with respect to REF. This filler effect when using percentages substitution below 10% has been already reported for limestone filler and other raw materials with low particle size (48-51). This performance of LTA mortars is very interesting for construction applications since a more fluid cementitious material makes its placing easier.

Regarding the mechanical properties of the fabricated mortars, Figure 5 shows the evolution of the flexural strength and Figure 6 depicts the evolution of the compressive strength over time. Any significant conclusion is obtained from the flexural strength values but interesting conclusions can be obtained from the compressive strength results. Regarding LTA mortars, they show higher initial compressive strength but a very slow increase is detected from 7 to 90 days of curing, except for M_{LTA-5} sample. The higher initial strength showed in LTA mortar agrees with the filler effect previously mentioned. The very low particle size of LTA-type zeolite allows that they acts as nucleation sites from the hydration of the cement hydrates. This effect has been reported in mortars and concretes

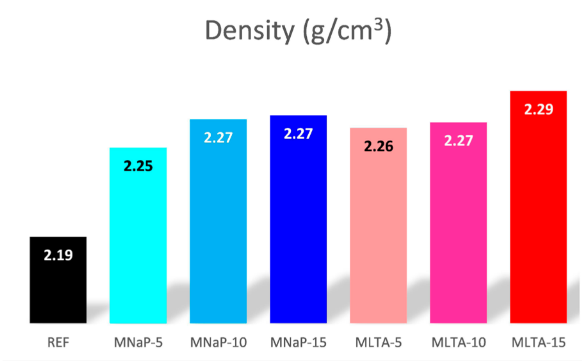

FIGURE 3. Fresh density of the mortars with LTA (red) and NaP (blue) zeolites.

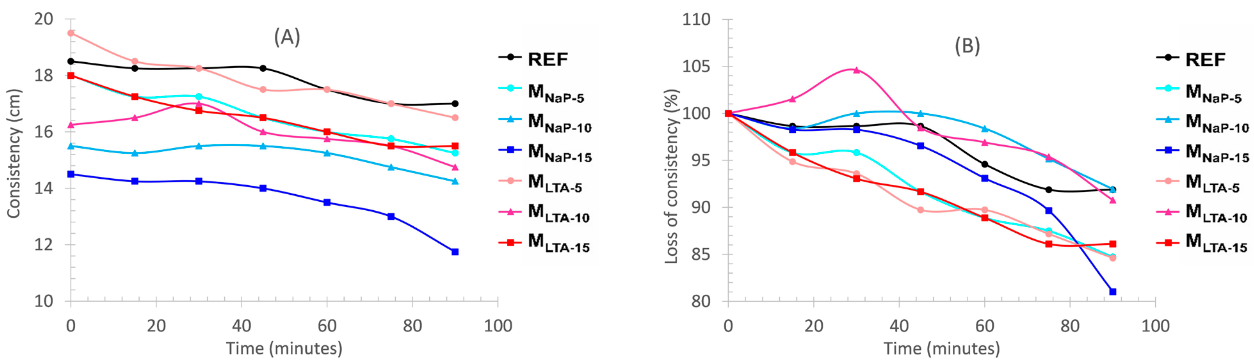

FIGURE 4. (A) Evolution of the consistency measured in the fresh state of the fabricated mortars; (B) % of loss of consistency over time.

with limestone filler with similar particle size than LTA-type zeolites (48-51). Moreover, the slightly higher specific surface are of LTA-type zeolite with respect to NaP-type one, can also explain a higher initial reactivity of the formers. Additionally, LTA-type zeolite has particles of TiO_2 (see Table 2) and previous studies have demonstrated the nucleation effect of TiO_2 particles with low particle size (52).

The filler effect is not clearly detected in NaP mortars, possibly due to the higher particle size of NaP-type zeolite. However, NaP-type zeolite clearly increases the long-term compressive strength. Furthermore, this increase is greater when the zeolite content increases, since the mortar with 15% NaP (M_{NaP-15}) shows the greatest value at 90 days. This, most likely, will be due to pozzolanic reactions of the silica in the zeolites with the portlandite in the cement, which agrees with published results with natural zeolites (13-19). In this sense, in the LTA mortars, the long-term pozzolanic reaction is only clearly detected in the one with the lowest zeolite content (M_{LTA-5}). Pozzolanic reactions also occur in M_{LTA-10} and M_{LTA-15} mortars because, if not, their respective compressive strength at 90 days will be lower than the ones measured (considering their lower cement content). In any case, the importance of the pozzolanic reactions in M_{LTA-10} and M_{LTA-15} mortars is lower than in M_{LTA-5} mortar and very much lower than in M_{NaP} mortars. This agrees with the higher silica content measured in NaP-type zeolite with respect to LTA-type zeolite (see Table 2).

It is noteworthy than, according to these results, while the maximum zeolite content allowed when using LTA zeolite agrees with the percentages already published in order to avoid the decrease of the long-term mechanical performance of cementitious materials (15-19), the maximum content when using NaP zeolite is higher. In this study, the substitution of 15% of cement by NaP-type zeolite has not limit but increase the long-term compressive strength of the fabricated mortars, so possibly higher contents could be used thus increasing the sustainability of the construction materials.

4. CONCLUSIONS

Two types of zeolites, coming from the total conversion of hazardous aluminum waste, have been considered in this study: NaP-type zeolite and LTA-type zeolite. Both zeolites are proposed to be used in cementitious materials and the main conclusions obtained in this study are the following:

- Both zeolites have interesting characteristics to be used as supplementary cementitious materials.
- The lower particle size of LTA-type zeolite promotes a filler effect when they are used in mortars. In this sense, they increase the fluidity of the mortar mixes in the fresh state and they also acts as nucleation sites for the cement hydrates, thus accelerating the cement hydration reactions. This acceleration of the cement hydration promotes the increase of the initial compressive strength of the mortars fabricated with this zeolite type. However, the long-term compressive values are limited if the zeolite content used is equal or higher than 10% of the weight of the cement.
- The higher silica content of NaP-type zeolite, 25% higher than the one of LTA zeolite, promotes pozzolanic reactions that significantly increase the long-term compressive strength of the fabricated mortars. Moreover, the higher the zeolite content, the higher the compressive value measured at 90 days is. These results open the possibility of increase the NaP zeolite content used in the mortars, thus increasing in a greater way the sustainability of the construction materials fabricated.

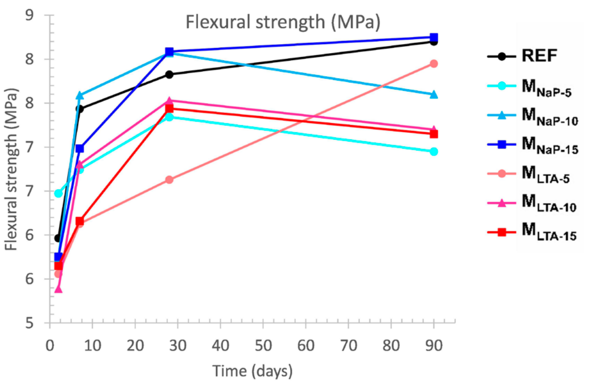

Figure 5. Evolution of the flexural strength of the fabricated mortars.

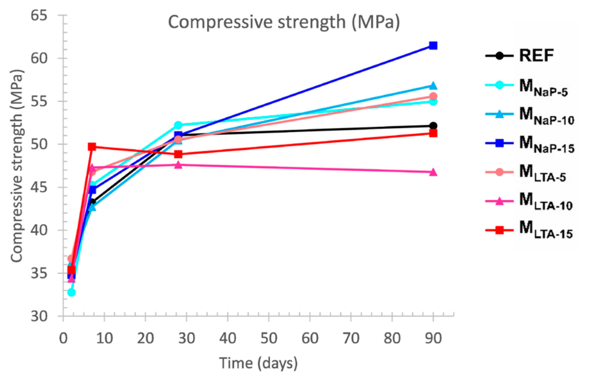

Figure 6. Evolution of the compressive strength of the fabricated mortars.

The microstructural hypothesis extracted from the performance observed in the fabricated mortars must be corroborated in further microstructural studies. Moreover, in order to applicate the zeolytes fabricated in the real market, a scalability of the studies made in concrete scale must be carried out. In addition, this scalability should be achieved by thinking not only of conventional concretes, that would be the first step, but also of certain types of special concretes with advanced properties. Obtaining this type of concretes in a more sustainable way, such as the use of zeolites from aluminum waste, will have a positive impact on achieving the sustainability requirements that have been imposed on the construction sector. Furthermore, the durability of the new more sustainable concretes must be evaluated.

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Authorship contribution statement

José Luis García Calvo: Conceptualization, Data Curation, Formal analysis, Investigation, Methodology, Resources, Supervision, Writing-original draft, Writing - review & editing.

Pedro Carballosa: Data Curation, Investigation, Methodology, Writing-review & editing.

Rocío Jarabo: Investigation, Writing-review & editing.

Maximina Romero: Investigation, Writing-review & editing.

Isabel Padilla: Investigation, Writing - original draft, Writing - review & editing.

Aurora López-Delgado: Funding acquisition, Investigation, Project administration, Resources, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

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