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Mineral, Chemical and Technical Characterization of Altered Pyroxenic Andesites from Southeastern Spain for Use as Eco-Efficient Natural Materials

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Abstract: Climate change is already an undeniable reality, and it is a direct consequence of our society's lifestyle and the indiscriminate use of certain materials, such as Portland cement, which causes the emission of gases and waste that contributes to the greenhouse effect. The object of this work is to present the results obtained from research on pyroxenic andesites that have become altered to zeolite and their use as alternative, eco-efficient materials that improve the quality of cement through a standardized partial substitution. In this work, four samples of pyroxenic andesites altered to zeolites (PAAZ) and two samples of unaltered andesites (UPA) were analyzed. The methods used in this study are as follows: petrography of thin section (PTS), chemical analysis of X-ray fluorescence (XRF) and phase determination by X-ray diffraction (XRD). Other tests were carried out to determine the quality of the PAAZ from a technical and practical application point of view, such as chemical analysis of pozzolanicity (CPT) at 8 and 15 days, as well as mechanical compression tests at 2, 7, 28 and 90 days. Petrographic and phase analyses show that the original mineral components of the samples such as pyroxene, amphibole, plagioclase and mica were leached and replaced by more than 90% with mordenite and smectite. XRF analyses indicates an anomalous rise in SiO_2, a drastic reduction in alumina Al_2O_3 and a significant increase in alkaline compounds over alkaline-earth compounds in samples of altered pyroxenic andesites (PAAZ) with respect to samples of unaltered andesites (UPA). The pozzolanicity test establishes that the samples of unaltered andesites do not behave like pozzolans at 8 or 15 days; however, altered andesites experienced remarkable pozzolanic reactivity in the same periods. The mechanical compression tests carried out on specimens made with PAAZ and Portland cement showed a growing increase in mechanical resistance from 2 days (15.2 MPa) to 90 days (72.1 MPa). These results suggest that pyroxenic andesites altered to zeolite can be an ideal alternative to partially replace Portland cement, which in turn could contribute to the preservation of the environment and a more rational use of traditional resources.

Keywords: altered pyroxenic andesite; zeolite; cement; pozzolanicity; eco-efficient materials; mortars

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1. Introduction

The use of new materials for the improvement of cements is currently a common practice, since experience indicates that in this way the negative effects on the environment due to the manufacture of cement together with the premature degradation of modern construction structures can be mitigated. Among these materials, andesites have been widely used in many fields of sustainable construction. Hamidi et al. [1] consider andesites as pozzolans capable of replacing Portland cement by up to 40%, and this substitution is more effective when the rock is heated between 700° and 900 °C. Davraz et al. [2] highlight the positive effect of andesite as a pozzolan on the mechanical behavior of high-strength concretes, indicating that a substitution of cement by andesite of 10% is the most effective proportion to obtain maximum mechanical resistance. Along the same lines, the works of Özkan and Ceylan [3] as well as those of Özkan et al. [4] stand out. Andesites have been used effectively in the manufacture of mortars with mechanical strengths greater than 50 MPa in 48 h of curing [5], and studies have clarified the mechanisms that form microfractures in mortars to predict trends in their growth [6,7]. The properties of andesites as aggregates have been mentioned for many other uses by several researchers in the following fields: to improve the properties of specific asphalts [8,9]; to determine the hydrodynamic abrasion resistance of concrete [10]; to improve light concretes [11]; in the use of sewage sludge from wastewater treatment plants generated during the processing of andesitic materials [12] and to pave roads [13,14]. On the other hand, andesites have traditionally been used in the construction of historic and modern buildings due to their high chemical resistance [15], physical resistance [16], mechanical strength [17], resistance to freeze–thaw cycles [18] and abrasion resistance [19].

The object of this work is the mineral, chemical and technical characterization of pyroxenic andesites altered to zeolite that lie in the volcanic complex of the southeast Iberian Peninsula, and researching their influence in mixtures with Portland cement through standardized formulations. It is expected that the use of this material will improve the quality and rheology of cements, mortars and concretes. It is also expected that with the results obtained, zeolitized pyroxenic andesites can be designated as eco-efficient materials capable of contributing to environmental sustainability and a reduction in CO_2 emissions into the atmosphere.

2. Materials and Methods

2.1. Materials

In the development of this research, 4 samples of pyroxenic andesites altered to zeolite and another 2 samples of unaltered andesites were selected. All samples come from outcrops inside the Caldera de Los Frailes, in the southeastern part of the Iberian Peninsula (Figure 1) [20]. Both altered and unaltered andesites are the main host rocks of zeolitic mineralization previously studied in detail by other researchers [21–23]. The samples have varied colors ranging from dark green to light gray. In the outcrops, they have varied structures of columnar type, disjunctive, sometimes breccious and pyroclastic. The weight of the samples ranged from 15–20 kg.

A Type I Portland cement (PC) was used, with strength class equal to 42.5 R. The methodology indicated in the Standard UNE EN 197-1:2011 [24] was followed, in which the characteristics of this binder are detailed extensively. A standard fine aggregate (CEN NORMANSAND DIN EN 196-1) with a SiO_2 content >95% was used to produce the mortar specimens; the procedure followed the Standard UNE EN 196-1:2016 [25]. The chemical composition of the cement used in this research is shown in Table 1.

In the preparation of mortars, two fundamental proportions of Portland cement and pyroxenic andesites altered to zeolites (PC/PAAZ) equivalent to 75:25% and 70:30%, respectively, were used.

Table 1. Chemical composition of Portland cement used in this research.

Portland Cement (PC)	Compounds in Mass Percentage (% Weight)											LOI * (%)	% Total
	S_iO_2	Al_2O_3	K_2O	Na_2O	MgO	Fe_2O_3	CaO	TiO_2	SO_3	MnO	P_2O_5		
	17.47	5.61	1.35	0.091	0.639	3.37	64.01	0.325	4	0.094	0.071	2.44	99.47

* Loss on ignition.

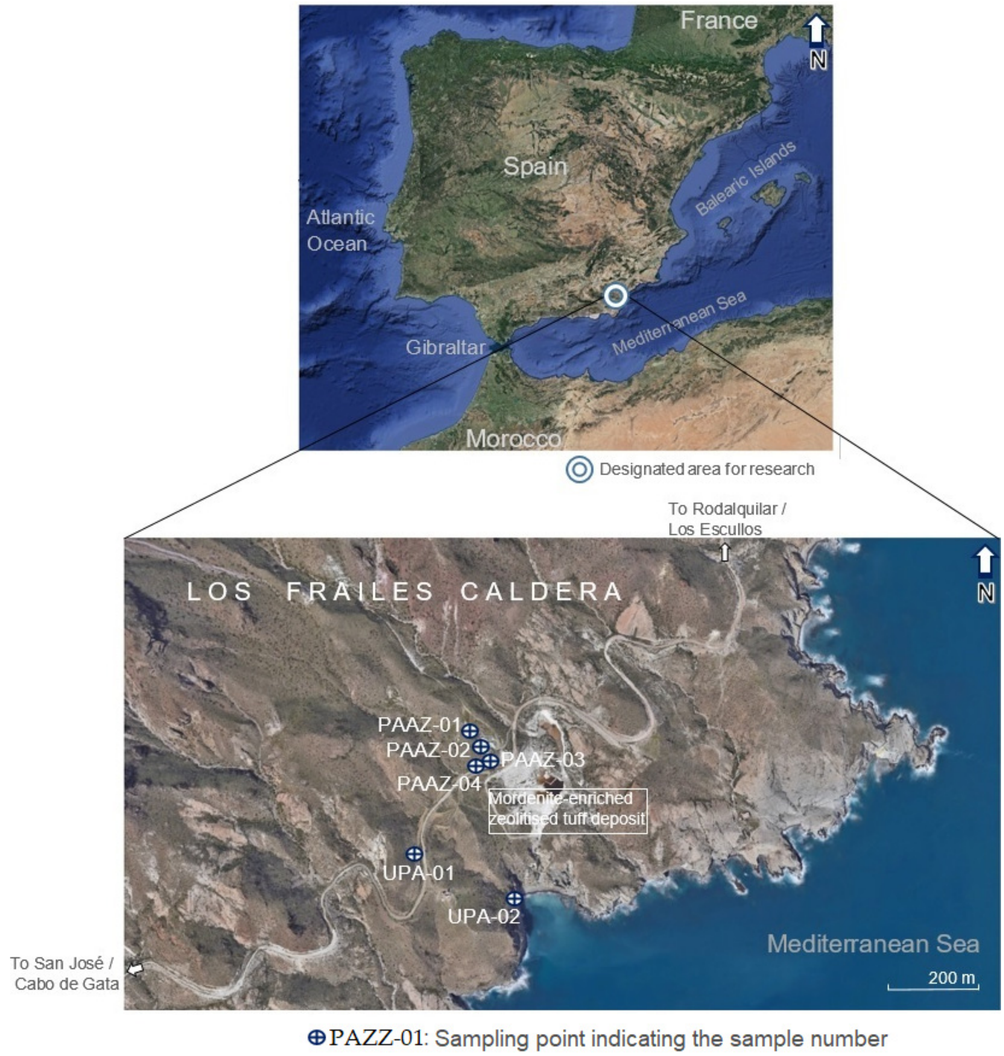

Figure 1. Location of the study area [20].

2.2. Methods

A thin-section petrographic study was carried out to identify the different non-metallic mineral species present in the researched samples, as well as the texture, morphology, size and alterations present. To carry out this study, a Leica DM600M Scope microscope was used, equipped with a DTA-13 system of monochromator filters of visible and infrared light for 13 wavelengths (400 nm to 1000 nm), at intervals of 50 nm. This microscope has an integrated system called Cameva, developed and maintained by the Universidad Politécnica de Madrid and AITEMIN (Association for Industrial Research and Development of Natural Resources). It also has an integrated LAS control and an automated Märzhäuser plate, which are all monitored from a DELL workstation. For the measurement of the VNIR spectra, the Ocean Optics high- and low-reflectance standards were used as reference. For the processing and interpretation of the images, Aphelion software was used.

Chemical analysis by X-ray fluorescence (XRF) was carried out to establish the chemical composition of both altered and unaltered pyroxenic andesite samples. This analysis was performed with a Phillips model PW-1404 (Madrid, Spain). The equipment has an integrated system (collimator) that converts the divergent beam into a parallel beam, thereby homogenizing the X-ray trajectory and concentrating it into a single beam, which strengthens it considerably. The radiation intensity of the samples was 10–100 kV. A monochromator was used to isolate the radiation and obtain a suitable wavelength. The research samples were previously ground to 74 μ. Then, 6 to 8 g were taken and pressed with the help of a Herzog press until 5 cm diameter analysis tablets were obtained. Finally, the samples were introduced into the X-ray spectrometer for quantitative XRF analysis.

X-ray diffraction (XRD) analysis was carried out to determine the mineral phases present in the samples. A Rigaku Miniflex 600 X-ray diffractometer (version, Madrid, Spain) was used for qualitative and quantitative analysis. This equipment works with an X-ray tube at 600 watts. In addition, it has an automatic sampler with 6 positions, a HyPix-400 MF-2DHPAD detector (version, Madrid, Spain), SmartLab Studio II software (version, Madrid, Spain) and an interface with a profile view, phase data view, 3D view and crystal structure view. The required power is 100–240 v, while the frequency is 50/60 Hz. For this analysis, 500 milligrams per sample were weighed, crushed and screened up to 74 µ. One pill was manufactured for each sample in their sample holder molds and placed in the sample holder for analysis.

The determination of pozzolanic reactivity was conducted in order to monitor the behavior of the samples as natural pozzolans and establish their capacity to partially replace Portland cement in mortars. This analysis consists of comparing the volume of $Ca(OH)_2$ existing in an aqueous solution with hydrated cement and pozzolan, with enough calcium hydroxide needed to obtain a saturated solution of the same alkalinity as the previous one. The chemical test for pozzolanicity was based on the Standard UNE-EN 196-5:2006 [26]. Distilled water (100 mL) was heated to 40 °C for the pozzolanicity test, and 20 g of sample and cement were poured with a formulation of 75:25% on the one hand, and 70:30% on the other. The test took place at two different times, on days 8 and 15. After each period, the solution was filtered. Finally, the hydroxyl ion $[OH^-]$ concentration as well as the calcium oxide (CaO) concentration were calculated.

The pozzolanicity test is considered positive when the concentration of calcium hydroxide in the solution is lower than the saturation concentration [26].

A test of mechanical resistance to compression was performed after 2, 7, 28 and 90 days to determine the mechanical stability of samples made with partial replacement of Portland cement by altered andesites (PC/PAAZ), in standardized proportions of 70:25% and 70:30%, respectively (Table 2). The main purpose of this survey was to check how much mechanical resistance could increase from initial ages to later normalized periods. To carry out this test, the Standard UNE EN 196-1:2016 [25] was used as a reference.

Table 2. Formulation of mortar mixtures made with different proportions of PC/PAAZ (70:30% and 75:25%).

Nomenclature of specimens	Mortar components				
	NA [1] (%)	Formulation I (PC/PAAZ) (%)	Formulation II (PC/PAAZ) (%)	PC [2] (%)	DW [3] (g)
PCS [4]	100	-	-	100	225
PC/PAAZ-01[5]	100	75:25	70:30	-	225
PC/PAAZ-02	100	75:25	70:30	-	225
PC/PAAZ-03	100	75:25	70:30	-	225
PC/PAAZ-04	100	75:25	70:30	-	225

[1] Natural fine aggregate; [2] Portland cement; [3] Distilled water; [4] Portland cement specimen; [5] Specimen made of Portland cement and pyroxenic andesite altered to zeolite.

3. Results and Discussion

3.1. Petrographic Thin-Section Study (PTS)

Figure 2a–d provides several microphotographs of the analyzed samples (PAAZ-01, PAAZ-02, PAAZ-03 and PAAZ-04). The mineral composition consists of mordenite, altered hornblende crystals, plagioclase, muscovite, interstitial glass, opaque minerals (possibly ilmenite) as well as sericite. The texture is varied, highlighting the porphyry, glomeroporphydic, intersertal, granular-xenomorphic, granular-hypidiomorphic, inequigranular and merocrystalline textures. In all cases, an advanced zeolitization process can be observed that has affected both the matrix and the original minerals. In Figure 2a,b,d, it is possible to observe how the secondary mordenite has penetrated the interior of the hornblende crystals following the exfoliation lines. Another feature to highlight is the dark halo originating at the edges of the relict crystals due to the reaction of the crystal with the fluids forming mordenite and smectite. In the process of alteration of pyroxenic andesite by zeolite, the protominerals have been completely replaced by mordenite, as indicated in Figure 2a–c, in which the total replacement of a pyroxene crystal by mordenite within a devitrified matrix can be observed.

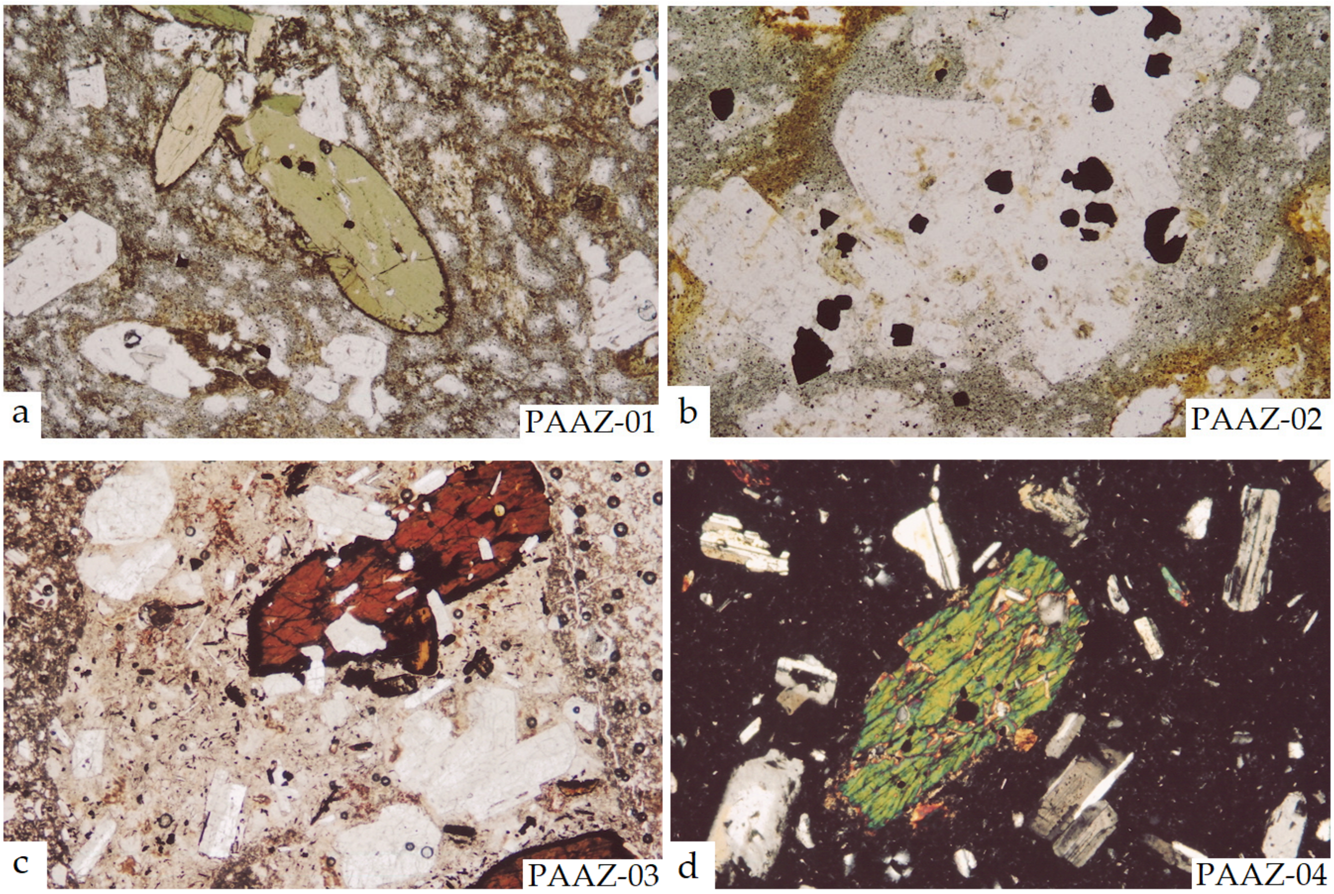

Figure 2. Microphotographs of the thin sections (**a**–**d**) with Obj x.2.5 and parallel (N//) (**a**,**b**,**d**) and crossed nicols (Nx) (**c**).

The microphotographs shown in Figure 3a,b show the mineral composition of the samples of unaltered pyroxenic andesite (UPA-01 and UPA-02) that have not undergone the zeolitization process and that are considered as unaltered samples. Both samples are composed of plagioclase, pyroxene, amphibole, glass, opaques, sericite and iron oxide. The texture is porphyry, poikilitic, pilotaxitic, glomero-porphyry, fluidal, inequigranular, merocrystalline and pseudomorphic.

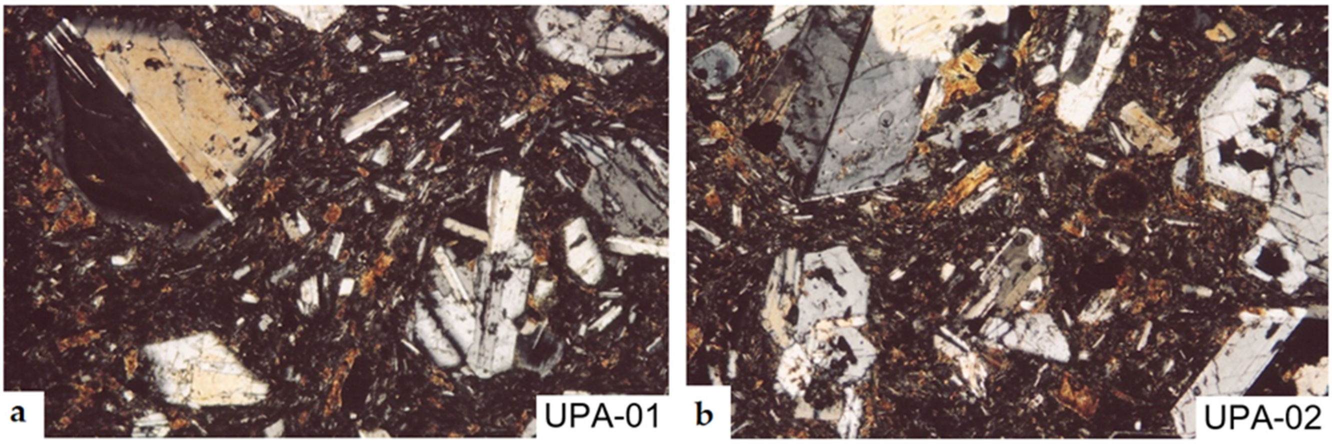

Figure 3. Microphotographs of samples of unaltered pyroxenic andesites (**a**,**b**) obtained with Obj x.2.5 and crossed nicols (Nx).

3.2. X ray Fluorescence (XRF)

The results of the study of the chemical composition of the samples are listed in Table 3. The high values of SiO_2 in the most altered andesite samples are highlighted, such as PAAZ-01 (65.17%) and PAAZ-02 (64.49%), respectively, although they are also significant in the case of samples PAAZ-04 (62.4%) and PAAZ-03 (61.2%). In samples of unaltered andesites (UPA-01 and UPA-02), the SiO_2 contents are markedly lower than in the altered samples, which leads us to conclude that the high percentages of SiO_2 are a direct consequence of the processes of zeolitization and smectization caused by hydrothermal activity [27–29]. Through these processes, it is deduced that the contents of alkaline compounds (Na_2O and K_2O) experienced an increase with respect to the alkaline earth (CaO and MgO), as shown in Table 3 for the groups of altered and unaltered samples. On this same criterion, the high values of loss on ignition (LOI) in the altered samples, specifically PAAZ-01, PAAZ-02 and PAAZ-04, compared to the practically insignificant values detected in the unaltered samples, are also highlighted. The high values of SiO_2, the predominance of alkaline compounds and the LOI are factors that establish their nature as pozzolans of the altered andesites studied in this work. These three factors have been mentioned before by several authors, such as [28,30], in their research on other types of pozzolanic materials.

Table 3. Chemical composition of the samples studied by X-ray fluorescence (XRF).

Sample	(% weight)								LOI (%)
	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	Fe_2O_3	TiO_2	
PAAZ-01 [1]	65.17	13.19	0.88	3.92	2.99	2.09	1.60	0.119	11.70
PAAZ-02	64.49	13.57	0.96	2.94	2.36	2.10	1.40	0.113	11.50
PAAZ-03	61.20	14.70	2.58	1.63	1.69	3.17	4.30	0.47	3.40
PAAZ-04	62.40	13.82	2.45	2.78	2.26	2.44	4.70	0.49	9.75
UPA-01 [2]	52.30	18.20	10.20	2.02	0.59	5.08	9.68	0.80	0.70
UPA-02	51.90	19.10	10.14	2.01	0.60	5.11	9.66	0.77	0.60

[1] Pyroxenic andesite altered to zeolite; [2] Unaltered pyroxenic andesite.

3.3. X-ray Diffraction (XRD)

The study to determine the different mineral phases present in the PAAZ-01 and PAAZ-04 samples (Figure 4) established the dominant presence of neoforming mineral species such as mordenite and smectite, accompanied by secondary phases such as halloysite, illite and quartz, which were formed by a hydrothermal process that caused particularly intense zeolitization and smectization [31]. Section 3.1 describes in detail how the neoforming minerals have replaced the original minerals. On the other hand, Leone et al. [32] describe these isomorphic and pseudomorphic substitution processes as an enthronement of new mineral varieties. This process is interpreted in this work as a diffusive event of bidirectional character by which the hydrothermal solutions captured ions from the host rock (original pyroxenic andesite) and provided foreign ions that created mordenite and smectite. As can be seen in Figure 4, there are some compositional and morphological differences in both samples. The PAAZ-01 sample presents more pronounced and intense peaks that show a high crystallinity of the mineral species present, mainly mordenite, while in the PAAZ-04 sample, the intensity of these peaks tends to attenuate significantly. Another detail to highlight in this last sample is the presence of amorphous phases, possibly produced by the formation of glass in the places where the hydrothermal solutions, still hot, experienced rapid cooling [28]. Another interpretation could be that this amorphous phase was deposited during the pyroclastic events that took place in this region during the Neogene period [33].

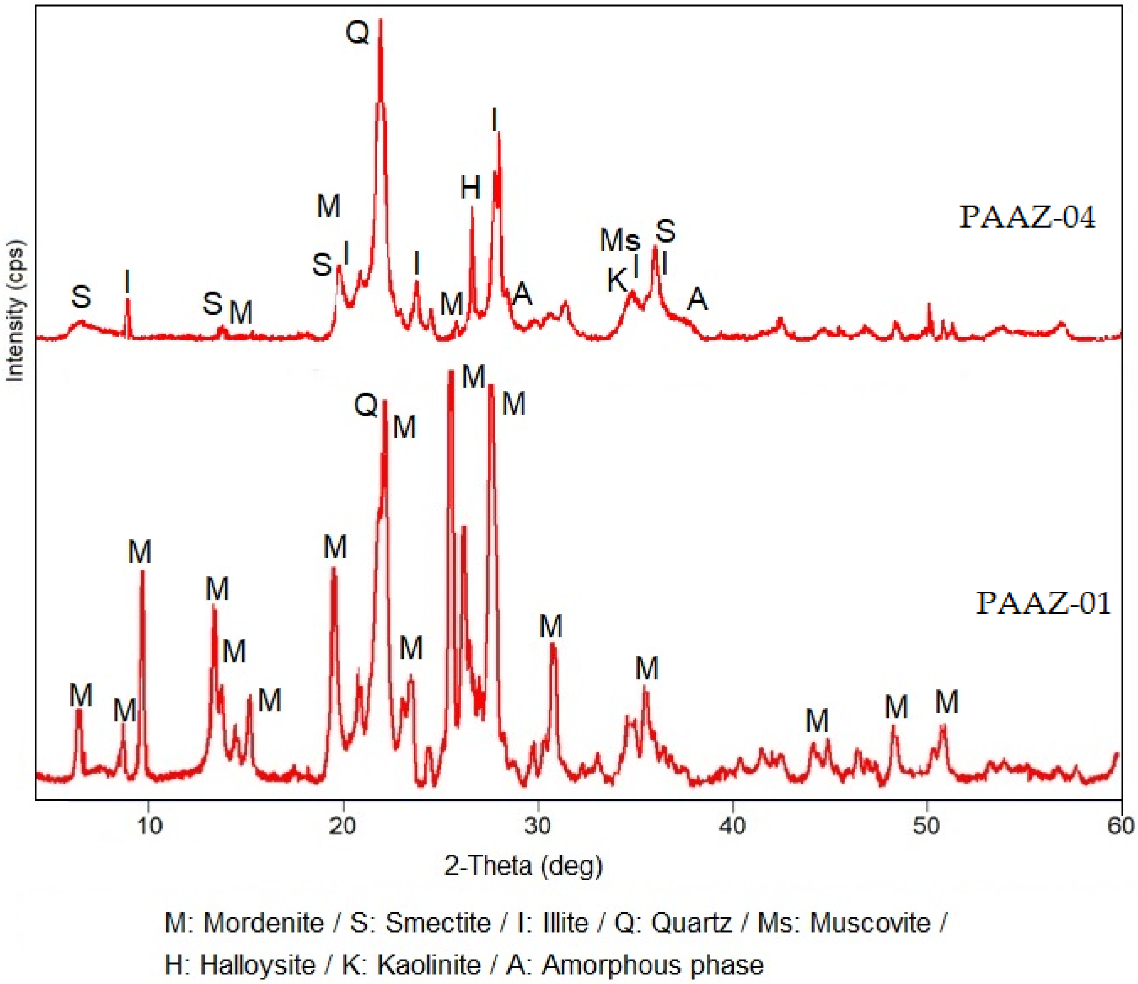

Figure 4. Diffractograms obtained from the study of the phases present in the PAAZ-01 and PAAZ-04 samples.

3.4. Chemical Analysis of Pozzolanicity (CAP)

Figure 5a–d presents the results of the chemical analysis of pozzolanicity, both at 8 and 15 days. As can be observed, the samples of unaltered pyroxenic andesites UPA-01 and UPA-02 do not show any pozzolanic behavior at 8 days of testing (Figure 5a); however, even though after 15 days they tend to move imperceptibly towards the isothermal solubility curve (Figure 5b), they do not come into contact with it. For this reason, it is concluded that samples of unaltered pyroxenic andesites lack pozzolanic activity in their natural condition without being ignited. The reason why these samples do not have pozzolanic reactivity could be mainly due to their mineral composition, meaning that the SiO_2 present in the structure of pyroxenes and amphiboles is strongly combined in the silicate structural group, forming stable crystalline structures, which prevents their reaction with cement. However, Martín et al. [34] have achieved hydraulic reactions of materials of volcanic origin through a very fine grinding process which causes an increase in the surface area of the grains and consequently their pozzolanic reactivity.

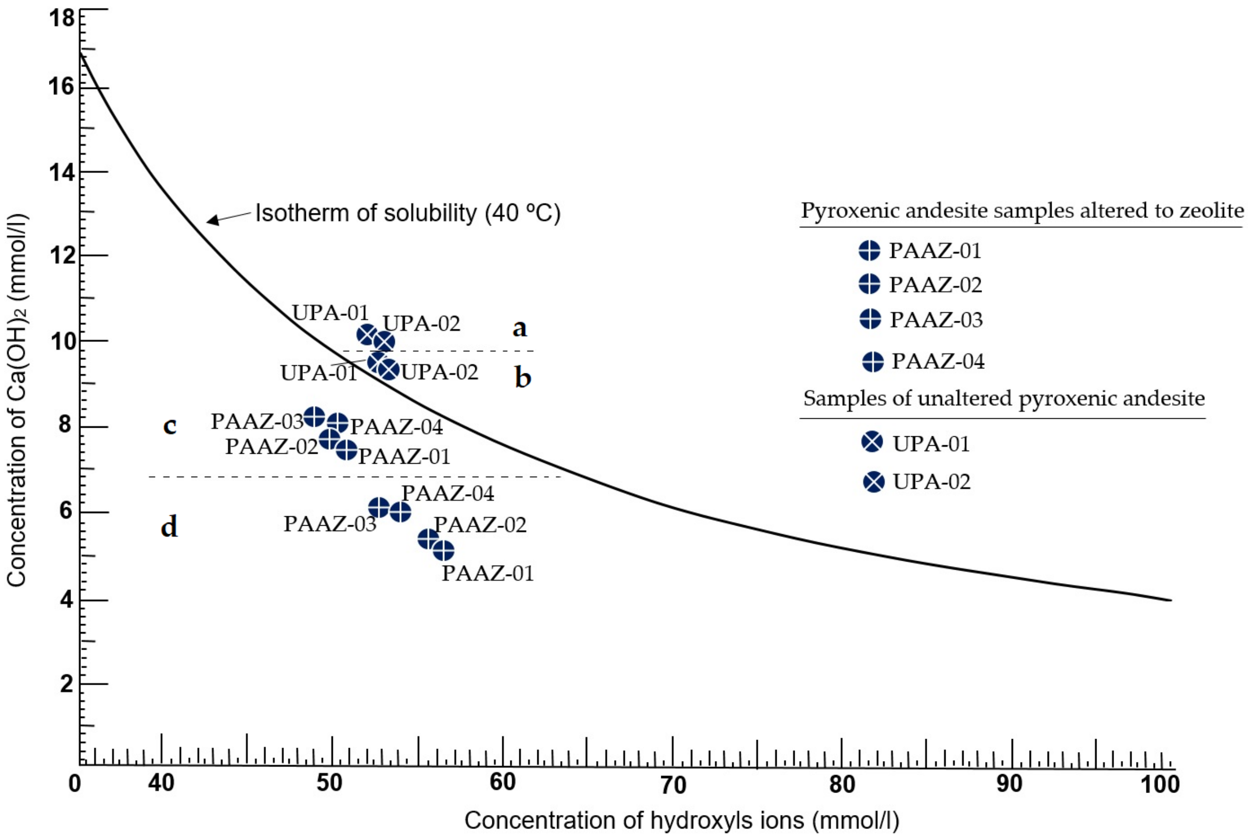

Figure 5. Evolution of the pozzolanic behavior of the samples: a and c correspond to 8-day test periods, whereas b and d represent 15-day periods.

A very different situation has been found in the analysis of samples of pyroxenic andesites altered to zeolites. In Figure 5c, after just 8 days of testing, the pozzolanic nature of all samples can already be established, specifically PAAZ-01 and PAAZ-02; also noteworthy are PAAZ-04 and PAAZ-03. At 15 days (Figure 5d), the pozzolanic behavior of the samples seems to be visibly reinforced, with PAAZ-01 and PAAZ-02 being the most reactive. The mineral constitution of these samples, characterized by an increase in the contents of mordenite and smectite, the albitization and sericitization of plagioclase with formation of smectites, the presence of amorphous products, as well as the chemical composition with a high presence of reactive SiO_2 [28], seem to be the fundamental causes behind the pozzolanic behavior of these materials.

3.5. Mechanical Resistance to Compression at 2, 7, 28 and 90 Days

Figure 6 shows the results obtained in the test of mechanical resistance to compression done on the specimens made with the formulation PC/PAAZ and PCS-R, with percentages of substitution of 75:25% at 2, 7, 28 and 90 days.

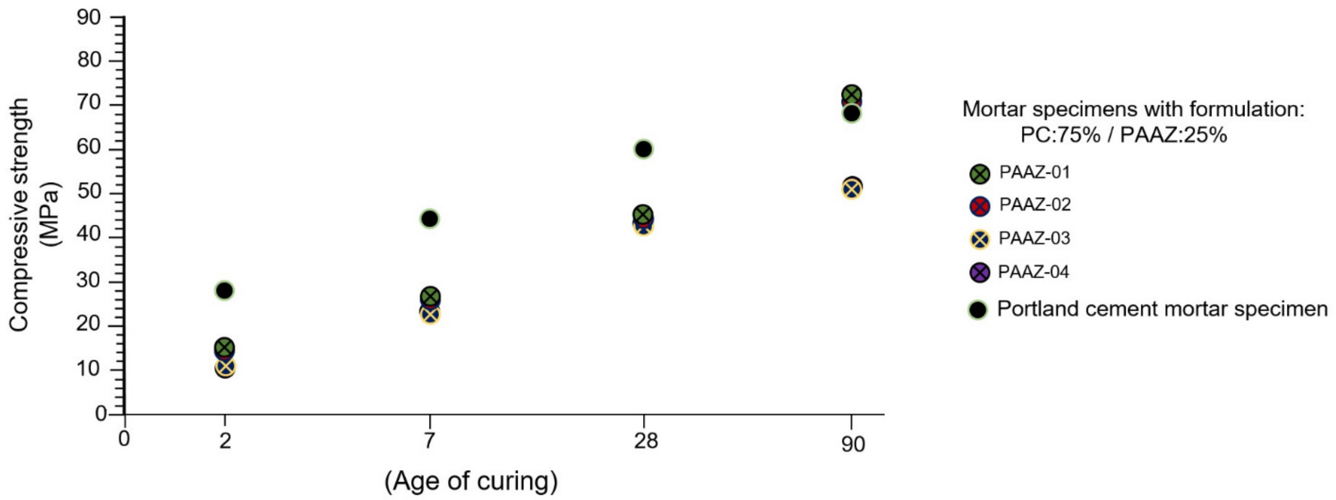

Figure 6. Behavior of mechanical resistances at different ages of curing, with the formulation PC: 75%/PAAZ: 25%.

Among the most notable features highlighted is a trend in the exponential growth of mechanical resistance from 2 to 90 days. Note that all samples made with PC/PAAZ show only slight differences in their resistances between 2 and 28 days of curing; however, this difference is accentuated in later periods (90 days) in which the PAAZ-01 and PAAZ-02 samples reach values of 72.1 and 71.4 MPa, respectively, which not only exceed the two remaining samples (PAAZ-03 and PAAZ-04), but also the reference specimen (PCS-R). Khan and Amin [35] have shown that mortar and concrete specimens made with different types of pozzolans, such as volcanic ash, can match the rate of resistant activity of mortars above 90 days of setting. Another noteworthy highlight from this analysis is the influence of the chemical and mineral composition of the samples on the pozzolanic and hydraulic activity that takes place inside the mortar; thus we see that the samples PAAZ-01 and PAAZ-02, which have undergone a more intense process of zeolitization, are more reactive and develop greater mechanical strength than the samples PAAZ-03 and PAAZ-04, which come from areas of the deposit with a lower influence of the zeolitization process.

Figure 7 represents the variations in the mechanical compressive strength determined by testing mortar specimens manufactured with a proportion of PC-PAAZ and PCS-R, where part of the PC has been replaced by 30%. As can be seen, the gain of mechanical resistance follows a temporal pattern that increases as the curing time passes; with few exceptions, the resistance values do not differ much from each other, nor do they differ much from the behavior of the resistance values observed in Figure 6. It seems that the substitution of Portland cement at both 25% and 30% does not significantly affect the development in mechanical strength of this type of specimen. Martín et al. [36] have opted to increase in a controlled manner the replacement of cement with natural aggregates above 70% with satisfactory results.

According to the data observed in Figure 6, we calculated that the increase in initial mechanical resistances (2 and 7 days) in the most reactive samples is 11.5% and between 18.8 and 26.9% for normal resistance (28 days), when the PC/PAAZ formulation is 75:25%. In the case of the formulation PC/PAAZ-70:30% (Figure 7), the initial mechanical resistance increases by 8.6%, while the normal resistance increases by 22.8%.

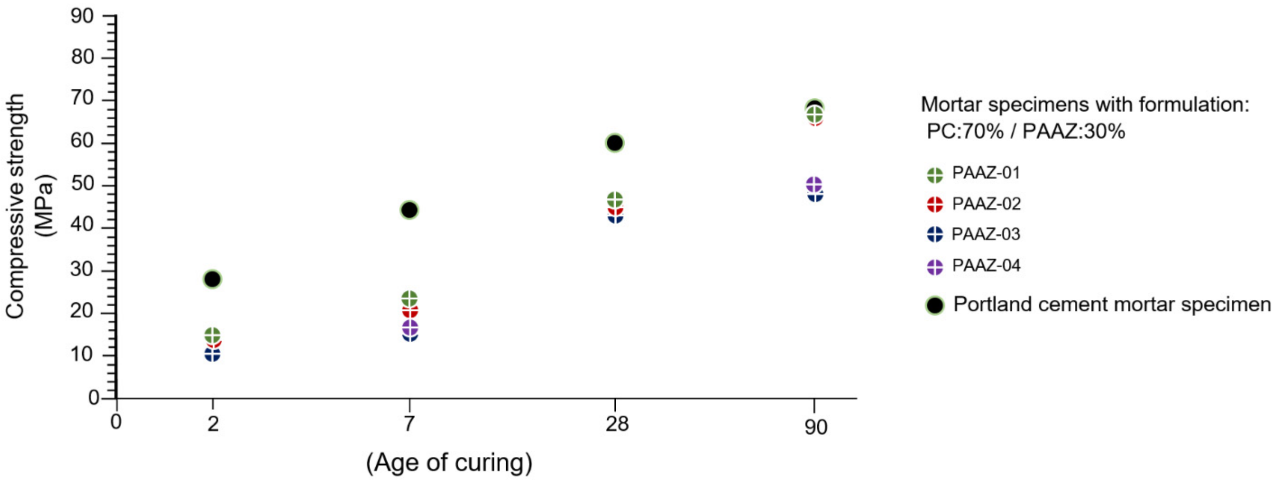

Figure 7. Mechanical resistance of specimens made with PC: 70% / PAAZ: 30%.

4. Conclusions

The samples studied show a visible replacement of the original minerals (pyroxene, amphibole, plagioclase and mica) by secondary species consisting of mordenite and smectite, and their presence favors the behavior of these andesites as typical natural pozzolans. This fact can be explained by the inherent characteristics of zeolites, such as their high content of reactive SiO_2, their cation exchange capacity and their marked pozzolanic reactivity.

In the chemical composition of the samples of altered pyroxenic andesites compared to unaltered ones, there is an increase in reactive SiO_2, alkaline compounds on alkaline-earth and loss on ignition, as well as a decrease in Al_2O_3, causing a better pozzolanic response.

The mechanical strengths of the specimens prepared with partial substitution of Portland cement by altered pyroxenic andesites increases exponentially from the initial curing ages (2 and 7 days) to normal and late (28 and 90 days), reaching equal, and even occasionally exceeding, the values of resistances of the reference specimen.

The values of mechanical resistance obtained by the formulations of 75:25% and 70:30% show an increase in resistance when the substitution is 25%; however, these differences are not very high, so for practical purposes both dosages could be equally profitable in the production processes of pozzolanic cements.

The samples of altered pyroxenic andesites are part of the host rocks of the deposit of natural zeolites located in the Caldera de Los Frailes; therefore, the establishment of their pozzolanic properties could be considered for rational and simultaneous exploitation of both materials, to a better use.

The results presented in this work could be used as a practical guide within the applied sciences to guide local industries in the optimal use of natural resources of volcanic origin.

The results achieved suggest that the altered pyroxenic andesites investigated in this work could guarantee the quality of more environmentally friendly cements, through which CO_2 emissions to the atmosphere and global warming could be mitigated. In addition, these results could be taken into account in sustainable development objectives, in the circular economy and in the recycling of new materials.

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