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Improvement of the Mechanical Properties of Mortars Manufactured with Partial Substitution of Portland Cement by Kaolinitic Clays

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Abstract: Presently, the search for urgent solutions to mitigate climate change has become a global priority. One of the most important challenges is the characterization, standardization, and technology of sustainable natural raw materials, which will significantly improve the quality of common types of cement, the production process of which emits large amounts of greenhouse gases into the atmosphere. This work is focused on the study of natural kaolinitic clays (NKC) from the eastern part of the Iberian Peninsula and its main objective is to define and normalize their properties as natural pozzolanic materials. This research consists of an initial study to determine the morphological and chemical properties using SEM and XRF. Furthermore, the physical properties of the samples were studied, such as thermic treatment (TT), Blane particle finesse (BPF), real density (RD) and apparent density (AD), porosity (P), volume stability (VS) and start and final setting time (SFST). On the other hand, technological analyses were carried out as follows: chemical analysis (CATQ), pozzolanicity (CAP), mechanical compression strength tests at 7, 28, and 90 days (MCST) as well as the ultrasonic pulse velocity (UPV). XRF results indicated that the SiO_2 content (49.9–51.0%) of kaolinitic clay in its natural state (NKC) increases to 57.41 and 58.10%, respectively, when calcined (CKC). The chemical analysis of pozzolanicity established that the NKC does not show pozzolanic activity during the first 8 and 15 days; however, once calcinated, its pozzolanic reactivity increases substantially. On the other hand, the results of the mechanical stress tests (MCST) indicate an exponential increase in mechanical resistance from 7 to 90 days, which is higher in mortars made with CKC; similarly, and according to the results of the calculation of the Resistant Activity Index (RAI), it shows that the substitutions of Portland cement (PC) by NKC are effective between the ranges of 10 and 25%, while in the case of the substitution of PC by CKC, all formulations (10, 25 and 40%) are effective. This research establishes that the kaolinitic clays of the east of the Iberian Peninsula can be considered quality pozzolanic materials, capable of partially replacing Portland cement. The results presented here could be used as guidelines for the understanding and application of natural pozzolanic materials contributing to the improvement of types of cement, mortars, and concretes, which would positively affect the quality and preservation of the environment as well as the sustainability of eco-efficient construction materials.

Keywords: kaolinite; mortars; calcination; pozzolanicity; mechanical strength

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1. Introduction

Presently, kaolinitic clay is well known, studied, and used today in many scientific and industrial fields, as it is a highly valued and versatile raw material from the point of view of its use as a pozzolan. In this sense, the work of Tironi et al. [1,2] established that kaolinitic clays have sufficient pozzolanic reactivity even when they replace Portland cement by 30%, which is also confirmed by Cao et al. [3], Almenares et al. [4] and Alujas et al. [5]. On the other hand, Marvila et al. [6] managed to partially replace hydrated limestone with kaolinitic clays, establishing that this substitution becomes effective even when using 50%. Msinjili et al. [7] developed bricks based on calcined kaolinitic clays achieving a significant improvement in the resistance to chloride penetration. In the research of Boakye et al. [8], a study of the mechanical and chemical properties of mortars containing kaolinitic clays was carried out to establish their suitability in the construction industry; According to their conclusions, a proportion of 20% of these clays is suitable for this purpose. These conclusions have also been confirmed in the work of Singh [9]. In the manufacture of cement, there is much research today that validates the effectiveness of the use of kaolinitic clays as supplementary cementitious material capable of partially replacing Portland cement clinker by 30–50%, which also has an important effect which is to greatly reduce the vast amounts of CO_2 being released into the atmosphere, as well as improvements in mechanical strength and durability [10–15]. Nevertheless, kaolinitic clays are used in many applications and new fields, such as in the manufacture of ceramic materials [16], the adsorption of methane, Ni(II) and Mn(II) [17,18], the manufacture of cosmetic and pharmaceutical products [19] as well as in soil stabilization [20]. Finally, the current rise of the ternary mixture of limestone, calcined clays, and cement, known as "LC^3 cement", should be highlighted as an ideal formula for the production of more efficient and less environmentally aggressive cement; authors such as Scrivener et al. [21], Krishnan et al. [22], and Canbek et al. [23], among others, have highlighted the advantages of these cementitious mixtures in their recent studies.

The specific purpose of this research is to establish the nature of the kaolinitic clays that lie in the eastern part of the Iberian Peninsula as pozzolans (Figure 1) and prove their ability to replace part of the Portland cement (PC) in mortar mixtures. This research has been developed in several stages; first, a characterization of the morphological, mineralogical, and chemical features of kaolinitic clays was made through SEM and XRF; second, the characterization of physical properties was also made; and third, a chemical analysis study of pozzolanicity was made as well as mechanical resistance tests and non-destructive analysis of ultrasonic pulse which established parameters of quality and technical viability of the kaolinitic clays.

Figure 1. Location of the research area [24].

The data and conclusions established in this work could be considered to be a methodology to characterize and normalize kaolinitic clays, used mainly to improve pozzolanic cement, mortars, and concretes adapted to the demands of environmental care and with low CO_2 emission into the atmosphere.

2. Materials and Methods

2.1. Materials

To carry out this work, a representative sample of kaolinitic clays weighing 60 kg was chosen and taken directly from the outcrops located in the eastern region of the Iberian Peninsula (Figure 1). The sample is characterized by its light colors, which can be pale gray, white, and pinkish. It is not very compact, earthy, and powdery in appearance (Figure 2).

Figure 2. Natural kaolinitic clay (NKC) sample appearance.

Before submitting the sample to the study planned in this research, a series of initial preparations were carried out in phases, as follows: a grinding phase in a planetary ball mill Retsch, model PM 100, for 10 s and at 250 rpm; a standardized homogenization phase using an approved cracker machine; and a selection phase of standard quantities of samples according to the guidelines in each of the standards used in this research.

2.2. Methods

2.2.1. Analysis Using SEM and XRF

A SEM study was carried out to monitor the textural, structural, and morphological properties of the sample under study, both in the natural state (NKC) and calcined (CKC). A Hitachi S-570 electron microscope, owned by the E.T.S.I.M.E. of the Polytechnic University of Madrid, was used. The microscope is equipped with a Kevex-1728 analyzer and a BIORAD Polaron, as well as a power supply and a Polaron SEM coating system. It uses two different pieces of software, namely Winshell and Printerface.

XRF analysis was applied to obtain information on the chemical composition of the natural kaolinitic clay (NKC) sample. To develop this analysis, a portion of natural kaolinitic clay was mixed with a flux with the following ratio: NKC/Flux: 0.3–5.5. Next, this mixture was melted together with a lithium tetraborate compound, with the help of the Perl ′3 induction device, by Philips. Finally, the sample obtained was subjected to XRF spectrometry analysis, using wavelength dispersion (WDXRF) in PANalytical's apparatus conditioned with a Rhodium tube.

2.2.2. Physical Characterization Tests (PCT)

The natural kaolinitic clay sample was subjected to a thermic treatment (TT) test to expel moisture and other undesirable substances that could interact negatively with the experiments. Initially, the sample was heated in a Binder stove, model 9010-0101 ED 240, to 105 °C for 8 h. It was then calcined in a Thermo Scientific Heraeus muffle furnace, model M 110 Muffle Furnace, at 800 °C for 1 h. A granulometric analysis was conducted to match the size of the kaolinitic clay particles with that of Portland cement following the guidelines of the Standard UNE-EN-196-6:2019 [25].

Other tests were carried out to determine the real density (RD) using the Micromeritics Accupyc 1330 air pycnometer (Standard UNE-EN-80103:2013) [26], apparent density (AD) and porosity (P) (Standard UNE-EN 1097-3:1999) [27]. Volume stability (VS) was carried out in accordance with the guidelines given by the Standard UNE-EN 196-3:2017 [28]. This method determined the volumetric expansivity of the paste composed of PC/NKC.

Finally, the start and final setting time (SFST) was calculated through the Standard UNE-EN 196-3:2017 [28].

2.2.3. Technological Tests for the Qualitative Assessment of Natural (NKC) and Calcined Kaolinitic Clays (CKC)

A chemical analysis was carried out to determine the technological quality (CATQ) of natural (NKC) and calcined kaolinitic clays (CKC) to study the pozzolanic properties of these samples and monitor their influence on the partial substitution of Portland cement (PC). This analysis also determined the amount of SiO_2 capable of reacting with $Ca(OH)_2$, as well as the percentage of insoluble residue formed as a reaction product, the presence of sulfates, chlorides, magnesium oxide, and free lime. The reason for doing this test was the Standard UNE-EN 196-2:2014 [29].

The chemical analysis of pozzolanicity (CAP) to monitor the pozzolanic reactivity of NKC and CKC samples was performed following the guidelines of the Standard UNE-EN 196-5:2011 [30]. The fundamental criterion of this test is to determine the degree of pozzolanicity of the samples by comparing the concentrations of calcium ions (expressed as calcium hydroxide) dissolved in the solution with an amount of calcium ions capable of saturating a solution of the same alkalinity. When the amount of calcium ions is less than the saturation concentration, the analysis is considered positive, and the samples analyzed are considered to be suitable pozzolans. To determine the hydroxyl ion $[OH^-]$ concentrated in the solution, as well as the CaO the following formulas were used:

$$\left[OH^-\right] = \frac{1000 \times 0.1 \times V_3 \times f_2}{50} = 2 \times V_{3\times} f_2 \quad (1)$$

where:

- $[OH^-]$: is the concentration in hydroxyl ions (mmol/L).
- V_3: is the volume of the hydrochloric acid solution (0.1 mol/L).
- f_2: is the factor of the hydrochloric acid solution (0.1 mol/L).

$$[CaO] = \frac{1000 \times 0.03 \times V_4 \times f_1}{50} = 0.6 \times V_4 \times f_1 \quad (2)$$

where:

- [CaO]: is the concentration of calcium oxide (mmol/L).
- V_4: is the volume of EDTA solution used in the titration.
- f_1: is the factor of the EDTA solution.

Mechanical compressive stress tests (MCST) were carried out at 7, 28, and 90 days to monitor the rate of increase in the mechanical resistance of the specimens manufactured with NKC and CKC compared to the reference specimen made exclusively from Portland cement (RMS). Additionally, in the preparation of the mortar mixtures, 225 g of demineralized water (DW) and 1350 g of natural sand (NS) used as fine aggregate were selected. Table 1 provides details of the proportions of each material. The dosages used in each of the mixing projects rigorously adhered to the criteria of the Standard UNE-EN 196-1:2018 [31].

Table 1. Design of dosages of mixtures of natural kaolinite clay (NKC) and calcined clay (CKC) partially replacing Portland cement (PC).

Sample	Proportion (Ratios)			Temperature of Calcination (°C)
	NKC [1]/CKC [2]:PC [3] (%)	NS [4] (g)	DW [5] (g)	
RMS *	PC:100	1350	225	-
NKC-01-10	10:90			-
NKC-01-25	25:75			-
NKC-01-40	40:60			-
CKC-01-10	10:90			800
CKC-01-25	25:75			800
CKC-01-40	40:60			800
NKC-02-10	10:90			-
NKC-02-25	25:75			-
NKC-02-40	40:60			-
CKC-02-10	10:90			800
CKC-02-25	25:75			800
CKC-02-40	40:60			800

[1] Natural kaolinite; [2] Calcined kaolinite; [3] Portland cement; [4] Normalized sand; [5] Demineralized water. * Reference mortar sample.

The method to determine the ultrasonic pulse velocity (UPV) is a non-destructive test applied to the specimens of mortars already consolidated and is based on calculating the time an ultrasonic pulse takes to travel through each specimen. In addition to the propagation time, it also allows the calculation of the speed of the pulse. Through the data obtained, a reliable interpretation can be made of the structural makeup of the specimens, the degree of homogeneity, the influence of the materials on the interfaces, and the possible defects produced during the setting process, among other phenomena. Each stage of this test has been carried out in accordance with the Standard UNE-EN ISO 16810 [32].

To determine the UPV the following formula was used (3):

$$\mathrm{UPV}^* = \frac{\mathrm{d}}{\mathrm{t}} \tag{3}$$

where:

d: distance (km).
t: time(s).
*UPV is in km/s.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

Figure 3a–d shows several microphotographs made with an electronic microscope of the samples of natural kaolinitic clays (NKC) and calcined clays (CKC). The samples in the natural state (Figure 3a,b) have pseudo-hexagonal and tabular aspects, although they also appear as subrounded to rounded aggregates of irregular texture, exhibiting discontinuous and intermittent edges. The sizes range from very fine to thick, and their color varies from light gray to white. The surfaces of the grains have small pores of unimportant dimensions. The morphology exhibited by kaolin grains seems to indicate an alluvial sedimentary origin [33].

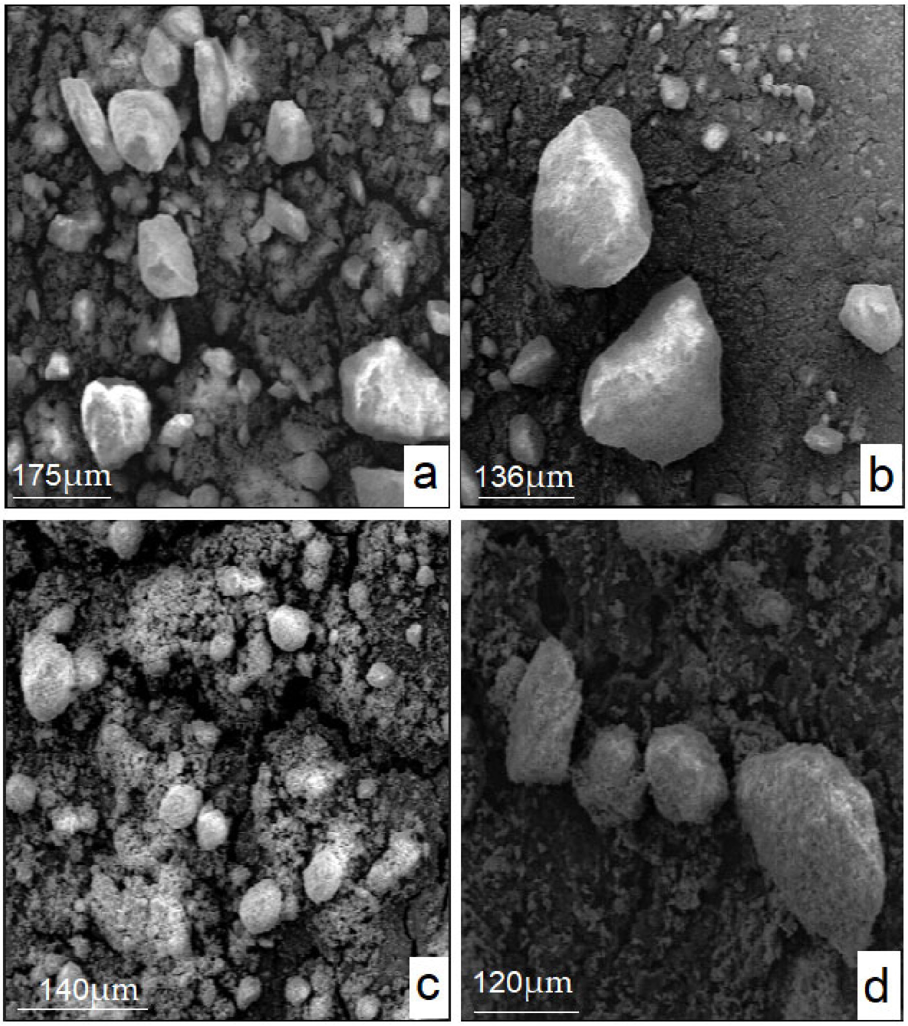

Figure 3. Microphotographs taken from samples of natural kaolinitic clays in (NKC) (**a**,**b**) and later after being calcined (CKC) (**c**,**d**).

In calcinated samples (Figure 3c,d), an increase in porosity due to heating is highlighted [34]; some of the original texture has been modified, markedly increasing the surface area of the samples [35].

3.2. X-ray Fluorescence (XRF)

The data provided by the analysis of the chemical composition of the samples and seen in Table 2 suggest three fundamental facts: high contents of SiO_2 (NKC-01: 49.9%/NKC-02: 51.0%), Al_2O_3 (NKC-01: 31.5%/NKC-02: 33.5%) and high values of loss by calcination (NKC-01: 12.0%/NKC-12.1%). According to the work of the authors in [36], the samples of kaolinitic clays seem to have sufficient quality as sources of kaolin.

Table 2. Results of chemical analyses obtained by X-ray fluorescence (XRF).

Sample	Compounds in % Weight											
	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	SO_3	K_2O	MgO	P_2O_5	Na_2O	Cl	LOI *
NKC-01	49.9	31.5	2.5	1.9	0.43	0.17	0.8	0.34	0.13	0.0	0.01	12.0
NKC-02	51.0	33.5	1.0	0.3	0.27	0.56	0.54	0.23	0.08	0.0	0.0	12.1
PC [1]	17.47	5.57	3.39	64.01	0.33	4.0	1.39	0.64	0.07	0.09	-	2.41

* Loss on ignition; [1] Portland cement.

3.3. Physical Tests (PT)

Table 3 and Figure 4 detail the results obtained by granulometry analysis. It also shows the graphs with the variations in particle size distribution of the NKC-01 and NKC-02 samples.

Table 3. Details of the results of the granulometric analysis performed on the samples of natural kaolinitic clays NKC-01 and NKC-02.

Sample	Size (µm)	Retained (%)	Passing Through (%)	Percentage (%)	Size (µm)	(B.P.F.) [1] (cm^2/g)
NKC-01	32	26.3	73.7446	10	1.352	6643
	45	23.2	76.8439	50	7.309	
	63	20.5	79.4973	63.2	13.859	
	90	18.0	81.9845	90	221.703	
NKC-02	32	17.1	82.8706	10	1.215	7640
	45	14.6	85.4088	50	5.699	
	63	12.5	87.5494	63.2	9.207	
	90	10.6	89.3754	90	104.952	

Sample NKC-01	Sample NKC-02
Type of distribution: volume	Type of distribution: volume
Average diameter D[4,3]: 56.159 µm	Average diameter D[4,3]: 37.716 µm
Distribution width (10–90%)/50%: 30.150	Distribution width (10–90%)/50%: 18.204
Mode: 4.551 µm	Mode: 4.371 µm

[1] Blaine particle fineness.

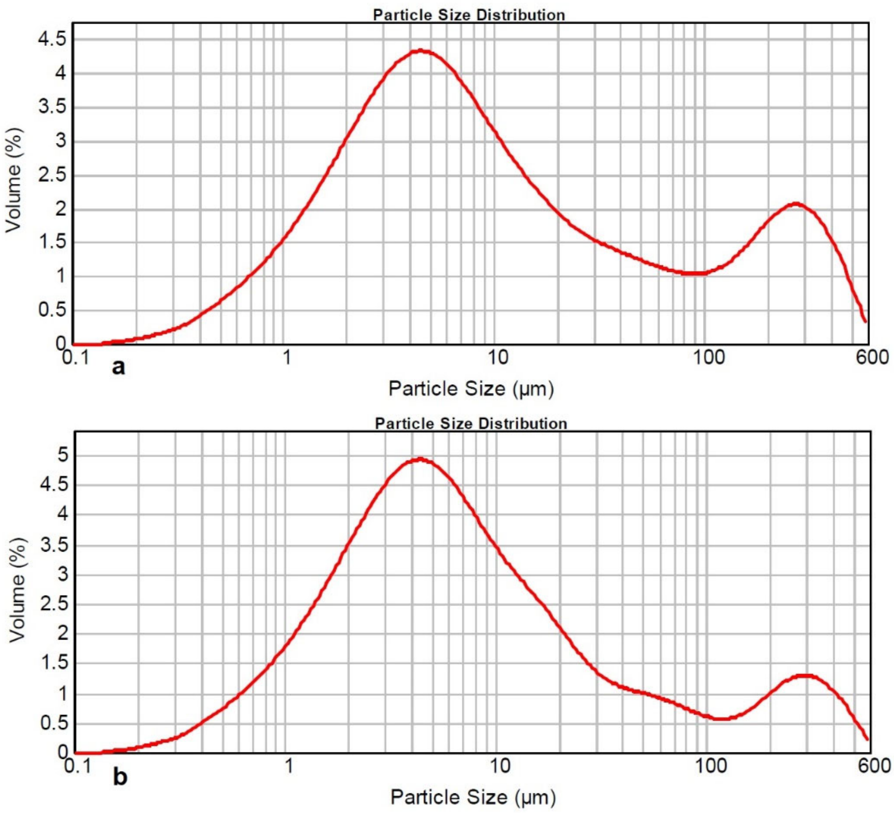

Figure 4. Granulometric distribution obtained by granulometric analysis of natural kaolinitic clay samples; (**a**) NKC-01 and (**b**) NKC-02.

Table 4 shows the remaining results of the physical properties of natural kaolinitic clay samples, such as real density (RD), apparent density (AD), and porosity (P). On the other hand, the results of the study of volume stability (VS) start and final setting time (SFST) are presented in Table 5.

Table 4. Results of the calculation of the real density, apparent density, and porosity of the samples of natural kaolinitic clays NKC-01 and NKC-02.

Sample	Mass (g)	Volume (cm^3)	R.D. [1] (g/cm^3)	A.D [2] (g/cm^3)	Porosity (%)
NKC-01	10	57.23	2,74	0.172	0.913
NKC-02	10	58.76	2,73	0.173	0.911

[1] Real density; [2] Apparent density.

Table 5. Results of the volume stability test and the start and final setting time of the samples of natural kaolinitic clays (NKC) and calcined clays (CKC).

Sample	Volume Stability (mm)			Start and Final Setting Time	
	A [1]	C [2]	C-A	Start (min)	Final (min)
RMS [3]	0	0	0	170	230
NKC-01-10 [4]	0	1	1	160	205
NKC-01-25	0	1	1	180	225
NKC-01-40	0	0	1	230	275
NKC-02-10	0	0	0	155	215
NKC-02-25	0	1	1	160	225
NKC-02-40	0.5	0.5	0	210	225
CKC-01-10 [5]	3	3	0	165	200
CKC-01-25	0	0	0	180	215
CKC-01-40	0	1	1	190	225
CKC-02-10	0	0	0	135	205
CKC-02-25	0	0	0	150	215
CKC-02-40	0	0	0	155	220

[1] Distance measured between the tips of the needles after resting the Le Chatelier equipment for 24 h ± 30 min at 20 ± 1 °C in the wet chamber; [2] Distance measured between the tips of the needles after allowing the Le Chatelier equipment to cool to room temperature; [3] Reference mortar sample; [4] Natural diatomite at 40, 25 and 10%; [5] Calcined diatomite at 40, 25 and 10%.

According to the data of the real and apparent density, as well as the porosity, it seems that both samples have similar characteristics, which can be interpreted to mean that the geological conditions under which they were formed were influenced by the same natural factors [34,37]. Another aspect to note is that the presence of kaolinitic clays in the cement paste hardly influences the volume stability of the paste and exhibits practically insignificant values in the order of 0.5 to 1 mm (Table 5). Similarly, it seems that pastes made with NKC in which they replace Portland cement (PC) between 10 and 25% experience a significant decrease in the start and final setting time, which is even lower than Portland cement (PC). A similar but even more remarkable case occurs with pastes containing CKC (Table 5), where the start and final setting times of the process are shortened even more. This is very significant, as pozzolans usually produce the opposite effect [38–40].

3.4. Chemical Analysis of Technological Quality (CATQ)

The results of the chemical analysis of the technological quality of the samples (NKC and CKC) are shown in Table 6. The results show that these kaolinitic clays in their natural state have a high content of SiO_2 (NKC-01: 52.39%/NKC-02: 50.97%) and Al_2O_3 (NKC-01: 31.80%/NKC-02: 31.56%) that increase significantly after the calcination process between 88 and 91% and 88%, respectively. The increase of these compounds, mainly in the case of SiO_2, seems to be a consequence of the transformation process of the crystalline siliceous phase, present in the insoluble residue, to the amorphous siliceous phase, due to calcination [41]. The formation of this new amorphous phase makes the samples react even more and improves their qualities as pozzolans [42].

Table 6. Results of the chemical composition and pozzolanic quality of the samples.

Compounds	NKC-01 [1] (%)	CKC-01 [2] (%)	NKC-02 (%)	CKC-02 (%)	Limit Allowed * (%)
Total SiO_2	52.39	57.41	50.97	58.10	-
Reactive SiO_2	35.84	44.36	34.99	47.81	>25
Total CaO	0.21	0.48	0.39	0.53	-
Reactive CaO	0.0	0.39	0.03	0.47	-
Al_2O_3	31.80	36.05	31.56	35.84	<16
MgO	0.19	0.49	0.15	0.12	<5
Fe_2O_3	1.24	1.53	0.61	1.06	-
SO_3	0.01	0.01	0.01	0.01	<4
Humidity	2.33	-	2.24	-	-
IR [3]	24.59	15.62	23.35	15.82	<3
LOI [4]	11.57	0.33	11.90	0.35	-
Cl [5]	0.0	0.0	0.0	0.0	<0.1
$SiO_2/(CaO + MgO)$	130.9	59.18	94.38	89.38	>3.5

[1] Natural kaolinite; [2] Calcined kaolinite; [3] Insoluble residue; [4] Loss on ignition; [5] Chlorides; * [26].

The high values determined for reactive SiO_2 are highlighted, from which it follows that for samples NKC-01 and NKC-02 about 68.4 and 68.6%, respectively, of the total SiO_2 can have a pozzolanic reaction. In the case of calcined samples (CKC-01 and CKC-02), this percentage increases to between 77.3 and 83.3%, respectively. On the other hand, a decrease of 64–68% of the insoluble residue takes place after the calcination process of the samples, which seems to contribute to the increase in the pozzolanic properties of these kaolinitic clays [43–45]. In relation to the Loss on Ignition (LOI), a comparatively similar situation seems to occur, where the values decrease drastically by up to 2.8–3%. The total loss of moisture after calcination, added to the low contents of Cl, SO_3, and MgO, makes the samples increase their qualities as pozzolans [46].

3.5. Chemical Analysis of Pozzolanicity (CAP)

Figure 5a,b graphically shows the results of the chemical analysis of pozzolanicity (CAP) to which the samples of kaolinitic clays were subjected both in natural state (NKC-01, NKC-02) and calcined (CKC-01, CKC-02). This is in accordance with the results shown in Figure 5a, which establishes that samples NKC-01 and NKC-02 do not manifest pozzolanic properties at 8 or 15 days of research, which is deduced by the position that both occupy above the isothermal solubility curve.

According to the authors in [30], the pozzolanic capacity of a sample is determined when its location occurs below the above-mentioned curve. The low pozzolanic response of the samples analyzed in their natural state could be due to an excess of crystalline silica present in them. As already seen in Table 6, it could also be due to the presence of non-reactive organic matter [47].

A comparatively different fact occurs when the samples have undergone a calcination process (CKC-01 and CKC-02) (Figure 5b), where it is evident that the samples have acquired significant pozzolanic properties, mainly the CKC-02 sample. In both cases, there is a tendency to increase the pozzolanic properties from 8 to 15 days of testing. The cause of this increase could be found in the fact that during the calcination process, crystalline silica could be converted into amorphous silica, which is more likely to react in solution with $Ca(OH)_2$ [48]; this contribution of silica could reinforce the original contents of reactive silica (Table 6) and enhance the pozzolanic character of the samples [49]. It could also be argued that after calcination substances of organic origin and other non-reactive residues have been removed [50].

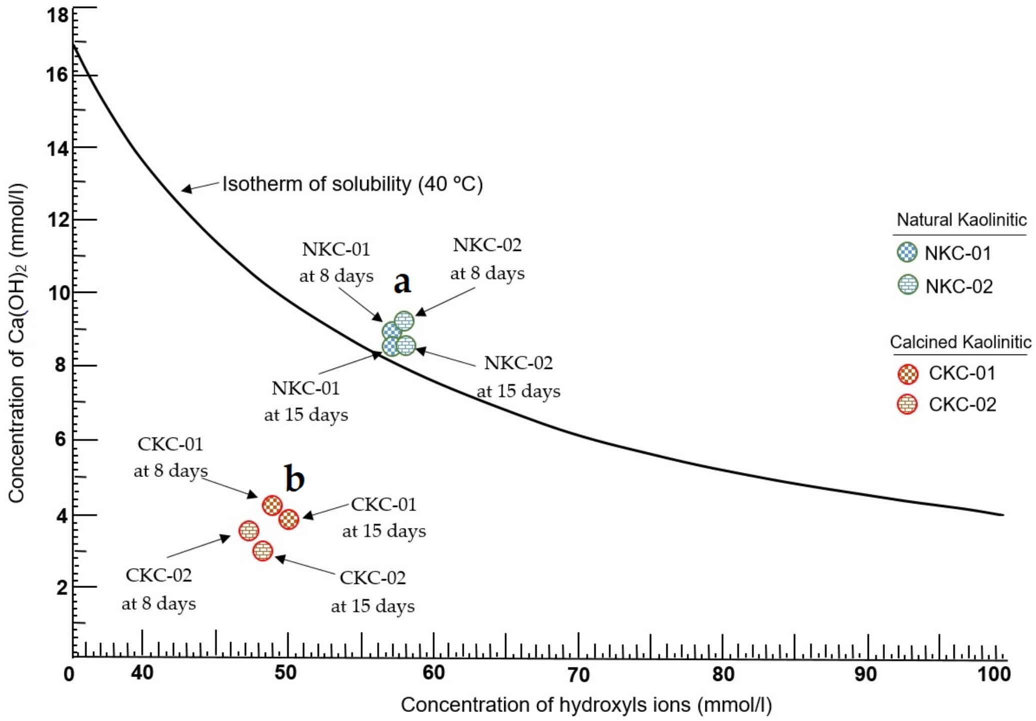

Figure 5. Evolution of the pozzolanic behavior of the samples of kaolinitic clays in natural state (**a**) and calcined (**b**) analyzed at 8 days and 15 days.

3.6. Mechanical Strength Tests (MST) at 7, 28, and 90 Days

Figure 6 shows the results of the mechanical strength test (MST) performed at 7, 28, and 90 days of setting. It seems evident that the dosages of mortar specimens with the presence of natural (NKC) and calcined (CKC) kaolinitic clays, in proportions of 10, 25, and 40%, contribute to the gain of mechanical strength throughout the period of research. During the monitoring of the mechanical behavior, it is noted that the specimens made with 10% of NKC and CKC are those that have higher values of mechanical resistance, followed by those formulated with 25% and 40%. The specimens made with each mixture maintain a homogeneous mechanical behavior over time, although the case of the sample NKC-01/PC 10/90% is highlighted, as it practically equals the value of mechanical resistance of the reference specimen (RMS) at 90 days of age.

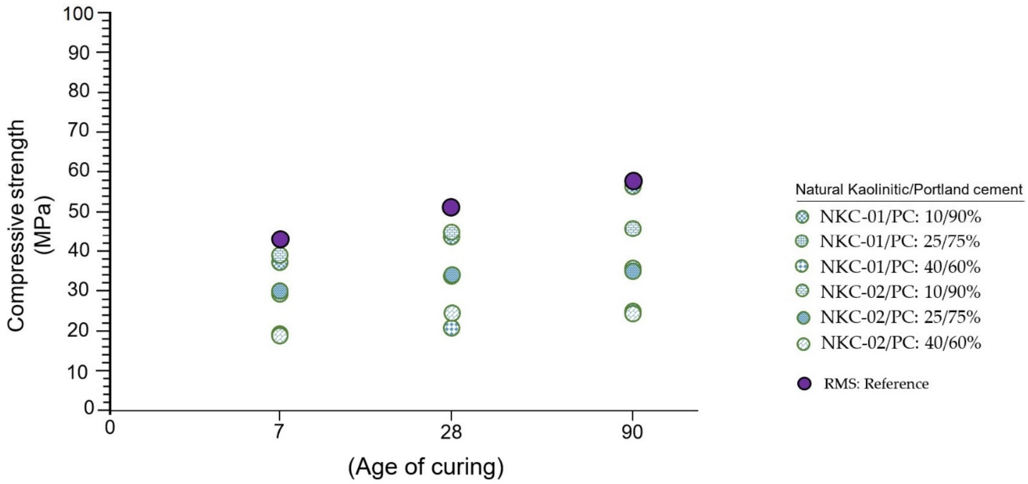

Figure 6. Mechanical behavior of samples of mortar specimens made with natural kaolinitic clay (NKC) at 7, 28, and 90 days.

Figure 7 shows the evolution of the mechanical compressive strengths of mortar specimens manufactured with standardized amounts (10, 25, and 40%) of calcinated kaolinitic clay (CKC). In relation to what is observed in Figure 6, the scenario is very different; the pozzolanic behavior of the calcined samples positively influences the hydraulic reactivity of the CKC-PC interface, leading to significant values of compressive strength from 7 to 90 days. In the specific case of the 7 days of curing, note how all specimens made with 10 and 25% CKC have equaled or exceeded the reference specimen (RMS); this trend is still observed at 28 and 90 days, where even specimens with a proportion of 40% CKC equal or significantly approach the RMS.

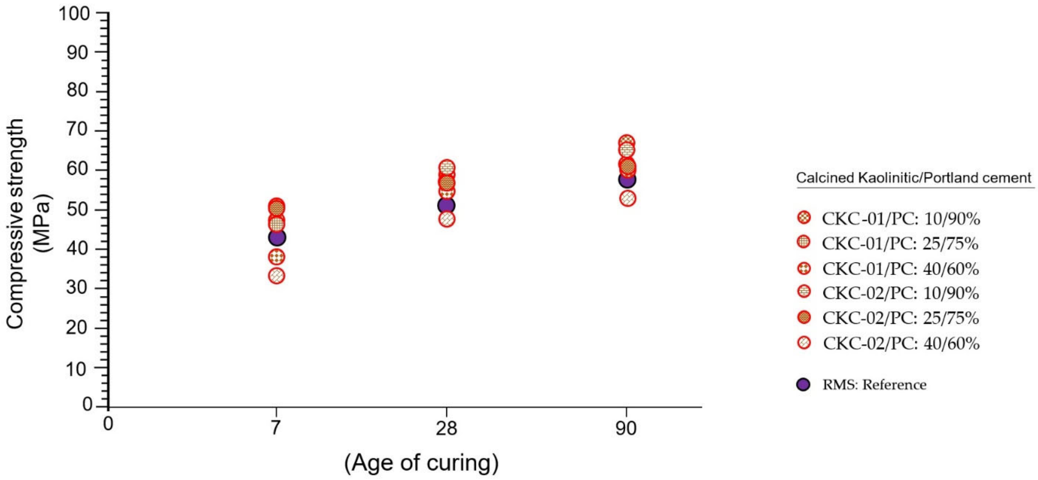

Figure 7. Results of the tests of mechanical resistance to compression obtained from the study of specimens made with calcined kaolinitic clay (CKC) at 7, 28, and 90 days.

This seems to show that several factors analyzed above, such as the chemical composition and physical properties of the samples, improve significantly after the calcination process, which not only influences the pozzolanic reactivity but also the hydraulic reactivation, which in turn implies an improvement in the mechanical properties of the mortar specimens. Researchers have demonstrated these anomalous increases in mechanical resistance in their investigation with other pozzolans such as natural zeolites [51], dacitic tuffs [52], volcanic ash [53], and bentonite clays [54].

The data in Figures 6 and 7 show the Resistance Activity Index (RAI) calculated for all the mortar specimens dosed with natural kaolinitic clay (NKC) and calcined clay (CKC) studied in this work (Table 7). The calculation was made through Formula (4), by which the values of mechanical resistance to compression of all the specimens are related to the reference (RMS); the resulting values of the calculation equal to or greater than 75% are considered positive.

$$\mathrm{RAI} = \frac{V_{1\times \mathrm{f}_{(\%)}}}{\mathrm{V}_2} \tag{4}$$

where:

- V_1: Mechanical compressive strength (MPa) of mixed mortar specimens produced according to NDT/PC and CDT/PC formulations.
- V_2: Mechanical compressive strength (MPa) of reference mortar specimens.
- $f_{(\%)}$: Percentage factor with a value of 100%.

The assessment of the data that appears in Table 7 establishes an RAI value pattern of behavior that depends directly on the percentage of kaolinitic clay present in the mortar mixtures, either in the natural state (NKC) or calcined (CKC). On this basis, it is observed that the specimens with 10% NKC are the only ones capable of exceeding 75% of the normalized RAI calculated for the periods of 7, 28, and 90 days; and although the values calculated for NKC at 25% are quite close to the reference limit value, the truth is that it does not reach it at any of the study ages, in the same way as NKC at 40%. However, specimens that include calcined kaolinitic clay (CKC) at 10, 25, and 40% in their composition not only reach the limit value of the RAI but also exceed it abnormally from initial curing periods up to 90 days. The calculation of the Resistant Activity Index (RAI) has once again permitted the recording of the criteria established in this work regarding the influence of the chemical constitution, porosity, specific surface, and pozzolanic activity of the samples studied and their increase once they have been subjected to high normalized temperatures. The papers of Presa et al. [55], Martín et al. [56], and Rosado et al. [57] describe similar conclusions that support the arguments discussed in this research.

Table 7. Calculation of the values of the Resistance Activity Index (RAI) from the mechanical resistances of the mortar specimens manufactured with NKC and CKC with 10, 25, and 40%.

Sample	7 Days of Curing		28 Days of Curing		90 Days of Curing	
	Compressive Strength (MPa)	RAI [1] Calculated (%)	Compressive Strength (MPa)	RAI Calculated (%)	Compressive Strength (MPa)	RAI Calculated (%)
RMS [2]	42.7	-	51.6	-	57.8	-
NKC [3]-01-10	37.1	86.9	44.0	85.2	56.1	97.05
NKC-01-25	29.7	69.6	33.8	65.5	35.9	62.1
NKC-01-40	19.5	45.7	20.8	40.3	24.5	42.4
CKC [4]-01-10	47.8	111.9	59.0	114.3	66.4	114.9
CKC-01-25	46.7	109.4	56.9	110.3	61.7	106.7
CKC-01-40	38.0	89.0	54.5	105.6	60.1	104.0
NKC-02-10	39.2	91.8	45.9	89.0	48.0	83.04
NKC-02-25	29.8	69.8	33.8	65.5	35.7	61.8
NKC-02-40	18.8	44.02	24.5	47.4	24.8	42.9
CKC-02-10	51.2	119.9	60.2	116.7	64.7	112.0
CKC-02-25	50.9	119.2	56.7	109.9	60.3	104.3
CKC-02-40	33.9	79.4	47.9	92.8	52.2	90.3

[1] Resistant activity index; [2] Reference mortar sample; [3] Natural kaolinitic clay (10, 25 and 40%); [4] Calcined kaolinitic clay (10, 25 and 40%).

3.7. Ultrasonic Pulse Velocity (UPV)

Table 8 shows the values obtained by calculating the UPV on mortar specimens containing natural kaolinitic clay (NKC) and calcined clay (CKC) with proportions of 10, 25, and 40%. As can be seen, the lowest value of the propagation time of the ultrasonic wave corresponds to the reference specimen (RMS). Specimens made with only 10% NKC and CKC are very close to the value of the ultrasonic pulse propagation time of the reference specimen (RMS) [55]; however, a growing increase in propagation time can be observed as the percentage of natural (NKC) and calcined (CKC) kaolinitic clays in the specimens increases, being comparatively higher in formulas with 25 and 40%, respectively. Regarding the calculated ultrasonic pulse velocity, there is an inverse relationship is established with respect to the UWPT, meaning that the values tend to decrease when the percentages of NKC and CKC increase in the specimens [58]. Furthermore, the formulas with 10 and 25% have higher values regarding the velocity parameter. According to the results shown in Table 8, it seems that the cause of this behavior lies in the complex composition of the kaolinitic clays themselves, mainly in the mineral, chemical, pozzolanic properties, porosity, and calcination conditions [59–61]. This heterogeneity inherent to the mass of the specimens studied is more marked as the percentage of NKC and CKC increases.

Table 8. Ultrasonic wave propagation time (UWPT) and ultrasonic pulse velocity (UPV) of the samples.

Samples	UWPT [1] (µs)	UPV [2] (km/s)
RMS	36.33	4.40
NKC [1]-01-10	36.73	4.36
NKC-01-25	39.20	4.08
NKC-01-40	41.47	3.86
CKC [2]-01-10	37.80	4.23
CKC-01-25	39.30	4.07
CKC-01-40	40.13	3.99
NKC-02-10	37.57	4.26
NKC-02-25	39.63	4.04
NKC-02-40	41.40	3.86
CKC-02-10	36.83	4.34
CKC-02-25	38.63	4.14
CKC-02-40	40.50	3.95

[1] Ultrasonic wave propagation time; [2] Value of Ultrasonic Pulse Velocity calculated.

4. Conclusions

The samples of natural kaolinitic clays (NKC) are characterized by their high contents of SiO_2 (>50%) and Al_2O_3 (>30%); However, despite this, they do not have pozzolanic behavior at 8 or 15 days. Nevertheless, once the samples were subjected to the calcination process, the pozzolanic properties manifested and increased markedly for the test periods. The reason for this behavior could be found in the highly crystalline nature of the silica present in the natural sample, which is not prone to react; however, after the calcination process, it seems that this silica passes into its amorphous phase, making it more reactive.

Kaolinitic clays, both natural (NKC) and calcined (CKC), at 10, 25, and 40%, contribute to the increase of the mechanical resistance of mortar specimens from 7 to 90 days. In the case of NKC at 10%, the gain is very positive in relation to the formulas of 25 and 40%. However, the increase in mechanical resistance grows exponentially when the kaolinitic clays have been calcined (CKC). It is significant that at 7 days, the specimens with CKC at 10 and 25% equal or exceed the value of the resistance of the reference specimen; this phenomenon continues to manifest at 28 and 90 days of curing, a period in which specimens with 40% formulations also match the mechanical strength of RMS.

Specimens made with NKC only exceed 75% of the Resistant Activity Index when their proportion was 10%, a fact that is different from what happens with specimens containing CKC in which all calculated RAI values significantly exceed the normalized limit value.

The nature and proportion of the kaolinitic clays (NKC and CKC) used in this research seem to cause an increase in the propagation time of the ultrasonic wave and a decrease in the speed of the ultrasonic pulse through the specimens, which depends directly on the proportion of NKC and CKC in the specimens. Therefore, specimens with a content of 10% NKC and CKC are those that behave closest to the reference specimen (RMS).

All of the above emphasizes that the materials analyzed in this research could not only be capable of replacing Portland cement in a standardized way but could also be used to improve eco-efficient pozzolanic cement that is more environmentally friendly, therefore reducing the emission of greenhouse gases into the atmosphere and contributing to the process of reversing climate change. Furthermore, for industrial processes, costs could be comparatively lower due to the use of geologically abundant and easily accessible natural materials.

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