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Bentonite Clays from Southeastern Spain as Sustainable Natural Materials for the Improvement of Cements, Mortars and Concretes

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Abstract: The effects of global climate change are becoming more evident and accelerating at an unprecedented pace. For this reason, human activities urgently need a paradigm shift to stop this entropic process before the consequences become irreversible. In this sense, the use of highly eco-efficient materials aimed at conveniently neutralizing CO_2 greenhouse gas emissions entering into the atmosphere can contribute significantly to mitigating and reversing this process. This work aims to demonstrate the positive effects obtained when Portland cement is partially replaced by bentonite clays of volcano-sedimentary origin. The samples were initially characterized by various methods, such as Thin-Section Petrographic Study (TSP) and the analysis of mineral phases with XRD, chemical composition was determined via XRF, and morphological analysis was determined via scanning electron microscopy (SEM). To determine the technical properties of the samples, a qualitative chemical analysis (QCA) was performed, as well as a chemical analysis of pozzolanicity (CAP) at 8 and 15 days, respectively, and a study of the mechanical compressive strengths at 2, 7, 28 and 90 days. Characterization studies using TSP, DRX, FRX and SEM established that these bentonite clays have a complex mineralogical variety, composed mainly of smectite, mordenite, plagioclase and biotite, as well as altered volcanic glass and sericite. The results of the qualitative chemical analysis establish that more than 93% of the SiO_2 present in the samples is reactive. Chemical analysis of pozzolanicity (CAP) showed significant pozzolanic behavior in all samples analyzed at both 8 and 15 days, while mechanical tests highlighted significant increases in mechanical strengths, with maximum values varying between 52.2 and 70.6 MPa at 90 days. These results show that the materials can be used as quality pozzolans for the manufacture of cements, mortars and concretes, which could be considered as a favorable factor and, therefore, relevant in the management and control of greenhouse gas emissions responsible for the deterioration of the environment.

Keywords: bentonite clays; pozzolanicity; Portland cement; sustainability; environment

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1. Introduction

Bentonite has been known since ancient times, and with an increase in the understanding of its properties as well as the emergence of new technologies, its use has increased considerably in a variety of applications in diverse and different fields. For example, in medicine, many authors have mentioned the role of bentonites in detoxifying the human body, improving the quality of hair and skin, treating ulcers and the gastro-intestinal tract. They also allude to the use of bentonites to heal kidney problems, as an antibacterial agent, in the maintenance of bones, in therapies aimed at alleviating the effects of cancer, as well as inflammation in general [1–4]. The use of bentonites in the pharmaceutical industry has been described by numerous modern authors [5,6], and the use of these materials in the field of cosmetics has also been highlighted [7,8]. Bentonites are used consistently and standardized in animal feed in the form of additives, specific products and compounds [9–11]. The role of bentonites in the process of refining and the catalytic cracking of petroleum is well known [12–14]. However, one of the most widespread uses is in the drilling of wells during prospecting and the exploration of metallic, non-metallic and gas–petroleum deposits; In these operations, bentonites play a very important role in the lubrication of the drill bit and walls of the well, as well as in the suspension and extraction of the rock debris accumulated at the bottom. Sodium bentonites are usually the most widely used for these purposes, however, with the improvement of activation techniques, calcium bentonites are also being used effectively [15–18]. The effectiveness of bentonite in soil decontamination has been documented given its adsorption capacity of certain metals such as cesium [19], copper [20] and arsenic [21]. It is also effective in immobilizing municipal solid waste saturated with heavy metals and harmful organic materials [22], as well as in improving soil microbial properties [23]. Bentonites are widely used in enology for the clarification of wine due to their property of eliminating the unstable proteins that cause the characteristic turbidity in the early stages of the manufacturing process [24]. In addition, it has been found to be effective in the extraction of phenols from red wine [25], as well as in the correction of protein and tartaric instability [26]. Bentonites are in high demand in cement production as they can replace it in the clinkerization process to improve its pozzolanic properties and reduces the emission of CO_2 into the atmosphere [27], with increases in mechanical strengths [28], physical and chemical stability, as well as resistance to acid attack [29,30]. It has also been documented that the benefits of bentonite in its natural state can be markedly increased with the use of modified bentonites [31]. Despite the uses and advantages of the use of natural materials such as bentonite in the preservation of the environment, some authors such as Li et al. [32] propose that other types of binders such as the so-called supersulfate cement (SSC) guarantee low carbon emissions. In the same line of research, Liao et al. [33] have proposed a method to improve the flowability, setting time and compressive strength of supersulphate cement, establishing its quality not only for the environment but also in engineering applications.

This work was carried out in the outcrops of bentonite that lie at an unexplored point to the west of the San José-Los Escullos zeolite deposit, located within the Caldera de Los Frailes in the southeast of Spain (Figure 1), and the central target is the investigation of the mineral, chemical, pozzolanic and technological properties in its natural state to test its ability to partially replace Portland cement in mortars. The results obtained in this research could constitute a guide for the correct selection of very abundant and easily accessible natural materials that contribute to neutralizing the emission of CO_2 and other waste that is highly harmful to the environment.

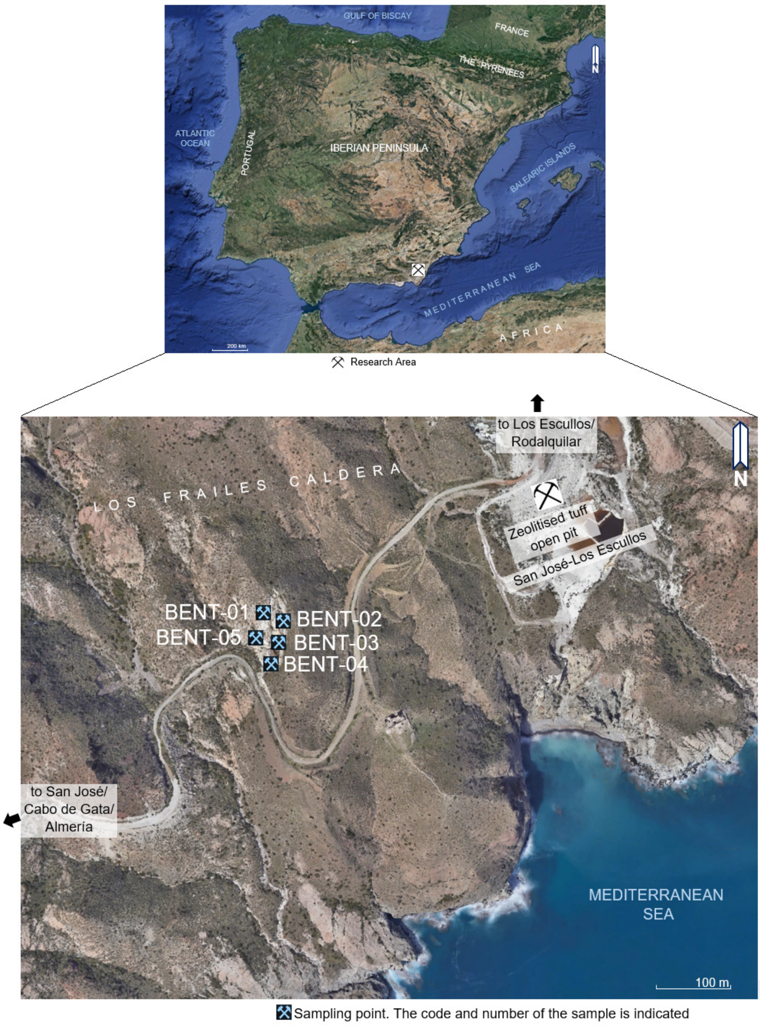


Figure 1. Location of the research area [34].

2. Materials and Methods

2.1. Materials

The samples selected to carry out this study come from an outcrop located 695 m WSW of the San José-Los Escullos zeolite deposit, in the central part of the Caldera de Los Frailes; this has been an unexplored area until now. 5 samples weighing 10 kg each were chosen and sampled in the study area by the lithogeochemical sampling of outcrop fragments. The samples are made up of altered bentonite of tuffaceous composition; with predominantly light gray, beige, yellow and white colors; and friable and not very compact in appearance, due to breccia materials altered to bentonite being interspersed (Figure 2).

In this study, a Portland cement (PC) Type 1, 42.5 N, of normal strength, with the characteristics and parameters as indicated in the Standard UNE-EN 197-1:2011 [35], was used in order to produce mixed mortar specimens composed of a standardized mixture of PC with bentonite, in a ratio of 70:30% and 75:25%, respectively. Normalized sand (NS) of the Normsand-CEN EN 196-1 type was used as a fine aggregate in this work.

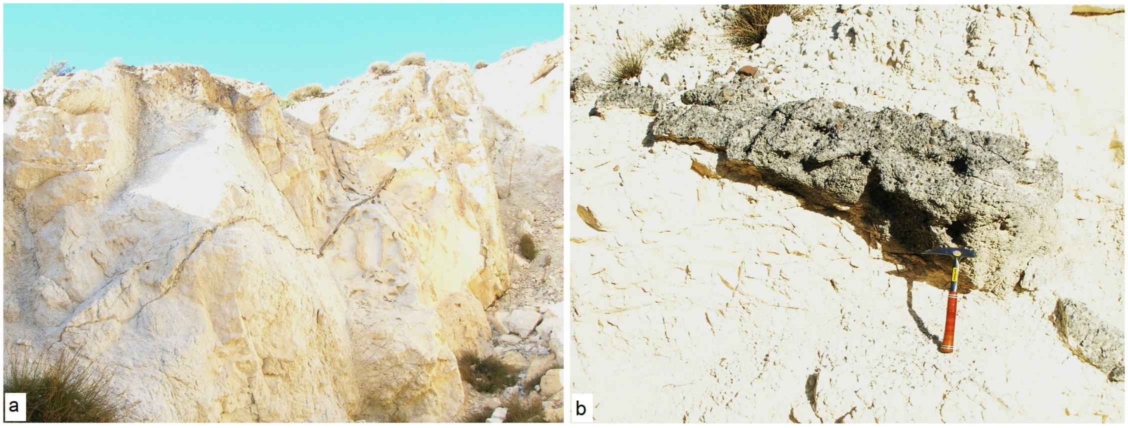


Figure 2. Partial views of bentonite outcrops in the research area: (**a**) reddened bentonite on the north-eastern side; (**b**) section of a lapilli horizon lying concordantly within the bentonite sequence.

2.2. Methods

A mineral analysis with transmitted light was carried out to determine the petrographic mineral phases present in the samples, as well as to study the textures, morphology, intergranular relationships, matrix characteristics, pseudomorphic substitutions, degrees of the mineral mesostasis reaction and secondary alteration products. In the development of this study, a microscope of the brand "Leica DM600M Scope" was used, equipped with a DTA-13 system of monochromating filters of visible and infrared light for 13 wavelengths, from 400 nm to 1000 nm, at intervals of 50 nm. The microscope is integrated into a Cameva Complex, owned by the Universidad Politécnica de Madrid and AITEMIN (Asociación para la Investigación Industrial y el Desarrollo de los Recursos Naturales). This microscope also has a LAS-CS System and an automated Märzhäuser stage integrated into the DELL station. In this research, high and low reflectance "Ocean Optics" standards were used as references for the measurement of VNIR spectra. Aphelion software was used for image processing.

An X-ray diffraction (XRD) study was developed to determine the crystalline mineralogical phases present in the investigated samples, as well as to distinguish and describe non-crystalline phases such as volcanic glass and other amorphous compounds. To carry out this analysis, the crystalline powder method (PTE-RX-004) was applied. The measurements were made with PANalytical's XPERT PRO MPD equipment, with a copper tube (45 kV, 40 mA), a graphite monochromator and an automatic aperture. For data acquisition, PANalytical's X'Pert Data Collector 5.1 (5.1.0.156) was used. In addition, HighScore 3.0.4 software (PANalytical), PDF-2 databases (ICDD) and CODJanuary2012 were employed for data processing. The equipment used belongs to the Escuela Técnica Superior de Ingenieros de Minas y Energía of the Universidad Politécnica de Madrid.

To determine the chemical composition of the samples analyzed in this work, the XRF method was utilized, whereby the contents of SiO_2, Al_2O_3, CaO, Na_2O, K_2O, MgO and Fe_2O_3, necessary for the objectives set in this research, were determined. To carry out this test, the Philips PW 1404 was employed, equipped with a collimator to reduce the angle of divergence of the X-rays. The radiation intensity of the sample ranged from 10 to 100 kV. At the same time, a monochromator filter was used to isolate the radiation and set a suitable wavelength for identification. A phase of grinding and conditioning of the samples was carried out up to 200 meshes. An amount of 6–8 g was mixed with 1.5 mL of elbaite. It was then dried at room temperature for 5 min. An analysis tablet with a diameter of 5 cm was manufactured. To determine the loss on ignition (LOI), 1 g of sample was utilized.

A scanning electron microscopy (SEM) study was carried out in this research to determine the morphological, structural and textural characteristics of the samples analyzed. This research also aims to study the process of the formation of new secondary mineral phases from the zeolitization and bentonitization of pre-existing mineral species, which due to their characteristics provide pozzolanic properties to the samples. To carry out this analysis, a Hitachi S-570 electron microscope was used from the Central Laboratory of the Escuela Técnica Superior de Ingenieros de Minas y Energía de la Universidad Politécnica de Madrid. The equipment has a Kevex-1728 analyzer, a BIORAD Polaron, a power supply for evaporation and a Polaron SEM coating system. Winshell and Printerface were used to manage the information obtained and to obtain the microphotographs. The samples were previously reduced to a diameter of 0.2–0.5 cm. They were then covered with a layer of graphite and placed in the microscope specimen sampler for study.

The qualitative chemical analysis, of a technological nature, was carried out to establish the capacity and quality of the samples studied to replace Portland cement by 25 and 30%. In this analysis, the contents of the following compounds were found: total and reactive silica, total and reactive calcium oxide, aluminum oxide, magnesium oxide, sulphates and insoluble residues present. At the same time, the $SiO_2/(CaO + MgO)$ and $SiO_2 + Al_2O_3 + Fe_2O_3$ ratios were calculated. This analysis was carried out following the indications of the Standard UNE-EN 196-2-2014 [36].

A pozzolanicity chemical test was performed to determine the pozzolanic nature of the samples in this study, and their ability to react with $Ca(OH)_2$ was determined in a solution at 40 °C. The samples were initially crushed to a grain size of less than 50 μm. The test procedure was developed considering the requirements of the Standard UNE-EN 196-5:2011 [37]. Specifically, an amount equivalent to 100 mL of distilled water was taken and heated to 40 °C for 60 s, to which 20 g of sample made of bentonite and Portland cement were added. Two solutions were prepared simultaneously, one of them was to be analyzed at 8 days, while the other was to be analyzed at 15 days. After both periods of time, the solutions were filtered and evaluated. After the titration, the concentration of hydroxyl ions (OH^-) and the concentration of calcium oxide (CaO) were determined. The test is considered positive if a calcium hydroxide concentration lower than the saturation concentration is obtained.

To perform the mechanical tests, the samples were previously subjected to grinding to obtain an adequate granulometry. An Alas brand jaw crusher was used to ensure particle sizes of about 3 cm. A second crusher of the brand Controls was used to reduce the particle size by up to 1 cm. In a third and final phase, a Siebtechnik vibratory mill was used to obtain particle diameters close to 63 μm. The development phases of this test were in accordance with the indications of the Standard UNE-EN 196-1:2005 [38]. Subsequently, several series of mortar specimens made of standardized diversified mixtures of bentonite and Portland cement were prepared. In these mixtures, a portion of the Portland cement was partially replaced by bentonite by 25% and 30%, respectively. Details on the number of mortar specimens, materials and their proportions within the mixtures are listed in Table 1.

Table 1. Standard proportions of bentonite, Portland cement, standard sand and water in mixtures used for the manufacture of mortar specimens.

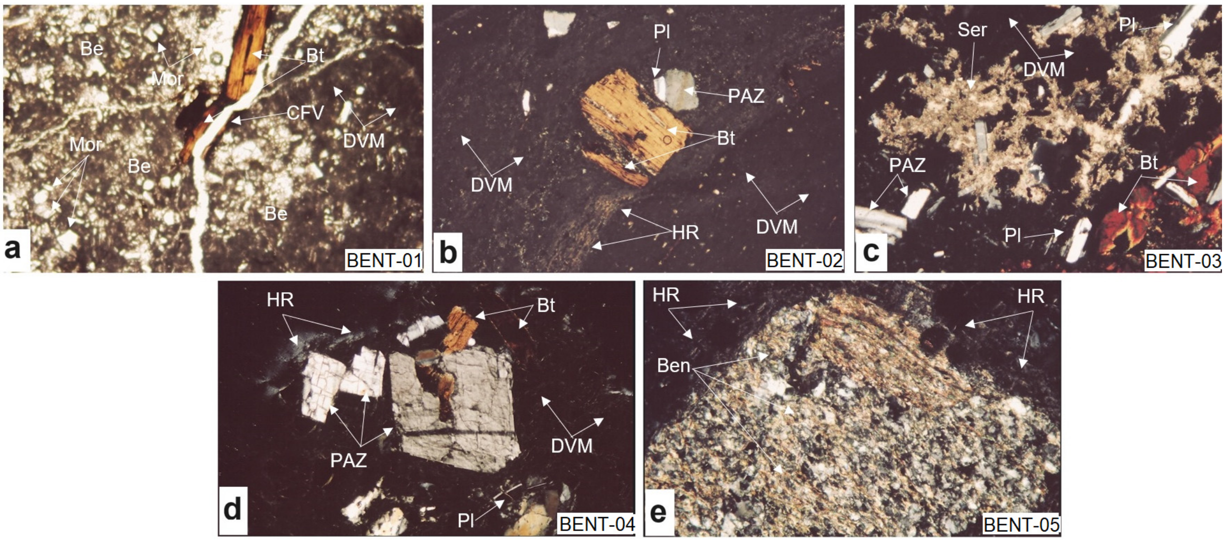
Sample	Component Ratios				
	BENT [1]:PC Formulations I (%)	**BENT:PC Formulation II (%)**	**PC [2] Formulation III (%)**	**Natural Sand (g)**	**Distilled Water (g)**
RMS [3]	-	-	100		
BENT [1]/PC-01 [4]					
BENT/PC-02					
BENT/PC-03	75:25	70:30	-	1350	225
BENT/PC-04					
BENT/PC-05					

[1] Bentonite sample; [2] Portland cement; [3] Specimen mortar made with Portland cement as reference; [4] Specimen mortar made of a standardized mixture of bentonite and Portland cement.

3. Results and Discussion

3.1. Thin-Section Petrographic Study Using (TSP)

Figure 3a–e show the microphotographs obtained by studying the petrographic thin sections using transmitted light. According to this study, several predominant mineral phases were detected, such as smectite (Sme) and mordenite (Mor); in addition, biotite (Bt), plagioclase (Pl) and sericite (Ser) are present. All the mineral species mentioned coexist on a visibly devitrified vitreous matrix (Figure 3a–d). The plagioclase and pyroxene crystals are altered to mordenite and sericite (Figure 3a,c), and are almost entirely replaced by pseudomorphism. Some late veins re-filled with carbonate are visible (Figure 3a). Some reaction processes between the vitreous matrix and biotite crystals and the smectite masses are observed (Figure 3b–d). The textures present in the studied samples are of porphyry, glomeroporphyry, poikilitic and substitution typology [39].



Bt: Biotite; Pl: Plagioclase; Be: Bentonite; Ser: Sericite; PAZ: Protomineral altered to zeolite; DVM: Devitrified vitreous matrix altered to bentonite; CFV: Carbonate-filled vein; RH: Reaction halos.

Figure 3. Microphotographs obtained by studying thin petrographic sections; (**a**–**e**) represent samples BENT-01 through BENT-05. The images were taken with Obj x.2.5 and crossed nicols (Nx).

3.2. Mineralogical Phase Study Using XRD

Figure 4 highlights the different phases present in the samples analyzed. The main and most developed peaks indicate the smectites as the dominant phases associated with the mordenite. The subordinate phases consist of plagioclase, orthoclase, biotite, quartz, kaolinite and sericite. An amorphous glass phase, abundant and altered, makes up the matrix of these samples.

3.3. Chemical Composition Study Using XRF

Table 2 lists the results of the XRF analysis of the samples analyzed in this research, from which a calco-alkaline chemism can be deduced [40,41]. The predominance of SiO_2 is highlighted in all samples; however, they are particularly high in samples BENT-01, BENT-04 and BENT-05, while the lowest level was calculated in sample BENT-03. However, these values are far from below average. It is observed that the behavior of some compounds in the samples appear to be variable; for example, in the samples BENT-01, BENT-04 and BENT-05 the ratio between the average contents of SiO_2:Al_2O_3 = 4.66, while for the samples BENT-02 and BENT-03, this ratio is equal to 3.92, indicating that the latter have undergone a greater bentonitization process than the former, which have undergone a marked zeolitization process [37]. In the alkaline and alkaline-earth compounds present in the samples BENT-01, BENT-04 and BENT-05, it is observed that the ratio of

Na_2O:CaO = 2.77, MgO:K_2O = 1.07 and Na_2O:MgO = 1.29, which also confirms the predominance of zeolitization over bentonitization. In the case of samples BENT-02 and BENT-03, the behavior of these compounds appears to be very different, that is, Na_2O:CaO = 1.15, MgO:K_2O = 15.75 and Na_2O:MgO = 5.78, which establishes a marked magnesium chemism, which characterizes the bentonites of some sectors of the interior of the Caldera de Los Frailes [42].

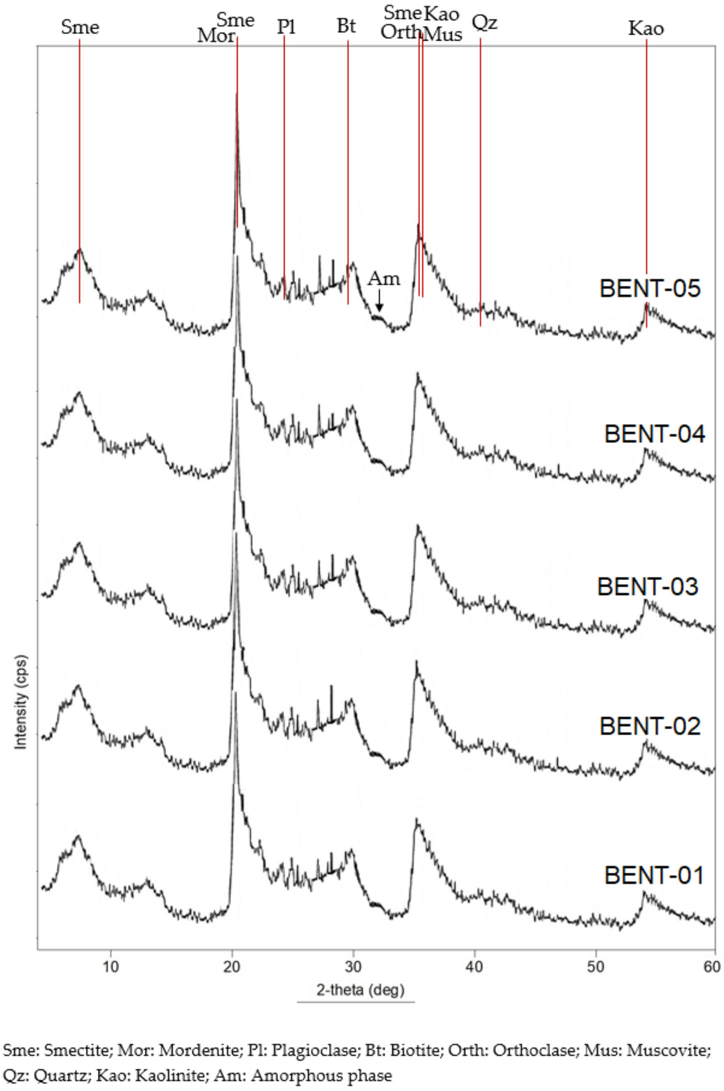


Figure 4. Diffractograms obtained from the study of samples using XRD.

Table 2. Results obtained by X-ray fluorescence.

Sample	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	Fe_2O_3	TiO_2	LOI *	Si/Al
BENT-01	64.83	13.91	1.07	2.21	2.13	2.40	1.77	0.115	9.22	4.60
BENT-02	52.14	13.15	1.13	1.41	0.291	7.63	2.69	0.121	19.3	3.90
BENT-03	52.92	13.63	1.15	1.23	0.678	7.65	2.77	0.122	20.6	3.88
BENT-04	64.32	13.71	1.08	3.12	2.21	2.41	1.41	0.134	11.6	4.69
BENT-05	63.01	13.59	1.11	2.77	3.13	2.12	1.75	0.119	9.4	4.63

* Loss on ignition.

Additionally, the relationship between MgO and Fe_2O_3 has been calculated for both groups of samples, obtaining ratios of MgO:Fe_2O_3 = 1.40 (BENT-01, BENT-04 and BENT-05) and MgO:Fe_2O_3 = 2.79 (BENT-02 and BENT-03). These results indicate an anomalous increase in Fe_2O_3 and MgO in the latter group of samples, which is caused by the rubefaction process that affected the bentonites of this region [43], characterized by the anomalous enthronement of Fe and Mg ions due to the effect of hot hydrothermal solutions [44].

The values calculated for the Si/Al ratio indicate a low to medium ratio (3.88–3.90 and 4.60–4.69, respectively), which shows the tendency of these bentonites to moderately to highly swell [39]. It is highlighted that for ratios of Si/Al > 4, the predominance of silica will slightly impede the swelling process [42]. For ratios of Si/Al < 4, the swelling process will be more noticeable. On the other hand, and according to Section 3.2, the presence of smectite in these samples contributes to increased swellability.

3.4. Scanning Electron Microscopy

Figure 5a–e show the series of microphotographs obtained by scanning electron microscopy, in which the habits and morphological properties of the various mineral species that make up the samples can be appreciated. The major presence of smectite (Figure 5a–e) and mordenite (Figure 5a,c,e) are main minerals highlighted, although plagioclase and biotite (Figure 5a,c) as well as amorphous glass-like materials (Figure 5d) are also observed. The textures of the different mineral species are variable, in the form of globular, fibrous aggregates and as compact masses. Both mordenite and smectite are observed to grow at the expense of protominerals, possibly pyroxenes, amphiboles and plagioclase, as well as from volcanic glass (Figure 5a,c,d).

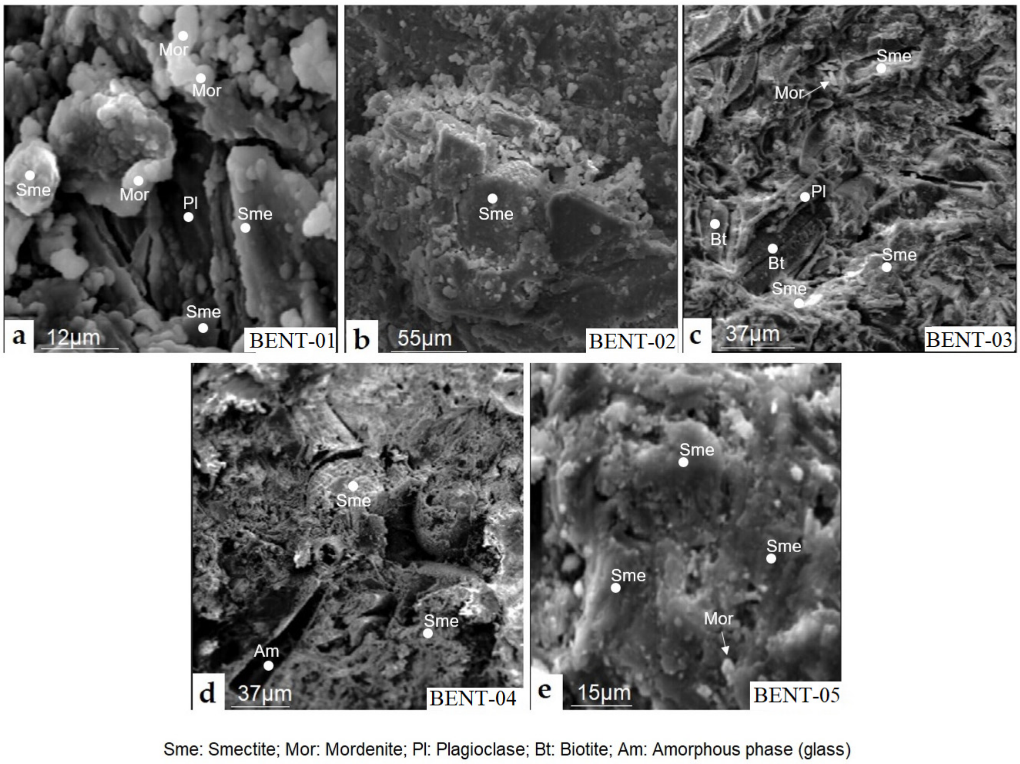


Figure 5. Microphotographs (**a**–**e**) from the electron microscope.

Several authors [45–47] consider the mineral and petrological composition of bentonites from southern Spain to be complex, most of the above-mentioned authors agree that their origin is due to the hydrothermal alteration of glass-rich volcano-sedimentary deposits that formed during the Neogene.

3.5. Qualitative Chemical Analysis

Table 3 shows the results of the study of the technical suitability of the samples analyzed by means of qualitative chemical analysis of pozzolanic quality, through which the efficacy of the materials to be mixed with Portland cement can be established [36]. The remarkable percentage of SiO_2 capable of reacting (reactive SiO_2) present in the samples analyzed is noteworthy.

Table 3. Results of the qualitative pozzolanic quality chemical test.

%	Samples					Maximum Allowed Content (%)
	BENT-01	BENT-02	BENT-03	BENT-04	BENT-05	
Total SiO_2	64.90	52.47	50.98	64.65	63.34	-
Reactive SiO_2	60.70	48.27	46.7	60.45	59.14	>25
Total CaO	1.27	1.18	1.40	1.13	1.16	-
Reactive CaO	1.22	1.15	1.37	1.10	1.13	-
Al_2O_3	13.87	13.17	13.15	13.67	13.55	<16
MgO	1.37	2.15	1.41	1.68	1.39	<5
Fe_2O_3	2.01	2.61	2.80	2.33	2.27	-
SO_3	0.02	0.02	0.01	0.03	0.01	<4
I.R.	4.2	3.7	3.78	4.41	3.73	<5
SiO_2/(CaO + MgO)	24.58	15.75	18.14	23.0	24.83	>3.5
$S_iO_2 + Al_2O_3 + Fe_2O_3$	79.78	72.05	71.57	80.65	79.16	>70

The calculation of the percentage of SiO_2 that has reacted in each case has yielded the following results: BENT-01: 93.53%; BENT-02: 92.0%; BENT-03: 91.6%; BENT-04: 93.50%; and BENT-05: 93.36%. From these results, it can be inferred that samples BENT-01, BENT-04 and BENT-05 are the ones with the highest pozzolanic reactivity; however, the remaining samples (BENT-02 and BENT-03), despite having somewhat lower values of reactive SiO_2, are also considered highly pozzolanic. The above procedure is also applied to reactive CaO, showing that in a general sense, this compound reacts between 96.06 and 97.41%, with respect to the total amount, for BENT-01, BENT-04 and BENT-05, while for BENT-02 and BENT-03, it varies between 97.45 and 97.85%, respectively.

As can be seen, the samples studied have Al_2O_3, MgO, SO_3 and insoluble residues below the permitted thresholds (Table 2) [36]. Conversely, both the SiO_2/(CaO + MgO) and $SiO_2 + Al_2O_3 + Fe_2O_3$ ratios abnormally exceed the normalized limits [36]; both results are considered positive. All that has been stated in this subsection allows us to conclude that the samples analyzed meet the quality requirements as natural pozzolanic materials.

3.6. Chemical Analysis of Pozzolanicity

Figure 6a,b graphically represents the variations in the pozzolanic behavior of the samples, both at 8 and 15 days. According to the point location of each sample in the diagram, it can be observed that they are entirely under the isothermal solubility curve (I.S.C.) at 40 °C, which represents a standardized requirement to designate the pozzolanic capacity of any material [37]. After 8 days of tests, the following samples stood out from highest to lowest degree of pozzolanic reactivity: BENT-01, BENT-04, BENT-05, BENT-02 and BENT-03 (Figure 6a).

At 15 days, a greater tendency towards a pozzolanic reaction continues to manifest in the set of samples (Figure 6b), with the pozzolanicity of each one standing out remarkably at about 8 days. The work of Rosell et al. [48] points out that early pozzolanic reactions ensure a continuity of reactions in later periods. These properties are of great importance for the appointment if materials intended to be mixed with clinker in the production process of pozzolanic cements [49–51].

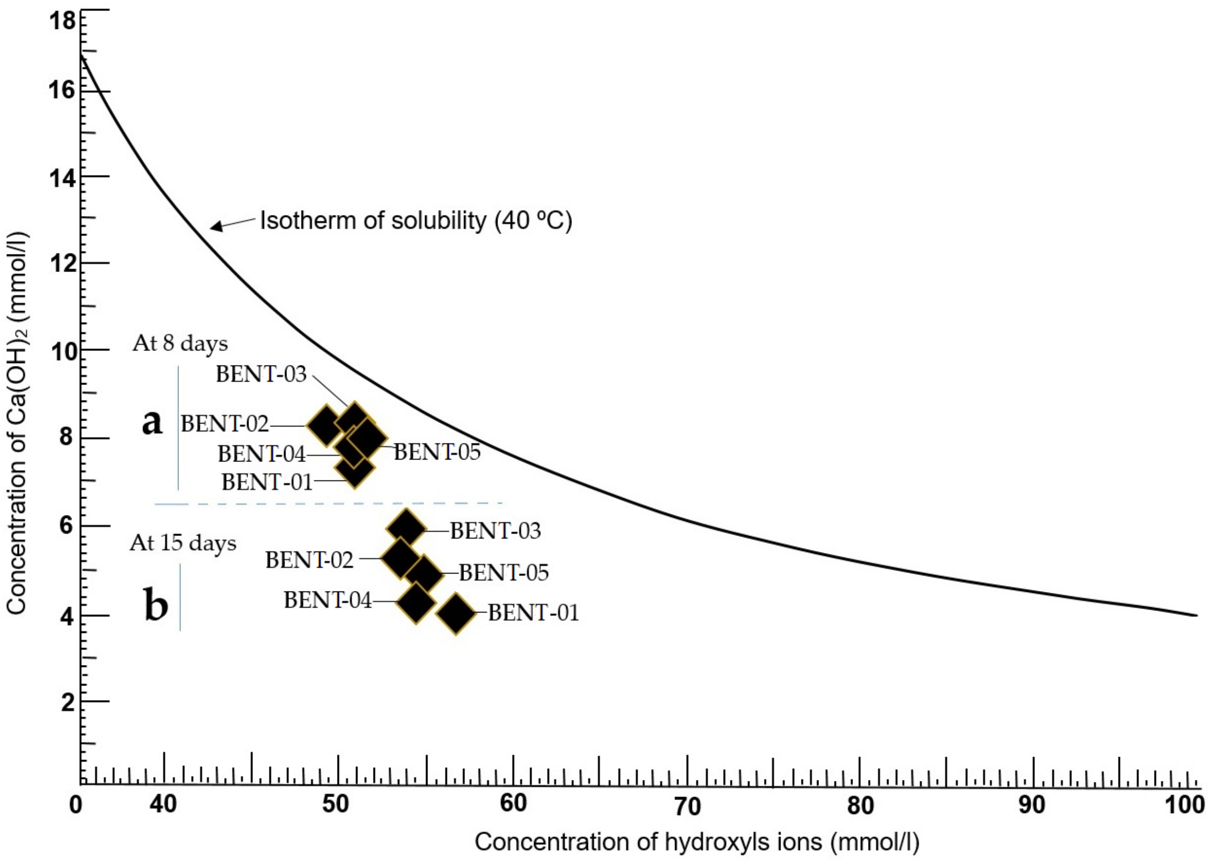


Figure 6. Variations in the pozzolanic behavior of the samples: (**a**) represents the results obtained at 8 days, while (**b**) refers to those obtained at 15 days.

3.7. Mechanical Compressive Strength Tests

Figure 7 shows the results of the mechanical compressive strength test at 2, 7, 28 and 90 days performed on specimens made of mixtures of bentonite clay and Portland cement in a normalized ratio of 75:25%. The way the graph is depicted, in a general sense, can be interpreted as an efficient development of the hydraulic reactions within the mortar specimens throughout the entire curing period, since all the strengths increase exponentially.

A notable increase in the value of mechanical strength is observed in all samples, from the initial (2 days) to the final (90 days) periods, which can be observed in the following order: BENT-01: 12.5–70.6 MPa; BENT-04: 11.9–70.1 MPa; BENT-05: 11.1–66.0 MPa; BENT-02: 10.5–56.6 MPa; and BENT-03: 10.2–52.2 MPa. Between 2 and 28 days, the reference sample (RMS: 24.5–51.0 MPa) exceeds the resistance of the rest of the samples analyzed; however, a visible approximation is observed in samples BENT-01 (49.0 MPa) and BENT-02 (48.1 MPa) at 28 days. The appearance is different after 90 days of curing, as the aforementioned samples exceed the mechanical strength value of the reference specimen. The behavior of the other samples in this period indicates that they have good quality as pozzolans, evidenced by the value of the mechanical resistance to compression which is greater than 50 MPa. Several authors, such as Costafreda [39] and Costafreda et al. [52], describe in their works how the mechanical resistance of mortars made with certain pozzolans, such as volcanic tuffs and some varieties of zeolites, can equal and exceeding the mechanical resistance of Portland cement.

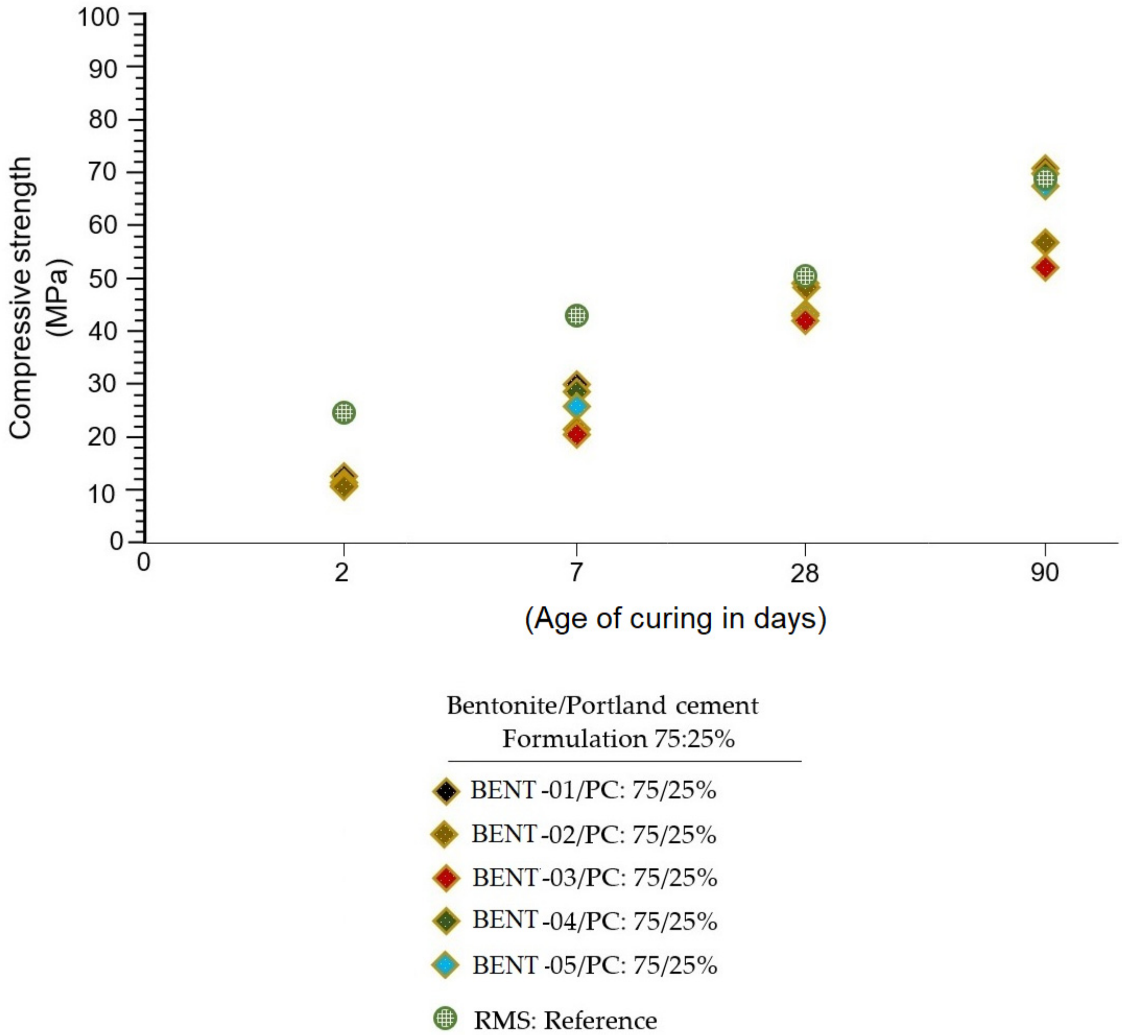


Figure 7. Behavior of mechanical strengths over time with formulations of standard mixtures of bentonite and Portland cement (BENT/PC) of 75:25%.

Figure 8 shows the results of compressive strength tests performed on specimens composed of BENT/PC in a ratio of 70:30%. An examination of the diagram shows that the behavior of the samples analyzed with respect to the reference sample does not differ too much from that observed in Figure 7. Indeed, the general trend is an increase in resistance from the earliest to the latest stages. The increase in the amount of bentonite in the mixture to 30% has produced subtle delays in the increase in resistances at 2 and 7 days, which continues to be observed in the final periods; however, even so, the BENT-04 (68.5 MPa) and BENT-01 (68.7 MPa) samples equal and exceed, respectively, the resistance value of the reference sample (RMS: 68.5 MPa) at 90 days. On the other hand, it should be noted that the remaining samples behave adequately in the curing process, given the resistance values provided.

Finally, it is established that both formulations (BENT/PC-75:25% and BENT/PC-70:30%) are suitable to produce cements, mortars and pozzolanic concretes.

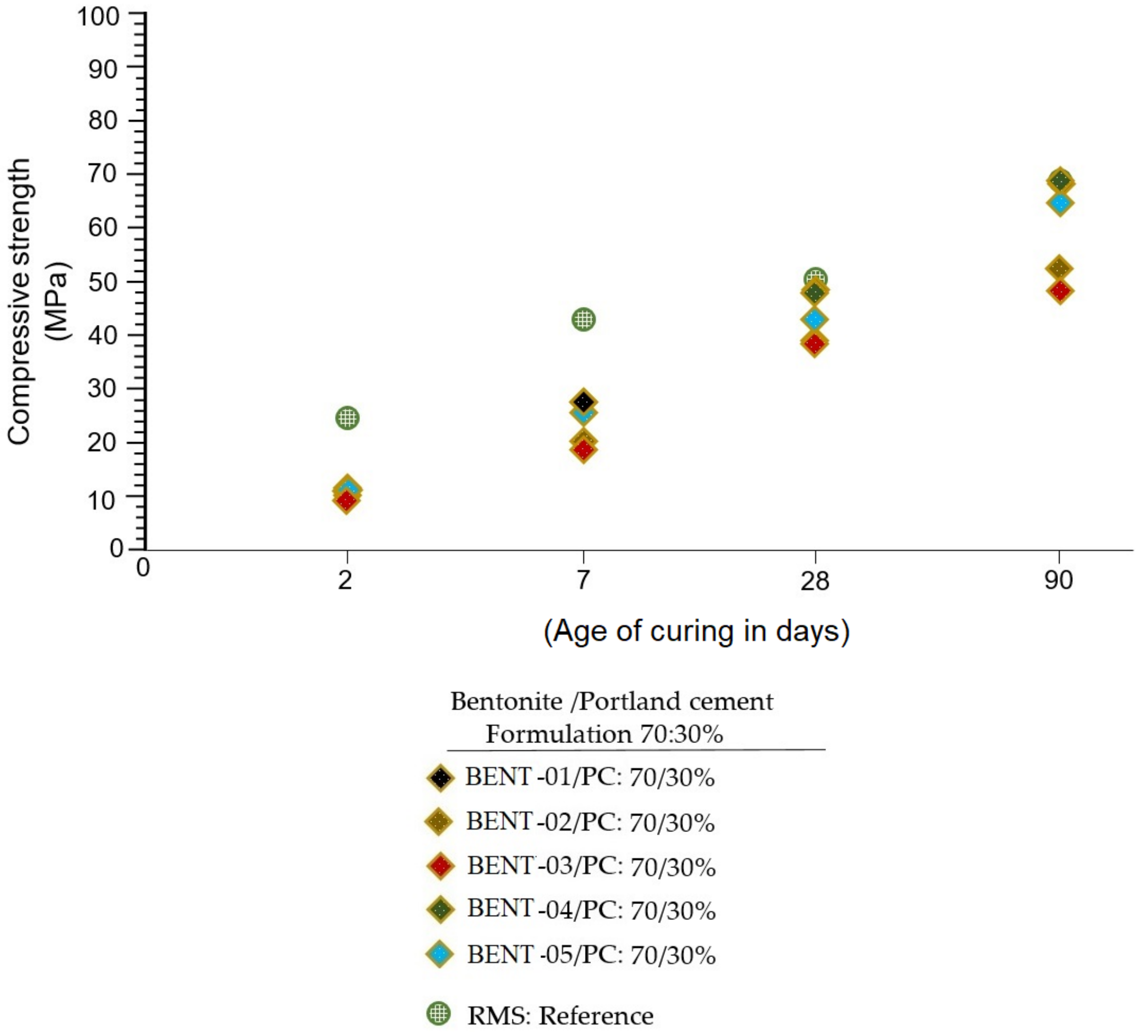


Figure 8. Behavior of mechanical strengths over time with formulations of standard mixtures of bentonite and Portland cement (BENT/PC) of 70:30%.

According to what has been analyzed and discussed throughout this work, it seems that the petrographic and mineralogical characteristics of the samples analyzed, despite their heterogeneity and complexity, favor the pozzolanic reactivity and hydraulicity of the bentonites in the mortars; this may be due to the presence of phases such as smectite, mordenite and amorphous material (volcanic glass) [39]. The first two mentioned species possess special properties, such as the ability to exchange cations [53], absorption and hydration capacity [54]. On the other hand, volcanic glass is very reactive at the paste–cement interface of mortars, capable of developing pozzolanic reaction and remarkable mechanical strength at 28 days [52]. All of the above can also be related to the chemical composition of these samples, in which the high SiO_2 and Al_2O_3 contents seem to be decisive in the behavior of most pozzolans [39]. On the other hand, the percentages of reactive SiO_2 and reactive CaO confirm and justify the properties of bentonite as pozzolans and demonstrate once again the high mechanical strength values achieved at 28 and 90 days, respectively.

4. Conclusions

The bentonites studied have a varied and heterogeneous mineral and petrological composition, typical of volcanic environments with marked pyroclastic activity in which minerals and volcanic glass coexist.

The study of the chemical composition indicates high contents of SiO_2 and Al_2O_3, a distinctive feature that characterizes the pozzolanic materials of the Caldera de Los Frailes.

The samples with higher alkaline content (BENT-01, BENT-04 and BENT-05) are more zeolitized, while the calcoalkaline samples (BENT-02 and BENT-03) are bentonitized and rubefacted.

As regards the technological properties, it is established that the samples are within the parameters required in the standards that regulate the selection and use of materials for the improvement of cement quality.

All samples analyzed show pozzolanic reactivity after 8 days of testing, increasing this behavior up to 15 days.

The results of the mechanical tests show increases in compressive strength from initial periods of 2 days to later ages of curing (90 days) for both the BENT/PC-75:25% and BENT/PC-70:30% formulations.

The normal mechanical strengths of some samples equal and even exceed the mechanical strength of Portland cement at 28 and 90 days of setting.

In the industrial manufacture of pozzolanic cement, both formulations (BENT/PC-75:25% and BENT/PC-70:30%) could be used while minimizing energy costs and preserving the inherent properties of the cement.

The results of this research provide solid criteria to consider the bentonite clays of the Caldera de Los Frailes, in the southeast of Spain, as quality products for the improvement of common cements. Therefore, this could be a practical guide for their further exploitation.

Additionally, the sustainable use of these materials such as pozzolans would avoid CO_2 emissions into the atmosphere and therefore function as a more effective conservation method for the environment.

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