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Bentonite Clays Related to Volcanosedimentary Formations in Southeastern Spain: Mineralogical, Chemical and Pozzolanic Characteristics

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Abstract: The volcanism that took place during the Neogene in the southeastern Iberian Peninsula caused a large accumulation of volcanosedimentary materials, which were subsequently altered and transformed into bentonite deposits. The mineral composition and technical quality of these deposits have been demonstrated and established in this work. The main object of this research is the mineral, chemical and thermal characterization of the bentonites that lie in the southeastern region of Spain and to demonstrate their technical capabilities to be used as pozzolans. The first phase of characterization of the samples was carried out by X-ray diffraction (XRD), oriented aggregates (OAs), X-ray fluorescence (XRF) and thermogravimetric analysis (TGA). In the second phase, a chemical–technical quality test (CTQT) was carried out, aimed at determining reactive SiO_2 and reactive CaO, whereas in the third phase, a chemical pozzolanicity test (CPT) was carried out to establish the pozzolanic behavior of the samples over two test periods: 8 and 15 days. The XRD and OA analyses showed that the bentonite samples are made up of a main phase formed by montmorillonite, quartz, plagioclase-albite and chabazite–Ca. The results obtained by XRF on the bentonite samples indicated that the SiO_2 contents are high and vary between 43.33% and 64.71%, while Al_2O_3 ranges between 15.81% and 17.49%. The CTQT established that more than 80% of the SiO_2 and CaO present in the samples are reactive, which was confirmed by the results of the chemical pozzolanicity test (CPT). The results obtained show that the bentonites in this study present technical qualities that are undoubtedly reinforced by their mineral constitution and chemical composition. These tests could become a practical guide for the selection of eco-efficient materials in the production of pozzolanic cements and environmentally friendly ceramic products.

Keywords: bentonite; pozzolanicity; SiO_2 reactive; CaO reactive; cement

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1. Introduction

According to Murray's definition [1], bentonites are clays consisting essentially of minerals of the smectite group. One of their main characteristics is to increase several times their size when in contact with water, when their composition is preferably sodic. The vast majority of bentonites are calcium bentonites. Bentonites have applications in various fields, such as well drilling, in the foundry industry, cat sands, as well as in various adhesives, such as starch, latex and asphalt.

Spain has large bentonite deposits. For several decades, the bentonites of SE Spain have been studied and characterized in detail by many researchers, who almost unanimously agree that their origin is hydrothermal [2–6]. Caballero and Jiménez de Cisneros [7] have investigated the origin of the hydrothermal precursor solutions, as well as the formation temperature of the bentonites by interpreting the δ^{18O} and d2H values and their correlation with chemical and isotopic parameters. In recent times the research of these bentonites has been directed to their practical application in many fields of technology and industry. Recently, some authors [8–12] have succeeded in developing methodologies for the safe storage of nuclear waste in enclosures composed of compacted bentonite granules and blocks. Huertas et al. [13] have carried out studies that demonstrate the ion exchange capacity of bentonites and highlight that they have a greater preference for K^+, Ca^{2+} and Mg^{2+} ions than for Na^+. Viseras and López–Galindo [14], as well as Srasra and Bekri-Abbes [15], have demonstrated the effectiveness of bentonites as excipients for pharmacological tablets, reassuring that they are totally innocuous and without any negative impact on health. Costafreda and Martín [16] have classified bentonites from the southeast of the Iberian Peninsula from a mineral and technical point of view, proving that they can be used in cements, mortars and concretes. The works carried out by Van Geet et al. [17] show the effectiveness of bentonites from Cabo de Gata (Spain) in the sealing of borehole walls and highlight this effectiveness in relation to the control of water, gas and radionuclide migration. Delaleux et al. [18] have achieved better performance of borehole geothermal heat exchangers by improving the conductivity of bentonite slurries. Pandey [19] established that bentonite can be used as an adsorbent material in wastewater treatment process. Nadziakiewicz et al. [20] have carried out conclusive investigations on the physicochemical properties of bentonites, confirming their use as an effective and essential additive in animal feed. Matei et al. [21] have succeeded in manufacturing bentonite-based ceramic matrix composites with high compressive strength. Several researchers, such as Da Silva et al. [22], Stojiljković and Stojiljković [23], and Di Prima et al. [24], have carried out studies assuring the suitability of bentonites in the manufacture of cosmetic products.

Recently, bentonites have been considered as pozzolans [25], based on their chemical composition, mineral constitution and origin. A pozzolan is a material with significant SiO_2 and Al_2O_3 contents that does not have cementitious properties on its own, but which, when ground and mixed with cement, behaves as an effective binder [26]. Pozzolans can be of natural or artificial origin [27]. Among the best known natural pozzolans are zeolites [28], ignimbrites, altered andesites, diatomites, among others [29–31]. Artificial pozzolans include slag, fly ash, silica fume and calcined clay. Pozzolans significantly improve the properties of so-called pozzolanic cements, the production of which avoids the emission of greenhouse gases [32].

The main objective of this work is the classification of the bentonites found in the southeastern part of the Iberian Peninsula according to their mineral, chemical, thermal and technical aspects (Figure 1) and to establish their pozzolanic properties with a view to using them as sustainable natural aggregates in more environmentally friendly pozzolanic cements.

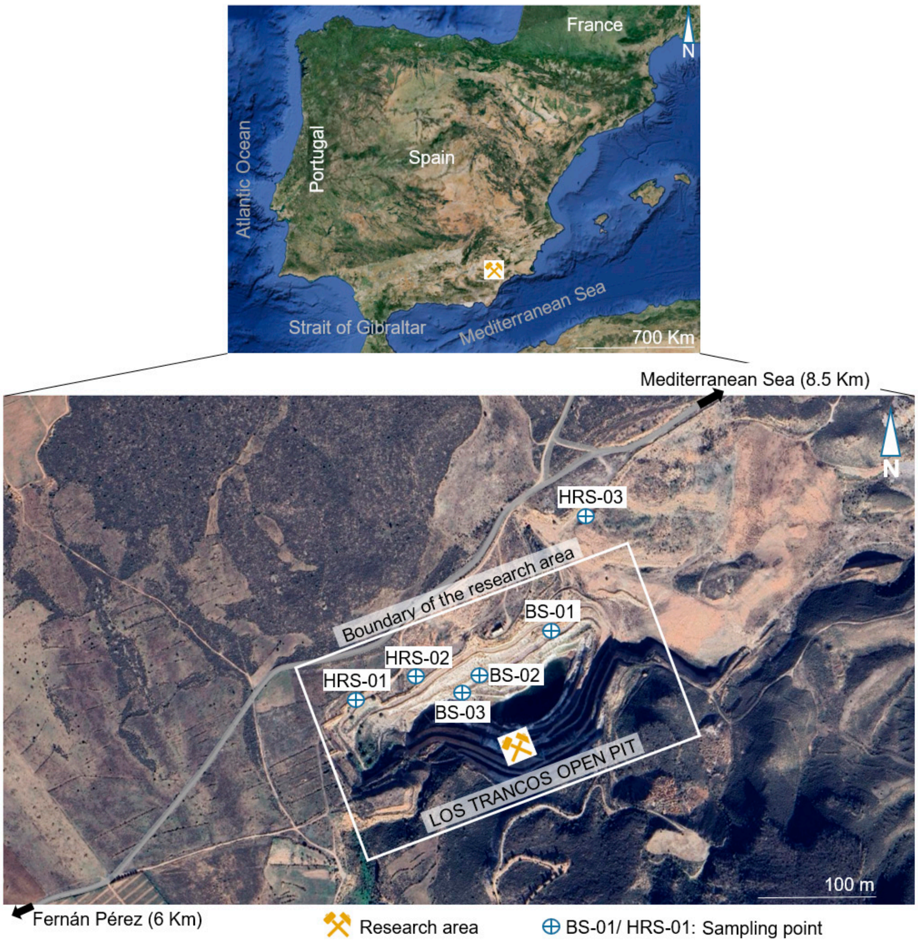

Figure 1. Location of the research area indicating the sampling points [33].

2. Materials and Methods

2.1. Materials

In order to develop this research, six volumetric samples were taken in the study area, which is located in the old bentonite open pit known as Los Trancos, whose operations are currently interrupted (Figure 1). All samples (BS–01, BS–02, BS–03, HRS–01 and HRS–02) were extracted from the northern slope of the open pit, while the sixth sample (HRS–03) was taken directly from the overlying host rock, about 360 m from the center of the deposit, in a northerly direction. All samples were taken by the outcrop lithogeochemical method, each weighing 40 kg. Samples BS–01, BS–02 and BS–03 consist of bentonite of dacitic–rhyolitic origin, which looks friable in appearance and is white to gray in color. Samples HRS–01 and HRS–03 correspond to a fine-grained, compact and stratified calcarenite lying discordantly over the bentonite horizons. Sample HRS–02 represents a lithologic level consisting of friable and weathered material of highly altered dacite. A summary of the samples analyzed in this research is given in Table 1.

Table 1. Samples analyzed in this research.

Sample	Type of Lithology	Position in the Outcrop
BS–01 BS–02 BS–03	Bentonite clay	Central part of the deposit
HRS–01	Calcarenite	Proximal host rock
HRS–02	Dacite altered	Proximal host rock
HRS–03	Calcarenite	Distal host rock

2.2. Methods

Mineral phases were identified using powder X-ray diffraction (XRD) with a Bruker D8 advance diffractometer equipped with a copper (Cu) anticathode, located at the Unidad de Técnicas Geológicas from Universidad Complutense de Madrid. Diffractograms were continuously recorded at 2θ angles ranging from 2° to 68°, with 0.02° stepping intervals and a 1 s duration per step. Phase identification was carried out with X'Pert software, using the ICDD Powder Diffraction File (PDF2), and the Crystallography Open Database (COD 2021). The semiquantitative analysis was performed using the Chung method, with X'Pert software. This method involves determining the reference intensity ratios (RIRs) of the existing phases, allowing for the normalization of intensity calculations based on the assumption that the total of all phases in the sample equals 100%.

For correct identification of clay minerals, samples taken from the open pit were prepared for the oriented aggregates XRD method (OA) by taking an additional fraction of the original sample (0.1–0.5 g) and dispersing it in distilled water. The fraction smaller than 0.5 µm was then separated and extracted according to Stokes's law and pipetted onto three glass slides, prepared as follows: (1) oriented aggregates without further treatment (air dried, AD), (2) oriented aggregates treated with ethylene glycol for 24 h (EG), and (3) oriented aggregates heated at 550 °C for 90 min (thermal treatment, TT). The same diffractometer was used, recording diffractograms at 2θ angles from 2° to 35°, with 0.02° stepping intervals and 0.8 s per step.

Chemical analyses of samples were obtained by means of energy-dispersive X-ray fluorescence spectrometry (EDXRF), using a Malvern PANalytical, mod. Axios spectrometer that belongs to the CAI de Técnicas Químicas at the Universidad Complutense de Madrid. For obtaining semiquantitative data, PANalytical's Omnian software with a set of internal standards was used. Sample preparation included grinding until reaching a grain size of less than 100 µm, and the preparation of a pressed powder pill. In addition to the bentonite clay samples (BS–01, BS–02 and BS–03), the chemical composition of three samples of host rocks (HRS–01, HRS–02 and HRS–03) was determined to compare their chemistry with that of the bentonites under study.

A thermogravimetric analysis was carried out to study the thermal behavior of the bentonite samples and to establish the main thermal events that took place until their final collapse. In this test, a thermobalance with the serial number N5190152 was used, which employs Software Version 4.00. The charging temperature is 25.0 °C, the temperature rate is 100.0 °C/min, and the filter factor is 3. The samples were analyzed by thermogravimetry (TGA) under air atmosphere conditions and at 20 °C/min. The heating range was between 25 °C and 950 °C. This analysis was carried out at the Laboratorio de Tamices Moleculares del Instituto de Catálisis y Petroleoquímica del Centro de Investigaciones Científicas (CSIC) de Madrid (Spain).

A chemical–technical quality test (CTQT) was carried out following the European Standard UNE–EN196–2–2006 [34]. Two fundamental compounds were revealed as a priority: reactive SiO_2 (RS) and reactive CaO (RC), in addition to other compounds, such as total SiO_2 (TS), total CaO (TC), MgO, Al_2O_3 and Fe_2O_3. This test is of vital importance to establish the quality of the samples as pozzolans and to determine if they can be used in the improvement of pozzolanic cements. Additionally, the insoluble residue (IR) was determined with a hydrochloric acid solution.

A chemical pozzolanicity test was carried out at 8 and 15 days to determine the pozzolanic reactivity of the samples. The procedure in this test strictly followed the Standard UNE–EN196–5:2006 [35], according to which, pozzolanicity is calculated by comparing the concentration of calcium ion (expressed as $Ca(OH)_2$) contained in the aqueous solution in contact with the hydrated cement, with the amount of calcium ion capable of saturating a solution of the same alkalinity, in a fixed period of time. The test is considered positive when the calcium ion concentration in the solution is less than the saturation concentration [35].

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

According to the XRD data, calcite and dolomite were determined as the main minerals in samples HRS–01 and HRS–03 (56%–55% and 36%–37%, respectively; Table 2). Additionally, quartz and albite-like plagioclase were also present in smaller amounts (6%–5% and 1%, respectively; Table 2). The latter is evident by the presence of peaks and spacings of 4.04, 3.75, 3.2 and 3.17 Å. A broad band around 14 Å was also observed, which probably corresponds to the presence of smectite-type clays (1%; Table 2). Sample HRS–02 also contained plagioclase, although in a higher content (32%; Table 2), and, in this case, it was identified as anorthite (Figure 2). Next to it, there are clays of the smectite group, as well as quartz and cristobalite, in an amount of 6%, 51% and 11%, respectively (Table 2). The smectite was identified as dioctahedral in structure, since the 060 reflection appears at 1.50 Å spacing [36]. Some peaks were observed that could be amphibole or pyroxene-type phases, but the intensity is weak and does not allow them to be identified clearly; however, they could be residual phases of hydrothermally altered mafics that were transformed into bentonite. Some authors [16,37,38] have identified relict phases of pyroxenes and amphiboles in the bentonites that lie in the San José–Los Escullos deposit, located 25.2 km south of the study area.

Table 2. Mineralogical analysis (%) of the samples obtained by XRD.

Samples	% Mineral Content [1]							
	Cal	**Dol**	**Crs**	**Qz**	**Plg**	**Sme**	**Zeo**	**Amp/Px**
HRS–01	56	36	-	5	1	1	-	-
HRS–02	-	-	11	51	32	6	-	t
HRS–03	55	36	-	6	1	1	-	-
BS–01	-	-	-	9	21	70	-	-
BS–02	25	-	-	-	-	73	2	-
BS–03	22	-	-	-	-	78	-	-

[1] Mineral abbreviations as suggested by [39]: Cal—calcite; Dol—dolomite; Crs—cristobalite; Qz—quartz; Plg—plagioclase; Sme—smectite group; Zeo—zeolite; Amp—amphibol group; Px—pyroxene group; t = traces.

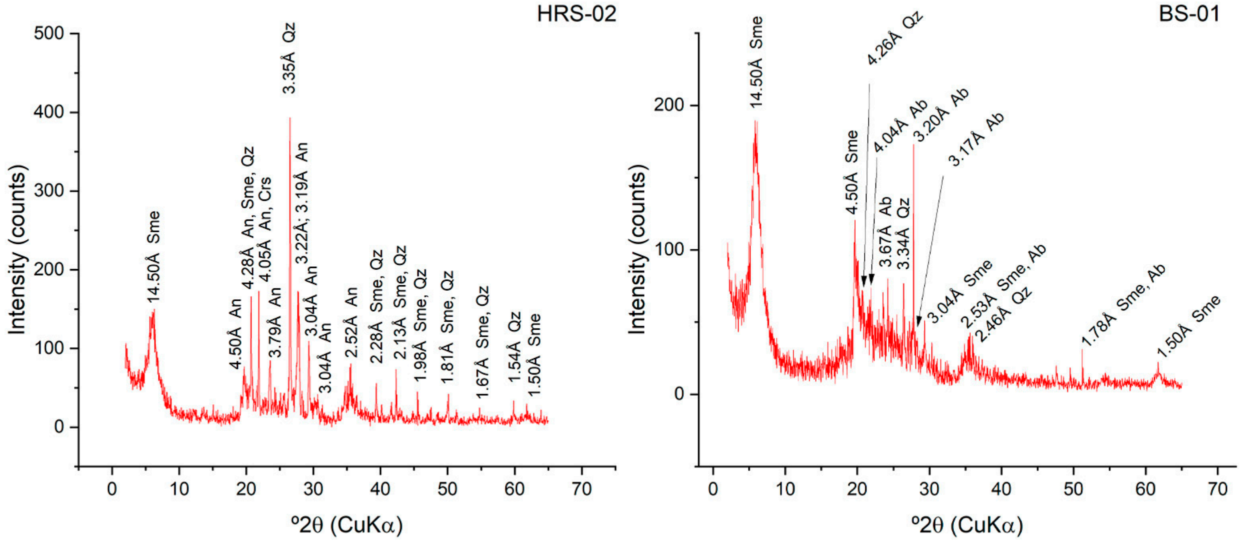

Figure 2. Selected powder XRD patterns of HRS-02 and BS-01 showing the main peaks and mineral assignment. The spacing *d* is expressed in Å, and mineral abbreviations as suggested by [39].

Plagioclase (probably albite due to the presence of peaks at 3.20 and 3.17 Å) and smectite are the main minerals in sample BS–01, plus some smaller amount of quartz

(Table 2). Samples BS-02 and BS-03 are quite similar, with abundant clay (smectite) in more than 70% (Table 2) and calcite (25%–22%, respectively; Table 2) as the main phases. In the case of BS-02, although the intensity of the peaks is weak, it could be affirmed that a zeolite is present, identified as chabazite-Ca by the COD 96-90-9307 card from the Crystallography Open Database [40]. In the work by García–Romero et al. [41], zeolite, mainly present as mordenite, is mentioned as always accompanying smectite clay, identified as montmorillonite.

Regarding the clay content determined by oriented aggregates, all the samples show a very intense peak at 15 Å, which undergoes a shift to 17 Å spacings with the ethylene glycol (EG) treatment and drops to a spacing of 10 Å after the thermal treatment (TT) (Figure 3). This behavior indicates the presence of smectite-group clays that were previously identified as montmorillonites and beidellites [42].

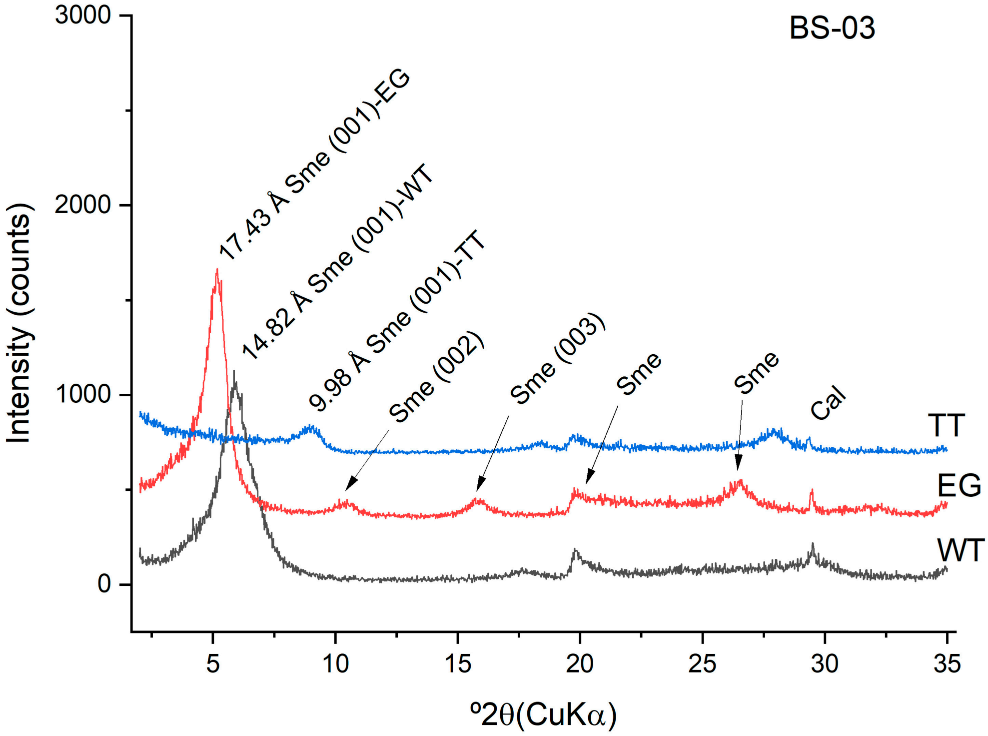

Figure 3. Oriented aggregates XRD patterns of clay fraction from BS-03 showing the main peaks, including the *hkl* basal reflections and mineral assignments: (WT) without treatment; (EG) treatment with ethylene glycol; (TT) with heat treatment. The spacing *d* is expressed in Å, with mineral abbreviations used as suggested by [42].

The increase in montmorillonite spacing has been described by other researchers [36,40,43] in the bentonites from the southeast of the Iberian Peninsula, which ensures an increase in the expansivity of these materials from 14 Å to 17 Å, corroborating the results obtained in this work. Table 3 shows the main peaks of the clay minerals detected by the oriented aggregate method.

Table 3. Main peaks of clay minerals of the smectite group obtained by AOs.

Sample	OA–WT [1] (Å)	OA–EG [2] (Å)	OA–TT [3] (Å)	Mineral Found
BS–01	15.11	17.3	9.91	Smectite
BS–02	14.79	17.41	10.08	Smectite
BS–03	14.82	17.43	9.98	Smectite

[1] Without treatment. [2] Treatment with ethylene glycol. [3] With heat treatment.

3.2. X-ray Fluorescence (XRF)

The XRF results (Table 4) show compositions that correspond well with the mineral phases identified by XRD. Samples HRS–01 and HRS–03 contain CaO (77.81%–25.9%wt.) and MgO (12.03%–17.83%), respectively, as major components, together with minor amounts of SiO_2 (6.27%–6.80%), Al_2O_3 (1.57%–1.60%) and Fe_2O_3 (1.02%–0.70%), and some other elements at trace levels (e.g., K_2O = 0.38%–0.36% and TiO_2 = 0.13%–0.12%). The samples HRS–02 and BS–01 are clearly more siliceous, with contents of 58.05 and 64.71%wt in SiO_2 and 15.99 and 17.49%wt in Al_2O_3, respectively. MgO, K_2O and Na_2O present similar contents in both samples, but both Fe_2O_3 and CaO are more abundant in HRS–02 (8.42 vs. 3.49 and 6.74 vs. 2.87%wt, respectively). The samples BS–02 and BS–03 are very similar, with a chemical composition fully marked by SiO_2, CaO, Al_2O_3, MgO and Fe_2O_3 (approx. 45%, 30%, 16%, 6% and 3%, respectively) and a much lower proportion of Na_2O, TiO_2, K_2O and MnO (approx. 0.5; 0.2; 0.15; and 0.15%wt., respectively).

Table 4. Chemical composition of the samples obtained by XRF.

Samples	% Oxides Weight												
	SiO_2	Al_2O_3	CaO	Na_20	K_2O	MgO	Fe_2O_3	TiO_2	MnO	SO_3	LOI	Si/Al	Si/ (Al + Fe)
BS–01 [1]	64.71	17.49	2.87	1.77	2.44	5.87	3.49	0.24	0.25	0.08	9.8	3.69	3.08
BS–02	43.33	15.81	30.41	0.54	0.17	6.01	2.97	0.23	0.13	0.03	23.4	2.74	2.38
BS–03	45.27	16.69	27.63	0.56	0.16	6.05	2.95	0.22	0.15	0.03	23.0	2.71	2.30
HRS–01 [2]	6.27	1.57	77.81	0.3	0.38	12.03	1.02	0.13	0.03	0.20	41.1	3.99	2.42
HRS–02	58.05	15.99	6.74	2.14	2.24	5.01	8.42	0.75	0.13	0.09	9.1	3.63	2.37
HRS–03	6.80	1.60	25.9	0.53	0.36	17.83	0.70	0.12	0.03	0.96	44.1	4.25	2.95

[1] BS (01–03): bentonite sample; [2] HRS (01–03): host rock samples.

In the sample BS–01, the SiO_2/Al_2O_3 ratio of 3.7 is higher than in the samples BS–02 (2.74) and BS–03 (2.71), respectively.

On the other hand, it should be noted that the SO_3 contents are negligible in almost all the samples, the exception being the markedly carbonated samples (HRS–01 and HRS–03), where, in any case, the values never reach 1%. Likewise, it is observed that whatever the origin of the CaO, the values of loss on ignition (LOI) are always higher in those samples where the percentages of this compound are markedly high. Therefore, it is established that the higher the SiO_2 content, the lower the loss on ignition experienced by the samples in this study. Conversely, the higher the CaO content, the higher the LOI becomes.

Indeed, there seems to be an inversely proportional relationship between SiO_2 and CaO (Table 4), whereby the higher the SiO_2 content, the lower the CaO content becomes, and vice versa. It is possible that the action of hydrothermal fluids caused the remobilization of the Ca^{2+} ion and its subsequent deposition in the proximal areas of the reservoir [44]. The high CaO contents could indicate the presence of a high pH at which SiO_2 could be dissolved, giving very low contents relative to CaO [45]. In the same order, it seems that when the SiO_2 content increases, Na_2O and K_2O increase relative to CaO.

According to Table 4, the appreciable CaO contents and the low SiO_2 and Al_2O_3 contents seem to confirm that the samples HRS–01 and HRS–03 are sedimentary carbonate bedding rocks of different origin than bentonites. However, the abundance of SiO_2 and Al_2O_3 in sample HRS–02 seems to confirm a volcanosedimentary origin with a very marked degree of alteration.

3.3. Thermogravimetric Analysis (TGA)

Figure 4 (a–c) shows the TGA curves of the samples BS–01, BS–02 and BS–03. The curve for sample BS-01 (Figure 4 (a)) shows a simple decomposition process with very few multistage features, suggesting the decomposition and transformation of poorly stable materials that stabilize near 850 °C. Approximately three main thermogravimetric events stand out. The first begins at 23 °C, showing a rapid desorption of the physisorbed water on the surface of the sample, which lasts until approximately 240 °C. In this interval, a mass loss equivalent to 12.6% occurred. The second event takes place between 240 and 500 °C, while the third occurs in the 500–850 °C range. In the last two events, a common feature predominates, and that is a lower mass loss (2.32% and 2.17%, respectively), which indicates the presence of materials with relatively low stability. At 850 °C and above, the curve finally stabilizes indicating the formation of stable phases, with no mass loss or mass gain. The DTA curve clearly shows three endothermic events, the first and most important being near 90 °C; the second at 180 °C, and the third near 650 °C.

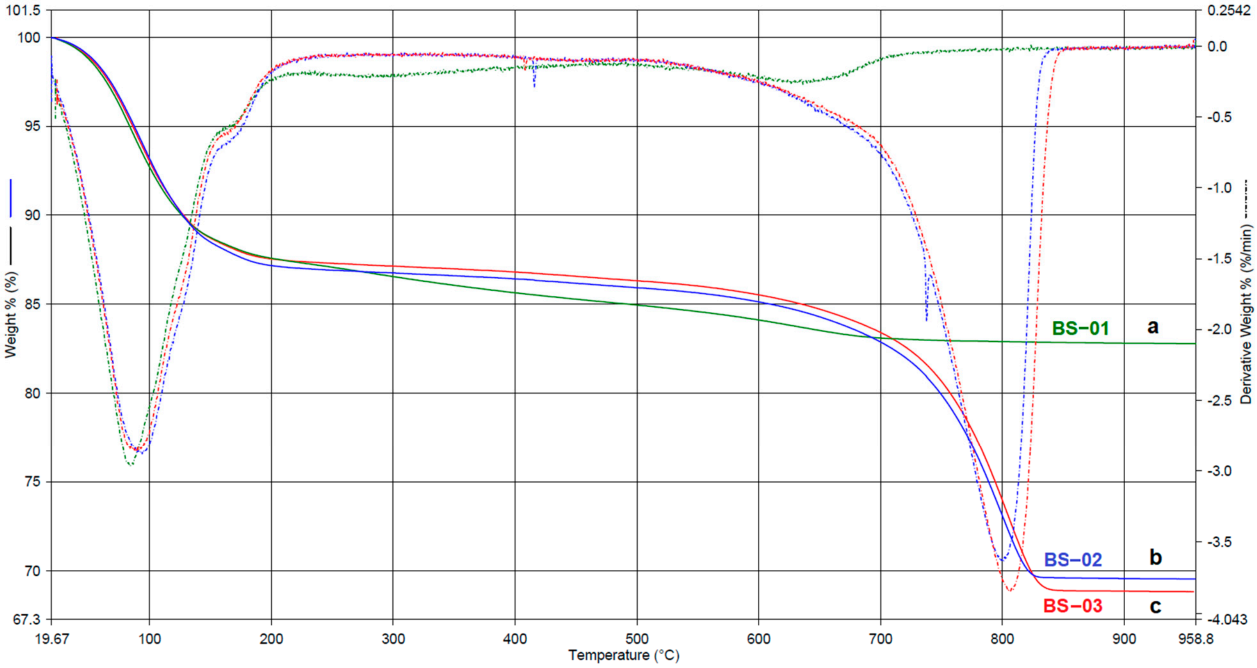

Figure 4. Combined thermograms (a, b and c) of samples BS–01, BS–02 and BS–03.

Figure 4 (b) corresponds to sample BS–02 and shows a thermogravimetric event with multistage decomposition in more or less stable intervals. Basically, four events are defined. The first one is triggered at about 20 °C and is maintained up to 250 °C. A steep slope of the TG curve is observed, indicating a rapid desorption of the sample, specifically between 98 °C and 150 °C, with a significant mass loss of 13%. Relative stability is seen in the second event, occurring in the thermal range from 250 °C to 500 °C, with a negligible mass loss of only 1%. The third event takes place between approximately 500 °C and 830 °C, with the highest mass loss of more than 16% in this range. The fourth and last event occurs at 830 °C and above, at which point the final stability of the curve is reached. The DTA curve shows five endothermic peaks formed at 98 °C, 170 °C, 420 °C, 740 °C and 800 °C, the first and last being the most pronounced, respectively.

The behavior of the thermograms in the sample BS–03 (Figure 4 (c)) is relatively similar to those shown in Figure 4 (b). It is a multi-stage event that manifests in three main thermal intervals with a rapid and noticeable initial weight loss of 12.5%, from 20 °C and up to about 200 °C, in which materials weakly adhering to the sample surface are removed and the rapid drying of the sample occurs. From 200 °C and up to about 520 °C, there is a slight stabilization in the behavior of the curve where only a weight loss of 1% is seen. However, from this point up to 840 °C, there is a rapid weight loss of more than 17%, which exceeds the value of the previous stages. From 840 °C to temperatures above 900 °C, the curve remains stable.

The DTA curve also shows some similarity with the one described in Figure 4 (b), except for some details, such as a less pronounced extension of the endothermic peaks formed at 90 °C and 410 °C, respectively, and the absence of the endothermic peak in the thermal range of 740 °C, which is clearly defined in Figure 4 (c).

Finally, considering Figure 4 (a–c) together, it is established that all three curves show rapid moisture loss, surface dehydration and extraction of weakly adsorbed gas phases on the surface and nanopores of the samples. According to MacKenzie [46], the dehydration endothermic reactions occur between 25 and 300 °C for phyllosilicates, due to the loss of adsorbed water from the outer surface, as well as the interlayer water from the inner surfaces and the hydration shells of the interlayer cations. Indeed, when the presence of clays is confirmed in the sample, an endothermic reaction below about 200 °C usually indicates the presence of montmorillonite [47].

In the studied samples, the strong gradient of the TGA curves in the first event (~70–200 °C) can be ascribed to the dehydration of mineral phases, such as smectites [43] and zeolites [37,38], which possess properties such as ion exchange [34]. In this thermal range, mass losses seem to manifest similarly (BS–01 = 12.6%, BS–02 = 13%, BS–03 = 12.5%) in the samples, although they are slightly higher in the sample BS–02.

Between 290 °C and 690 °C, the curves stabilize slightly. This is caused by the unstable phases in the process of relative stabilization, during which there was a possible loss of crystalline water, constitution or structure of smectite through a process of dehydroxylation caused by the disintegration of the $(OH)^-$ group inside its structure. In this interval, the sample BS–01 loses more mass (2.32%) compared to the samples BS–02 and BS–03 (1%), respectively. From 690 °C onwards, the curve of the sample BS–01 stabilizes definitively, while samples BS–02 and BS–03 show a second mass loss (BS–02 = 16.35%, BS–03 = 17.45%), much higher than that observed in the first thermogravimetric event (~70–200 °C). The stabilization of the curves of these last two samples takes place from 830 °C and 850 °C, respectively, caused by a structural rearrangement in post-dehydration–dehydroxylation conditions, with the absence of decomposition processes and mass losses.

3.4. Chemical-Technological Quality Test (CTQT)

The chemical–technological quality analysis was carried out to determine the quality of the samples as pozzolans, by monitoring the behavior of total SiO_2 and total CaO during their hydraulic reaction with the reference cement components. The results obtained from this test are shown in Table 5, and they establish that the researched bentonites possess the quality of pozzolanic material. According to the data observed, it seems that sample BS–01 is the most representative of the set, a fact that is proven by the higher content of total SiO_2 and reactive SiO_2, indicating that about 86% of the original silica is able to react with the $Ca(OH)_2$ of the cement. In the works of many authors [37,48,49], this fact is emphasized, pointing out that this is one of the characteristic features of pozzolans. The samples BS–02 and BS–03 possess practically less than half of the total SiO_2 compared to the sample BS–01; however, even so, they exhibit an important hydraulic reactivity, between 89.3% (BS–02) and 83% (BS–03), respectively.

Table 5. Results of the chemical–technological quality test.

% Weight	Samples			Allowed Levels (%)
	BS–01	**BS–02**	**BS–03**	
Total SiO_2	63.61	34.78	33.60	-
MgO	2.78	3.26	3.35	<5
Total CaO	2.25	23.55	21.39	-
Fe_2O_3	2.21	1.50	1.47	-
Al_2O_3	15.13	11.82	11.16	<16
Reactive SiO_2	54.42	31.08	27.91	>25
Reactive CaO	0.12	6.59	4.92	-
Insoluble Residue	14.53	7.84	8.52	<3
$SiO_2/(CaO + MgO)$	12.6	1.3	1.4	>3.5
$SiO_2 + Al_2O_3 + Fe_2O_3$	80.95	48.1	46.23	>70

Another detail to highlight is the low proportion of the total CaO inherent in sample BS–01(2.21%), of which 0.12% is capable of reacting (~5%); however, in the samples BS–02 and BS–03, both the total CaO (BS–02: 23.55%; BS–03: 21.39%) and the reactive CaO (BS–02: 6.59%; BS–03: 4.92%) are remarkably high when compared to BS–01. This is a factor to highlight, since, in any case, the CaO present is able to react in the presence of the cement–water–pozzolan interface. However, this excess CaO could be counteracted by the high Al_2O_3 contents present in each sample [37].

It seems evident that the mineralogical and petrological complexity of these samples, as described in the previous subsections, is the cause of the high contents of insoluble residue (IR) observed in Table 5, which exceed the minimum set thresholds [34]. This residue could then be composed of very stable crystalline phases, incapable of developing hydraulic reactions within the interface, and which would result in the physical and chemical stability of the reaction products generated by the hydraulic interaction between the cement and the bentonites studied.

3.5. Chemical Pozzolanicity Test (CPT)

Pozzolanicity is the ability of some materials to react more or less actively with $Ca(OH)_2$ and other compounds present in Portland cement clinker in the presence of water, during a standardized period of 8 and 15 days [35,48]. The pozzolanic capacity of a sample can be represented graphically in a diagram (Figure 5) at a point where the reaction is monitored by the variation in the CaO concentration and the concentration of hydroxyl ions. This correlation indicates that the sample is pozzolanic whenever its position is just below the CaO solubility isotherm at 40 °C [35].

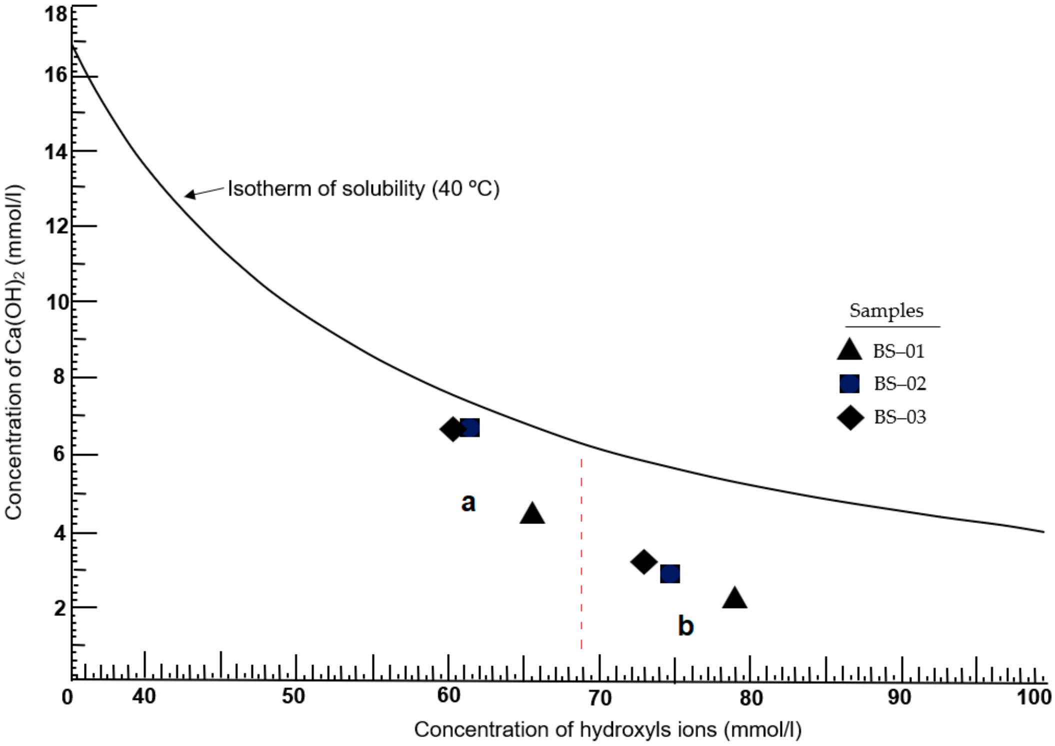

Figure 5. Behavior of pozzolanic reactivity at 8 (a) and 15 days (b) of assay.

According to Figure 5, all the bentonite samples in this study behave as pozzolans. The behavior of sample BS–01 is notably more pozzolanic compared to the other samples. This may be due to the high contents of total SiO_2 (>50%), the high percentage of SiO_2 that is able to react with $Ca(OH)_2$, and a significant portion of reactive CaO (Table 5). However, it should be noted that although the SiO_2 contents are lower in samples BS–02 and BS–03, this does not prevent them from behaving as typical pozzolans, although the reactive SiO_2 present is only 31.08% and 27.91%, respectively (Figure 5). Martín et al. [50] have described materials capable of showing significant pozzolanic behavior despite having CaO contents higher than 30%. Another aspect to highlight is that the $SiO_2/(CaO + MgO)$ and $SiO_2 + Al_2O_3 + Fe_2O_3$ ratios in the samples BS–02 and BS–03 show values below the limits set by standard [34] (Table 5); however, this does not seem to interfere negatively with their pozzolanic behavior.

4. Conclusions

After presenting and discussing the results of this research, the following conclusions are presented below:

1. The samples have a complex mineralogy, being fundamentally composed of minerals of the smectite group (montmorillonite), quartz, cristobalite and calcite. To a lesser degree, there are traces of pyroxene, amphibole and zeolite of the chabazite–Ca type.
2. From a chemical point of view, the bentonites have much more SiO_2 and Al_2O_3 compared to their proximal and distal host rocks (HRS–01 and HRS–03), which may be related to their origin from the alteration of calc-alkaline volcanic rocks in the southeast of the Iberian Peninsula. It seems that these anomalous contents are specifically due to the alteration of the feldspars and the presence of quartz contained in the dacites and rhyolites.
3. The bentonites have a marked pozzolanic reactivity, both at 8 and 15 days; therefore, they can be considered as natural pozzolanic materials, qualitatively suitable from a technical point of view.
4. In terms of the production processes, the chemical and mineral composition of these bentonites could be beneficial to produce eco-efficient pozzolanic cements. This is confirmed by the high contents of reactive SiO_2, reactive CaO and Al_2O_3, as well as by their low SO_3 contents.

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