Variations in the Texture Profile Analysis (TPA) Properties of Clay/Mineral-Medicinal Water Mixtures for Pelotherapy: Effect of Anion Type

Manuel Pozo [1],* , Francisco Armijo [2] , Francisco Maraver [2] , Pilar Zuluaga [2] , José Manuel Ejeda [2] and Iluminada Corvillo [2]

[1] Dpto. Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain
[2] Facultad de Medicina, Universidad Complutense de Madrid, 28040 Madrid, Spain; farmijoc@ucm.es (F.A.); fmaraver@ucm.es (F.M.); pilarzul@med.ucm.es (P.Z.); jmejeda@ucm.es (J.M.E.); corvillo@ucm.es (I.C.)
* Correspondence: manuel.pozo@uam.es; Tel.: +34-91-4974808

Abstract: A peloid's liquid phase can be mineral, sea or salt-lake water. This study examines the interactions among three materials, two special clays (bentonite and sepiolite) and one common clay, and three chemically different mineral-medicinal waters. In all clay–water mixtures, the hardness and adhesiveness decreased with the amount of water in the mixture. For a given hardness or adhesiveness, sepiolite retained more water than the other clays, especially in the presence of sulphate-rich mineral-medicinal water (73%). In contrast, the common clay retained the least amount of water (26%), and the bentonite samples returned an intermediate value for the amount of retained water (52–53%). These differences had a strong influence on the thermal behaviour of the mixtures and, hence, should be taken into account for their use in thermotherapy applications. There were no significant differences in the instrumental texture of the clay pastes according to the predominant anion in the mineral-medicinal waters.

Keywords: instrumental texture; hardness; adhesiveness; bentonite; sepiolite; common clay; mineral-medicinal water

1. Introduction

The preparation of peloids for therapeutic applications in spas and thalasso centres is, today, common practice. Peloids are composed of several clays that are mixed with mineral water and then left to mature for a variable length of time [1]. This maturation process required for a peloid to form is complex and involves physical, chemical, biological and physiochemical mechanisms. Peloids are semisolid systems with a solid phase often rich in clay minerals dispersed in mineral or sea water [2,3]. The main factors controlling the characteristics of a peloid are the clay's composition and grain-size distribution and the mineral water used in the mixture [4–9].

In the field of pelotherapy, much emphasis is placed on sensory perception, though the impressions of users are subjective and, thus, difficult to be measured. Instrumental procedures are usually more sensitive and reproducible than subjective sensory tests in which variations in measures are generally attributed to heterogeneity among samples and to individual perception [10]. Researchers should be able to count on a set of empirical instrumental tests to quantify these properties. For a clay paste or peloid to be suitable for pelotherapeutic use, it should have certain properties such as a low cooling rate, a high absorption capacity and cation exchange capacity (CEC), good adhesiveness, ease of handling and a low hardness offering a pleasant feeling when applied to the skin [1,11–13].

In the field of materials science, texture profile analysis (TPA) serves to examine the behaviour and properties of materials, solids and semisolids when subjected to compression. Through TPA, accurate and repeatable quantitative data can be obtained on the physical properties of food, cosmetics, pharmaceuticals and chemical products, along with peloids and clay/water mixtures for pelotherapy [7,14]. Variables such as hardness and adhesiveness can be estimated by calculating force peaks and areas under the curve [15,16]. Hardness, which is the compression force needed to produce a given deformation, is measured as the compression force peak in grams (g) in the first TPA cycle. Adhesiveness or the work needed to pull a material away from a surface is defined as the negative area for the first compression and is measured in grams second (g.s), and the instrumental definition is the negative area for the first compression. Variations in these parameters seem to be related to the rheological behaviour of clay/water mixtures. A positive correlation between instrumental hardness and abrasiveness has been described [7].

In previous work, we reported variations in the instrumental hardness and adhesiveness of mixtures of distilled water and several clay materials [14] but also of special clays (bentonite and sepiolite) mixed with seawater to assess the role played by salinity and pH. The present study was designed to assess the influence of anion type in mineral-medicinal waters and of clay mineral composition on instrumental hardness and adhesiveness variability in clay/water mixtures. For this study, we used, as reference, the values for instrumental hardness and adhesiveness reported by Pozo et al. [7] in Spanish peloids.

In this study, we compare the behaviour of clay/mineral-medicinal water mixtures for their use in pelotherapy. Clay composition is important because ab/adsorption capacity is related to thermal properties, especially in terms of retaining large water volumes. According to Casas et al. [17], salinity and ion contents affect the thermal behaviour of absorbent clays such as bentonite. Thus, clays composed of special clay minerals (e.g., bentonite and sepiolite) give rise to better thermal performance compared to common clays [18,19]. The hydrochemistry of the water in the mixture is related to its ion composition and affects the therapeutic behaviour of peloids [6,20–22].

2. Materials and Methods

2.1. Studied Materials

The absorbent clay samples examined, bentonite (M1) and sepiolite (M2), were supplied by the companies Clariant and Tolsa and mined from deposits in the Madrid Basin (Spain). The third clay sample is a common clay (M3) supplied by Innovarcilla S.A. from deposits in Bailén in southern Spain. The mineral-medicinal waters used were from the Spanish spas Mondariz (W1), La Hermida (W2) and Fuentepodrida (W3). Water samples were collected at the springs in polymer material bottles and were stored refrigerated until use. Distilled water (WD) was used as the control. The sites of both the clay deposits and the mineral-medicinal water springs are shown in Figure 1.

The samples were prepared by adding water to the solids, leaving the mixture to soak and then manually homogenizing it. After preparing a paste with very little water, further water was added to obtain a more moistened and easier to manipulate product as the first of the dilution series. The series was continued until the hardness of the sample was such that the instrument did not detect it as a sample. The water contents of the different preparations were determined by drying at about 105 °C in an oven until constant weight and were expressed as percentages relative to the whole mixture.
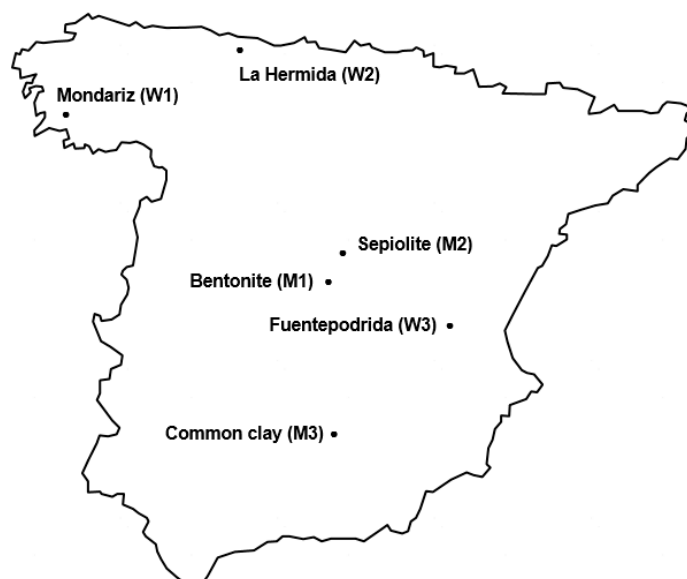
Figure 1. The geographical locations of the clays and mineral-medicinal waters in Spain.

2.2. Analytical Methodology

The mineralogical characterization of the clay samples was performed by X-ray diffraction (XRD) in a Bruker instrument model D8 ADVANCE. The bulk samples were X-rayed in the interval 2°–65° 2θ using randomly oriented powder and CuKα radiation at a scanning speed of 1° 2θ/min. The clay fraction (<2 μm) was separated by centrifugation, and the samples were prepared from dispersions oriented on glass slides. The identification of clay fraction minerals was carried out on three oriented samples, including an air-dried sample, solvated with ethylene glycol and heated at 550 °C for 2 h. Diffractograms were obtained in the interval 2°–35° 2θ. The mineral intensity factors (MIF) method was applied to XRD peak intensity ratios normalized to 100% with calibration constants for the quantitative estimation of mineral contents [23]. This method is empirically determined to modify the reflection heights for differences due to the scattering power of different unit cells. The MIF constants provided for each mineral phase are referred to the unit intensity for a selected reference mineral (commonly corundum) as the base for normalization. The measure of the d(060) reflection in the random polycrystalline powder of the clay fraction was used to establish the dioctahedral (1.49–1.50 Å) or trioctahedral (1.52–1.53 Å) nature of the clay minerals.

The grain-size distribution was determined in the 0.01–1000 μm range using a laser diffraction particle size analyser (Malvern Mastersizer 3000). The statistical parameters considered were the mode, median (Dv50) and volume mean diameter (D [3,4] and Dv10 and Dv90 percentiles [24]).

The nitrogen adsorption–desorption isotherms of the samples were measured at 77 K using a Micromeritic ASAP2020 (static volumetric technique). The total specific surface area (SBET) was determined through the BET equation [25].

The hardness and adhesiveness (texture profile analysis) were determined in a Brookfield Texture Analyzer, model LRFA 1000. The working parameters of this instrument were load 0 to 1000 g, resolution 0.10 g, precision ± 0.5% full scale range and probe speed 0.1 to 10 mm/s in 0.1 mm/s steps or 1 to 10 mm/s in 1 mm/s steps with an accuracy of ± 0.1% of the set point. The probe position can be adjusted from 0 to 75 mm with a resolution of 0.1 mm and precision of 0.1 mm. The probe used here was a stainless steel, spherical 10 mm diameter probe (reference TA 38), manufactured with a tolerance better than 0.1%. The samples were placed in a polymer recipient shaped like an inverted conical trunk, eliminating air bubbles [7,26]. The instrument provides numerical and graphical data for each product analyzed. The samples were tested in triplicate, and the mean value was recorded for each sample.

The equations best describing hardness and adhesiveness variations according to the water content of each clay–water mixture were obtained using the statistics software package Origin Pro 8 (Origin Lab Corporation, Northampton, MA, USA).

Distilled water (pH around 6.9), obtained using a Fistreen Cyclon distiller, Water Pro PS system Labconco and Synergy UV Millipore, was employed to prepare several mixtures of each clay.

The analytical procedures for the three mineral-medicinal waters were taken from Vademecum II [27]. For the sample collection method and tests described in this Vademecum, we followed the procedures from Standard Methods for Examination of Water and Wastewater (Edition 21), Official Methods of Analysis of the Association of Official Analytrical Chemists (AOAC) and US EPA.

The thermal behaviour of clay/water mixtures is defined by parameters such as specific heat capacity and cooling kinetics. To calculate the specific heat capacities of the clays, we used the equation proposed by Armijo et al. [19]. The velocity of heat loss is important, and this can be determined using curves of temperature decrease over time (cooling curves) and its derived variable: relaxation time (t_r) [19].

The cooling curves for the clay/water mixtures were prepared according to the procedure described by Rambaud et al. [28] using baths Alpha RA 8 and E-100 (Lauda) and a thermopar (model 91100-50 Digi-Sense, Cole-Parmer Instrument Co., Vernon Hills Illinois, IL, USA). For this procedure, a 250 cm^3 polystyrene flask plus screw cap with a central hole was used. The flask was filled with the sample eliminating the air bubbles. The temperature probe was introduced through the hole in the cap, and the vessel was placed in a hot water bath at 45 °C. When the probe reached this temperature, the flask was kept for 30 min in the bath to evenly distribute the heat and was then introduced into another bath at 36 °C. Using a thermometer with a Pt 100 probe, the temperature of the sample was measured at 15 s intervals until a temperature of 36 °C. The software package Origin 8 (Origin Lab Corporation, Northampton, MA, USA) was used to obtain temperature vs. time graphs and to describe the equations for the curves that best fitted the experimental data [19].

For each clay mineral, a regression analysis was used to model the relationship between hardness/adhesiveness and water content (%). Scatter plots showed an exponential relationship. To assess the goodness of fit of our regression model, the coefficient of determination (R-squared) was calculated. After linearization of these models, slope comparison tests (F) were used to assess the differences between the water types. The same procedure was followed for temperature against time in Thermal Properties. Statistical tests implemented in STATGRAPHICS served to determine whether the slopes of the lines were significantly different. All the statistical tests were performed using the software package STATGRAPHICS CENTURION XVIII. The significance was set at $p < 0.05$.

3. Results

3.1. Characterization of the Clay Samples

Bulk and clay mineral contents, grain-size distributions and BET specific surface areas of the three clays analysed are provided in Tables 1 and 2.

Sample M1 shows a predominance (95%) of mainly trioctahedral clay minerals (d(060) = 1.529 Å). Quartz and feldspar (K-feldspar and plagioclase) were detected in proportions lower than 5%. The clay fraction (<2 µm) shows Mg-smectite as the main component (92%), with minor amounts of illite (8%) and traces of kaolinite and sepiolite (Figure 2). The Mg-smectite content of the bulk clay sample was 87%. The 001 reflection of smectite appeared at 15.17 Å in the randomly oriented powder sample, indicating divalent cations in the interlayer.

Table 1. The mineralogical composition and BET specific surface areas.

Sample	Bulk Mineralogy (wt. %)	Clay Mineralogy (wt. %)	BET (m^2/g)
M1	Phyllosilicates (95) Quartz (2) K-feldspar (2) Plagioclase (1)	Smectite (92) Illite (8) Kaolinite (Tr) Sepiolite (Tr) (d(060) = 1.529 Å)	145
M2	Phyllosilicates (99) Quartz (<1) Plagioclase (<1)	Sepiolite (98) Smectite (2)	293
M3	Phyllosilicates (67) Quartz (10) Calcite (10) Plagioclase (4) Dolomite (4) Pyrite (2) K-feldspar (2) Cristobalite (<1) Gypsum (<1)	Smectite (52) Illite (41) Kaolinite + Chlorite (7)	29

Table 2. The particle size parameters.

PARAMETER	UNIT	M1	M2	M3
D [3,4]	µm	16.2	16.4	29.4
Dv (10)	µm	3.21	3.86	3.97
Dv (50)	µm	10.2	9.45	18.0
Dv (90)	µm	36.0	40.6	63.2
Mode	µm	8.36	7.33	23.8
Uniformity		1.04	1.13	1.15

Sample M2 was composed largely of clay minerals (99%), showing traces (<1%) of quartz and plagioclase (Figure 2). The clay fraction showed a predominance of sepiolite (98%) and minor amounts of smectite (2%). The sepiolite content of the bulk clay sample was 97%. According to Pozo et al. [29], the XRD powder pattern is characteristic of a high "crystallinity" sepiolite (HCS).

In the common clay sample (M3), dioctahedral clay minerals (d(060) = 1.501 Å) predominate (67%) along with lower contents of quartz (10%) and calcite (10%) and minor percentages (<5%) of dolomite, plagioclase, K-feldspar, pyrite, cristobalite and gypsum (Figure 2). The clay fraction (<2 µm) shows Al-smectite (52%) and illite (41%) as the main components, with minor amounts of kaolinite + chlorite (probably clinochlore) (3%).

The particle-size distributions including both frequency and cumulative plots are shown in Figure 3. Samples M1 and M3 show a more symmetric and unimodal frequency plot, whereas sample M2 displays an asymmetrical bimodal frequency plot. When we compared the particle-size distributions, the higher modes (7.33–23.8 µm) and medians (9.45–18.00 µm) were the higher values recorded in the common clay sample (M3), whereas the special clays (M1 and M2) showed similar lower values (Table 2). The volume mean diameter (29.40 µm) and Dv90 (63.2 µm) of M3 reveal this is the coarser-grained sample.
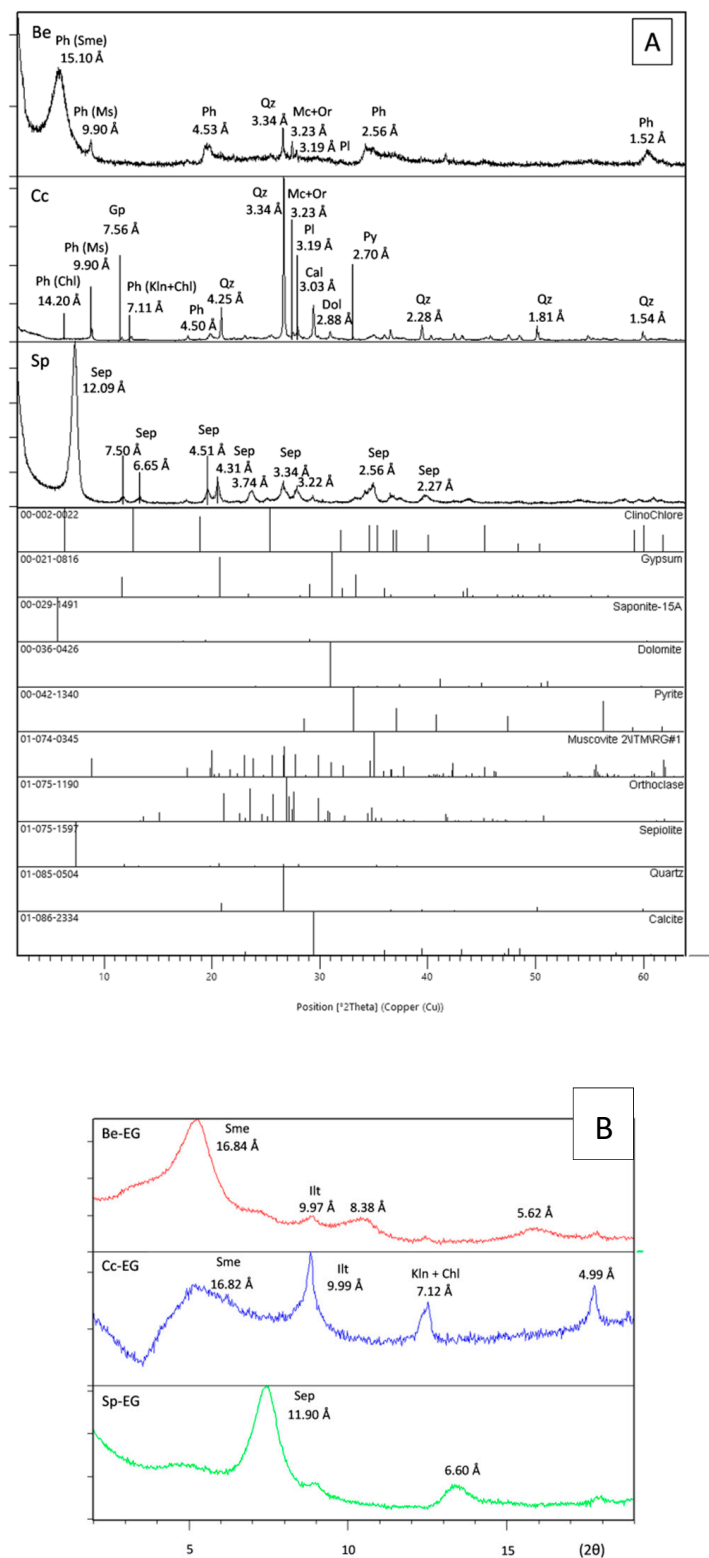
Figure 2. The XRD diffraction patterns of the M1 (Be), M2 (Sp) and M3 (Cc) samples: (**A**) the bulk sample and (**B**) the clay fraction (ethylene glycol solvated oriented mounts). With the exception of phyllosilicates (Ph), the IMA (International Mineralogical Association) abbreviations were used. Gp = Gypsum. Qz = quartz. Mc + Or = K-feldspar. Pl = Plagioclase. Cal = Calcite. Dol = Dolomite. Kln + Chl = Kaolinite+chlorite. Sme = Smectite. Sep = Sepiolite. Ilt = Illite. Ms = Muscovite. Py = Pyrite.
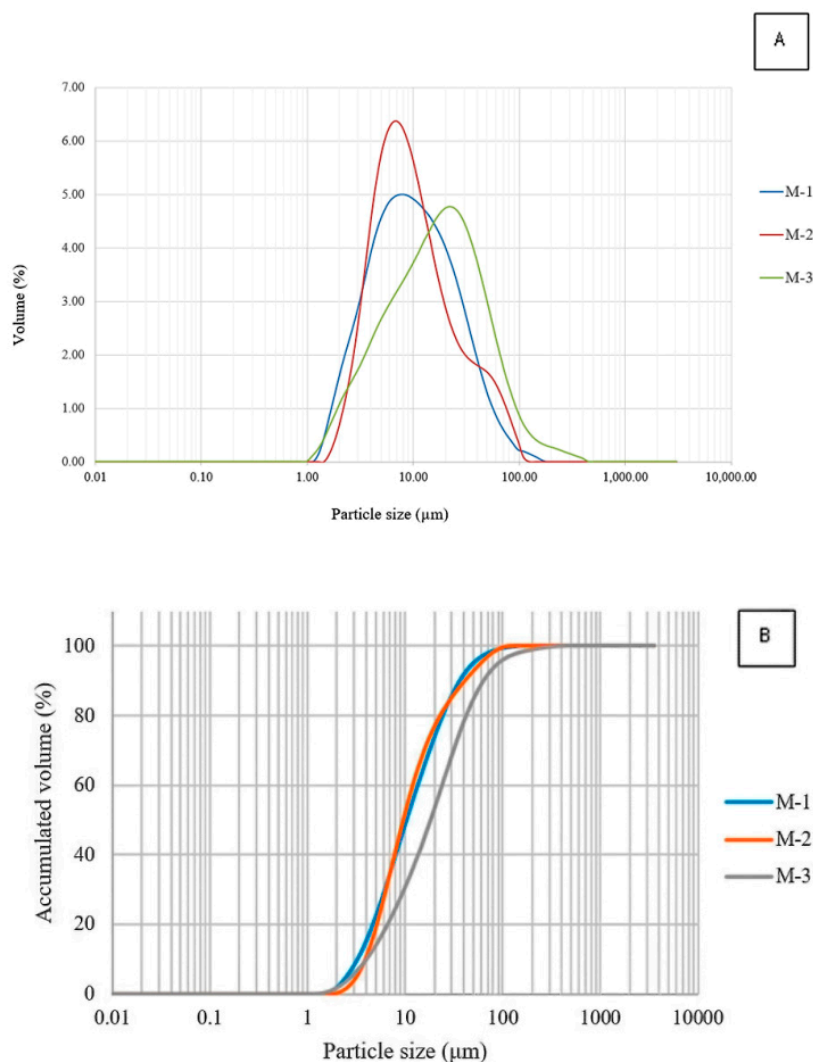
Figure 3. (**A**) The particle-size distributions of samples M-1, M-2 and M-3 and (**B**) the accumulated curves of samples M-1, M-2 and M-3.

Uniformity is a measure of the absolute deviation from the median. It is a dimensionless parameter, and higher values of uniformity indicate more polydispersed samples.

The BET specific surface area of the sepiolite sample (M2) was the highest, with values reaching 293 m^2/g (Table 1). The different grain-size distributions and mineralogical assemblages could explain the significant differences in BET between sample M1 (145 m^2/g) and M3 (29 m^2/g).

3.2. Mineral-Medicinal Waters

Table 3 lists the results of our physicochemical analysis of the three mineral-medicinal waters used to prepare the pastes. All three waters are of strong mineralization and classified as bicarbonates (W1), chlorides (W2) and sulphates (W3), since HCO_3^-, Cl^- and SO_4^{2-} concentrations exceeded 20% equivalent in all three cases to more than 1 g/L of dry residue [27].

Table 3. The chemical composition and properties of the natural mineral waters used in this study.

	W1	W2	W3
Type of Water	**Strong Mineralization Sodium-Bicarbonate**	**Strong Mineralization Sodium-Chloride**	**Strong Mineralization Calcium-Magnesium-Sulphated**
Flavour	saline	saline	saline
Odour	Odourless	Odourless	Rotten eggs
Colour	Colourless	Colourless	Colourless
Spring water temperature (°C)	15.2	51.2	17.8
Conductivity to 25 °C ($\mu S \cdot cm^{-1}$)	2998	4223	3876
pH (to the water spring temperature)	5.0	7.4	6.8
Turbidity (UN)	0.0	0.0	7.2
Dry residue to 180 °C (mg/L)	1814	2732	2640
Dry residue to 110 °C (mg/L)	1827	3032	2728
Hardness (mg/L $CaCO_3$)	208	412	1870
Alkalinity (mg/L $CaCO_3$)	1505	110	95
Cl^- (mg/L)	93.7	**1054.8**	116.7
F^- (mg/L)	3.3	0.4	2.6
HCO_3^- (mg/L)	**1836.1**	134.2	115.9
CO_3^{2-} (mg/L)	0.0	0.0	0.0
NO_3^- (mg/L)	0.0	2.8	0.0
SH^- (mg/L)	0.0	0.0	16.3
SO_4^{2-} (mg/L)	2.9	320.5	**1759.8**
Na^+ (mg/L)	624.1	629.9	77.4
K^+ (mg/L)	26.7	11	7.6
Li^+ (mg/L)	3.4	0.2	0.3
Ca^{2+} (mg/L)	37.1	129.8	516.1
Mg^{2+} (mg/L)	28.0	21.5	141.3
Sr^{2+} (mg/L)	0.0	0.0	0.0
Fe total (mg/L)	2.4	0.1	0.0
CO_2 dissolved (mg/L)	528	4.9	71.1
H_2S dissolved (mg/L)	0.0	0.0	27.3

3.3. Hardness (TPA)

The hardness variations with clay/water proportions for the three clays analyzed are shown in Figure 4. The bentonite, sepiolite and common clay samples showed similar behaviour in the clay/water mixtures with the hardness decreasing with increasing water content.
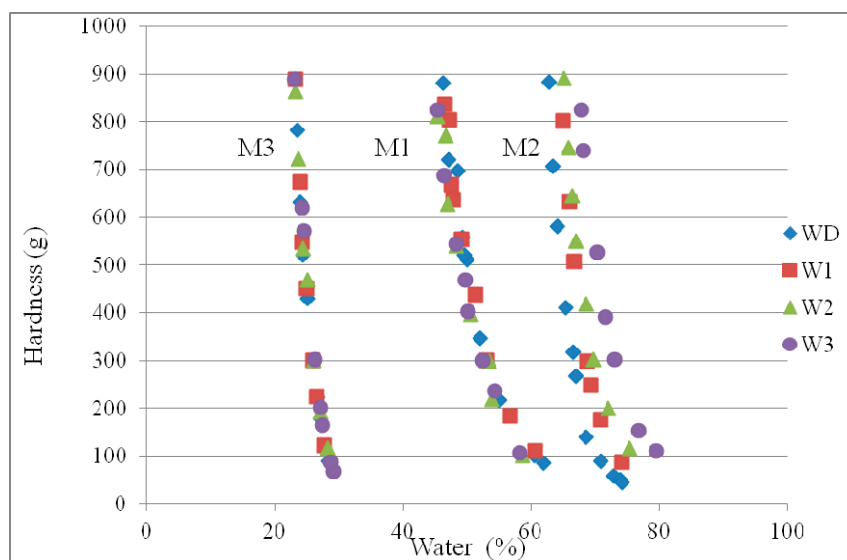
Figure 4. Hardness variations with water (%) content.

Sample M3 was observed to retain the least amount of water (<40%) for any hardness value considered. In contrast, the M2 sample retained the higher water content (>60%), while M1 showed an intermediate behaviour such that any hardness could be obtained using water contents greater than 40%.

When we examined the effect of the main anion of the mineral-medicinal waters used to prepare the paste, a small variation was detected between M1 (bentonite) and M3 (common clay), such that

the curves for the three waters and for the distilled water blank overlapped. In sample M2 (sepiolite), significant differences in terms of water retention were observed according to the type of water used. Thus, the sulphate-rich waters (W3) seemed to favour water retention for a given hardness value. In other words, a particular hardness could be obtained using a smaller amount of clay when the sepiolite sample (M2) was mixed with the water containing sulphates (W3). This means that for any hardness requirement, the amount of water necessary will always be greater when sepiolite is used, especially in mixtures with sulphate-rich waters.

Armijo et al. [14] reported that the hardness of different clay/water mixtures decreases with increasing water content according to a negative exponential curve. These authors proposed the measurement of the parameters H_0, X_0 and X_{300} where H_0 is defined as the hardness of the mixture, X_0 as the minimum water percentage of a product that could be used as a peloid and X_{300} as the amount of water needed to obtain that hardness. A_0 is the adhesiveness of the mixture for water percentage X_0, and X_A is the additional percentage of water needed for adhesiveness to decrease to the number e. According to the hardness values determined by Pozo et al. [7] for peloids used in Spanish spas, the mean hardness is 300 g.

The values of H_0, X_0 and X_{300} obtained for the mixtures of the clays M1, M2 and M3 with different water types are shown in Table 4. These results are consistent with the interpretation of the graph in Figure 4. For each clay mineral, an exponential regression analysis was used to model the relationship between hardness and water content (%). To assess the goodness of fit of our regression model, the coefficient of determination (R-squared) was calculated, and after linearization of these models (Table 5), slope comparison tests were used to assess the differences between the water types (Table 6).

Table 4. The characteristic hardness and adhesiveness parameters of the tested products.

Clay	Water	X_0 (%)	H_0 (g)	X_H (%)	X_{300} (%)	A_0 (g.s)	X_A (%)
M1	W1	46.6	728.9	4.9	53.0	8611.8	5.1
	W2	45.4	609.0	3.4	52.5	8702.4	3.4
	W3	45.5	801.6	6.7	52.4	8756.1	3.5
	WD	46.3	823.3	4.6	53.1	9514.6	6.6
M2	W1	65.0	745.1	2.9	68.8	6963.8	2.5
	W2	65.0	828.0	3.9	69.8	8904.2	4.1
	W3	67.9	747.6	4.5	73.1	7980.1	3.8
	WD	62.8	861.4	3.3	66.2	8950.7	3.7
M3	W1	23.3	874.9	2.4	26.1	8238.2	2.0
	W2	23.2	921.3	3.1	26.1	7936.9	2.6
	W3	23.1	980.1	3.3	26.3	8590.2	3.1
	WD	23.5	785.5	2.6	26.2	7297.9	2.7

Table 5. The intercept (A), slope (B) and determination coefficients (R^2) of the regression lines for hardness (or adhesiveness) by types of clay and water.

Clay	Water	Hardness			Adhesiveness		
		A	B	R^2	A	B	R^2
M1	W1	13.8175	−0.1522	0.9950	16.2078	−0.1509	0.9974
	W2	13.4291	−0.1444	0.9935	16.0578	−0.1484	0.9970
	W3	13.8319	−0.1556	0.9825	16.5729	−0.1612	0.9856
	WD	13.7352	−0.1539	0.9914	16.4404	−0.1583	0.9934
M2	W1	23.1746	−0.2623	0.9923	25.5167	−0.2598	0.9889
	W2	22.5248	−0.2442	0.9951	25.0833	−0.2453	0.9902
	W3	19.6927	−0.1992	0.9936	21.7983	−0.1940	0.9972
	WD	18.5847	−0.1756	0.9948	20.3335	−0.1658	0.9959
M3	W1	16.5680	−0.4201	0.9878	17.6202	−0.3708	0.9943
	W2	16.8025	−0.4294	0.9912	19.5497	−0.4498	0.9973
	W3	15.8456	−0.3895	0.9954	17.6237	−0.3724	0.9907
	WD	16.7569	−0.4253	0.9895	18.9594	−0.4250	0.9926

Table 6. The p-values of the statistical test for comparing slope regression lines for hardness (or adhesiveness) by types of clay.

Clay	Hardness			Adhesiveness		
	p-Value All Water	Waters	*p*-Value	*p*-Value All Water	Waters	*p*-Value
M1	0.5114			0.6624		
M2	0.0004	WD-W1	0.1954	0.0034	WD-W1	0.0006
		WD-W2	0.0001		WD-W2	0.9431
		WD-W3	0.0000		WD-W3	0.0419
		W1-W2	0.0000		W1-W2	0.0031
		W1-W3	0.0010		W1-W3	0.2712
		W2-W3	0.0194		W2-W3	0.0397
M3	0.0842			0.1350		

No significant differences were observed in the hardness variations shown by the peloids as water contents were varied for W1, W2, W3, WD and the clays M1 (F = 0.79, *p* = 0.5114) and M3 (F = 2.60, *p* = 0.0842). For the sepiolite, M2 differences in hardness depended on the water type used (*p* = 0.0004). Between WD and W1, no significant differences were detected (F = 1.85, *p* = 0.1954). When we compared the hardness of the peloids prepared with the three different clays (Figure 4), significant differences appeared among the three types: M1, M2 and M3 (F = 26.95, *p* = 0.0000).

To obtain a reference hardness of 300 g, sample M1 retained the greater amount of water when W1 was used in similar proportions to that necessary with distilled water (53%). Using W2 or W3, the water retention was slightly lower.

In the case of sample M2, the greatest water retention (73%) was noted for W3. For the use of waters W1 and W2, this retention was somewhat lower but still higher than the value recorded for distilled water.

The lowest water content (greater proportion of clay) to obtain a hardness of 300 g was observed for the common clay sample M3, such that a hardness of around 26% was attained using any one of the four waters.

3.4. Adhesiveness (TPA)

The variation in adhesiveness according to the clay/water proportion for the three samples examined is shown in Figure 5.
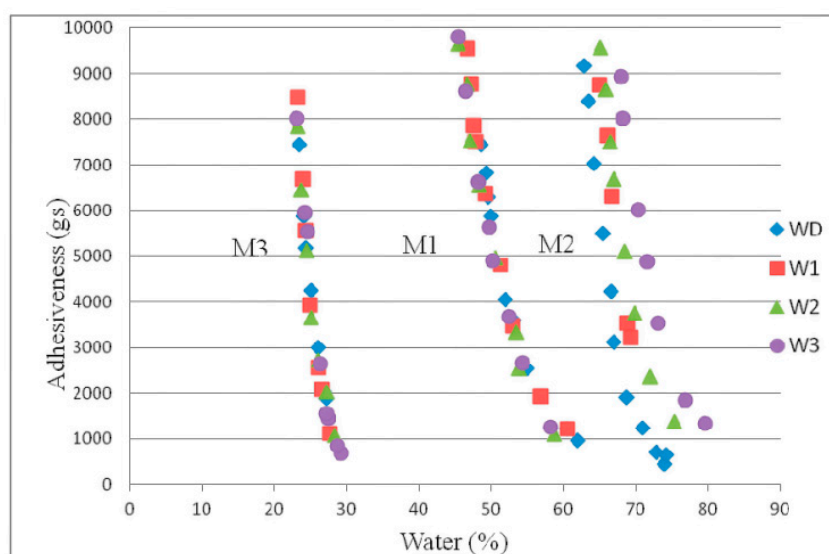

Figure 5. Adhesiveness variations with water (%) content.

Adhesiveness diminishes as the proportion of water in the mixture increases such that its behaviour is similar to that of hardness. As a reference, the mean value of the peloids employed in Spanish spas is of the order of 4500 g.s [7]. To obtain this level of adhesiveness in the bentonite mixtures, the greater clay contents (lowest amount of water) were observed for sample M3 with any type of water (Table 4). Conversely, this adhesiveness was recorded in sample M2 using the highest water content, especially when the mineral-medicinal water W3 was employed. In the case of M1, the content of water retained was between those of M2 and M3.

No significant differences in the adhesiveness of the peloids emerged when we modified the contents of the waters W1, W2, W3 and WD and the clays M1 ($F = 0.54$, $p = 0.6624$) and M3 ($F = 2.29$, $p = 0.1350$). In contrast, significant differences according to the water used in the mixture did arise for sample M2 ($F = 6.22$, $p = 0.0034$). However, among all the comparisons possible, there were no significant differences for WD versus W2 ($F = 0.01$, $p = 0.9431$) or for W1 versus W3 ($F = 1.34$, $p = 0.2712$). When comparing the three clays, differences in this variable were always significant ($F = 14.90$, $p = 0.0000$).

3.5. Thermal Properties

For the desired thermal properties of clay/water mixtures or peloids, a large volume of water is important. The clay particle size determines the adsorption capacity as does the presence of external and internal surfaces where water molecules are retained [18,30].

Considering the percentages of the different waters used to prepare the clay/water mixtures with the same hardness of 300 g, it is possible to calculate the heat capacities and, therefore, assess their potential thermotherapeutic effects [31]. To calculate the specific heat capacities of the clays, the equation proposed by Armijo et al. [19] was used.

The variable that describes cooling velocity t_r is designated as the relaxation time. This measure is defined as the time needed for a variable in exponential decrease to fall from its initial value by 63.2% of its amplitude. In this case, for a starting temperature of 45 °C and a final temperature of 36 °C, the amplitude is 9 °C and the first relaxation time t_r will be the time taken for the temperature to drop to ($36 + 9/e$), that is, 39.3 °C [19].

Our results (Table 7) indicate that pastes with a hardness of 300 g can be prepared with specific heat capacities that range from 2659 to 2685 J/(kgK) for the M1 clay/water mixtures, 3133 to 3357 J/(kgK) for the M2 clay/water mixtures and 1712 to 1721 J/(kgK) for the M3 clay/water mixtures. Taking into account the different types of water, the paste consisting of M2 and W3 presented the highest specific heat capacity.

Table 7. The thermal parameters of the pastes prepared to a hardness of 300 g.

Clay	Water	H_2O %	Ash %	C_p J/(kgK)	t_r min
M1	W1	53.0	43.7	2682	9.1
	W2	52.5	44.6	2663	9.2
	W3	52.4	45.4	2659	9.2
	WD	53.1	43.3	2685	9.1
M2	W1	68.8	27.9	3218	10.0
	W2	69.8	27.5	3249	9.9
	W3	73.1	24.5	3357	10.0
	WD	66.2	30.9	3133	10.2
M3	W1	26.1	67.1	1712	5.2
	W2	26.1	67.0	1714	5.3
	W3	26.3	66.8	1721	5.3
	WD	26.2	66.8	1717	5.4

Obviously, these differences are related to the percentage of water retained and, thus, to the type of clay minerals forming the clay/water mixture. Another aspect that needs to be considered

when assessing the thermal behaviour of a clay/water mixture or peloid is its capacity to slow release heat [7,19,32]. The cooling curves shown in Figures 6 and 7 were used to calculate the relaxation times (t_r) of the clay–water mixtures. For each clay mineral, an exponential regression analysis was used to model the relationship between temperature and time by each type of water. The linearization of these models is presented in Table 8. A large value of the relaxation time indicates a slower velocity of heat release. In Table 7, those variables are provided for the clay/water mixtures prepared with mineral-medicinal waters and distilled water for a hardness of 300 g.
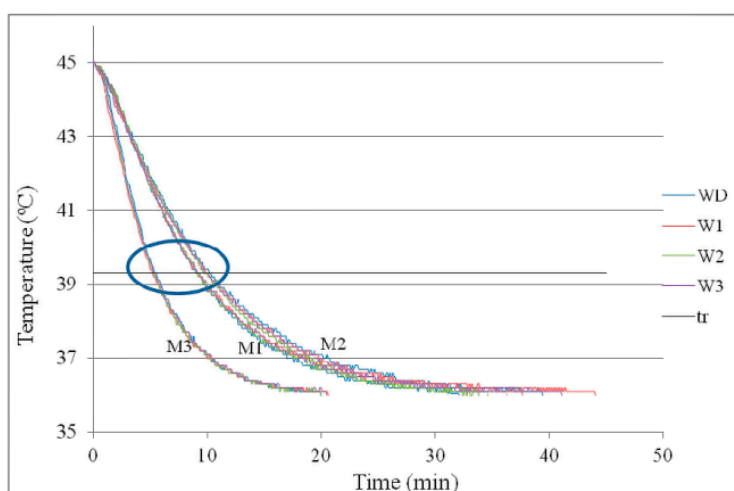
Figure 6. The cooling curves for the mixtures of the three clays and four waters. t_r = relaxation time.
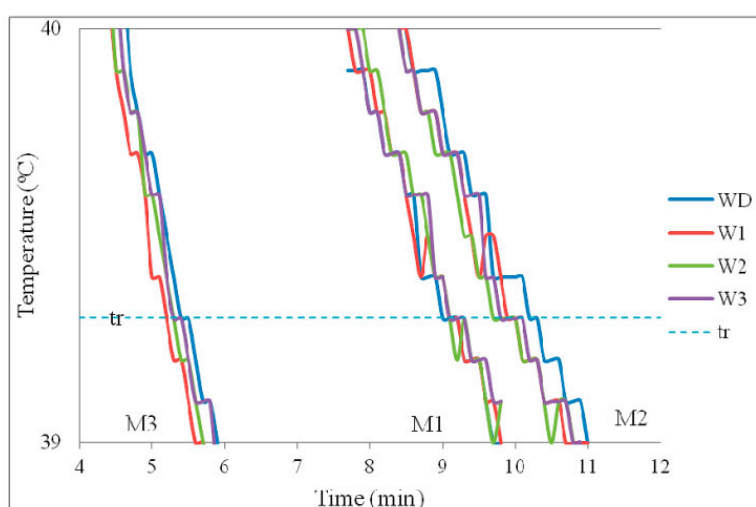

Figure 7. The cooling curves for the mixtures of the three clays and four waters. t_r = relaxation time (extension of the area marked with oval).

These data indicate that the clay/water mixtures prepared with sample M2 and any water show the least heat loss (nearly 10 min), whereas that prepared with M3, also with any water, will lose heat more rapidly (around 5 min).

Our statistical study of the cooling curves, which show the temperature variation of the peloid over time, indicates that for the pastes formed using the materials M1 (F = 0.30, p = 0.8259), M2 (F = 0.44, p = 0.7226) and M3 (F = 1.06, p = 0.3641), no differences exist among the four waters employed.

When comparisons were made among the pastes consisting of the three clays mixed with the four types of water, significant differences in temperature changes over time were detected for the three clays (F = 3.18, p = 0.0005).

Table 8. The intercept (A), slope (B) and determination coefficients (R^2) of the regression lines by types of clay and water.

Clay	Water	A	B	R^2
M1	W1	3.7502	−0.0064	0.8367
	W2	3.7220	−0.0040	0.7230
	W3	3.7443	−0.0058	0.8139
	WD	3.7289	−0.0045	0.7508
M2	W1	3.7411	−0.0050	0.8150
	W2	3.7426	−0.0052	0.8239
	W3	3.7529	−0.0062	0.8523
	WD	3.7451	−0.0055	0.8393
M3	W1	3.7493	−0.0104	0.8163
	W2	3.7403	−0.0096	0.7987
	W3	3.7455	−0.0010	0.8081
	WD	3.7445	−0.0099	0.8062

4. Discussion

This study reports an increase in both the instrumental hardness and adhesiveness of a clay/water mixture as its clay content increases and, thus, also as the mixture's viscosity increases. In every mixture, the proportion of water was higher when the clay was sepiolite rather than bentonite or common clay. In effect, sepiolite has a high water-retention capacity and may absorb an amount of water equivalent to 200–250% of its own weight [33].

The solid phase of a clay/water mixture will, in large measure, determine its viscosity [17,33]. This factor is conditioned by how the clay particles are arranged in a coherent network and by the composition, size and shape of these particles. Further, clay mineral particles aggregate, and these aggregates will assemble through different mechanisms determined mostly by the composition, pH and ion strength of the clay [34,35].

The clay/water mixtures prepared for this study contained high solid concentrations (>20% wt.%), and this conditions the aggregation state and properties of the mixtures. The water used to prepare the clay pastes varied in ion composition, and this, as described by Casás et al. [17,31], gives rise to pastes with different properties, depending especially on the electrolytes present in the mud [6,32,36–38]. The rheological properties of the mixtures are important as they affect their application and spreading [39] along with their thermotherapeutic properties.

Clay/water mixtures used to prepare peloids are highly concentrated clay suspensions and, thus, show the rheological features of semisolid products [39–41]. The different behaviour and rheological properties of concentrated laminar or fibrous clay mineral particle suspensions may be explained by individual aggregation mechanisms and aggregate size [42–44].

The interactions of sepiolite, bentonite and common clay with water may be conditioned by particle size, morphology and structural features. Clay minerals mostly form gels in water [45].

The swelling capacity and colloid behaviour of bentonites composed of smectites are determined by layer composition, their charge and the exchangeable interlayer cation [46,47].

As sepiolite is a non-swelling fibrous clay mineral, the fibre length and silanol groups on the fibre surfaces play a key role in aggregating the fibres in bundles to form a random network, which captures water and enhances viscosity. Thus, sepiolite is less sensitive to electrolytes than smectite [48,49].

The common clay used here is composed mostly of Al-smectite and illite, with a high proportion of non-clay minerals (33%), which explains the differences in the grain size distribution and, hence, its lower capacity to retain water.

The water contents of clay/water mixtures determine their thermophysical properties [16–18]. For purposes of thermotherapy, the best thermal behaviour was shown by the mixture containing

sepiolite and sulphate-rich mineral water, which had a specific heat of 3357 J/(kgK) and a t_r of 10 min. This mixture also had a higher water content than the mixtures containing bentonite or common clay.

5. Conclusions

Instrumental hardness and adhesiveness showed an exponential decrease with the content of mineral-medicinal or distilled water in the mixtures prepared. The clay/water concentration affected the viscosity of the clay/water mixtures and, thus, their instrumental hardness and adhesiveness.

Sepiolite retained more water (>60%) that the other clays for a particular instrumental hardness or adhesiveness of the mixture. In contrast, the common clay retained the least amount of water in the mixture when prepared with any of the waters tested.

For a reference instrumental hardness of 300 g, a sepiolite content of around 27% was needed, and this increased to 74% when the common clay was used. For the bentonite, an intermediate content of around 47% (53% of water) was needed.

When mixed with sulphate-rich mineral-medicinal water, sepiolite showed the best thermal behaviour because it was able to retain 73% of water and showed a specific heat capacity of up to 3357 J/(kgK) and a t_r value of 10 min. The common clay showed the worse thermal behaviour because it could only retain 26% of water.

The instrumental hardness and adhesiveness of the tested clay/water mixtures were poorly affected by the predominant anion in mineral-medicinal water. Only for the sepiolite sample was a slight difference observed among distilled, sulphate-rich, chloride-rich and bicarbonate-rich waters.

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