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Q1 Thermal behaviour of clays and clay-water mixtures for pelotherapy

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ABSTRACT

To prepare peloids for thermotherapy, the thermal behaviour of their component clay pastes needs to be known. This study was designed to experimentally determine the specific heat capacity and cooling kinetics of pastes prepared by adding different proportions of water to eight commercially available clays of different composition. According to exponential equations fitted to the cooling curves for the pastes, a new parameter designated the relaxation time is proposed. Using this parameter, the clayey pastes could be classified on the basis of rate of heat release. According to its specific heat capacity and relaxation time, Na-activated magnesium bentonite emerged as the most suitable clay material to prepare peloids with applications in thermotherapy.

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1. Introduction

The use of heat for therapeutic purposes is known as thermotherapy and this is one of the most important healing effects of peloids (Hattori, 1963; Beer et al., 2003; Maraver et al., 2015). Peloids are defined as a mixture solids and mineral water or seawater that acquire healing and/or cosmetic properties after maturation (Gomes et al., 2013, and references therein). The solid component of peloids may be inorganic (clay minerals), organic (peat) or even a mixture of both. Clays are the most commonly used inorganic materials to prepare peloids. Clay minerals forming raw or modified clays should be considered the materials of the 21st century, given their abundance, low cost and environmental friendliness (Bergaya and Lagaly, 2006).

Lewis (1935) was the first author to analyze the thermal properties of peloids. This author suggested that specific heat capacity increased as the percentage of water increased, while thermal conductivity decreased. Veniale et al. (2004) indicate that thermal behaviour varies depending on the thermal water used during the maturation process, while the temperature reached by the peloid 20 min after application depends on its water retention capacity (Legido et al., 2007).

The thermal behaviour of clay minerals-forming peloids is defined by parameters such as specific heat, heat capacity and cooling kinetics. According to the principles of thermodynamics, the heat applied to a system is used both to increase its internal energy, which may be transferred to an adjacent body, and to perform external work.

The heat Q that a system may transfer is given by the equation (Sears and Zemansky, 1954):

$$Q = m c_p (T_i - T_f) \quad (1)$$

where m is the mass, $(T_i - T_f)$ the temperature gradient and c_p the specific heat. For a fixed mass of product m and a similar temperature gradient, the specific heat will be the only varying factor and will be determined by the specific heats of their solid and liquid phases. For a similar water concentration, the specific heat of a peloid will be related with the solid phases used in its preparation, and hence the importance of characterizing this variable in these products.

The heat capacity of a system is defined as the amount of heat that needs to be supplied to the system to raise its temperature by one degree. If the system consists of a single substance or dissolution and its weight is one gram, this factor is known as the specific heat capacity. The value of this property, as mentioned above, is used to calculate the amount of heat that a system can supply as its temperature drops (Ferrand and Yvon, 1991; Nashchokin, 1979). This drop in temperature creates a flow of energy from the heat source to the cold source, and this

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is an irreversible process that can be expressed by phenomenological laws, in this case, that of Fourier (de Groot, 1951).

Ferrand and Yvon (1991) proposed an empirical equation to calculate the heat capacity of a paste (2):

$$C_p = 0.498 + 3.79 (W)/100 \quad (2)$$

where (W) is the weight percentage of water in the paste.

In contrast, Cara et al. (2000) argued that the specific heat of bentonite pastes could be correlated with their water proportions by linear regression (3).

$$C_p = 0.2914 + 0.0393 \text{ wt}\%(W) \quad (3)$$

where $\text{wt}\%(W)$ is the weight percentage of water in the product.

Several authors have reported specific heats of clay minerals. Effectively the specific heats of cation-saturated montmorillonites and kaolinites were early determined by Goranson (1942), and Oster and Low (1964). Skauge et al. (1983) used a differential scanning calorimeter (DSC) at temperatures between 300 and 700 K to obtain the heat capacities of sodium and calcium kaolinite, sodium and calcium montmorillonite, illite and attapulgite (palygorskite). Gailhanou et al. (2007) measured the specific heats of smectite, illite and a mixed-layer illite-smectite. Casás et al. (2011), using a Calvet calorimeter, measured the specific heats of magnesian bentonite (saponite) mixtures prepared with seawater and distilled water. Knorst-Fouran et al. (2012) measured the specific heats of the peloid TERDAX® and its dilutions at atmospheric pressure using a commercial calorimeter based on the Calvet principle with temperature control. More recently the effect of water salinity on the thermal behaviour of magnesian bentonite pastes was reported by Casás et al. (2013).

The cooling kinetics of a material is also crucial to understand the thermal behaviour of peloids (Ferrand and Yvon, 1991; Cara et al., 2000; Legido et al., 2007; Rebelo et al., 2011). Ferrand and Yvon (1991) and Legido et al. (2007) addressed the cooling kinetics of pastes prepared with bentonite, kaolinite, silt or sand and water using the equation:

$$T = T_0 + A e^{-kt} \quad (4)$$

where T is the temperature reached in the time period t , T_0 is the temperature of the cold source, A is the amplitude or initial difference in temperature between the hot and cold source, and k is given by the ratio between p , a constant of the measuring device, and c the specific heat capacity of the paste.

Legido et al. (2007) determined the cooling rates of bentonite, sepiolite and other clays often used in pelotherapy. These authors expressed k for a temperature T using the equation:

$$k = DT + E \quad (5)$$

where E and D are constants. They calculated the specific heats of the dry clays using the values obtained for the pastes with Eq. (4).

The present study examines the thermal behaviour of pastes prepared by mixing clays with different proportions of distilled water. The aim of the study was to determine variability in thermal parameters as a function of the clays used to elaborate each paste.

2. Materials and methods

Eight clays previously characterized by X-ray diffraction (Carretero et al., 2014; Armijo et al., 2015) were selected for this study: smectite-rich clays (M1, M2, M5, M6, M7), palygorskite (M3), sepiolite (M4), and kaolin (M8) (Table 1). All samples were provided by companies as powders.

Table 1
Clay materials used in this study along with their trade names and providing companies.

Sample	Trade name	Company
M1	Volcangel ^a	Benesa
M2	Atox ^a	Tolsa
M3	Palygel SMV ^a	Tolsa
M4	SPLF ELITE ^a	Tolsa
M5	Clay 1 ^b	Süd Chemie España
M6	Clay 2 ^b	Süd Chemie España
M7	Clay 3 ^b	Süd Chemie España
M8	Caolín G-40/77M ^a	Avisa

^a Clays studied in Armijo et al. (2015).

^b Clays studied in Carretero et al. (2014).

Grain size was measured using a Malvern Mastersizer (3000) Microlaser analyzer for particles in the range 0.01–3500 μm after processing bulk samples by high volume dispersion unit Hydro EV.

To check grain size and shape, a textural scanning electron microscope (Hitachi S-510) study was performed by fixing the mineral powders to an aluminium sample holders using adhesive carbon tape and later metalizing the samples with a thin layer of gold (5–10 nm thick).

Swelling in smectite-rich samples was measured using the standard ASTM D5890-06 test method.

The distilled water to prepare the clay pastes was obtained using a Fistreen Cyclon distiller, Labconco Water Pro PS system and Millipore Synergy UV system. Pastes were prepared by adding water to the solids, leaving the water to penetrate the products over a 24 h-period, and then manually homogenizing the mixtures.

Specific heats were determined using an air-cooled differential scanning calorimeter DSC1 (Mettler, Toledo) equipped with STARe software for data acquisition and treatment. The characteristics of this system are a temperature accuracy of ±0.02 K, heating speed of 0.02–300 K/min and cooling speed of 0.02–50 K/min.

The samples were previously dried at 105 °C and kept in bags made of a polymer material in silica gel desiccators. Next, they were pulverized to a particle size of about 0.1 mm, and compacted in aluminium crucibles using a Teflon pestle to remove trapped air, which could impair heat conduction, and achieve good contact with the base of the recipient. These crucibles had a centring pin for correct positioning in the oven. The reference crucible remained in the same position during all measurements, which were made at a heating rate of 10 K/min. The system provides graphs and tables with variations in specific heat produced with temperature.

Cooling curves for the pastes were prepared according to the procedure described by Rambaud et al. (1986) using baths Alpha RA 8 and E-100 (Lauda) and a thermopar (model 91100-50 Cole-Parmer). For this procedure, a 250 cm³ polystyrene flask plus screw cap with a central hole was used. The flask was filled with the sample eliminating air bubbles. The temperature probe was introduced through the hole in the cap and the vessel 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 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 describe the equations for the curves that best fitted the experimental data.

3. Results and discussion

3.1. Mineralogical considerations

The mineralogical characterization of the eight samples under study was previously reported by Carretero et al. (2014) for samples M5, M6 and M7, and by Armijo et al. (2015) for the remaining five samples.

Table 2

Bulk mineralogy and grain size distributions (<64 μm , <20 μm and <5 μm). Main clay mineral contents in each sample appear in bold. For samples M1, M2, M5, M6 and M7, some smectite parameters are also reported.

Mineralogy (wt%)	M1	M2	M3	M4	M5	M6	M7	M8
Smectite	75	57	7	3	99	85	85	2
Illite	13	tr		5		9	13	26
Sepiolite		38	5	91				
Palygorskite			78					
Kaolinite								64
Kao + Chlo			1					
Quartz	<5	<5	7	<1	1	2	1	7
K-feldspar	<5	<1					<1	<1
Plagioclase	<5	<1				3	<1	<1
Calcite	<5			<1		1	1	
Dolomite		<5	<5					
Others		<1 nacholite		<1 cristobalite				
<i>Smectite</i>								
d(060) Å	1.526	1.523			1.498	1.528	1.524	
Interlayer cation	X ⁺	X ⁺			X ²⁺	X ²⁺	X ²⁺	
FWHM (2 θ)	1.040	1.102			1.021	1.161	1.581	
Swelling (cm ³ /2 g)	30	30			11.5	12	5.5	
<i>Grain-size (%)</i>								
<5 μm	31.43	30.16	27.01	25.33	31.04	17.8	17.98	20.45
<20 μm	77.59	77.51	74.53	77.58	79.78	63.56	47.05	66.11
<64 μm	97.15	98.02	99.86	96.86	99.73	99.38	88.71	98.73

Table 2 shows the contents of the clay minerals recalculated for bulk samples from the data provided by the above mentioned authors, but also including variables related to smectite type, ordering (FWHM) and swelling capacity.

Among the bentonites (57–99 wt% smectite) samples M1 and M6 are mostly composed of trioctahedral smectites ($d_{(060)} \sim 1.52$ Å), sample M2 is a mixture of trioctahedral smectite and sepiolite and sample M5 consists of dioctahedral smectite ($d_{(060)} \sim 1.49$ Å). Smectite shows moderate to good ordering with FWHM values between 1.021 and 1.161 2 θ . Sample M7 is made up of poorly ordered smectite (FWHM = 1.581 2 θ) identified as stevensite.

The position of the $d_{(001)}$ reflection indicates that the smectites in samples M1 and M2 were Na⁺-activated ($d_{(001)} \sim 12.5$ Å) whereas samples M5, M6 and M7 contain mainly divalent cations in the interlayer ($d_{(001)} \sim 15$ Å). The different interlayer cations explain the differences in swelling observed: samples M1 and M2 30 cm³/2 g, samples M5 and M6 close to 12 cm³/2 g, and sample M7 only 5.5 cm³/2 g.

The remaining samples include two composed of fibrous clay minerals, palygorskite (78 wt%) in the case of M3 but sepiolite (91 wt%) in M4. Sample M8 consists mainly of kaolinite with subordinated illite-mica.

3.2. Grain size analysis

Grain size distributions indicate low contents of particles larger than 64 μm (<5%). Sample M7 was the exception showing around 12% of this particle size along with the highest median value (Table 2). Sample M7 showed a reduced <20 μm fraction (47.05%) compared with the remaining samples (63.56–79.78%). Samples M6, M7 and M8 featured the lower contents of particles < 5 μm . These differences in grain size were clear when cumulative weight percent curves were compared (Fig. 1), sample M7 showing the coarser grain sizes.

In the smectite-rich samples, grains are mostly aggregates commonly sub-angular in shape (Fig. 2A, C). Grain sizes are mainly <30 μm in samples M1, M2 and M5, but larger in M6 (Fig. 2D). Samples M3 and M4 also show grain sizes < 30 μm consisted of fibre bundles (Fig. 2B). Coarser sub-rounded grains were observed in sample M7 composed of stevensite (Fig. 2E). Finally, sample M8 displayed a mixture of kaolinite aggregates and mica flakes of variable grain size smaller than 30 μm is (Fig. 2F).

3.3. Specific heat capacity

The specific heat capacity of a body varies across the thermometer scale and this needs to be considered when trying to obtain accurate measurements. In practice, such variations are nevertheless so small that mean specific heat capacities can be worked without appreciable error. For solids and liquids, specific heats at constant pressure and volume are practically of the same magnitude because of the minimal effects of pressure when a body is in these states.

Table 3 shows the specific heat capacities of the eight clays from 36 to 45 °C, temperatures commonly used for peloid application in spas (Fernández-Torán, 2014). The mean values used in subsequent calculations are also provided. Sample M4 (sepiolite) showed the highest specific heat capacity and M3 (palygorskite) the lowest, consistent with values reported in the literature (Legido et al., 2007; Skauge et al., 1983).

The specific heat capacity observed for M1 (Na activated magnesian bentonite) is similar to that described by Skauge et al. (1983) of 853 J/(kg K) at 47 °C for Na-montmorillonite and that provided by Casás et al. (2013) of 851–889 J/(kg K) at temperatures in the range 20–44 °C for a trioctahedral smectite (saponite) of similar characteristics to that analyzed here.

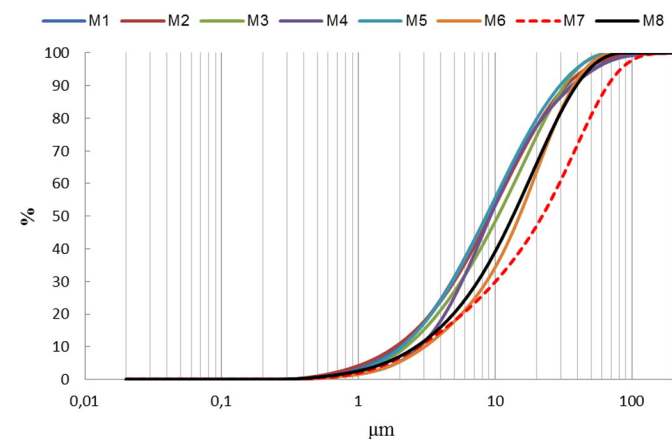


Fig. 1. Cumulative weight percentage curves. The dotted line shows the sample with the coarsest grain distribution (M8).

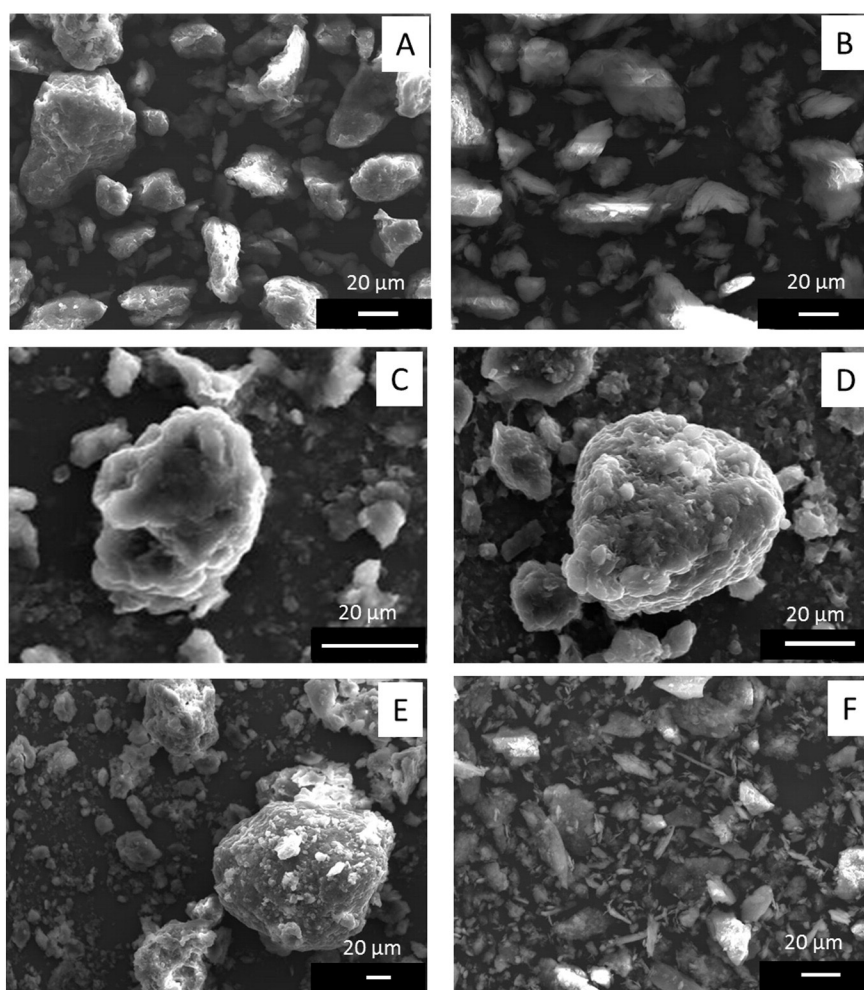


Fig. 2. SEM images of clays. A. Sample M1 (Na-activated magnesian bentonite) B. Sample M4 (sepiolite). C. Sample M5 (aluminian bentonite). D. Sample M6 (magnesian bentonite). E. Sample M7 (stevensite). F. Sample M8 (kaolin).

For the other smectite-rich clays, mean specific heat capacities of 865 J/(kg K) were observed for M5 (Al-bentonite), 892 J/(kg K) for M6 (Mg-bentonite) and 894 J/(kg K) for M7 (Mg-clay rich in stevensite), in agreement with the values reported by Carretero et al. (2014). The heat capacity of M2 is difficult to compare with reported values since it is a mixture of Mg-bentonite and sepiolite. The mean value observed for M3 is consistent with the value provided by Skauge et al. (1983) for palygorskite of 742–780 J/(kg K) for temperatures ranging from 27 to 47 °C. Finally, the specific heat capacity observed for M8 (kaolin) is in accordance with the value of 977 J/(kg K) cited by Skauge et al. (1983) for a calcium kaolinite at 47 °C, as well as the values of 946 J/(kg K) at 23 °C provided by King and Weller (1961) and 974 J/(kg K) at 20 °C provided by Waples and Waples (2004).

Table 3
Specific heat capacities of the studied clays.

Sample	Specific heat capacity (36–45 °C) J/(kg K)	Mean specific heat capacity J/(kg K)
M1	895–900	898
M2	873–892	882
M3	751–776	765
M4	1245–1264	1253
M5	855–865	859
M6	940–1010	981
M7	859–876	870
M8	971–975	972

For peloids or pastes, the specific heat capacity of the system is given by the sum of those of their components according to the general equation (Casás et al., 2011):

$$c_p(P) = \frac{(S_i)c_p(S_i) + (100 - S_i)c_p(W)}{100} \quad (6)$$

where (S_i) is the weight percentage of the different solid constituents and $c_p(S_i)$ and $c_p(W)$ are the specific heat capacities of both solid and water. Using this equation, it is possible to calculate this property if the heat capacities of the individual components of the system are provided. In the case of natural peloids or pastes for which neither the solid phase nor heat capacities are precisely known, we used approximations that provide a fairly acceptable idea of the heat capacity of these products according to the percentage of water they contain, as described in the introduction.

Prát and Brožek (1963) published a series of graphs that enable the calculation of certain physical properties of peloids, including their specific heat capacity as a function of their water and ash contents. The latter is the given percent of residue remaining after the peloid is heated at 850 °C.

Based on these graphs, Armijo (1991) proposed an Eq. (7), with which the specific heat of a peloid can be calculated as a function of its ash (A) and water (W) contents:

$$c_p = 1.26023 + 0.02926 (W) - 0.00628 (A) + 0.000063 (W) (A). \quad (7)$$

By mixing the clays with distilled water, we prepared 8 pastes and calculated their heat capacities according to their clay and water contents using Eq. (6) along with the mean heat capacities determined and the mean specific heat capacity of water in the temperature range 45–36 °C, i.e., 4179 J/kg K.

The heat capacity of the pastes was also estimated using Eq. (7) according to their water and ash contents along with the values obtained using Eqs. (2) and (3). These data are provided in Table 4 as well as percentage differences between values calculated with Eqs. (7), (2) and (3), and those calculated using the mean values measured (Table 3) and Eq. (6).

According to Table 4, the mean values calculated with Eq. (7) show a difference of <2% with respect to the experimental data, whereas the remaining equations gave rise to greater mean value differences of 3.1% for Eq. (2) and 7% for Eq. (3).

Eq. (7) may also be used to calculate the specific heat capacity of peloids (Armijo, 2007). For the TERDAX® peloid, Knorst-Fouran et al. (2012) obtained specific heat capacity values for a 45.2% water content in the range 2319 J/kg K at 25 °C to 2322 J/kg K at 41 °C. This value only differs by 5% from the heat capacity determined by (Armijo, 2007) using Eq. (7) for another sample of this peloid containing 46.1% water (2440 J/kg K).

3.4. Cooling curves of peloids

Another aspect that needs to be considered when assessing the thermal behaviour of a peloid is its capacity to slowly release heat (Berbenni, 1965; Veniale et al., 2004; Pozo et al., 2013). Heat loss from the peloid to the user is defined by the cooling law of Newton, whereby the velocity of heat loss from a heated system is proportional to the difference between its own temperature and the temperature of its cold surroundings.

Newton's law follows the differential equation (Besson, 2010):

$$dT/dt = -k(T - T_0) \quad (8)$$

where T is the instant temperature of the cooling body, T_0 is the temperature of the cold surroundings and k is a constant that defines the rate of cooling.

The solution to this differential equation is that cited in this paper as Eq. (4) ($T(t) = T_0 + A e^{-kt}$) where k is equal to $1/tr$, and tr is designated as the relaxation time (Alonso and Finn, 1968; Diab et al., 2009; Purcell, 2011). This parameter is defined as the time needed for a variable in exponential decrease to fall from its initial value by 63.2% of its amplitude.

A large value of the relaxation time (t_r) indicates a slower velocity of heat release. Newton's law is fulfilled when the difference in temperature between the hot and cold object is not too great as occurs for peloids or pastes.

Table 4

Specific heat capacities (J/kg K) of the clay pastes calculated using different equations (numbers in brackets) provided in the text. Water and ash contents are provided as percentages also included.

Sample	% H ₂ O	% Ash	C _p [6]	C _p [7]	C _p [2]	C _p [3]	[7]/[6]%	[2]/[6]%	[3]/[6]%
M1	62.9	35.2	2963	3020	2883	2765	1.9	2.7	6.7
M2	64.1	33.5	2977	3026	2929	2812	1.0	2.3	6.2
M3	62.8	33.5	2911	3021	2881	2762	3.8	1.1	5.1
M4	63.3	33.6	3106	3036	2899	2781	2.3	6.7	10.5
M5	65.1	32.7	3020	3094	2965	2850	2.4	1.8	5.6
M6	63.9	33.9	3026	3055	2922	2805	0.9	3.4	7.3
M7	63.6	34.2	2974	3043	2908	2790	2.3	2.2	6.2
M8	60.3	35.3	2907	2938	2785	2663	1.1	4.2	8.4

The temperature T_r when the relaxation time t_r has been reached will be:

$$T_r = T_0 + A/e. \quad (9)$$

In our determinations, the equation that best fitted the cooling process given by the Origin 8 software according to the experimental curves was:

$$T = T_0 + A \cdot e^{-(t-t_0)/tr}. \quad (10)$$

In this equation, t_r is the relaxation time, and t_0 corresponds to the inertia time of a small initial zone of the plateau across which the temperature remains constant (Armijo, 2007).

In this case, for a starting temperature of 45 °C and final temperature of 36 °C, the amplitude is 9 °C and the first relaxation time will be the time taken for the temperature to drop to $(36 + 9/e)$, that is 39.3 °C. This will be the same time needed for the temperature then fall to $[36 + 9/(e^2)]$, or 37.2 °C. After a similar third interval, a temperature of $[36 + 9/(e^3)]$, or 36.4 °C will be reached, and after a further such interval the temperature will be 36.16 °C. As a good approximation, the time needed to reach the end of its useful temperature gradient will be three times the relaxation time.

The cooling curves shown in Fig. 3 were used to calculate the relaxation times of the pastes prepared using different dilutions of clays in distilled water (Table 5). The percentage of water (i.e., 60, 70, 80%) was chosen considering the most favourable conditions for peloid elaboration as established by Armijo et al. (2015) in a previous paper.

If we compare the results for all the pastes containing between 60% and 80% of water (Fig. 4), it may be noted that relaxation time increases with water content. The plot shows that the magnesian bentonites (M1,

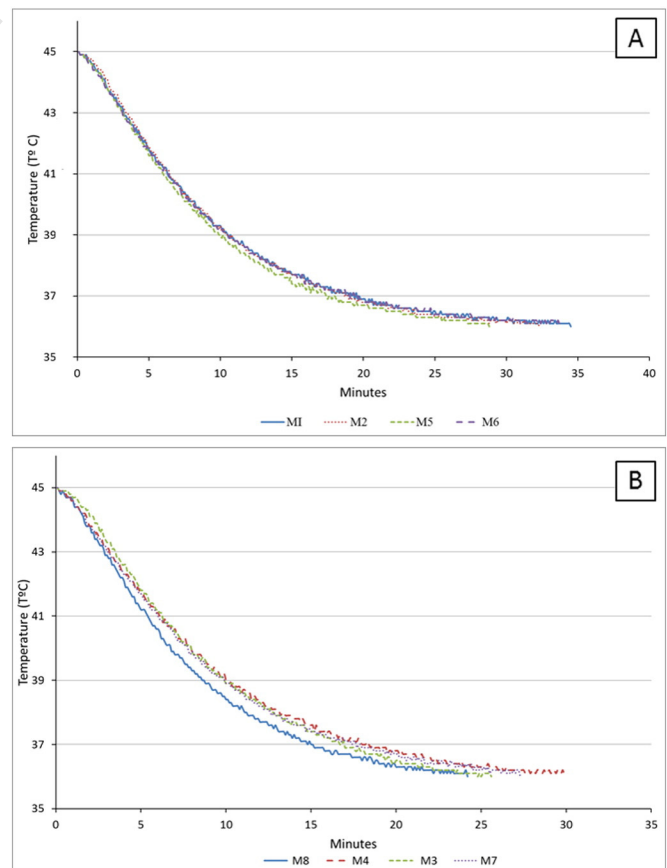


Fig. 3. Cooling curves (60% H₂O). A. Bentonites (M1, M2, M5, M6). B. Palygorskite (M3), sepiolite (M4), stevensite (M7) and kaolin (M8).

Table 5
Relaxation times (minutes) calculated for pastes containing 60, 70 and 80% water.

M1		M2		M3		M4	
% H ₂ O	t _r (min)	% H ₂ O	t _r (min)	% H ₂ O	t _r (min)	% H ₂ O	t _r (min)
60.10	8.7	60.17	8.5	60.09	7.8	60.05	8.3
70.04	9.0	70.08	9.0	70.06	9.1	70.14	8.7
80.16	9.6	79.99	9.3	79.88	9.8	80.17	9.2
M5		M6		M7		M8	
% H ₂ O	t _r (min)	% H ₂ O	t _r (min)	% H ₂ O	t _r (min)	% H ₂ O	t _r (min)
60.16	8.1	59.93	8.8	59.93	7.7	40.10	5.5
69.92	8.7	70.05	9.0	70.05	8.0	49.95	6.1
79.97	9.2	79.92	9.3	79.92	8.4	59.86	7.0

M2, M6) and palygorskite (M3) may attain a relaxation time of around 9 min in pastes containing 70% of water, whereas aluminian bentonite (M5) and sepiolite (M4) need 80% of water for a similar relaxation time, and stevensite (M7) even at this water content shows a shorter time. For kaolin (M8), the lack of consistency with high water contents explains its single value at 60%.

At a low water content (60%), the role of the solid phase is especially relevant and the samples showing the longest relaxation time for this water content, and thus releasing heat more slowly, were the Mg-bentonites (M1, M6), followed by Al-bentonite (M5) and sepiolite (M4), whereas the sample losing heat most quickly was kaolinite (M8) with the shortest relaxation time.

At higher water contents (70–80%), the thermal behaviour observed for palygorskite (M3) differed in that this sample attained the highest relaxation time. These results fully agree with the cooling rates obtained by Legido et al. (2007) for bentonites and sepiolite containing 70% water.

Thermal behaviour depends on the clay and mineral water used to elaborate the paste. Clay composition is essential because its adsorption capacity is important for its thermal properties, especially with regard to retaining a large volume of water. This property is related to the size of clay particles and especially to the existence of external and internal structural surfaces where water molecules are held. The variations observed in this study are mainly related to the water retention capacity of the clays and the presence of fine-grained clay minerals, especially in those with adsorption capacity such as the smectite-rich clays (M1, M2, M5, M6) and fibrous clay minerals (M3, M4). Outstanding differences have been observed on the basis of dioctahedral or trioctahedral character and the type of predominant cation interlayer (Brigatti et al., 2011). Indeed, trioctahedral smectite-rich clays with Na⁺ in the interlayer (greater swelling capacity) show the best characteristics for pelotherapy purposes.

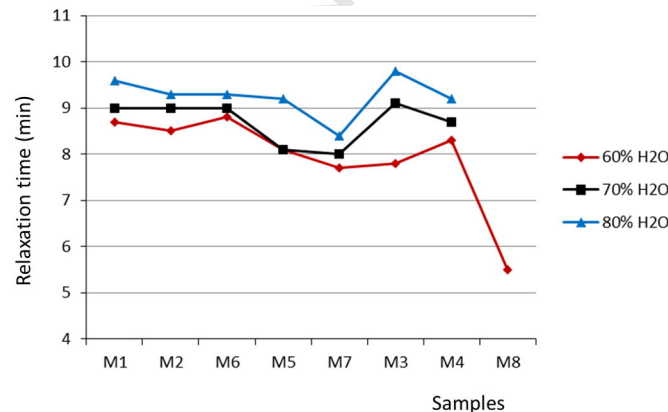


Fig. 4. Plot showing the effect of water content on the relaxation time (min).

Sample M7 is composed of stevensite, a magnesian smectite of low charge (Güven, 1988), which besides its coarser grain size distribution accounts for the lower relaxation time observed. As is well known, in smectites, layer charge and its location play an important role as they determine the hydration of the interlayer cations and thus the degree of moistness (Laird, 1999).

Fibrous clay minerals (sepiolite, palygorskite) have structural channels in which variable amounts of zeolitic water accumulate (Brigatti et al., 2006) explaining their significant thermal behaviour.

Sample M8, is mostly composed of kaolinite. This 1:1 layer clay mineral shows the practical absence of layer charge and only has external structural surfaces. These features serve to explain its lower water retention capacity and thus the lowest relaxation time compared to the other samples.

The complexity of factors influencing the relaxation time may be seen in Fig. 5 where the relationship of this parameter with the swelling of smectites and <20 µm fraction content are shown. Despite the relatively similar relaxation times obtained for the different clays analyzed, it is important to consider that for thermotherapeutic purposes, variations of only 1 min will make a substantial difference.

Knowing the specific heats of clays to be used in solid phase for the preparation of peloids, is useful to assess their thermotherapeutic applications. Also the relaxation time, t_r, serves to evaluate the heat release rate of a peloid. Eq. (7) is proposed as a valuable tool to determine with sufficient accuracy the heat capacity of a peloid without having to rely on expensive equipment.

4. Conclusions

Of the 8 clay samples examined in this study, M4, a sepiolite, showed the highest specific heat capacity and M3, a palygorskite, the lowest. The remaining clays featured similar heat capacities resulting in similar amounts of heat released by their peloids despite the high specific heat capacity of water.

The heat capacities of pastes prepared using the clays can be calculated using the proposed Eq. (7), resulting in differences below 4% when compared with experimental data.

Based on the relaxation times obtained from the cooling curves, pastes containing 60% water were classified according to their rate of heat release. Bentonites were the clays losing heat more slowly while kaolin was the product that released heat most rapidly. For a fixed content of water, the type of smectite plays a more important role than swelling capacity and/or grain size distribution. Based on the amount of heat available and the velocity of release of this heat, magnesian bentonites (especially Na-activated) and sepiolite, emerged as the most appropriate for their use to prepare peloids with applications in thermotherapy.

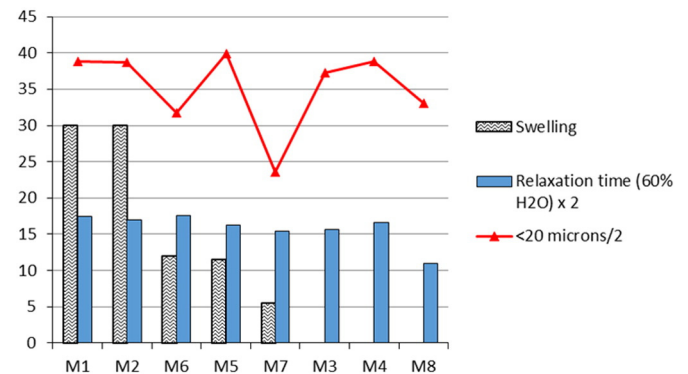


Fig. 5. Graph showing the effect of smectite swelling (cm³/2 g) and grain size (<20 µm) on relaxing time (min).

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