



## Research paper

## 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 <sup>a</sup>	Benesa
M2	Atox <sup>a</sup>	Tolsa
M3	Palygel SMV <sup>a</sup>	Tolsa
M4	SPLF ELITE <sup>a</sup>	Tolsa
M5	Clay 1 <sup>b</sup>	Süd Chemie España
M6	Clay 2 <sup>b</sup>	Süd Chemie España
M7	Clay 3 <sup>b</sup>	Süd Chemie España
M8	Caolín G-40/77M <sup>a</sup>	Avisa

<sup>a</sup> Clays studied in Armijo et al. (2015).

<sup>b</sup> 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  $\mu\text{m}$  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 Fiestren 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  $\pm 0.02$  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 cm<sup>3</sup> 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.

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