Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Thermal conductivity and density of clay pastes at various water contents for pelotherapy use

Victoria Caridad ^a, José M. Ortiz de Zárate ^{a,*}, Mohamed Khayet ^a, José L. Legido ^b

^a Departamento de Física Aplicada I, Universidad Complutense, 28040 Madrid, Spain

^b Departamento de Física Aplicada, Universidade de Vigo, 36280 Vigo, Spain

ARTICLE INFO

Article history: Received 12 September 2012 Received in revised form 8 February 2014 Accepted 10 February 2014 Available online 11 March 2014

Keywords: Applications of clays Pelotherapy Thermal conductivity Density

ABSTRACT

Experimental measurements are presented of the thermal conductivity (λ) and the density (ρ) of several clay pastes used in pelotherapy (peloids). Up to 22 peloids were tested. They were prepared by adding various amounts of water to seven mineralogically different powder clays or clay minerals. λ of each clay paste was measured at six different temperatures ranging between 293 K and 318 K, while ρ was measured at ambient temperature. A clear correlation was established between the density and the thermal conductivity of the peloids. © 2014 Elsevier B.V. All rights reserved.

1. Introduction

The preamble of the constitution of the World Health Organization (1948) defines 'health' not simply as the absence of disease, but as a complete state of physical, mental and social well-being. Among the many means used to increase a feeling of well-being, thermal centers (or, more recently, spas) are becoming increasingly important. One of the therapies traditionally employed in many of these centers is pelotherapy (mud therapy). The word *peloid* refers to different kinds of mineral sediments, whose composition usually includes a variable amount of organic matter. When mixed with sea water, spring waters or medical mineral waters, these minerals form pastes that, applied as mud packs or mud baths, have been used since ancient times as therapeutic agents (pelotherapy). In many southern European thermal centers, peloids based on clay pastes are traditionally used. An excellent review about several aspects of health resort medicine, describing different therapies and their benefits, has been recently published by Gutenbrunner et al. (2010). Viseras et al. (2007) have reviewed more specifically the uses of clays in pelotherapy. Historical evolution, classification and glossary have been recently reviewed by Gomes et al. (2013).

During the last years a number of scientific studies of the thermophysical properties of peloids have appeared (Beer et al., 2003; Cara et al., 2000; Casás et al., 2011, 2013; Ferrand and Yvon, 1991; Legido et al., 2007; Ortiz de Zárate et al., 2010). Continuing this effort, experimental measurements of the density (ρ) at ambient temperature, and of the thermal conductivity (λ) at various temperatures, of different clay pastes suitable for use in pelotherapy, are reported in this paper.

The measurements of λ have been performed with a KD2 Thermal Analyzer instrument, that is based on the transient hot-wire technique (Assael et al., 2008; Vázquez Peñas et al., 2008). Steady-state methods are not adequate to measure the λ of a peloid, because the sample may experience desiccation during the long equilibration times required. In contrast, the transient hot-wire technique is most adequate, since it allows for an almost instantaneous measurement of λ , so that the resulting values can be unambiguously ascribed to the water content with which the peloid was prepared. In addition, by a transient method, the λ measurements are conducted under a condition close to the peloid application.

2. Materials

Pastes were prepared based on one clay mineral (hectorite), two bentonites and four common clays. The clays or clay minerals were purchased from the suppliers as dry powder and were mixed with different amounts of distilled water to prepare the peloid pastes. The experimental measurements were carried out just after the preparation of the paste, without allowing for any maturation time. In previous publications (Legido et al., 2007; Ortiz de Zárate et al., 2010), the different clays or clay minerals were described in a great detail, and the chemistry



Note



^{*} Corresponding author.

E-mail addresses: jmortizz@fis.ucm.es (J.M. Ortiz de Zárate), kayetm@fis.ucm.es (M. Khayet).

and mineralogy of some of them were carefully studied. Hence, only brief general description of the seven samples is given next:

- The hectorite (Hect) used in this study comes from a quarry in Cádiz (southern Spain). It has the typical light rose color and, as most hectorites, is rich in lithium. It has a very high swelling capacity.
- Two different bentonites were employed: A magnesium bentonite (Mg⁺⁺Bent) obtained from a quarry in Toledo (central Spain), where is mined for industrial purposes (mainly sewage filtering), it has a greenish color. A sodium bentonite (Na⁺Bent) was obtained from another quarry located near Madrid (central Spain), where is mined for construction and other industrial uses. It has a grayish color and, mineralogically, it is composed of almost 100% of smectites.
- Three of the four common clays investigated were supplied by *Color Clay S.L.*¹ (Barcelona, Spain), that sells them for the cosmetic industry with the commercial names: cydonia, rosa, and cocoa. Clay cydonia has a yellow-greenish color and it contains aluminium and calcium. Clay rosa has a nice rose color and it contains sodium and potassium. Clay cocoa has a chocolate color and is rich in silicon and iron.
- The fourth common clay (clay sabhasana) was obtained from a quarry in Málaga (southern Spain), where is mined for the cosmetic industry. It displays a grayish color. It has an almost equal content of smectites (41%) and illites (38%).

Note that, although most of the clay powders are commercialized for the cosmetic industry, some are for industrial use and not controlled for potentially harmful trace elements. Of course, this issue needs to be study before actual use of these as peloids.

To prepare the peloids, the clay (or clay mineral) powders described above were mixed with distilled water. For each powder, two to four different pastes (peloids) were prepared by adding different quantities of water. Table 1 describes the 22 peloids investigated, showing in the first column the powder clay or clay mineral they are based on, and in the second column the amount of water added in mass fraction. To obtain suitable pastes, that give a pleasant feeling by touch and that provide an easy handling and application, the various clay powders required the addition of different quantities of water. The larger water intake was for hectorite (with peloids up to 94% water content in mass fraction, m/m) and the lower was for the common clay cydonia, cocoa and sabhasana (with a minimum 35% m/m of water in one of the peloids). To prepare the pastes, the quantities of powder and water were weighted with a digital balance (± 0.005 g), and mixed in a beaker. Strong mixing was applied by a mechanical stirrer, until a homogeneous paste is formed.

Before processing, powder clays or clay minerals were maintained overnight in a drying oven at 60 °C. The water used in this study was distilled in our laboratory, and filtered ($0.22 \mu m$) before use. Sample preparation and measurements were performed at atmospheric pressure.

3. Experimental results

When the paste homogenization process is finished a density measurement is performed using a pycnometer. A sample obtained from the homogeneous paste is analyzed and, to avoid mixing with the water contained in the clay paste, *n*-hexane is used as the reference liquid. Measurements were performed at ambient temperature, which never deviated more than ± 2 °C from 22 °C. The accuracy of the density measurements is estimated as $\pm 5\%$.

After the first density measurement, thermal conductivity (λ) of the clay pastes was obtained with the Decagon Devices Inc.² KD2 Thermal

Table 1

Peloid pastes used in this investigation, indicating the base clay or clay mineral powder and the amount of water added in mass fraction (m/m). Also reported is the paste density ρ_{av} at ambient temperature (2 α aprox.), obtained as an average of measurements done before and after performing the thermal conductivity measurements. Accuracy of the density values is estimated as 5%.

Clay or clay mineral	Water content	$ ho_{\rm av}({\rm kg}~{\rm m}^{-3})$
Hectorite (Hect)	94%	1040
	92%	1050
	90%	1090
Sodium bentonite (Na ⁺ Bent)	90%	1070
	85%	1120
Magnesium bentonite (Mg ⁺⁺ Bent)	75%	1170
	65%	1280
	60%	1310
	55%	1420
Common clay cydonia	80%	1120
	65%	1220
	45%	1450
	35%	1770
Common clay rosa	65%	1320
	55%	1340
	45%	1450
Common clay cocoa	55%	1340
	45%	1520
	35%	1720
Common clay sabhasana	55%	1350
-	45%	1500
	35%	1640

Analyzer instrument. This device is based on the transient hot-wire technique (Assael et al., 2008; Vázquez Peñas et al., 2008) and allows for quick measurements.

To perform the λ measurements at a controlled temperature, a glass test tube is filled with the clay paste (about 25 ml). Subsequently, the test tube was placed inside the bath, filled with water, of a circulation thermostat. Then, the measurement needle of the KD2 is stick into the clay paste. Finally, the test tube with the needle is covered with plastic film to avoid water evaporation. The measurement protocol was as follows: First the water bath was set at 20 °C, half an hour for temperature homogenization was needed, and six consecutive measurements with the KD2 probe were performed. Then, the temperature of the bath was increased by 5 K, waiting for another half an hour, and six new measurements at the new temperature were performed. The protocol was repeated until the bath temperature reached 45 °C, implying measurements at six different temperatures for each clay paste. The whole protocol lasted about 4 h. The purpose of this work is to obtain experimental data under conditions as close as possible to the conditions of actual use. Hence, the protocol is rather quick, and the data refer to fresh prepared pastes.

In each single measurement a value for the thermal conductivity λ is obtained from the KD2, and also the temperature *T* at which the acquired λ value is referred. For each bath temperature and each paste at least six individual measurements were carried out, the obtained mean λ values are reported in Table 2 together with the average *T* values and their corresponding standard deviations. Accuracy values reported in Table 2 represent only random or statistical errors. Systematic errors (precision of the measurement device) have to be also accounted for. For the KD2 device, the manufacturer reports the systematic errors to be \pm 0.05 K for the temperature readings and \pm 0.02 W m⁻¹ K⁻¹ for the thermal conductivity readings. In the final error, these quantities must be added to the random errors reported in Table 2.

To check clay paste stability, after finalizing the thermal conductivity measurements, a sample was taken from the test tube and a second density measurement was performed, following the same procedure as the first one. The differences between density values obtained before or after the λ measurements were, in most cases, below the accuracy of

¹ http://www.colorclay.com.

² http://www.decagon.com.

Table 2

Thermal conductivity, λ (at indicated temperature *T*), for the seven investigated powder clays or clay minerals, when mixed with different amounts of distilled water (m/m, mass fraction) as indicated. Quoted accuracy accounts only for random errors and corresponds to $1 - \sigma$ confidence intervals. In the final error, a 3% device precision must be added to all reported values.

Hectorite (Hect)								
94% (m/m) water content		92% (m/m) water content		90% (m/m) water content				
T (K)	λ (W/m K)	T (K)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)			
293.20 ± 0.05	0.601 ± 0.003	293.12 ± 0.04	0.608 ± 0.003	293.30 ± 0.05	0.621 ± 0.003			
298.43 ± 0.03	0.604 ± 0.005	298.33 ± 0.03	0.612 ± 0.004	298.50 ± 0.05	0.627 ± 0.004			
303.36 ± 0.03	0.618 ± 0.005	303.16 ± 0.03	0.620 ± 0.000	303.16 ± 0.03	0.630 ± 0.000			
308.17 ± 0.04	0.620 ± 0.000	308.20 ± 0.05	0.622 ± 0.004	308.06 ± 0.03	0.632 ± 0.004			
313.30 ± 0.05	0.622 ± 0.004	313.07 ± 0.04	0.625 ± 0.005	313.20 ± 0.05	0.634 ± 0.005			
318.30 ± 0.10	0.624 ± 0.005	318.19 ± 0.05	0.632 ± 0.003	318.32 ± 0.07	0.637 ± 0.004			

Sodium bentonite (Na⁺Bent)

90% (m/m) water content		85% (m/m) water content	
Т (К)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)
293.30 ± 0.07	0.607 ± 0.004	293.29 ± 0.05	0.630 ± 0.000
298.09 ± 0.05	0.608 ± 0.003	298.35 ± 0.10	0.630 ± 0.000
303.26 ± 0.06	0.615 ± 0.005	303.16 ± 0.03	0.637 ± 0.004
308.30 ± 0.05	0.620 ± 0.000	308.22 ± 0.04	0.645 ± 0.005
313.32 ± 0.07	0.624 ± 0.005	313.10 ± 0.05	0.652 ± 0.004
318.13 ± 0.04	0.630 ± 0.000	318.29 ± 0.05	0.654 ± 0.005

Magnesium bentonite (Mg⁺⁺Bent)

75% (m/m) water content		65% (m/m) water content		60% (m/m) water content		55% (m/m) water content	
Т (К)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)	T (K)	λ (W/m K)	T (K)	λ (W/m K)
$\begin{array}{c} 293.42 \pm 0.00 \\ 298.19 \pm 0.05 \\ 303.23 \pm 0.08 \\ 308.16 \pm 0.03 \\ 313.19 \pm 0.05 \\ 318.18 \pm 0.08 \end{array}$	$\begin{array}{c} 0.641 \pm 0.003 \\ 0.665 \pm 0.005 \\ 0.675 \pm 0.005 \\ 0.680 \pm 0.000 \\ 0.681 \pm 0.003 \\ 0.683 \pm 0.005 \end{array}$	$\begin{array}{c} 293.20 \pm 0.00 \\ 298.19 \pm 0.05 \\ 303.19 \pm 0.05 \\ 308.17 \pm 0.07 \\ 313.10 \pm 0.05 \\ 318.32 \pm 0.07 \end{array}$	$\begin{array}{c} 0.714 \pm 0.005 \\ 0.715 \pm 0.005 \\ 0.727 \pm 0.004 \\ 0.730 \pm 0.000 \\ 0.735 \pm 0.005 \\ 0.741 \pm 0.003 \end{array}$	$\begin{array}{l} 293.47 \pm 0.04 \\ 298.46 \pm 0.06 \\ 303.06 \pm 0.07 \\ 308.22 \pm 0.04 \\ 313.20 \pm 0.05 \\ 318.29 \pm 0.09 \end{array}$	$\begin{array}{c} 0.748 \pm 0.003 \\ 0.751 \pm 0.003 \\ 0.755 \pm 0.005 \\ 0.755 \pm 0.005 \\ 0.758 \pm 0.003 \\ 0.700 \pm 0.000 \end{array}$	$\begin{array}{c} 293.36 \pm 0.06 \\ 298.46 \pm 0.03 \\ 303.29 \pm 0.05 \\ 308.19 \pm 0.05 \\ 313.25 \pm 0.00 \\ 318.23 \pm 0.03 \end{array}$	$\begin{array}{c} 0.782 \pm 0.004 \\ 0.784 \pm 0.005 \\ 0.787 \pm 0.004 \\ 0.790 \pm 0.005 \\ 0.800 \pm 0.000 \\ 0.804 \pm 0.005 \end{array}$

Common clay cydonia

80% (m/m) water content 65% (m/m) w		65% (m/m) water o	content	45% (m/m) water content		35% (m/m) water content	
Т (К)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)	T (K)	λ (W/m K)
293.12 ± 0.04	0.674 ± 0.005	293.33 ± 0.03	0.752 ± 0.004	293.07 ± 0.07	0.875 ± 0.005	293.36 ± 0.06	1.008 ± 0.004
298.10 ± 0.10	0.672 ± 0.004	298.40 ± 0.05	0.764 ± 0.005	298.50 ± 0.05	0.878 ± 0.003	298.46 ± 0.03	1.010 ± 0.005
303.16 ± 0.03	0.701 ± 0.003	303.30 ± 0.05	0.774 ± 0.005	303.30 ± 0.00	0.875 ± 0.009	303.29 ± 0.05	1.014 ± 0.004
308.00 ± 0.00	0.711 ± 0.006	308.10 ± 0.05	0.792 ± 0.007	308.23 ± 0.03	0.882 ± 0.004	308.19 ± 0.05	1.015 ± 0.005
313.22 ± 0.04	0.765 ± 0.005	313.17 ± 0.04	0.817 ± 0.004	313.32 ± 0.04	0.882 ± 0.004	313.20 ± 0.00	1.017 ± 0.000
318.22 ± 0.04	0.760 ± 0.060	318.20 ± 0.05	0.830 ± 0.010	318.03 ± 0.03	0.890 ± 0.000	318.07 ± 0.03	1.017 ± 0.005

Common clay rosa

65% (m/m) water content 55% (m/m) water content		45% (m/m) water conte	nt		
<i>T</i> (K)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)	<i>T</i> (K)	λ (W/m K)
293.09 ± 0.05	0.758 ± 0.003	298.19 ± 0.04	0.851 ± 0.003	298.36 ± 0.06	0.947 ± 0.004
298.07 ± 0.04	0.767 ± 0.004	298.19 ± 0.05	0.855 ± 0.005	298.29 ± 0.05	0.957 ± 0.004
303.32 ± 0.04	0.780 ± 0.008	303.25 ± 0.05	0.861 ± 0.003	303.09 ± 0.05	0.957 ± 0.004
308.07 ± 0.03	0.785 ± 0.005	308.20 ± 0.05	0.867 ± 0.004	308.32 ± 0.04	0.965 ± 0.005
313.15 ± 0.00	0.787 ± 0.004	313.20 ± 0.07	0.874 ± 0.005	313.07 ± 0.07	0.968 ± 0.006
318.29 ± 0.05	0.800 ± 0.005	318.17 ± 0.04	0.880 ± 0.000	318.15 ± 0.00	0.960 ± 0.000
55% (m/m) water content	er content 45% (m/m) water content 35% (m/m) wa		35% (m/m) water conte	nt	
Т (К)	λ (W/m K)	T (K)	λ (W/m K)	T (K)	λ (W/m K)
Common clay cocoa					
293.32 ± 0.07	0.840 ± 0.008	293.27 ± 0.04	0.930 ± 0.000	293.22 ± 0.04	1.002 ± 0.004
298.39 ± 0.07	0.837 ± 0.004	298.12 ± 0.04	0.932 ± 0.004	298.15 ± 0.05	1.005 ± 0.007
303.05 ± 0.00	0.847 ± 0.007	303.22 ± 0.07	0.934 ± 0.005	303.39 ± 0.05	1.007 ± 0.007
308.20 ± 0.05	0.847 ± 0.004	308.42 ± 0.04	0.934 ± 0.005	308.09 ± 0.05	1.010 ± 0.008
313.22 ± 0.07	0.848 ± 0.003	313.17 ± 0.04	0.934 ± 0.005	313.17 ± 0.04	1.008 ± 0.008
318.22 ± 0.04	0.844 ± 0.007	318.16 ± 0.03	0.935 ± 0.007	318.18 ± 0.04	1.008 ± 0.006
Common clay sabhasana					
293.22 ± 0.04	0.762 ± 0.004	293.40 ± 0.05	0.836 ± 0.005	293.01 ± 0.05	0.934 ± 0.007
298.17 ± 0.04	0.774 ± 0.005	298.07 ± 0.04	0.843 ± 0.004	298.16 ± 0.03	0.944 ± 0.005
303.32 ± 0.04	0.782 ± 0.004	303.14 ± 0.03	0.848 ± 0.004	303.40 ± 0.05	0.960 ± 0.000
308.19 ± 0.05	0.788 ± 0.006	308.08 ± 0.04	0.849 ± 0.003	308.01 ± 0.05	0.987 ± 0.004
313.30 ± 0.10	0.801 ± 0.003	313.08 ± 0.04	0.850 ± 0.000	313.00 ± 0.00	0.987 ± 0.004
318.23 ± 0.03	0.804 ± 0.005	318.12 ± 0.04	0.850 ± 0.003	318.35 ± 0.00	0.990 ± 0.000

5%. In a couple of cases such difference was close to 10%. Although some rest time was allowed before doing the second density measurement, these were performed after the paste being at 45 °C for some time. However, since in no case this density difference was larger than $2 - \sigma$, it can be considered as no significative and concluded that no water had been lost during the thermal conductivity measurements. Hence, in the third column of Table 1 a single density value ρ_{av} is reported for each clay paste, it averages the actual measurements performed before and after the thermal conductivity series.

4. Discussion

4.1. Dependence of λ on temperature

The thermal conductivity data reported in Table 2 show that, in all cases, the λ of the clay pastes increases with temperature. This increment is more significant for the pastes with higher water content. As a representative example, two extreme cases are shown in Fig. 1: hectorite (Hect) with 92% (m/m) water content as solid symbols and clay cocoa with 35% (m/m) water content as open symbols. The error bars in Fig. 1 have been calculated by adding a 3% systematic error to the random errors reported in Table 2. The two thin solid straight lines are just a guide to the eye. One observes an increase of the λ in both cases, being more pronounced in the case of the sample with higher water content (Hect). As a thick solid curve, the reference data for the λ of water (Ramires et al., 1995) is indicated.

The observed behavior is expected because the thermophysical properties of the clay pastes are mostly determined by their water content. For the pastes with more water, the λ variation with temperature closely follows that of pure water, as obvious in Fig. 1 comparing the values measured for the hectorite (Hect) paste (92% m/m) with the reference data of water, that are undistinguishable within the experimental uncertainty. For the pastes with less water, the importance of the clay component is larger, and the increase of λ with temperature is less pronounced.

4.2. Dependence on water content. Correlation $\lambda - \rho$

The most important factor determining the thermophysical properties of the clay pastes is their water content. This is obvious when comparing the ρ (Table 1), or the λ (Table 2), of pastes based on the same clay but with different water contents. Indeed, the variation of λ with water content is more significant than with temperature.



Fig. 1. Thermal conductivity (λ) as a function of the temperature (*T*), for hectorite at 92% water content (open symbols) and for the common clay cocoa at 35% water content (solid symbols). Error bars are total error, systematic plus random. Thin straight lines are only a guide to the eye. The thick curve is the reference thermal conductivity of pure water (Ramires et al., 1995).



Fig. 2. Correlation of thermal conductivity (λ_{293}) vs. density (ρ_{av}) at 20 °C for the 22 clay pastes investigated (crossed circles). The solid line is a linear fit of the data, Eq. (1), and dotted lines represent this fit plus/minus a 7%. Solid stars are the measurements of Ortiz de Zárate et al. (2010), and a big circle encloses it with the current measurements of the equivalent systems. The solid circle in the upper right corner is the measurement of a compacted bentonite with the higher water content from Tang et al. (2008).

To quantify this important effect one can initially test models for the prediction of the λ of the pastes from the knowledge of the λ of pure water and of the solid clay (Ould-Lahoucine et al., 2002). The problem with this approach is the poor knowledge of the λ of the solid clay. Therefore, a more phenomenological approach is adopted here, and the correlation between λ and ρ is studied. Hence, Fig. 2 shows in the abscissa the average density ρ_{av} from Table 1 versus λ_{293} , the thermal conductivity measured at 20 °C bath temperature (i.e. with *T* in Table 2 close to 293 K), for all the 22 clay pastes investigated. A simple look at Fig. 2 shows the clear positive correlation between ρ_{av} and λ_{293} . Indeed, the Pearson coefficient is $r \approx 0.95$, indicating the high strength of the correlation. A linear fit of all 22 data points gives:

$$\lambda_{293} = 5.873 \times 10^{-4} \rho_{\rm av} - 0.0036, \tag{1}$$

where ρ_{av} is to be substituted in units of kg m⁻³ to give λ_{293} in units of W m⁻¹ K⁻¹. By substitution of $\rho_{av} = 999.8$ kg m⁻³ (density of pure water at 22 °C) into Eq. (1), one obtains a λ value that is just 3% lower than the reference value for the thermal conductivity of water at 22 °C (Ramires et al., 1995), inside the accuracy interval of the current measurements.

The solid line in Fig. 2 represents Eq. (1) and, for reference, two dotted lines that represent Eq. (1) plus or minus a 7% are added. Fig. 2 shows that Eq. (1) predicts the thermal conductivity of the peloids within a few percent deviation. Notice that in Fig. 2 data is plotted for clays of very different chemistry and mineralogy, see Section 2. Therefore, it is concluded that the main factor determining the thermal conductivity of the pastes is their density, being chemistry or mineralogy (and even temperature) much less important.

Other correlation studies are possible. From the data in Table 1 it is simple to plot the density vs. water content, a plot that shows a strong correlation between both magnitudes. However, the dependence of ρ on water content results clearly non-linear, and a parabolic fit is better than a linear fit to relate the two quantities. Similarly happens with the λ vs. water content correlation. The fact that the $\lambda - \rho$ dependence is linear, see Fig. 2, is the reason why this correlation is preferred over other possibilities here.

4.3. Comparison with other published data

Ortiz de Zárate et al. (2010) have recently reported density and thermal conductivity measurements of two clay pastes for pelotherapy that were based on two of the same powder clays used here, namely, magnesium bentonite and clay sabhasana. Ortiz de Zárate et al. (2010) measured λ with a custom-made transient hot-wire setup, that gives better accuracy but it is more tedious to use as compared with the KD2 instrument. Furthermore, the previous measurements were performed at a single temperature (40 °C) and with water content values slightly different from the ones investigated here. For an easy comparison, the two data points of Ortiz de Zárate et al. (2010) are added to the current data set in Fig. 2 as solid star symbols. In each case, a big circle encloses the previous measurements with the current measurement of the most similar system. An excellent agreement is found, within the experimental errors and the slightly different temperatures and water contents. This manifests good reproducibility of the experimental results when, for a given clay or clay mineral, pastes are prepared independently at similar conditions.

Other studies of the thermal properties of peloids for therapeutic or wellness purposes (Beer et al., 2003; Cara et al., 2000; Ferrand and Yvon, 1991; Legido et al., 2007) usually report only the cooling rates of particular samples. The cooling rate has to be considered a derived property, and it is precisely our final goal to be able to predict cooling rates from more fundamental properties like the thermal conductivity, heat capacity, and density. Very few authors have reported on actual thermal conductivities of peloids (Beer et al., 2003), and in that case peats and no clavs were investigated.

Because of the possible use as buffer materials in nuclear waste disposal, there has been interest lately in measuring the thermal conductivity of bentonites (Beziat et al., 1988; Ould-Lahoucine et al., 2002; Tang et al., 2008; Villar et al., 2006). The water content of the bentonite samples used in those investigations was much lower than in the ones used in the present study, so that an inhomogeneous porous structure was adopted and the air trapped into the pores was an important factor affecting their thermal properties, significatively reducing the thermal conductivity. In the present study, with much higher water content, the samples are homogeneous and trapped air is not an issue. Therefore, in general, a detailed comparison of these investigations with the current data is not feasible. Only in some cases (Beziat et al., 1988; Tang et al., 2008; Villar et al., 2006) the bentonite samples were compacted. The maximally compacted bentonites with the higher water content are more comparable with the current measurements. The solid circle in Fig. 2 represents one of the experimental data reported by Tang et al. (2008), corresponding to their sample with maximum water content (\approx 18%) compacted at maximum density (no trapped air). This single data compares well with the current measurements. Finally, it is interesting to mention that Eq. (1) is also consistent with very recent measurements of glacial till soils by Alrtimi et al. (2014).

Acknowledgments

Financial support of the "Consellería de Innovación e Industria de la Xunta de Galicia" (project 10PXIB310153PR) is gratefully acknowledged.

References

- Alrtimi, A., Rouainia, M., Manning, D.A.C., 2014. An improved steady-state apparatus for measuring thermal conductivity of soils. International Journal of Heat and Mass Transfer 72, 630–636.
- Assael, M.J., Antoniadis, K.D., Kakosimos, K.E., Metaxa, I.N., 2008. An improved application of the transient hot-wire technique for the absolute accurate measurement of the thermal conductivity of pyroceram 9606 up to 420 K. International Journal of Thermophysics 29, 445–456.
- Beer, A.M., Grozeva, A., Sagorchev, P., Lukanov, J., 2003. Comparative study of the thermal properties of mud and peat solutions applied in clinical practice. Biomedical Technology 48, 301–305.
- Beziat, A., Dardaine, M., Gabis, V., 1988. Effect of compaction pressure and water content on the thermal conductivity of some natural clays. Clay and Clay Minerals 36, 462–466.
- Cara, S., Carcangiu, G., Padalino, G., Palomba, M., Tamanini, M., 2000. The bentonites in pelotherapy: thermal properties of clay pastes from Sardinia (Italy). Applied Clay Science 16, 125–132.
- Casás, L.M., Legido, J.L., Pozo, M., Mourelle, L., Plantier, F., Bessières, D., 2011. Specific heat of mixtures of bentonitic clay with sea water or distilled water for their use in thermotherapy. Thermochimica Acta 524, 68–73.
- Casás, L.M., Pozo, M., Gómez, C.P., Pozo, E., Bessières, D., Plantier, F., Legido, J.L., 2013. Thermal behavior of mixtures of bentonitic clay and saline solutions. Applied Clay Science 72, 18–25.
- Ferrand, T., Yvon, J., 1991. Thermal properties of clay pastes for pelotherapy. Applied Clay Science 6, 21–38.
- Gomes, C., Carretero, M.I., Pozo, M., Maraver, F., Cantista, P., Armijo, F., Legido, J.L., Teixeira, F., Rautureau, M., Delgado, R., 2013. Peloids and pelotherapy: historical evolution, classification and glossary. Applied Clay Science 75–76, 28–38.
- Gutenbrunner, C., Bender, T., Cantista, P., Karagülle, Z., 2010. A proposal for a worldwide definition of health resort medicine, balneology, medical hydrology and climatology. International Journal of Biometeorology 54, 495–507.
- Legido, J.L., Medina, C., Mourelle, M.L., Carretero, M.I., Pozo, M., 2007. Comparative study of the cooling rates of bentonite, sepiolite and common clays for their use in pelotherapy. Applied Clay Science 36, 148–160.
- Ortiz de Zárate, J.M., Luis Hita, J., Khayet, M., Legido, J.L., 2010. Measurement of the thermal conductivity of clays used in pelotherapy by the multi-current hot-wire technique. Applied Clay Science 50, 423–426.
- Ould-Lahoucine, C., Sakashita, H., Kumada, T., 2002. Measurement of thermal conductivity of buffer materials and evaluation of existing correlations predicting it. Nuclear Engineering and Design 216, 1–11.
- Ramires, M.L.V., Nieto de Castro, C.A., Nagasaka, Y., Nagashima, A., Assael, M.J., Wakeham, W.A., 1995. Standard reference data for the thermal conductivity of water. Journal of Physical and Chemical Reference 24, 1377–1382.
- Tang, A.M., Cui, Y.J., Le, T.T., 2008. A study on the thermal conductivity of compacted bentonites. Applied Clay Science 41, 181–189.
- Vázquez Peñas, J.R., Ortiz de Zárate, J.M., Khayet, M., 2008. Measurement of the thermal conductivity of nanofluids by the multicurrent hot-wire method. Journal of Applied Physics 104, 044314.
- Villar, M.V., Pérez del Villar, L., Martín, P.L., Pelayo, M., Fernández, A.M., Garralón, A., Cuevas, J., Leguey, S., Caballero, E., Huertas, F.J., Jiménez de Cisneros, C., Linares, J., Reyes, E., Delgado, A., Fernández-Soler, J.M., Astudillo, J., 2006. The study of spanish clays for their use as sealing materials in nuclear waste repositories: 20 years of progress. Journal of Iberian Geology 32, 15–36.
- Viseras, C., Aguzzi, C., Cerezo, P., Lopez-Galindo, A., 2007. Uses of clay minerals in semisolid health care and therapeutic products. Applied Clay Science 36, 37–50.