Specific heat of mixtures of bentonitic clay with sea water or distilled water for their use in thermotherapy

L.M. Casás[a,*], J.L. Legido[a], M. Pozo[b], L. Mourelle[a], F. Plantier[c], D. Bessières[c]

[a] Departamento de Física Aplicada, Facultade de Ciencias Experimentais, Universidade de Vigo, Lagoas Marcosende s/n, 36310 Vigo, Spain
[b] Departamento de Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco s/n, 28049 Madrid, Spain
[c] Laboratoire de Thermodynamique et Energétique des Fluides Complexes - UMR 5150, Université de Pau et des Pays de l'Adour, BP 1155, 64013 Pau, France

ABSTRACT

In thermotherapy, an appropriate and detailed chemical and physical characterization of the different clays and thermal muds is necessary for the use of these products. In order to predict the thermal behaviour of a mud the analysis of its physical properties is required; among these, those that have bigger influence are the specific heat capacity, the thermal conductivity and the density. This work focuses on the study of the behaviour of the specific heat of a bentonitic clay (composed mainly of 55% Na-saturated smectite, 28% sepiolite, and 15% illite) mixed with distilled water or sea water as a function of the water concentration in the temperature range 293.15–317.15 K. The experimental data were measured using a Calvet calorimeter, SETARAM BT 2.15, which permits studying with high precision all kind of substances and materials (oils, polymers, hydrates, powders) and simulate almost any process condition (reactions, crystallisation, freezing, etc.). The obtained specific heat values in the studied temperature range are between 851 and 889 J kg^{-1} K^{-1} for mineral phase, 3479 and 3505 J kg^{-1} K^{-1} for 19.9% bentonite + distilled water, and 2724 and 2758 J kg^{-1} K^{-1} for 39.8% bentonite + sea water. The results of this study can be used in the spas or thermal centres to determine the suitability and quality of the bentonitic muds for pelotherapy.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The mixtures of clays and different types of waters (medicinal mineral waters, sea water or salt lake water) are the basis of the matured thermal muds (peloids), which have a wide range of uses in the field of thermotherapy from the therapeutic point of view [1] as well as from a cosmetic point of view [2]. In 1949, the International Society of Medical Hidrology, during its 6th Conference held in Dax (France), defined the term *peloid* as a natural product consisting in a mixture of medicinal mineral waters, sea water or salt lake water (liquid phase), and organic and inorganic compounds (solid phase) after having suffered physical, chemical, biological and geological phenomena. Contact between phases for a time is necessary for the formation of a peloid (maturation), and several processes happen having an influence on the final composition and properties of the peloid [3–5]. The peloids have been used as therapeutic agents in many spas and thermal centres since ancestral times, in mask, cataplasm or bath forms.

The utilization of peloids is very widespread everywhere in the world. This fact can be borne witness to by recent literature involving peloids used in Italy [4], Portugal [6], Spain [7], Turkey [8], Argentina [9], and Mongolia [10].

The peloids are used from the therapeutic point of view in order to make lighter chronic rheumatic diseases and after-effects of osteoarticular traumas. In cosmetics, they are used to moisturize the skin, to delay the development of cellulites, skin cleaning and dermatological treatments [11–14]. The suitable properties of a peloid in order to be used in peloterapy are [15]: high specific heat, low thermal conductivity, high density, and suitable rheological properties when applied to the skin, handling easiness, small particle size, high absorption/adsorption capacity, high cationic exchange capacity, and pH similar to skin.

Both from the medical point of view as the cosmetic one, the thermophysical properties of the clays and peloids are very important [4,16]; since the heat works as a therapeutic agent. In the recent years, experimental data concerning the thermal properties of clays and peloids have been published [16–19], without very high accuracy for specific heat data.

In the present work, the specific heat of mixtures of a bentonitic clay, suitable for the peloid preparation, with sea water or distilled water has been studied. The experimental data have been measured

* Corresponding author. Tel.: +34 986812294; fax: +34 986812295.
  E-mail address: lmcasas@uvigo.es (L.M. Casás).

Table 1
Chemical composition (g/kg) of sea water.

Cations	
Na^+	10.92
Mg^{2+}	1.300
Ca^{2+}	0.4173
K^+	0.4042
Sr^{2+}	0.0080
Anions	
Cl^-	19.60
SO_4^{2-}	2.747
HCO_3^-	0.1061
Br^-	0.0681
CO_3^{2-}	0.0145
$B(OH)_4^-$	0.0080
F^-	0.0013
OH^-	0.0001
Neutral ions	
$B(OH)_3$	0.0197
CO_2	0.0004

Table 2
Thermophysical properties of sea water at 298.15 K.

pH	7.92
Density/g cm^{-3}	1.0226
Refractive index	1.33876
Viscosity/mPa	1.007
Dry solid matter (%)	3.85

using a Calvet calorimeter, SETARAM BT 2.15 in the temperature range 293.15–317.15 K, and atmospheric pressure. The aim of this study is obtain accuracy specific heat data, in order to analyze differences between a mixture of clay with distilled water and with highly mineralized water (sea water).

2. Experimental

2.1. Materials

Bentonitic clay used in this work was supplied by the Spanish company "BENESA". Its mineralogical analysis is described in the next section. Clay was dried in a laboratory oven at 383.15 K for 24 h before use in order to prevent possible moisture. Sea water was supplied by Quinton Labs. Chemical composition and some thermophysical properties are gathered in Tables 1 and 2, respectively. The practical salinity of the sea water sample was determined from conductivity measurements with a Guidline 8410A Portasal salinometer that was calibrated with IAPSO Standard Sea water, using the equation proposed by UNESCO [20]. The concentration of major chemical species in the sea water sample was calculated from sea salt composition definition for reference salinity of the standard ocean, using table D3 (page 86) of McDougall et al. [21]. The pH was determined using a basic 20+ pH-meter. Density was measured with an Anton Paar DMA-4500. Before taking measurements, this instrument was calibrated with Millipore quality water and ambient air, respectively, in accordance with the instructions. Besides, the critical angle method was employed to measure the refractive index at the Na D-line wavelength (589.3 nm). Experimental refractive index was determined by means of an ABBEMAT-HP refractometer. In order to keep a constant temperature, the measuring prism was water-jacketed using a controller. Then, the viscosity measurement was performed with an automated viscometer Anton Paar AMV 200, connected to a PolyScience fluid circulation bath that ensures temperature stability. Finally, in order to determined dry solid matter, a significant quantity of sample was dry in an oven for at least 24 h at 383.15 K until constant weight was reached. Distilled water was from MiliQ system (Milipore). Both waters were used without further purification.

2.2. Mineralogical study

2.2.1. Methodology

For the mineralogical study the sample was grounded and sieved to a size lower than 63 μm. The mineralogical analysis of the sample was achieved by means of X-ray diffraction (XRD) using a

SIEMENS D-5000 equipment with a scanning speed of $1°2\theta$/min and Cu-Kα radiation (40 kV, 20 mA). The XRD analysis was carried out on randomly oriented samples (total sample) and on clay fraction samples (<2 μm), the last prepared from cation-saturated, ultrasonic treated suspensions oriented on glass slides. The identification of the clay fraction minerals was performed on oriented Mg^{2+}-saturated samples with ethylene glycol solvation, and also after heating at 823.15 K of K^+ – saturated samples. Quantitative estimation of the mineral content was carried out using the intensity factors calculated by Schultz [22], Barahona [23] and Van der Marel [24]. The crystallinity of the smectite was studied through measurement of the full width at half maximum peak intensity (FWHM) of the $d(0\,0\,1)$ peak after treatment with ethylene glycol (approximately at 17 Å). The crystallite size (coherent diffraction domain) was calculated using the Scherrer equation [25].

3. Results

The studied sample showed a high percentage of phyllosilicates in the total fraction (98%), with characteristic reflections at 1.50 Å, 1.52 Å, 2.56 Å, 4.51 Å and 12.04 Å. The first two d-spacing, which corresponds to $d(0\,6\,0)$ reflection, clearly shows a mixture of dioctahedral and trioctahedral phyllosilicates. The presence of other minerals was low (<5%), specifically limited to cristobalite, quartz, calcite, plagioclase and mordenite.

The study of the clay fraction revealed the existence of three minerals, which, after the appropriate treatments, led us to infer the existence of a predominant swelling phase and two highly subordinated non-swelling phases. Thus, the study of air-dried oriented aggregates (Mg-saturated) revealed d-spacings with a very intense reflection at 14.63 Å and two smaller reflections at 12.15 Å and 10.01 Å, respectively. Treatment with ethylene glycol caused the reflection at 14.63 Å to shift to 16.80 Å, which revealed a 2:1 swelling phyllosilicate. Treatment at 823.15 K revealed a shift in reflection to 9.9 Å, which was consistent with a structural collapse process in a mineral with the interlayer space occupied by hydrated exchangeable cations. All the identified features pointed to a smectite as the prevailing mineral of the sample. On the other hand, the 12.04 Å spacing of the $d(0\,0\,1)$ reflection of the smectite in the whole sample, suggests that the interlayer space was mainly occupied by Na+.

The subordinated clay minerals showed no changes in its basal d-spacing after application of the above described treatments, remaining around 10 Å and 12 Å with ethylene glycol, but collapsing to 9.9 Å after thermal treatment, identifying these mineral as sepiolite and illite.

Quantitative estimation revealed a 56% percentage of smectite in the clay fraction of phyllosilicates, whereas the percentage of sepiolite and illite were of 29% and 15%, respectively. Therefore the measured percentages of these clay minerals in the whole sample were 55% smectite, 28% sepiolite and 15% illite. The measurement of the smectite FWHM reaching a value of 0.86° 2θ indicates a moderate ordering, with a small crystallite size of 10 nm.