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The bentonites in pelotherapy: thermal properties of clay pastes from Sardinia (Italy)

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Abstract

On the basis of a previous detailed characterization of the Sardinian bentonites for pelotherapy applications [Cara, S., Carcangiu, G., Padalino, G., Palomba, M., Tamanini, M., 2000. The bentonites in pelotherapy: chemical, mineralogical and technological properties of materials from Sardinia deposits (Italy). Appl. Clay Sci. 16, 117–124 (this issue)], three commercial bentonites have been selected for detailed studies. The thermal properties of the pastes, prepared with these bentonites at different moisture, have been compared with the properties of a peloid, commonly used in the spa of Benetutti (northern Sardinia). The cooling kinetics of the bentonites along with the thermal mud have been studied using an experimental apparatus that reproduces the conditions during the application of a cataplasm. A mathematical model for the cooling kinetics has been obtained by means of a theoretical cooling equation, with instrumental constants derived from a reference paste (TiO_2 at 50% moisture). The heat capacity of the pastes introduced into the model was calculated from chemical and mineralogical data. The methodology developed can be used in other laboratories of the thermal centres to determine the quality and ability of the bentonitic materials for pelotherapy. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: bentonites; pelotherapy; thermal properties; Sardinia; Italy

1. Introduction

Thermal properties of pastes are considered as fundamental parameters for pelotherapy applications. During the cataplasm application, a good heat reten-

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tion is required. It is well-known that pastes consisting of bentonite–water mixtures are the best materials for thermal application (Ferrand and Yvon, 1991). It is mainly due to their high smectite content, high swelling properties and ability to retain large water percentages.

In order to define the thermal properties of Sardinian bentonites, three representative samples of regionally certified materials have been selected. The samples have been collected from Costa Paradiso, Busachi and Giba (northern, central and southern Sardinia, respectively) mines of Società Sarda di Bentonite, chosen for their proximity to natural thermal springs.

Mineralogical, chemical analysis and technological tests have been performed in all samples (Cara et al., 2000). The thermal behaviour of the pastes, obtained from adding different water percentages to these materials, has been tested in the laboratory. The experimental cooling curves have been compared with those of the mud used in the spa of Benetutti (central Sardinia). Empirical models of the cooling kinetics have been produced using multiple linear regression based on a theoretical cooling equation, applied on experimental data.

2. Materials and methods

All bentonite samples have been ground, homogenised and studied from mineralogical, chemical and technological point of view. Mineralogical analyses have been performed by XRD methodology utilising a Rigaku Geigerflex diffractometer, operating with Cu tube at 30 kV and 30 mA. Mineralogical phases have been recognized by comparison with the JCPDS FILE (1985). Chemical analyses have been carried out by a Philips PW 1400 XRF spectrometer, operating with a Rh tube at 30 kV and 60 mA. The intensities data have been elaborated with the Franzini program (Franzini et al., 1972). Chemical and mineralogical data have been elaborated to obtain a semi-quantitative evaluation of mineral phases. In order to verify the technological properties of these materials tests, including cation exchange capacity (CEC), water saturation (WS), swelling index (SI), determination of the fraction over 75 μm and $CaCO_3$ contents, have been carried out according to the 6716-70 UNI Standard Normative (1970).

The experimental pastes have been prepared both at about 60% of water and water percentage corresponding to the water limit. The cooling kinetics of these samples has been observed by a simple apparatus consisting of a cylindrical polyethylene terephthalate (PET) cell (250 ml), filled with 300 g of paste, plunged in a 30-l water thermostatic bath, regulated to 25°C. The samples have been conditioned at 60°C before the immersion into the bath. The temperature sampling, started from 50°C, has been performed by a thermometric probe, located in the center of the cell.

3. Results and discussion

Table 1 shows chemical analyses of the selected bentonites and the Benetutti thermal mud.

The chemical data show that northern and central bentonites are of Ca–Mg type, whereas southern bentonite shows a higher Na_2O content, with a lower CaO content ($Na_2O/CaO = 1.17$).

The mineralogical composition of all bentonite samples is relatively similar, as shown in Table 2. The thermal mud of Benetutti shows worse technological properties, compared with the bentonite samples (Table 3). The proportion of mineral phases present in the bentonites has been derived solving a system of linear equations based on chemical data and stoichiometric formulas, attributed to the constituent minerals, recognized by XRD analysis (Table 4).

3.1. Cooling kinetics

Experimental data of cooling tests of pastes prepared mixing three selected bentonites at two different water percentages (the second ones corresponding to the WS) have been represented in the Fig. 1A–C. The increase of water content in the pastes gives an improvement of the cooling kinetics proportionally to the difference in the water content between the two pastes.

The temperature sampling has been performed by a thermometric probe located at the centre of the cell at steps of 2 min. Data processing and mathematic model have been planned on the basis of a theoretical cooling equation that describes the thermal exchange between a hot body in contact with a cool body with an infinite heat capacity:

$$(T - T_{min}) = (T_{max} - T_{min})e^{-kt} \quad (1)$$

considering that $k = p/C$, where p is the instrumental constant of the apparatus and C is the heat capacity of the paste. The last parameter can be derived from

Table 1
Chemical analyses (wt.%) of the selected Sardinia bentonite and thermal mud from XRF data

Deposits	Northern bentonite	Central bentonite	Southern bentonite	Benetutti mud
SiO_2	50.42	54.74	59.41	58.93
TiO_2	0.26	0.72	0.18	0.54
Al_2O_3	27.29	16.15	18.93	18.00
Fe_2O_3	3.73	6.69	2.36	4.43
MnO	0.12	0.11	0.07	0.13
MgO	2.32	5.07	5.53	2.41
CaO	1.24	1.57	0.88	3.37
Na_2O	0.45	0.55	1.03	0.99
K_2O	0.13	0.60	0.49	1.65
P_2O_5	0.03	0.18	0.03	0.06
LOI	14.01	13.62	11.09	9.50
Na_2O/CaO	0.36	0.35	1.17	0.29

Table 2
Mineralogical qualitative analyses of selected Sardinian bentonites and thermal mud from XRD data

Deposits	Z	M	Q	P	I
Northern bentonite		*			*
Central bentonite	*	*	*	*	
Southern bentonite		*	*	*	
Benetutti mud	*	*	*	*	*

Legend: Z = zeolites, M = montmorillonite, Q = quartz, P = plagioclases, I = illite.

the equation $C = c_p * m$ with c_p the specific heat and m the quantity of the paste.

The specific heat of the paste can be written as:

$$C_p = \sum_i w_i c_{pi} \tag{2}$$

for a stable matrix of i constituents in w_i quantities with specific heat c_{pi}.

The experimental constant p derives from a cooling test of a reference paste (TiO_2 at 50% moisture). Eq. (1) can be written as:

$$\ln(T - T_{min}) = \ln(T_{max} - T_{min}) - kt \tag{3}$$

or

$$\ln(T - 25) = \ln(25) - kt \tag{4}$$

if the paste cools down from $T = 50°C$ to $T_{min} = 25°C$ corresponding to the thermostatic bath temperature.

Eq. (4), applied to the experimental measures for each paste, allows the apparent heat capacity of the paste to be obtained by a best fit regression. Best fit curves and theoretical curves, obtained by the heat capacity calculated from the mineralogical data according to Eq. (2), multiplied for the quantity of the paste m. The results are plotted in Fig. 2A–D.

Table 3
Technological properties of selected bentonites and thermal mud

Deposits	CEC (meq/100 g)	> 75 μm (wt.%)	C (wt.%)	WS (%)	Swelling (ml/2 g)
Northern bentonite	88	1.1	0.3	385	22.0
Central bentonite	75	1.4	*	330	22.0
Southern bentonite	85	20.0	1.5	320	22.0
Benetutti mud	30	32.4	*	175	6.0

Legend: C = total carbonates, (*) < 0.1 wt.%, WS = water saturation.

Table 4
Mineralogical semi-quantitative analyses of selected Sardinia bentonite and thermal mud from XRD and chemical data

Deposits	M	Q	P	I	Z
Northern bentonite	89	–	–	11	–
Central bentonite	78	12	9	–	1
Southern bentonite	66	16	18	–	–
Benetutti mud	50	16	20	10	4

Legend: M = montmorillonite, Q = quartz, P = plagioclases, I = illite, Z = zeolites.

Table 5 reports data for apparent and theoretical specific heat calculated assuming for each pure mineral the specific heat derived from the literature.

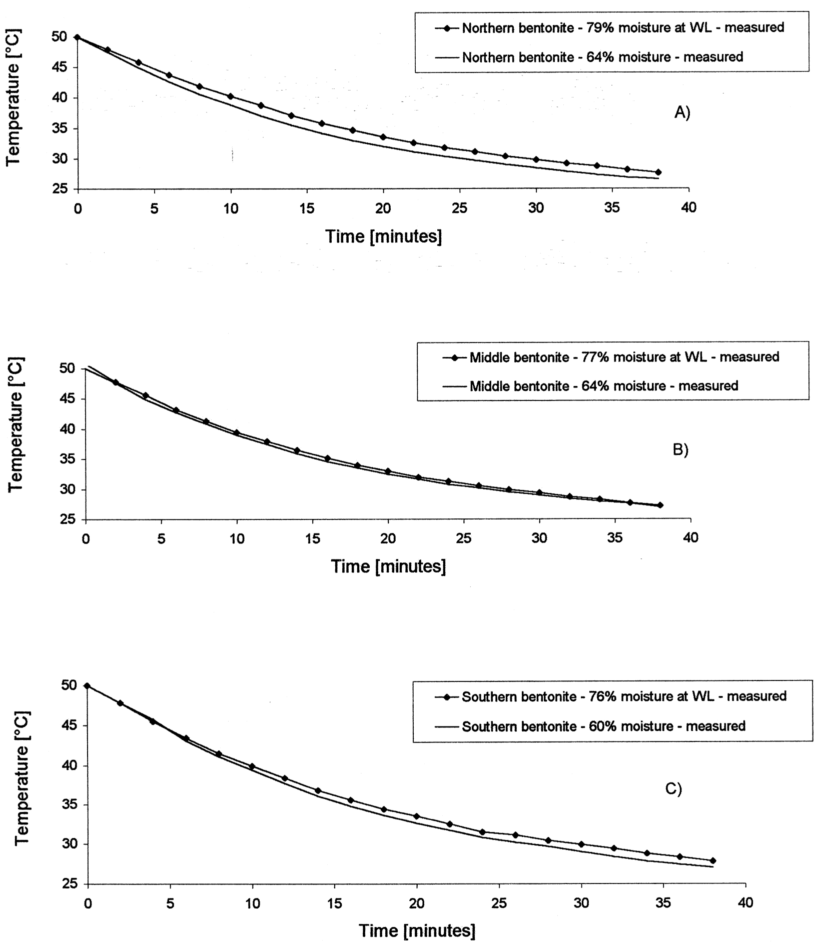

Fig. 1. Cooling kinetics of bentonites at different moistures.

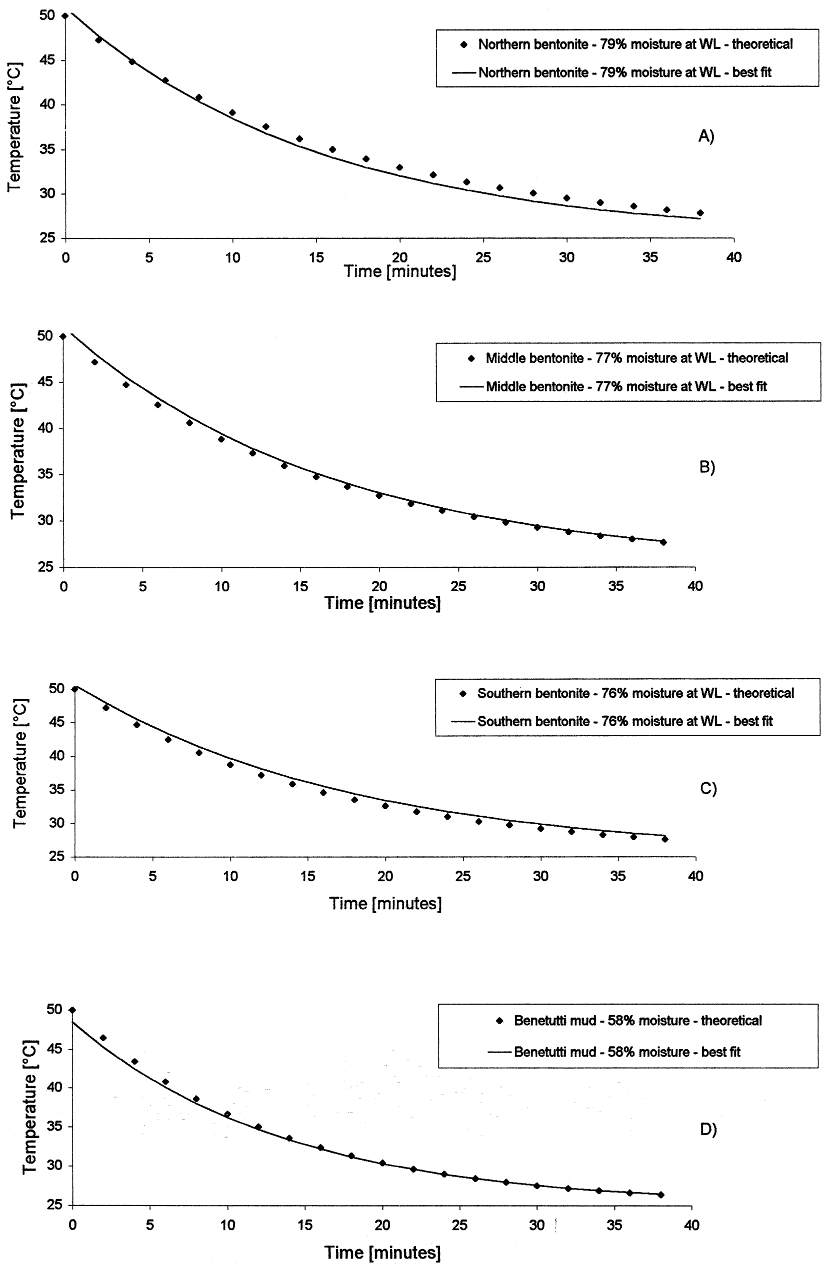

Fig. 2. Theoretical and best fit curves of cooling kinetics.

It can be seen that there is a satisfactory agreement between experimental curves and calculated curves (correlation coefficient very close to 1) for all samples in the 50°C–30°C range, that is up to the paste temperature after 30 min of application.

Table 5
Apparent (a) and calculated (c) specific heat of all pastes (J/g °C)

	C_p (a)	C_p (c)
Northern bentonite at 64% moisture	2.98	2.81
Northern bentonite at 79% moisture at WS	3.45	3.41
Middle bentonite at 64% moisture	3.18	2.81
Middle bentonite at 77% moisture at WS	3.31	3.30
Southern bentonite at 60% moisture	3.13	2.66
Southern bentonite at 76% moisture at WS	3.53	3.28
Benetutti mud at 58% moisture	2.64	2.56

The deviation of apparent specific heat from the theoretical values derived from mineralogical data can be attributed to:

(i) the mean values assumed for the pure mineral specific heats,
(ii) the inaccuracy typical of the mineralogical semi-quantitative analysis methods, and
(iii) the variation of the gradient when the temperature of the paste approaches the bath temperature, after a time no more significant for the application.

4. Conclusions

The pastes prepared with high quality bentonites (northern and central bentonites) show the best behaviour during the cooling, as can be observed from data reported in Tables 4 and 5.

The difference in the cooling kinetics is more pronounced comparing the experimental curves of the selected bentonites with the cooling curve of the thermal mud (Fig. 3). The Benetutti mud is a low-smectite content material with a worse heat retention due to a lower absorption of water.

It is possible to correlate the specific heat of the pastes with the water percentages by a linear regression: so the thermal behaviour of a mixture can be expected by means of a moisture measurement.

The equation is the following:

$$C_p = 0.2914 + 0.0393 * \%H_2O \tag{5}$$

The specific heat is proportional to the smectite content in a material due to its water retention capacity. Finally, the temperature (T_{20}) after 20 min of cooling derives from the solution of a multiple linear regression applied to C_p and $\%H_2O$ values of all tested pastes:

$$T_{20} = 14.62 + 38.22 * C_p - 1.40 * \%H_2O \tag{6}$$

We still point out the importance of the use of tested materials in order to guarantee maximum quality of the thermal muds.

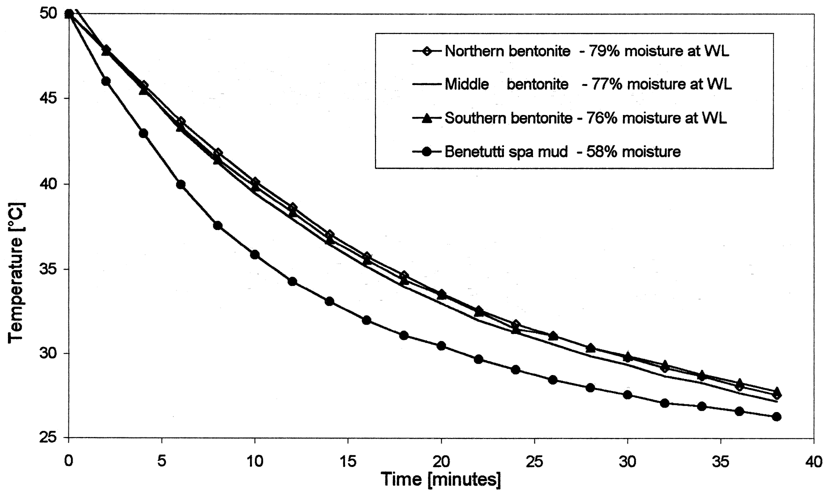

Fig. 3. Cooling kinetics of all pastes.

The methodology applied in this research can be easily used in other laboratories of the thermal centres in order to verify the quality and ability of the bentonitic materials. With a simple WS test, the application of expressions similar to Eqs. (5) and (6) allows the calculation of C_p and T_{20} upon determination of the instrumental constant.

The availability at relatively low price of these materials allows to extend of their application, besides the traditional uses, and in the pelotherapy field.

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