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Research paper

The specific heat of dry homoionic forms of bentonites SWy-2 and Stx-1b: An effect of the fraction of particles less than 2 μm

Tomasz Kozlowski *, Anna Rusin, Edyta Nartowska

Department of Geotechnical and Water Engineering, Kielce University of Technology, 25-314 Kielce, Poland

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ABSTRACT

The specific heat of Ca^{2+}-, Na^{+}- and K^{+}-forms of SWy-2 and Stx-1b has been determined in the range between −150 °C and 100 °C by use of Quasi Isothermal Modulated Differential Scanning Calorimetry. According to expectations, a strong temperature dependency is observed, but the results of ANOVA also show high statistical significance of the kind of initial clay and the kind of the exchangeable cation. The effect of the latter proved to be indirect, as the contribution from the heat capacity of the exchangeable cations appeared less significant, although its detailed analysis meets difficulties associated with a lack of data on the specific heat of the cations and its relation to the specific heat of the corresponding metals in bulk. A relatively high and statistically significant correlation of the specific heat at a given temperature and the fraction of particles less than 2 μm may indicate a contribution of surface atoms to the specific heat capacity, analogical to that observed and theoretically substantiated in relation to nanoparticles of metals and simple organic compounds. This thesis is supported by the kind of temperature-size dependence, resembling that reported for nanoparticles of cuprum oxide by Wang et al. (2006). However, a proposed simple power function model not taking into account the size effect can predict specific heat of montmorillonites with the standard error of the estimate SEE equal to 0.038 J g^{-1} K^{-1}.

1. Introduction

Soil thermal properties are of great importance in a variety of engineering and scientific applications, such as predicting frost depth, the numerical simulation of the heat and mass transfer phenomena, modeling the heat exchange at the ground surface or the geothermal gradients. Moreover, knowledge of the specific heat of a dry soil material is crucial in the investigation of the phase change phenomena in soil-water systems by calorimetry, including the unfrozen water content. Theoretically, the heat capacity of a material, being a thermodynamically well defined quantity, is the basis for determination of other thermodynamic quantities such as enthalpy and entropy changes, which, in turn, enable us to calculate the free (Gibbs) energy.

Despite this, there is very little data on the temperature dependence of the specific heat of dry soil material of various types and origin. As a rule, the available data are given for a "soil" in general. For example, Van Wijk (1964) (cited after Farouki, 1986) reported the value 0.175 cal/g °C (0.732 J g^{-1} K^{-1}) for "many soil minerals" (including quartz). The same value was recommended for engineering computations by Andersland and Ladanyi (2004). Anderson et al. (1978) reported 0.84 J g^{-1} K^{-1} for the specific heat of dry soil matter. Similarly, Bristow (1998) calculating the volumetric heat capacity of soil mixtures used 0.8 and 0.9 J g^{-1} K^{-1} for quartz and clay respectively. Comparing the values of 0.733 J g^{-1} K^{-1} for quartz and 0.8 J g^{-1} K^{-1} for granite (Andersland and Ladanyi, 2004), it seems that the effect of mineral composition may be of little significance. Data collected by Winter and Saari (1969) for 8 representative rock minerals speak in favor of such a thesis. Similarly, a graph given by Frivik (1982), illustrating the results of the specific heat measurements for clays, silt and sand suggests that the effect of the type of soil is not statistically significant. The effect of temperature for these soils is described as "moderate" and the average specific heat decreased from about 0.78 J g^{-1} K^{-1} at 20 °C to about 0.66 J g^{-1} K^{-1} at −40 °C (Frivik, 1982).

The specific heat of clays and clay minerals is only known fragmentarily. There is a need for models enabling to take into account the temperature dependence in numerical simulations relating to the heat transfer in soil, particularly at artificial ground freezing projects and a variety of special issues such as skating-rinks, cold stores, building foundations in permafrost regions and many others. Wolfe and Thieme (1964) measured the specific heat of a dry, not identified "gray, fire clay" at several temperatures down to −180 °C, obtaining a nonlinear decrease from 0.92 J g^{-1} K^{-1} at +30 °C to 0.34 J g^{-1} K^{-1} at −180 °C. Kay and Goit (1975) made specific heat measurements on several soil materials including clay at different temperatures in order to obtain a generalized functional relation between the specific heat and temperature. Specific heats were found to vary linearly with temperature from 200 to 300 K (−73 °C to +27 °C) and extrapolated

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* Corresponding author. Tel.: +48 603956567.
E-mail address: tomkoz@tu.kielce.pl (T. Kozlowski).

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close to zero at 0 K, according to the third law of thermodynamics. For clay, they obtained 0.75 J g^{-1} K^{-1} at −15 °C and 0.88 J g^{-1} K^{-1} at +10 °C. Robie and Hemingway (1991) measured the specific heats of kaolinite KGa^{-1} (7 to 380 K) by adiabatically shielded calorimetry. The observed temperature dependency was nonlinear and the values of the specific heat appeared relatively high (e.g. 1.1 J g^{-1} K^{-1} at +100 °C, 0.96 J g^{-1} K^{-1} at +30 °C and 0.38 J g^{-1} K^{-1} at −150 °C). The explanation could be that the samples were dried at room temperature under vacuum. Some forms of the adsorbed water may not be removed in such conditions and the resulting specific heat includes the adsorbed water component. Recently, data on the specific heat of kaolinites and a montmorillonite was determined between 40 °C and 215 °C before and after the dehydroxylation were reported by Michot et al. (2011), yet any information about a possible drying of the samples prior the experiments was not given. The significant decrease in the specific heat after the dehydroxylation was related to the hydroxyl group content. Kozlowski (2012) reported the temperature dependence of four homoionic forms of bentonite from Chmielnik between −70 °C and +30 °C obtained as a part of an experiment relating to the thermal properties of clay adsorbed water. However, his results were obtained by Modulated Differential Scanning Calorimetry (MDSC) at a relatively high scanning rate i.e. in strongly unsteady conditions, the samples were dried for too short a period and the temperature region cannot be regarded as satisfying. It seems that Quasi Isothermal Modulated Differential Scanning Calorimetry (QI-MDSC) may be a more suitable method for specific heat measurements because of the lack of smearing of results due to the continuous change of temperature during the experiment (Ding and Cheng, 2001; Wunderlich et al., 1997).

The main theses of the present paper are the following: i) the differences in the specific heats of different homoionic forms of the same clay are statistically significant, ii) the differences are significantly correlated with the fraction of particles <2 μm, the latter resulting from the cation composition.

2. Materials

In this study, homoionic forms of bentonite from Texas (Stx-1b) and Wyoming (SWy-2) were used as materials. The clays were obtained from the Source Clay Repository of the Clay Mineral Society. Three homoionic forms (Ca^{2+}, Na^{+} and K^{+}) were fabricated by the repeated saturation of the fraction less than 0.063 mm with an appropriate chloride and the subsequent purifying from chlorine anion by diffusion, until the disappearance of the characteristic reaction with $AgNO_3$. The clay pastes were then air-dried at room temperature.

In order to control the effectiveness of the cation exchange, the determination of the cation content in the clay matrices has been done by use of Atomic Absorption Spectrometry (AAS). The results, shown in Table 1, testify that the ion exchange process was carried out properly. According to the manufacturer's data (Perkin Elmer, model 3100 AAS), the error of metal determination in clays usually does not exceed 1% for the most common metals (Ca, Na, K, Fe), and can be in the order of 10% for Pb.

Other properties of the homoionic forms are characterized in Table 2.

3. Methodology

In the classical DSC (Differential Scanning Calorimetry) method, the temperature of a specimen changes linearly in time, while in the MDSC (Modulated Differential Scanning Calorimetry) method, on the linear plot of temperature the sinusoidal one is overlapped (Fig. 1). This technique provides measurement of the sample's heat capacity simultaneously with the total heat capacity. Yet, there is a measuring error related to the continuous change of temperature, which makes the system permanently thermally unstable. To measure the heat capacity avoiding the presented problem, the QI-MDSC method was used. In this method, temperature does not change linearly, but oscillates around a constant value (Fig. 1). At low amplitudes of modulation (normally between 0.01 and 0.5 K), the temperature is almost constant and the mode is said to be "quasi-isothermal". The possibility to determine the heat capacities even in the isothermal case is not provided by any other method (Höhne et al., 2003).

The TA DSC Q2000 differential scanning calorimeter with a liquid nitrogen cooling system (LCNS) was used in the experiment. The LCNS reaches a temperature range of −180 to 550 °C. After weighing an empty aluminum pan, a bentonite sample was put inside. A pinhole was punched in the lid of the sample pan which was placed in the calorimetric cell. Then the temperature was set at a constant value of 110 °C and the specimen was dried for 8 h. During the drying process and the following experiment, the calorimetric cell was purged with dry helium at a flow rate of 25 ml/min. Next, after the equilibration at 100 °C, the specific heat determination was done at every 10 °C down to −150 °C. The temperature modulation was ±0.26 °C/min around each measured temperature for 10 min. After the experiment, the specimen was heated to +20 °C and the mass of the dry bentonite was determined. Three samples of each homoionic form were examined at every 10 °C between −150 °C and +100 °C.

The calibration process consisted of making measurements of the specific heat of sapphire in a mode identical to that described above and the subsequent comparing of each measured value of the specific heat of sapphire to an analogical value for a given temperature taken from the references. All the measured values of the specific heat of clays were multiplied by temperature related ratios obtained in this manner.

Table 1
Exchangeable cation content in dry soil matrix (mg/kg).

Cation	Cation content in Stx-1 form				Cation content in SWy-2 form			
	Natural	Ca^{2+}	Na^{+}	K^{+}	Natural	Ca^{2+}	Na^{+}	K^{+}
Fe^{3+}	3412.08	3068.97	2617.65	3011.36	3063.09	3452.70	2347.15	2013.99
Ca^{2+}	10016.48	14594.83	730.39	687.50	4889.59	23300.68	2699.48	2657.34
Na^{+}	1054.95	211.21	8352.94	590.91	5009.46	344.59	6160.62	1500.00
K^{+}	972.53	448.28	1166.67	20892.05	1305.99	912.16	730.57	6653.85
Cu^{2+}	8.52	30.21	8.73	8.24	4.42	20.68	7.98	6.75
Cr^{3+}	8.19	12.16	6.18	7.22	7.41	8.58	6.17	5.10
Ni^{2+}	3.30	4.61	2.55	3.47	4.20	5.14	8.29	2.73
Zn^{2+}	18.68	24.00	27.21	27.22	38.52	53.34	45.08	54.51
Cd^{2+}	0.71	2.97	0.83	0.80	0.50	2.47	0.52	0.59
Pb^{2+}	13.30	131.25	13.14	46.48	34.67	129.80	31.87	27.17
Total	15508.74	18528.49	12926.29	25275.25	14357.85	28230.14	12037.73	12922.03