

Effect of dehydroxylation on the specific heat of simple clay mixtures

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Received 29 July 2010; received in revised form 7 January 2011; accepted 10 January 2011

Abstract

Specific heats of four clays (standard reference kaolins, commercial kaolin and montmorillonite) before and after dehydroxylation have been measured. The results were compared with handbook data for the thermal chemical properties of solids. Good agreement has been obtained for the reference kaolin before any thermal treatment. Then, following thermal treatments at 500 °C, 600 °C and 700 °C, dehydroxylation leads to a progressive decrease of heat capacity per unit mass. After dehydroxylation, heat capacity values for all the studied materials are rather similar and agree closely with those estimated by the rule of mixtures. Finally, an empirical relation describing the specific heat capacity (C) in $\text{J kg}^{-1} \text{K}^{-1}$ of dehydroxylated kaolin from 40 °C to 1100 °C is proposed: $C = 1128 + 0.102T - 36 \times 10^6 T^{-2}$ where T is in K.

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Keywords: A. firing; B. platelets; D. clays; Specific heat; Dehydroxylation

1. Introduction

The energy cost for large scale production of ceramic objects has become a critical issue. Nowadays, as a consequence of more ecologically aware policies, energy requirements during the firing cycle and also properties of the final product, such as the heat storage ability, have to be identified and predicted. Consequently, evaluation of the specific heat of the raw material and its subsequent variation with thermal treatment represents fundamental and vital knowledge.

In various sectors of the manufacturing industry, such as whitewares (earthenware, porcelain, etc.), structural clay products (tiles, roof tiles, brick, etc.) or refractories, the basic raw materials are constituted of clays. These are a mixture of clay minerals (phyllosilicates), associated minerals (feldspar, quartz, etc.) and impurities (iron, titanium, etc.). Typically, the fabrication process involves forming where the raw material mixture is worked into the required shape, for example by casting, drying and then firing to obtain a dense robust object. During firing both structural and microstructural changes take place in the clay material. Even if associated minerals and impurities can influence the kinetics of densification,^{1,2} the most important

evolution concerns the phyllosilicate phases. Indeed the original phyllosilicate is a hydrated aluminium silicate with a layered crystal structure in the form of fine grains. This transforms into an amorphous phase or a mixture of amorphous and crystallised phases depending on the thermal treatment.

In general, the specific heat of a material constituted of different solid phases can be calculated using the rule of mixtures. This rule also gives a useful approximation for a material of unknown specific heat providing its chemical composition can be broken up into constituent parts with known values. However, situations can occur where such an approach has its limits. According to Debye theory, because of a difference in terms of atomic structure and binding, two solids with the same chemical composition could have different specific heats particularly in the low temperature regime. For example, in the case of carbon, measurements with an adiabatic calorimeter by Lebedev et al. show that at room temperature there is a difference of 30% between the specific heats of diamond and graphite.³ Therefore, in order to test the validity of the rule of mixtures for complex clay based materials, measurements are necessary.

As early as 1887, Le Chatelier studied the thermal reactions occurring in clays on heating.⁴ Then work by Simpson, Knotte, MacGee and Cohn and reported measurements of the heat involved in clay transformations and also that related to the specific heat.^{5–8} The values cited for specific heat in these early papers correspond to average values measured for a large change in temperature (20–1050 °C). More recently

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measurements made on various clays show that, at room temperature, their heat capacities vary from 780 to 950 J kg⁻¹ K⁻¹.^{9,10} Unfortunately, the exact mineralogical compositions are not given, which makes further use more difficult. According to the handbook of the “Thermal Chemical Properties of Inorganic Substances”, the value at room temperature for kaolinite is 945 J kg⁻¹ K⁻¹.¹¹ Then, after dehydroxylation, which leads to metakaolinite, according to the same handbook, the room temperature heat capacity increases to 1006 J kg⁻¹ K⁻¹. These values were used for a previous study on thermal conductivity of kaolinite using the laser flash technique.¹² It should however be noted that the handbook curve for metakaolinite does not reveal the same sensitivity to temperature variation as that given for kaolinite. This behaviour merits further study.

In conclusion, only a few studies are available describing the evolution of the specific heat of clays and in particular phyllosilicates with thermal treatment. No established behaviour seems to exist. To clarify the situation and refine our results, measurements using an adiabatic calorimeter have been made. The aim of this article is therefore to measure specific heat for two pure kaolin clays before and after dehydroxylation. The approach is then extended to two slightly more complex commercial clays and the validity of the rule of mixtures is examined.

2. Experimental

Clay minerals are classified as either 1:1 or 2:1 phyllosilicates.¹³ The four chosen materials consist essentially of a mixture of 1:1 phyllosilicate (kaolinite) and/or 2:1 phyllosilicates (montmorillonite, illite, muscovite), secondary phases (quartz, feldspar, etc.) and impurities (iron). The model materials labelled KGa-1B and KGa-2 are standard reference kaolin clays from Georgia (USA) supplied by the “The Clay Minerals Society”. Both of them contain more than 95 wt.% of kaolinite.^{14–16} KGa-1B is well crystallised (high Hinckley index, i.e. 1.03), whereas KGa-2 exhibits a lot of defects (low Hinckley index, i.e. 0.37).¹⁷ The commercial raw materials are BIO kaolin from Echassière (Allier, France) supplied by “les Kaolins de Beauvoir” and a montmorillonite supplied by “Argiletz”. BIO kaolin consists principally of kaolinite (~80 wt.%), muscovite (~17 wt.%) and quartz (<4 wt.%).¹⁸ The studied montmorillonite contains less than 65 wt.% of 2:1 phyllosilicates (montmorillonite, illite), a high percentage of quartz (~30 wt.%) and iron (7 wt.%).¹⁹ The principal characteristics of these raw materials are summarized in Table 1.

It should be noted that a sample of KGa-1B was enriched with iron following the method of Arias et al.²⁰ Finally, measurement by Inductively Coupled Plasma-Atomic Emission Spectrometry

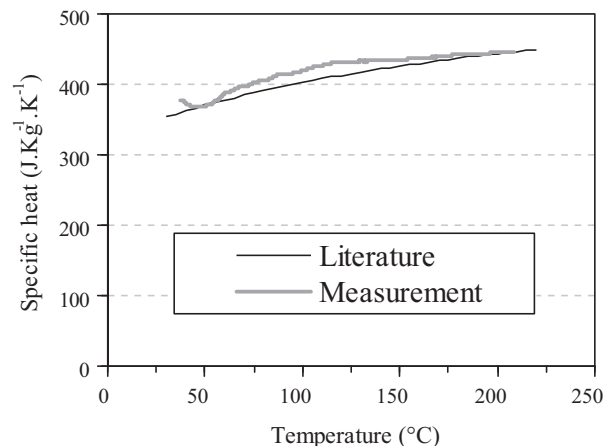


Fig. 1. Comparison of measured specific heat values and those of literature for a pure tin oxide powder.

shows that the powder contains 9.5 wt.% of Fe₂O₃. According to Soro, it is in the form of ferrihydrite nanometric particles.¹⁷

The transformations in the clays due to thermal treatment were studied using differential thermal analysis (DTA). Then green bodies and fired samples were characterized using X-ray powder diffraction (XRD).

Specific heat was measured, between 40 °C and 220 °C on raw or thermally treated powder using a Calvet type calorimeter (C80, Setaram). The apparatus was calibrated in energy through melting of an indium sample. Because of the thermal inertia of the furnace, the heating rate is slow (0.2 °C min⁻¹) between an initial 2 h dwell at 30 °C and the final 2 h dwell at 220 °C. The heat capacity is then calculated by:

$$C = \frac{A_e - A_B}{mv} \quad (1)$$

where A_e and A_B are the measured heat flows with and without the sample, respectively (mW), m is the sample's mass and v is the heating rate. The measurement validity was verified using a tin oxide powder (Aldrich, purity 99.9%), whose specific heat is well known.¹¹ The difference between literature and our measurement is less than 2% for all temperatures (Fig. 1).

For comparison to measured specific heat, the term “calculated specific heat” refers to those values obtained using the rule of mixtures, given by:

$$C_{\text{rom}} = \sum_i m_i C_i \quad (2)$$

where C_{rom} is the calculated specific heat, m_i and C_i are the mass fraction and specific heat of phase i , respectively. For each

Table 1
Principal characteristics of studied clays: kaolin KGa-1B,¹⁴ KGa-2,¹⁵ BIO,¹⁸ montmorillonite.¹⁹

	Material	Main phases	Comments
Model materials	KGa-1B	Kaolinite (>95%)	Well crystallised
	KGa-2	Kaolinite (>95%)	Numerous defects
Raw industrial materials	BIO	Kaolinite (~80%), muscovite (~17%), quartz (<4%)	/
	Montmorillonite	Montmorillonite (<65%), quartz (~30%), illite	High percentage of quartz and iron (~7%)

temperature T (K), C_i is calculated using a polynomial:

$$C_i = (a_i + b_i 10^{-3} T + c_i 10^6 T^{-2}) \quad (3)$$

where a_i , b_i and c_i are the coefficients given by the thermochemical data handbook.¹¹ The given coefficients were divided by the molar mass of the solid phase to obtain directly the specific heat in $\text{J kg}^{-1} \text{K}^{-1}$.

3. Results and discussion

3.1. Structure and microstructure

Phyllosilicates are hydrated aluminium silicates with a layered crystal structure in the form of fine grains. At an atomic scale, a layer consists of one octahedral sheet (Oc) and one or two tetrahedral sheets (Te) piled up in the c -axis direction (Fig. 2). In fact, clay minerals can be classified depending on the way that tetrahedral and octahedral sheets are packed into layers as 1:1 (Te–Oc) or 2:1 (Te–Oc–Te). If inside a layer the bonds, including those to the OH groups, are ionic or covalent in nature, between layers the bonds are weaker (hydrogen or Van der Waals) and in some cases space is provided for interlayer cations, such as potassium.

The loss of hydroxyl groups from the crystal structure, called dehydroxylation, is an endothermic phenomenon. Using differential thermal analysis, it was detected between 500 °C and 600 °C for all of the studied materials (Fig. 3). This phenomenon was less clearly seen in the case of the montmorillonite material

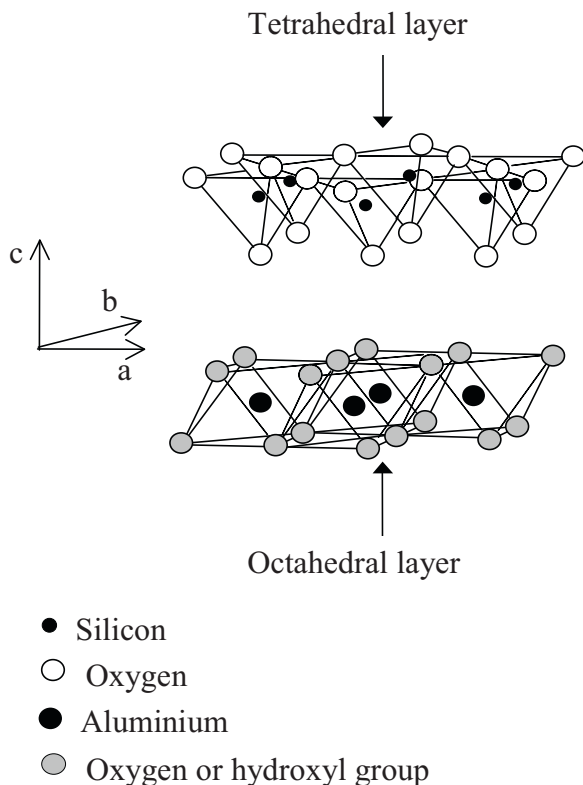


Fig. 2. Schematic of the octahedral and tetrahedral planes.

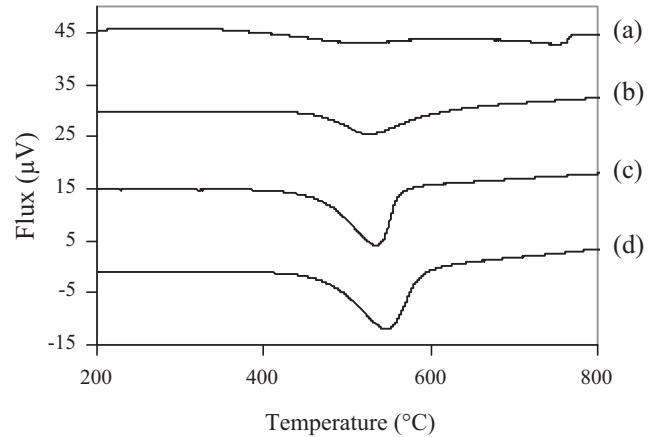


Fig. 3. DTA between 200 °C and 800 °C of (a) montmorillonite, (b) BIO kaolin, (c) KGa-1B kaolin and (d) KGa-2 kaolin.

because of the poor signal to noise ratio. Using X-ray diffraction, the main evolutions and characteristics of our samples before and after dehydroxylation were followed (Figs. 4 and 5). The X-ray diffraction patterns confirm that KGa-2 kaolin is less crystallised than KGa-1B kaolin, relating to peak broadening. They also indicate the presence of quartz and 2:1 phyllosilicate in the BIO kaolin and the studied montmorillonite. It should be noted that because of a high proportion of iron in the montmorillonite, the corresponding X-ray diffraction pattern contains more noise.

For KGa-1B and KGa-2 kaolins, after dehydroxylation, no crystallised phases, except anatase, can be detected even though the layer structure is maintained in a distorted form called metakaolin up to 900 °C. However, according to MacKenzie et al., approximately 10% of hydroxyl groups remain in the structure.²¹ For BIO kaolin and montmorillonite, since after

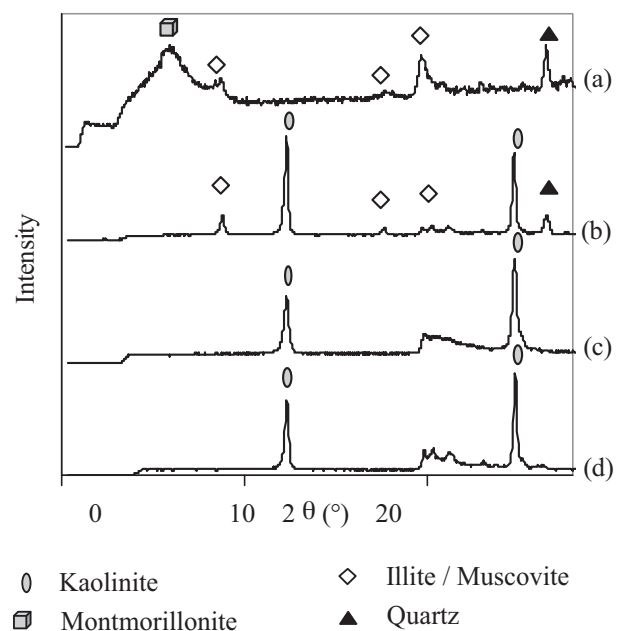


Fig. 4. XRD patterns for (a) montmorillonite, (b) BIO kaolin, (c) KGa-2 kaolin and (d) KGa-1B kaolin, as green bodies.

Table 2
Comparison of measured and calculated specific heat values for pure KGa-1B kaolin and for KGa-1B kaolin enriched with 9.5 wt.% iron as a function of temperature.

Temperature (°C)	Heat capacity (J kg ⁻¹ K ⁻¹)			
	KGa-1B		KGa-1B with iron	
	Literature	Measured values	Calculated values	Measured values
40	984	974	954	953
60	1023	999	992	980
80	1058	1043	1025	1014
100	1089	1085	1055	1054
150	1154	1176	1118	1140
200	1208	1223	1170	1187

dehydroxylation the muscovite and illite structures are maintained until 800 °C and above,^{22,23} only these 2:1 phyllosilicates are still detected in the diffraction patterns (Fig. 5).

3.2. Specific heat of raw materials

The measurements of heat capacities of KGa-1B and KGa-2 kaolins between 40 °C and 215 °C exhibit the same values within 0.3%. In this particular case, we deduce that there is no influence of crystallinity on heat capacity. Furthermore the measured heat capacity is in close agreement with literature yielding difference of less than 2.5% for all values in the temperature range.

A sample of KGa-1B kaolin was enriched with 9.5 wt.% of iron. According to calculation using the rule of mixtures, its specific heat should be about 3% lower than for kaolinite without iron. Measurements are in close agreement with the calculations (Table 2). From these results, the measurement accuracy is deduced to be better than 3%.

The heat capacity of untreated BIO kaolin is slightly lower than that of KGa-1B. The difference varies between 20 at 40 °C

and 40 J kg⁻¹ K⁻¹ at 200 °C. BIO kaolin contains 80 wt.% of kaolinite. Taking into account an upper limit of 4 wt.% of quartz, whose heat capacity is 735 J kg⁻¹ K⁻¹ at 23 °C, only a decrease of 10 J kg⁻¹ K⁻¹ can be explained. Therefore, the reduced value of heat capacity could also be attributed to the 17 wt.% of muscovite in BIO kaolin providing muscovite has a lower heat capacity than kaolinite. Finally, the heat capacity of montmorillonite is significantly decreased compared to KGa-1B kaolin by approximately 100 J kg⁻¹ K⁻¹ throughout the temperature measurement range 40–200 °C. This seems to be related to the high proportion of 2:1 clay minerals (~60 wt.%). Muscovite and montmorillonite are 2:1 clay minerals, and thus contain fewer hydroxyl groups than kaolinite (Table 3). It can be deduced that the proportion of hydroxyl groups has a significant effect on the specific heat capacity values.

3.3. Effect of thermal treatment

The measurements on the raw materials suggest that the value of heat capacity per unit mass is related to the OH content in the clay mineral. Thermal treatment for dehydroxylation constitutes another route to induce a strong change in the OH content of a clay mineral. The values of heat capacity per unit mass are therefore compared before and after dehydroxylation. However, the literature data for kaolinite and metakaolinite is somewhat ambiguous. In fact the two curves cross over at 70 °C so that the effect of dehydroxylation is an increase in specific heat below 70 °C and a decrease in specific heat for values above 70 °C (Fig. 6). Furthermore this behaviour is different from that predicted by the rule of mixtures. Based on the chemical composition of metakaolinite, the rule of mixtures predicts less than 1% difference between the specific heat values at 23 °C for a mixture of mullite and cristobalite (748 J kg⁻¹ K⁻¹) and that for a mixture of alumina and silica in the form of quartz (749 J kg⁻¹ K⁻¹). Detailed values are given in Table 4.

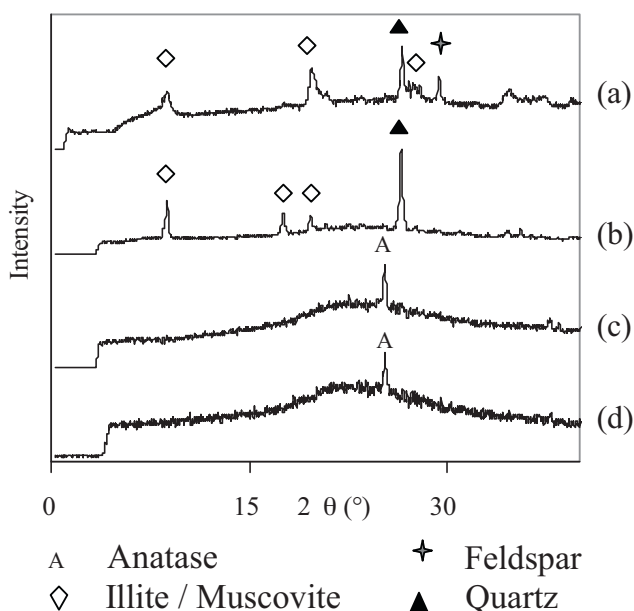


Fig. 5. XRD patterns for (a) montmorillonite treated at 650 °C and (b) BIO kaolin, (c) KGa-2 kaolin, (d) KGa-1B kaolin treated at 700 °C.

Table 3
Formulas of montmorillonite, muscovite and kaolinite.

	Formula
Montmorillonite	Si ₄ (Al _{2-x} R _x ²⁺)O ₁₀ (OH) ₂ CE _x ·nH ₂ O
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH)
Kaolinite	Si ₂ Al ₂ O ₅ (OH) ₄

Table 4

Example of calculated specific heat obtained in the case of dehydroxylated kaolin KGa-1B (a) with respect to its chemical composition (b) on the assumption that it has been entirely transformed into mullite and cristobalite.

Components	Specific heat at 23 °C (J kg ⁻¹ K ⁻¹)	Chemical composition (wt.%)	Calculated specific heat (J kg ⁻¹ K ⁻¹)
SiO ₂ (quartz)	735	52.25	749 (a)
Al ₂ O ₃ (alumina)	767	45.42	
TiO ₂	686	1.92	
Fe ₂ O ₃	654	0.24	
K ₂ O	895	0.02	
Na ₂ O	1103	0.03	
MgO	920	0.07	
CaO	751	0.03	
2SiO ₂ , 3Al ₂ O ₃ (mullite)	750	66	748 (b)
SiO ₂ (cristobalite)	744	34	

Experimentally, powders were thermally treated to 500 °C, 600 °C or 700 °C (heating rate: 5 °C min⁻¹), corresponding to the temperature range for dehydroxylation of KGa-1B kaolin (Fig. 3). The powders were cooled after reaching the maximum temperature of the cycle, except for the sample treated at 700 °C. In this case, the maximum temperature was maintained for one hour before cooling. The calorimeter measurements show that at the beginning of dehydroxylation, the heat capacity is the same as that of the raw material, and afterwards it corresponds to that calculated by the rule of mixtures (Fig. 7). For a thermal treatment at 600 °C, the heat capacity curve lies halfway between these two limits. In fact, the curves are approximately parallel and the particular behaviour reported by literature for metakaolinite was not observed.

Samples of KGa-1B kaolin were also treated at 1050 °C and 1400 °C. The thermal treatment at 1050 °C leads to the formation of an amorphous phase. At higher temperatures, it is composed of a mixture of amorphous phase, cristobalite and mullite (Fig. 8). However, measurements of the specific heats of these two samples exhibit values close to those calculated using the rule of mixtures. No particular effect of crystallisation was detected (Table 5).

Moreover according to a previous study, there is a good agreement between the calculated values and those measured at higher

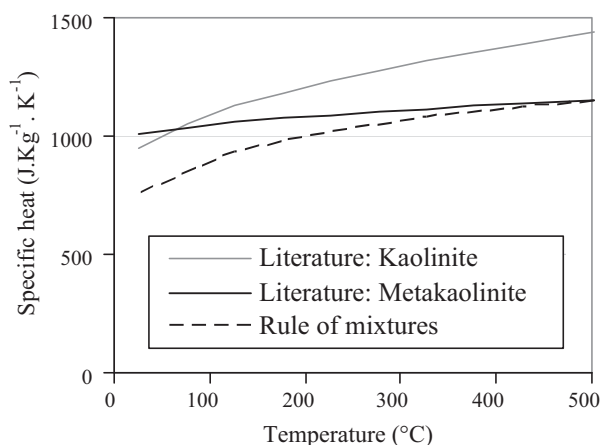


Fig. 6. Specific heat values of kaolinite, metakaolinite,¹¹ and those calculated by the rule of mixtures between 25 °C and 500 °C.

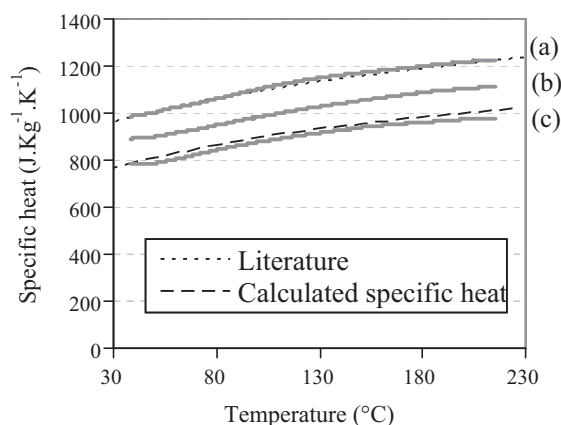


Fig. 7. Measured specific heat of KGa-1B kaolin treated at (a) 500 °C, (b) 600 °C and (c) 700 °C.

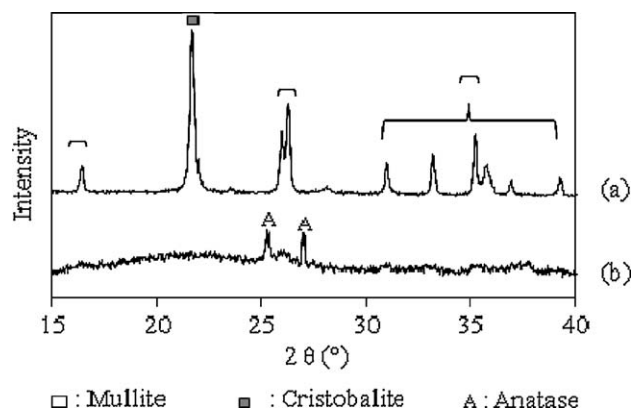


Fig. 8. XRD patterns of KGa-1B kaolin treated at (a) 1400 °C and (b) 1050 °C.

Table 5

Comparison of calculated and measured specific heat values of thermally treated KGa-1B kaolin as a function of temperature.

Temperature (°C)	Heat capacity (J kg ⁻¹ K ⁻¹)		
	Calculated	Treated at 1050 °C	Treated at 1400 °C
40	792	808	809
80	875	869	864
120	935	910	919
160	980	939	984
200	1015	976	988

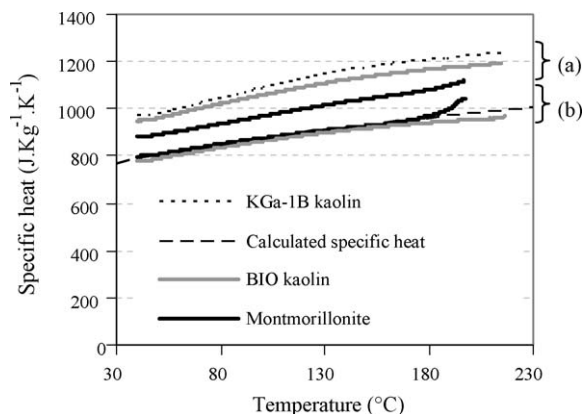


Fig. 9. Specific heat of BIO kaolin and montmorillonite (a) as green bodies and (b) treated at 650 °C and 700 °C, respectively.

temperatures (350–1100 °C).¹² For kaolinite treated at 700 °C (metakaolinite) and higher temperatures up to 1400 °C, we therefore propose an empirical relation, which describes the specific heat capacity as a function of temperature (T in K) between 40 °C and 1100 °C:

$$C = 1128 + 0.102T - 36 \times 10^6 T^{-2} \quad (4)$$

It can be noted that these more refined heat capacity values have a slight effect on room temperature values of thermal conductivity of thermally treated KGa-1B kaolin reported in a previous paper.¹²

Finally, the heat capacity values for BIO kaolin and montmorillonite after thermal treatment were estimated using the rule of mixtures and compared to experiment. First, without the OH groups the estimated values at room temperature are almost the same: 748 J kg⁻¹ K⁻¹ for BIO kaolin and 753 J kg⁻¹ K⁻¹ for montmorillonite. Second, the experimental data for BIO kaolin treated at 700 °C and montmorillonite treated at 650 °C are in close agreement with calculations (Fig. 9). The role of the OH group content in the heat capacity values of BIO kaolin and montmorillonite raw materials is revealed in Fig. 9 by comparing the curves before and after dehydroxylation.

4. Conclusion

Specific heat measurements on kaolin reference clays (95 wt.% of kaolinite), which have not been dehydroxylated, agree with literature. It has also been shown that crystallinity does not have a significant influence on these measured values. In contrast, for more complex clay mixtures, heat capacity decreases when the proportion of 2:1 phyllosilicates increases, which can be related to the hydroxyl group content.

Further measurements, during and after dehydroxylation, confirm the role of hydroxyl groups. Indeed, dehydroxylation leads to a progressive decrease of heat capacity values. Once dehydroxylation is completed, values for heat capacities are in agreement with those calculated by the rule of mixtures. These values are rather similar for all the studied materials.

Acknowledgements

Aurélien Michot would like to thank the Limousin Region and the European Social Fund for their financial support.

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