Variations of Strength, Resistivity and Thermal Parameters of Clay after High Temperature Treatment

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A b s t r a c t

This paper reports the variations of strength, resistivity and thermal parameters of clay after high-temperature heating. Experiments were carried out to test the physical properties of clay heated at temperatures ranging from room temperature to 800°C in a furnace. The experiment results show that below 400°C the uniaxial compressive strength and resistivity change very little. However, above 400°C, both increase rapidly. At a temperature under 400°C, the thermal conductivity and specific heat capacity decrease significantly. The thermogravimetric analysis (TG) and differential scanning calorimeter (DSC) test indicate that a series of changes occur in kaolinite at temperatures from 400 to 600°C, which is considered the primary cause of the variation of physical and mechanical properties of clay under high temperatures.

Key words: high temperature, clay, strength, resistivity, thermal parameters.

1. INTRODUCTION

Clay is a common material, with broad applications in geomechanical engineering. Under the influence of high temperature, the mineral composition

and microstructure of clay change significantly (Sato *et al.* 1992, Aparicio and Galan 1999, Wu and Zhou 2008, Zhu *et al.* 2008). Meanwhile, various physical and mechanical properties are changed in the clay matrix. After being cooled down to room temperature, these thermally-induced variations are to some extent irreversible. Hence, the macroscopic physical and mechanical properties of clay depend on the temperature history, especially the maximum temperature that they were exposed to. Knowledge on the variation of the mechanical and physical properties of clay which are affected by temperature is important to understand and simulate many processes in various engineering projects, such as nuclear water storage (O'Flaherty and Gray 1974, Dixon *et al.* 1985, Radhokrishra and Chan 1989, Witherspoon 2001, Abuel-Naga *et al.* 2009, Sundberg *et al.* 2009, Gens *et al.* 2010, Dupray *et al.* 2013), material modification (Sato *et al.* 1992, Zhang and Yuan 1993, Li *et al.* 2012), pollution controlling (Zheng *et al.* 2010, Sánchez *et al.* 2011), oil or gas industry (Cai 2003).

Numerous studies have shown that some properties of clay or claystone are correlated with thermal damage, such as mass, mechanical strength (*e.g.*, compressive strength), Poisson's ratio, elastic modulus (Laloui and Cekerevac 2003, Zhang 2012, Tian *et al.* 2014, Mao *et al.* 2015), porosity, permeability (Ślizowski *et al.* 2003, Nelskamp *et al.* 2008, Melenevsky *et al.* 2009, Peltonen *et al.* 2009), thermal parameters (Monfared *et al.* 2011), chemical and mineral composition (Sun *et al.* 2015a), and wave velocity (Zhang 2012).

Therefore, the research on the thermo-physical-mechanical of clay is extremely meaningful on a wide range. In this paper, the variations of uniaxial compressive strength, resistivity and thermal parameters are analyzed after high-temperature heating.

2.   EXPERIMENTAL TESTS

Clay samples used in these experiments are tan-eluvial soils collected from farmland in Xuzhou, Jiangsu Province. As shown in Fig. 1, the main composition was quartz and kaolinite.

The clay samples were first dried in a high temperature drying oven (keeps 2 hours under the temperature of 105°C), then ground into powder and screened by a 1-mm sieve to remove the impurities. The screened clay was shaped into cylindrical specimens of $\Phi\, 60 \times 70$ mm by adding a small amount of water with a compaction device. The average of moisture content and density of the cylindrical specimens were 5% and 2.11 g/cm^3, respectively. Finally, the samples experienced the several steps of heat treatment by an MTS652.02 high-temperature furnace. The temperature was set into fourteen levels (25, 60, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, and 800°C), with four samples as a set. The heating process was com-
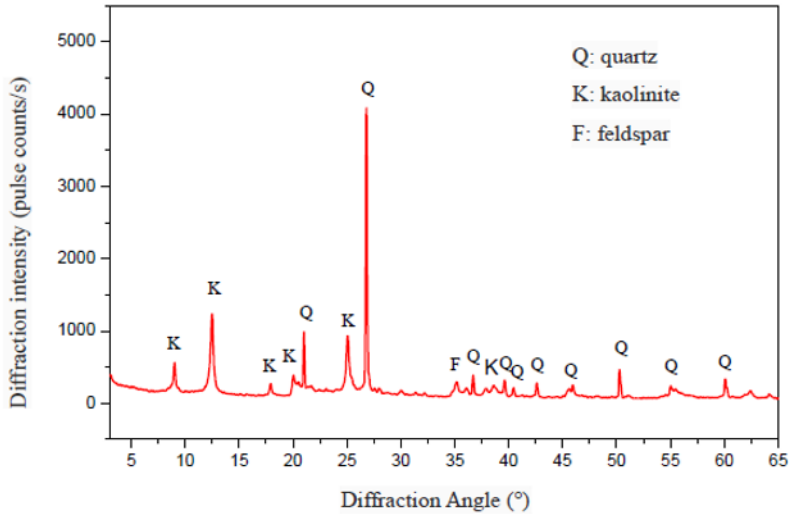
Fig. 1. XRD spectrum of a clay sample.

Fig. 2. The testing machine and resistivity detector: (a) loading apparatus, and (b) digital electrical instrument (SYSCAL-R2).

posed of three stages: ① clay specimens were heated in the high-temperature furnace at the heating rate 30°C/min until reaching the targeted temperature; ② the targeted temperature was kept for 3 min to ensure that the inside of the samples was heated evenly; ③ the furnace was cooled down to room

temperature by cutting off the power of furnace. The strength, resistivity, and thermal parameters of the specimens were tested before and after heating. The strength was tested with an electro-hydraulic servo-controlled testing machine (EHC-3000, produced by Sansi Instruments Co. Ltd. of Zhuhai, China, shown in Fig. 2a) at the loading speed of 0.5 kN/s. The load was measured by an oil pressure sensor connected to the hydraulic pressure cylinder, and a cylindrical capacitor displacement sensor fixed to the upper plate was used to measure the displacement of clay samples in the test. The electrical resistivity was measured with a digital electrical instrument (SYSCAL-R2, produced by IRIS Instrument Co. Ltd, France, shown in Fig. 2b), and the information on thermal parameters was simultaneously collected by a TPS test machine produced by Hot Disk Equipment Co. Ltd. In addition, the TG curve (thermogravimetric analysis) of clay specimen
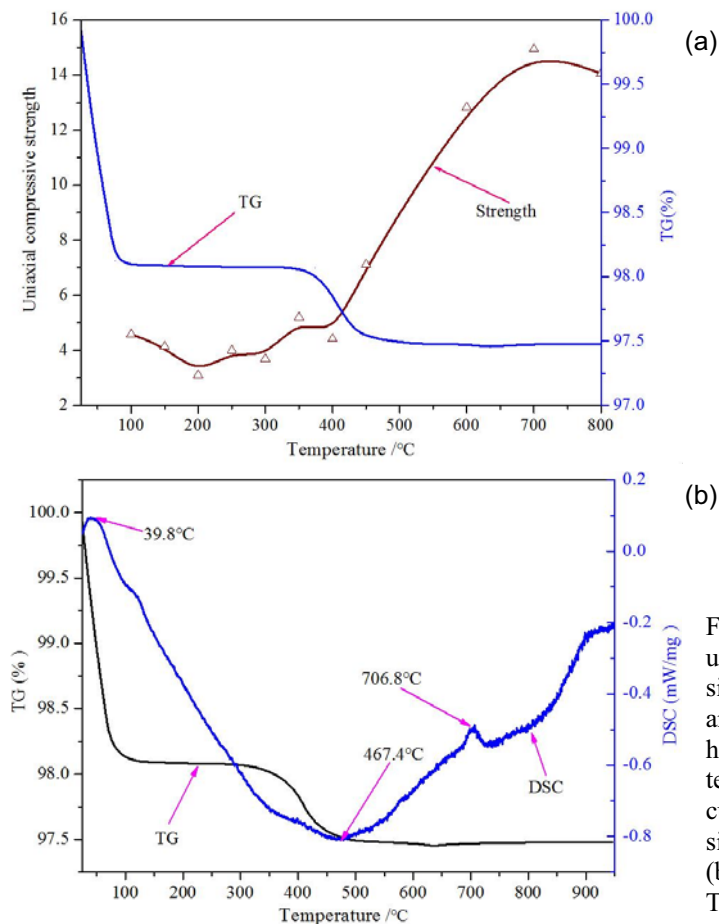

Fig. 3. Variation of uniaxial compressive strength, TG and DSC, after heating at different tempera-tures: (a) curve of compressive strength, and (b) curve of DSC-TG.

(shown in Fig. 3) was tested with a synchronous comprehensive thermal analyzer (type STA409C) produced by NETZSCH Co. Ltd., and in this test, the heating rate was set as 5 k/min and the gas flow rate was 100 mL/min.

3. THE TEST RESULT ANALYSIS

3.1 Variation of uniaxial compressive strength

The variation of uniaxial compressive strength with temperature is shown in Fig. 3. Two stages of variation can be identified: (i) Below 400°C, the strength changes subtly with the increase of temperature (the strength is around 4 MPa); (ii) When temperatures are higher than 400°C, the strength drastically increases with temperature. Combining this with the TG and DSC (differential scanning calorimeter) measurement curves shown in Fig. 4 (Zhu et al. 2008) and Fig. 5 (Wu and Zhou 2008), it can be deduced that when the temperature is higher than 400°C, the temperature effect is mainly caused by the alteration of mineral content. From differential thermal analysis (DTA) of clay (as shown by Figs. 4 and 5), the dehydroxylation reaction of clay is obviously verified at the range from 400 to 650°C. Therefore, in the heating process, kaolinite dehydroxylation yielding metakalinite occurs in the 400-650°C range (De Aza et al. 2014), as shown by the equations:

$$Al_2O_3 \bullet 2SiO_2 \bullet 2H_2O \rightarrow Al_2O_3 \bullet 2SiO_2 \bullet \frac{1}{2}H_2O + \frac{3}{2}H_2O \,, \tag{1}$$

$$Al_2O_3 \bullet 2SiO_2 \bullet \frac{1}{2}H_2O \rightarrow Al_2O_3 \bullet 2SiO_2 + \frac{1}{2}H_2O \,. \tag{2}$$
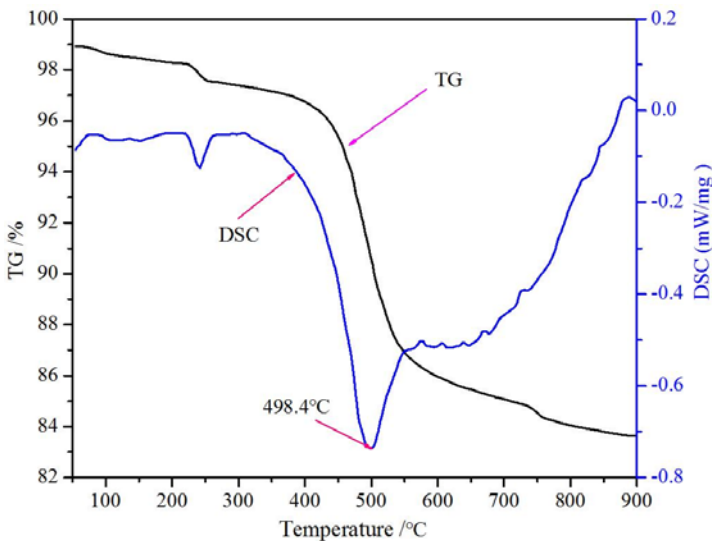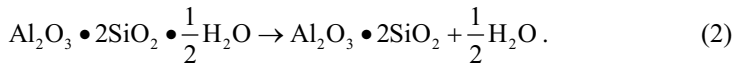

Fig. 4. DSC-TG diagram of Suzhou kaolinite (Zhu et al. 2008).
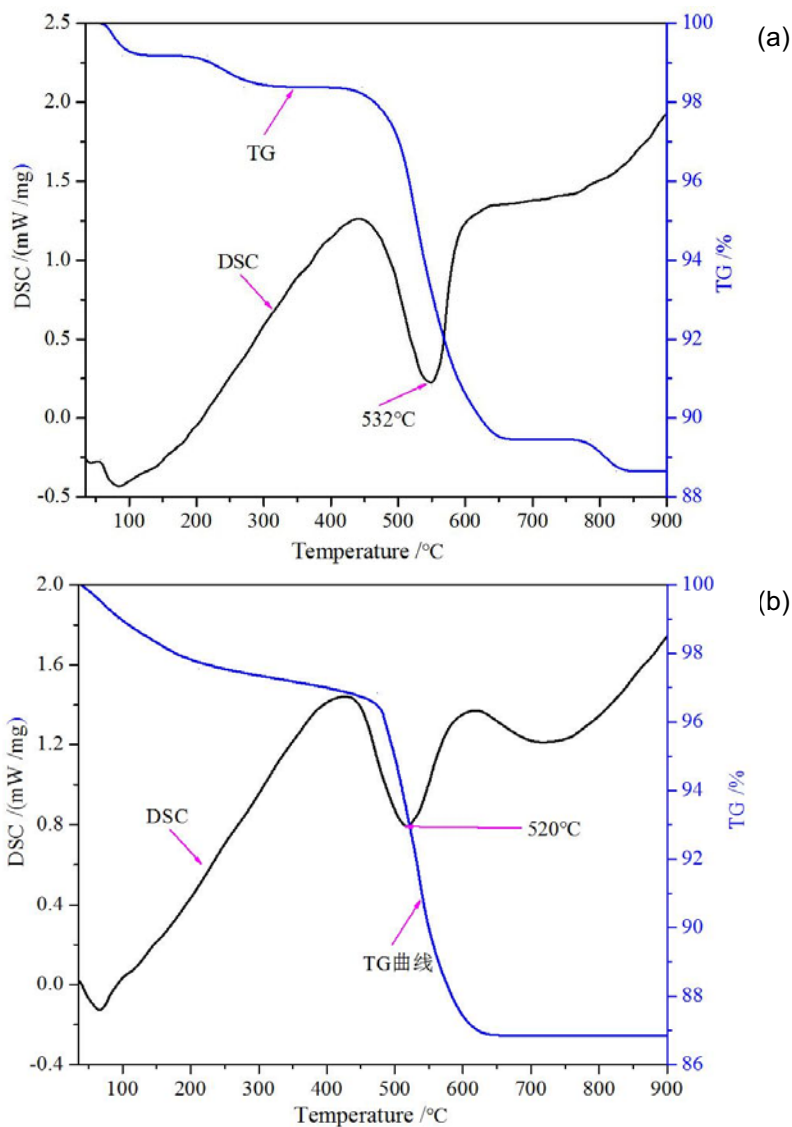
Fig. 5. DSC-TG diagram of kaolinite (Wu and Zhou 2008): (a) Tanwu kaolinite, and (b) Huling kaolinite.

In the heating process, kaolinite loses some hydroxyl (-OH) and the bond between particles is improved (Belloto *et al.* 1995, Lee *et al.* 1999). As a result, the improved cohesion between particles causes the increase of uniaxial compressive strength with temperature.

3.2 Variation of resistivity

The principle of resistivity measurement is shown in Fig. 6: powering both ends of the rock sample and then, using the measuring electrodes at the upper and lower ends, we observe the potential difference between MN when the electrical current passes through the rock sample, so the resistivity can be calculated with the following Eq. 3. As the clay resistivity is relatively large, the intensity of current is too small to be measured directly. It is obtained indirectly by measuring the voltages at both ends of a 1 kΩ standard resistor in the power supply circuit with the switch K (Fig. 6).

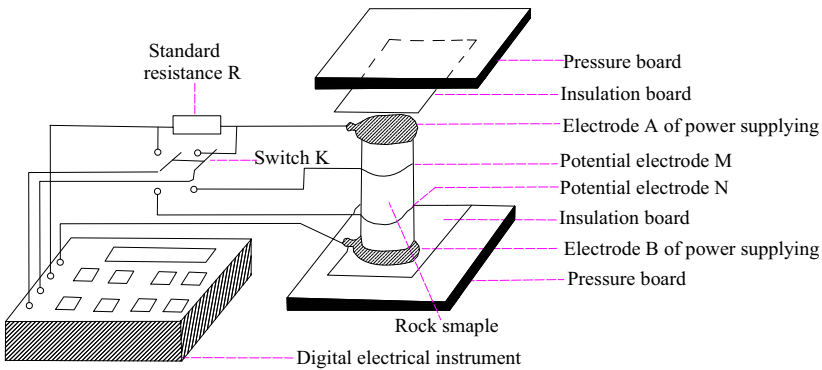$$\rho = K \frac{\Delta U_{MN}}{I} ; \quad K = A/L , \tag{3}$$

Fig. 6. Schematic diagram of the experimental system for stress and electrical resistance of clay under uniaxial compression (Sun *et al*. 2015b).
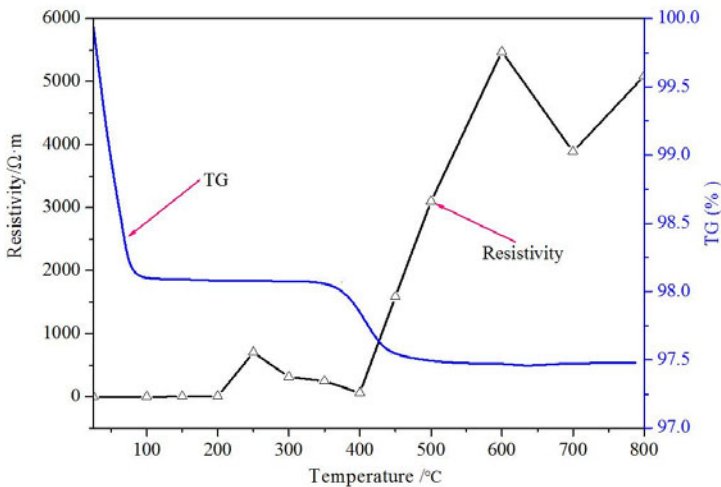

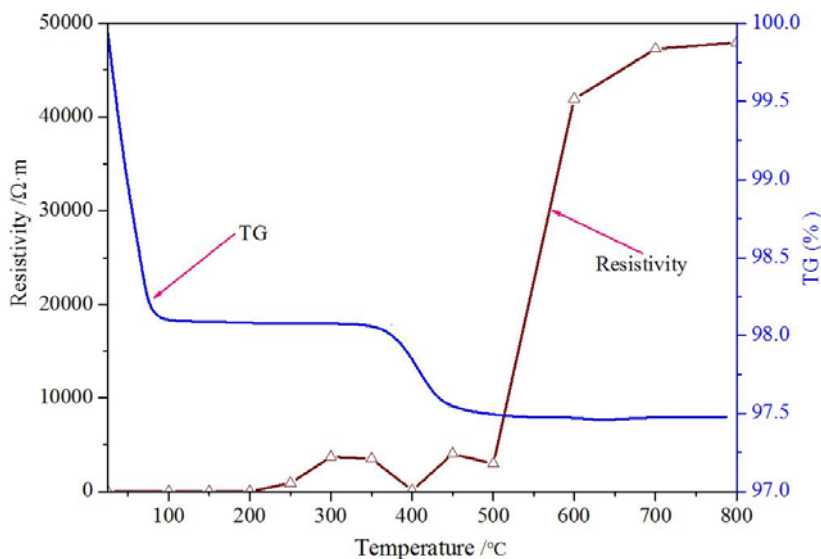Fig. 7. Variation of specific resistivity at different temperatures.

Fig. 8. Variation of resistivity (at the peak strength) at different temperatures.

where K is a coefficient determined by device, A is the cross-sectional area of rock sample; L is the distance between MN; ΔU_{MN} is the potential difference between MN; and I is current.

The variation of resistivity with temperature is shown in Figs. 7 and 8. Below 400°C, the resistivity changes very little with the increase of temperature. When the temperature is higher than 400°C, the resistivity quickly increases with temperature. This pattern of variation suggests that when the temperature is higher than 400°C, the varied thermal effect results from the changing mineral content of the sample (shown by Eqs. 1 and 2).

3.3 Variation of thermal parameters

After high-temperature heating, the thermal conductivity, specific heat capacity and thermal diffusivity of clay specimens change significantly (as shown in Figs. 9-11) in the temperature range of 20-800°C. From 25 to 400°C, conductivity decreases rapidly with temperature, which is mainly due to growing numbers of pores. Above 400°C, the thermal conductivity and specific heat capacity decrease a little bit. However, the thermal diffusivity presents a certain fluctuation, but the variation level is not apparent compared to thermal conductivity and specific heat capacity. It should be pointed out that the properties of clay in this phase (above 400°C) are close to rock. The variation of thermal conductivity with temperature is shown by Fig. 9 and the following Eq. 4
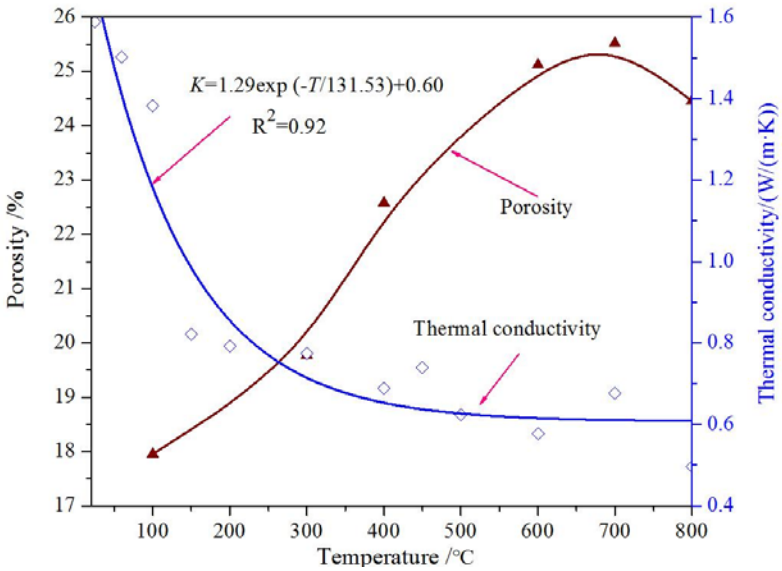
Fig. 9. Variations of thermal conductivity and porosity at different temperatures.
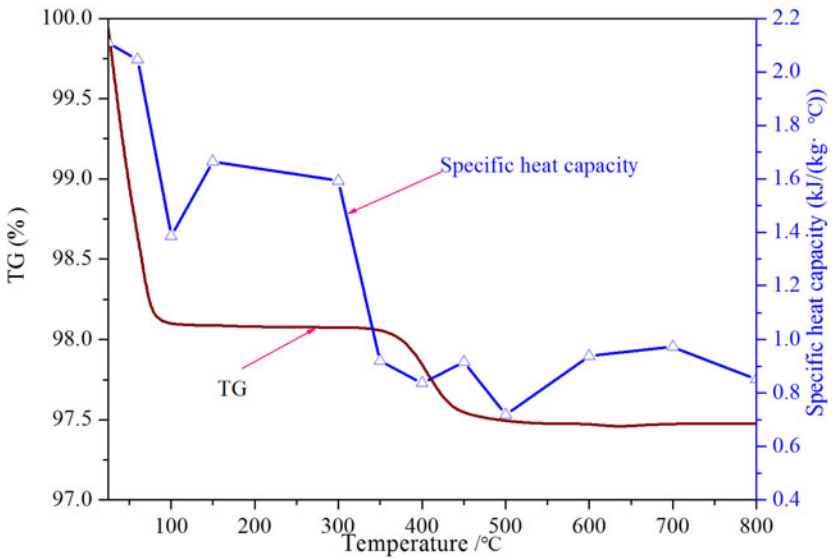

Fig. 10. Variations of specific heat capacity and TG at different temperatures.

$$K = 1.29\exp\left(-\frac{T}{131.53}\right) + 0.60; \quad R^2 = 0.92, \tag{4}$$

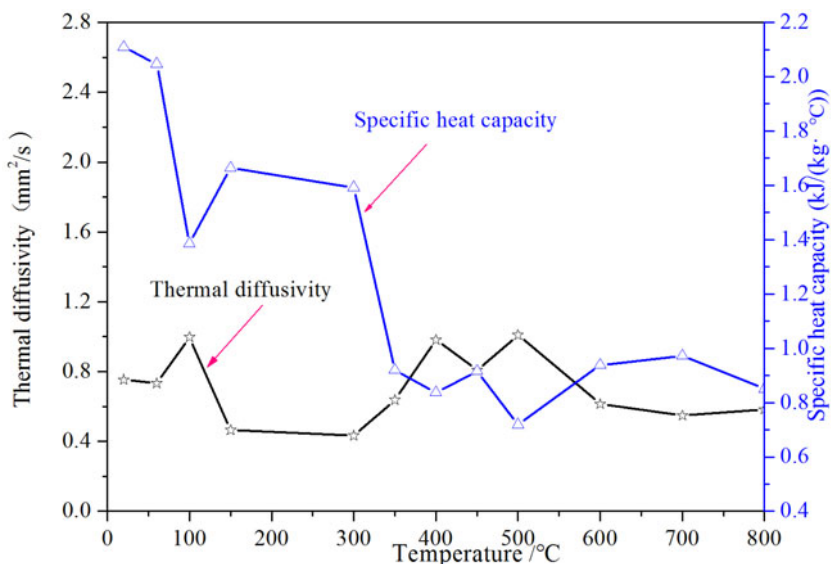where T *is* temperature, and K is thermal conductivity.

Fig. 11. Variations of specific heat capacity and thermal diffusivity at different temperatures.

4. DISCUSSION

The main mechanism of changes in physical properties of clay after thermal treatment is the damage of clay structure caused by thermal reactions. Generally speaking, clay is composed of different minerals. In the heating progress, there is a series of chemical reactions. Adsorbed and interlayer water can evaporate (*i.e.*, desorption) at the temperature range of 100-250°C, and the structural water is lost when the treatment temperature is higher than 300°C. When the heating temperature is lower than the threshold value, the variation of clay is mainly due to the change of all kinds of water. The existence of water seriously affects the porosity. Another reason: in the progress of losing structural water, some minerals are decomposed and evaporated (for example, the dehydroxylation of clay minerals), which may cause the increase of pore and fracture.

Organic matter is comparatively enriched in muddy sediments (Hunt 1996). Above 300°C, this organic matter begins to turn into char residue. The oxidation/decomposition reaction of organic matters is obviously evidenced in the range from 300°C (especially 400°C) to 500°C. Results of Fig. 12 show that the exothermal peak at 350°C is more strongly marked (Cai 2003, Cai *et al.* 2007), while the exothermal peak above 350°C disappeared. It indicates that organic matter is incorporated with clay minerals closely and stably. Therefore, oxidation/decomposition reaction of organic
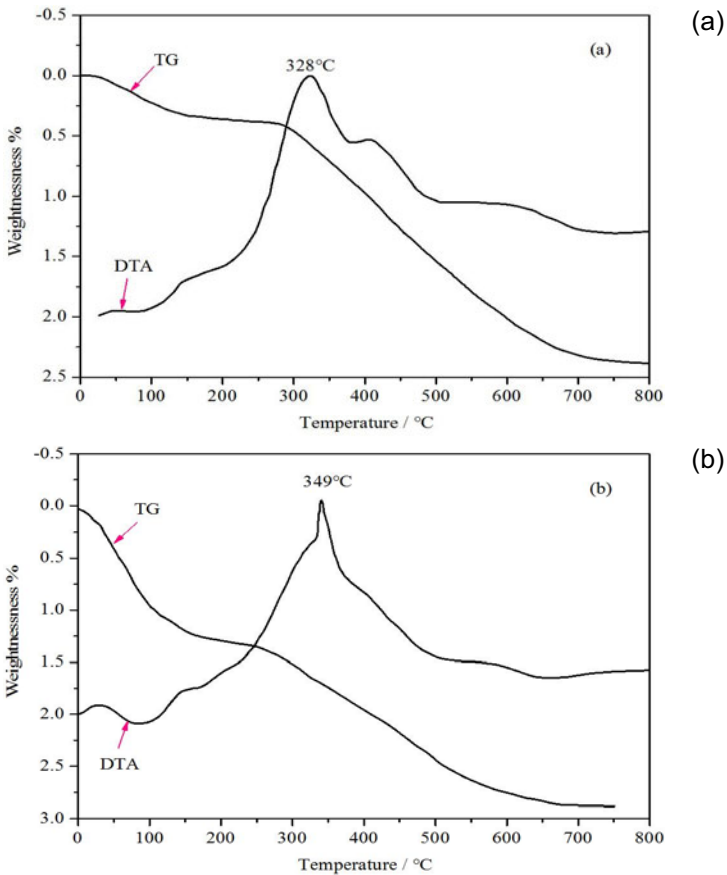
Fig. 12. The TG and DTA curves of clay samples No. 26 (a) and No. 3 (b) (Cai *et al.* 2007).

matters is obviously evidenced in the period ranging from 300 to 500°C, which leads to decrease of mass and increase of porosity. When the heating temperature reached the critical value, some of the carbonate minerals (such as calcium carbonate, magnesium carbonate, magnesite, dolomite) starts to decompose and results in the decrease of elastic modulus, compressive strength, tensile strength, and fracture toughness. Moreover, when the treatment temperature is higher than 400°C, the oxidation of organic matter is quickly increasing.

5. CONCLUSION

The study of characteristics of strength, resistivity, and thermal parameters of clay heated at different temperatures is reported in this paper. Based on the results, the following conclusions can be drawn:

❑ Temperature has a significant impact on the physical and mechanical properties of clay;

❑ Between 100 and 400°C, the uniaxial compressive strength and resistivity of clay change very little with temperature. Above 400°C, the strength and resistivity rise rapidly. The variations of uniaxial compressive strength and resistivity are significantly affected by altered mineral clay composition between 400 and 600°C;

❑ The thermal conductivity and specific heat capacity of clay specimens change significantly after treatment at high temperatures. From 20 to 400°C, they decrease rapidly with temperature. Above 400°C, both thermal conductivity and specific heat capacity decrease slightly.

Finally, it is worth mentioning that these characteristics of variation of clay properties were observed in laboratory tests. Permeability and ultrasonic measurement will also be included in future work.

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