

## THERMAL DEFORMATION THERMODYNAMICS OF A SMECTITE MINERAL

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A method has been purposed to calculate some of the thermodynamic quantities for the thermal deformation of a smectite without using any basic thermodynamic data. The Hançılı (Keskin, Ankara, Turkey) bentonite containing a smectite of 88% by volume was taken as material. Thermogravimetric (TG) and differential thermal analysis (DTA) curves of the sample were obtained. Bentonite samples were heated at various temperatures between 25–900°C for the sufficient time (2 h) until to establish the thermal deformation equilibrium.

Cation-exchange capacity (CEC) of heated samples was determined by using the methylene blue standard method. The CEC was used as a variable of the equilibrium. An arbitrary equilibrium constant ( $K_a$ ) was defined similar to chemical equilibrium constant and calculated for each temperature by using the corresponding CEC-value. The arbitrary changes in Gibbs energy ( $\Delta G_a^0$ ) were calculated from  $K_a$ -values. The real change in enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) was calculated from the slopes of the  $\ln K$  vs.  $1/T$  and  $\Delta G$  vs.  $T$  plots, respectively. The real changes in Gibbs energy ( $\Delta G^0$ ) and real equilibrium constant ( $K$ ) were calculated by using the  $\Delta H^0$  and  $\Delta S^0$  values. The results at the two different temperature intervals are summarized as below:  $\Delta G_1^0 = \Delta H_1^0 - \Delta S_1^0 T = -RT \ln K_1 = 47000 - 53T$ , (200–450°C), and  $\Delta G_2^0 = \Delta H_2^0 - \Delta S_2^0 T = -RT \ln K_2 = 132000 - 164T$ , (500–800°C).

**Keywords:** bentonite, cation exchange capacity, smectite, thermal analysis, thermal deformation, thermodynamics

### Introduction

The clays in which one of the smectite mineral is dominant are called bentonite. Smectite group includes sodium montmorillonite, calcium montmorillonite, saponite, nontronite and hectorite [1]. Bentonites and their major clay mineral smectites are among the most important industrial raw materials [2–5]. Smectites are the layer clay minerals. One layer has two silica tetrahedral sheets (T) joined to one central octahedral sheet (O). This layer is called as TOT or 2:1. There is a considerable substitution in the octahedral sheets of  $Al^{3+}$  with  $Fe^{2+}$  and  $Mg^{2+}$ , which creates a positive charge deficiency in the TOT layer. Also, there is some substitution of  $Si^{4+}$  with  $Al^{3+}$  in the tetrahedral sheets which again creates a charge imbalance. This net positive charge deficiency is generally balanced by exchangeable hydrated  $Na^+$  and  $Ca^{2+}$  cations between the TOT (2:1) layers and around the edges. The equivalence of exchangeable cations in one kilogram of a bentonite or a smectite has been defined as cation-exchange capacity (CEC). The exchangeable cations can be replaced by every other inorganic or organic cation. Also, the water associated with exchangeable cations can be replaced by polar organic molecules such as ethylene glycol, amines, polyalcohols, and the others. These are the important

properties which lead the preparation of useful products such as pillared clays and organoclays [6–9].

Some physicochemical properties, such as strength, swelling, plasticity, cohesion, compressibility, particle size, pore structure, adsorption capacity, surface acidity, catalytic activity, and cation-exchange capacity as well as the mineralogy of bentonites change considerably depending on thermal effects [10–20]. Bentonites may be subjected to high temperatures when used in some applications such as foundry, ceramics, catalysts, pillared clays, civil engineering, and the others. Before construction of bridges and building on smectite soils, the ground below the foundations may be heat-treated below the 600°C to harden the clays [21, 22].

As explained above, heat treatment leads to physical and chemical deformations in the microstructure of smectite minerals in bentonites. There are many studies about the thermal deformation kinetics [14, 23, 24]. However, there has not been enough study in literature about the thermal deformation thermodynamics of smectites minerals in bentonites. A method about this thermodynamics was proposed firstly in our previous study by using cation-exchange capacity data [25]. Therefore, the aim of this study is to develop this method by evaluating the temperature dependence of cation-exchange data.

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## Experimental

The Hançılı (Keskin, Ankara, Turkey) bentonite was used as a material in this study. This yellowish-green bentonite contains a sodium-rich smectite with the  $d(001)$ -value of 1.29 nm as clay minerals and also quartz, opal-C, feldspar, and dolomite as non-clay minerals. The percentage of the smectite in bentonite was estimated as 88% by volume. After heating at 100°C for 4 h, the bulk chemical analysis of the bentonite (mass%) is: SiO<sub>2</sub>, 61.25; Al<sub>2</sub>O<sub>3</sub>, 16.85; Fe<sub>2</sub>O<sub>3</sub>, 5.77; TiO<sub>2</sub>, 0.90; MgO, 2.78; CaO, 1.53; Na<sub>2</sub>O, 2.54; K<sub>2</sub>O, 1.12 and loss on ignition (LOI) is 7.05 [20].

The original sample was dried at 25°C for 4 h and stored in a polyethylene bag. The samples taken from this stock each of 10 g were heated at different temperatures between 25–900°C for the sufficient time intervals (2 h) until to establish the thermodynamic equilibrium. The heated samples were held in polyethylene bags.

A Netzsch Simultaneous TG-DTG-DTA Instrument Model 429, was used to determine the thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves of the original bentonite. Approximately 20 mg of sample was placed in a platinum crucible on the pan of the microbalance and was heated in the range 25–1400°C using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as an inert material. Analysis was performed under flowing nitrogen with the rate of 100 mL min<sup>-1</sup> using a heating rate of 10°C min<sup>-1</sup>. The CEC for natural and each heat treated sample was determined by the methylene blue standard procedure [26–28].

## Results and discussion

### Thermal analysis

Thermal behavior of smectites and their organic complexes has been determined by thermal analysis with combination some other instrumentations [29–41]. Several thermal analysis methods have been used to explain the thermal changes in natural and artificial materials [42–51]. TG, DTG, and DTA curves of the air dried (25°C) original bentonite are given in Fig. 1. The temperature interval and mass loss percentage by the dehydration (1), dehydroxylation (2), amorphization (3), and recrystallization (4) are observed from the DTA and TG curves as 25–450°C and 8.34%, 450–900°C and 4.16%, 900–1100°C and 0%, and 1100–1400°C and 0.45%, respectively. As seen in Fig. 1, the total mass% is 12.50% at 1000°C. Because the LOI measured by chemical analysis is 7.05%, the mass loss 25–100°C interval must be 12.50–7.05=5.45%. This value is the moisture of the

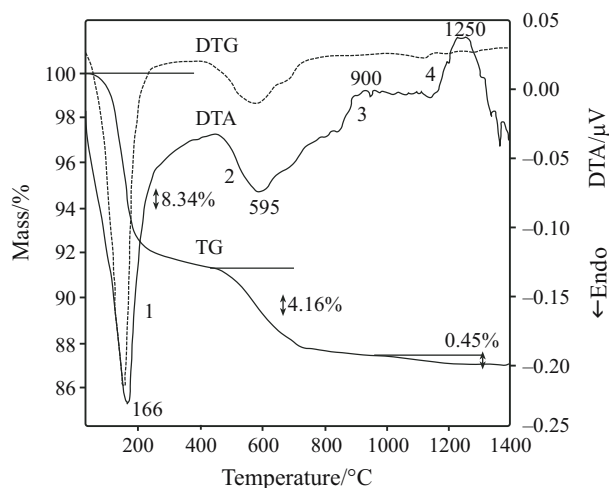


Fig. 1 The TG, DTG and DTA curves of the bentonite

air dried sample. It was seen in Fig. 1 that while the dehydration and dehydroxylation are endothermic changes, the amorphization is exothermic change.

### The effect of heating on CEC

The variation of CEC by thermal treatment temperature is given in Fig. 2. While the CEC is constant in 25–200°C intervals, it changes with displaying a convex curve (1) 200–450°C, and with displaying a concave curve (2) 500–900°C intervals. It is well known that the changes 1 and 2 occurred by the dehydration and dehydroxylation are known as reversible and irreversible, respectively. The contribution to the CEC of the non-clay minerals in the bentonite is negligible. It is fact that the exchangeable cations are almost located between the TOT (2:1) layers of smectite and do not disappear by increasing the heating temperature. However, it is known that the spacing between the TOT (2:1) layers decreases from  $d(001)=1.5$ –1.2 nm to  $d(001)=1.0$  nm at thermal treatment 550°C [25].

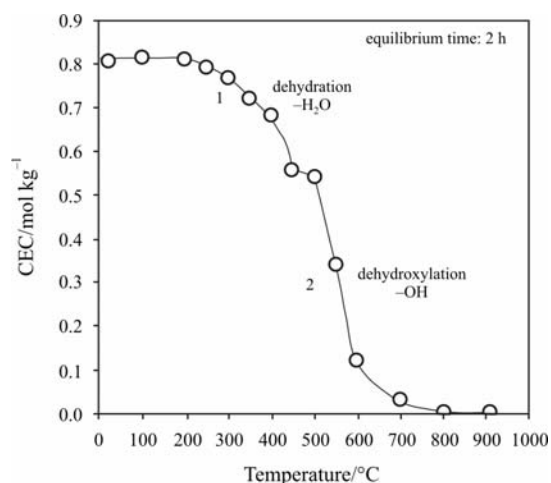


Fig. 2 Variation of cation-exchange capacity of the bentonite vs. the thermal-treatment temperature

This decrease creates difficulties to penetrate of the large methylene blue cations,  $[C_6H_{17}N_3S]^+$ , between TOT layers during the CEC measurements. In other words, thermal deformations in smectite cause a decrease in CEC. According to this fact each CEC-value is taken as a parameter for the thermal deformation equilibrium of smectite in the bentonite.

*Indirect thermodynamics considerations*

In many cases, since exact data for basic thermodynamic quantities such as molar heat capacity, standard formation enthalpy, and standard absolute entropy are not available for smectites and a lot of natural materials, direct thermodynamic calculations can not be performed for physical and chemical changes of them. Such difficulties increase by mineral mixture. To eliminate these difficulties, an indirect thermodynamic method without using the basic thermodynamic quantities has been purposed in our previous study [25]. The assumptions of indirect thermodynamics are described as follows.

- The heating time should be sufficient to establish the thermodynamic equilibrium for the thermal deformation in smectite.
- The CEC of a heated smectite should be permanent when it is cooled down room temperature and can be taken as equilibrium variable.
- A thermodynamic equilibrium for the thermal deformation of smectite and its arbitrary equilibrium constant ( $K_a$ ) have been described based on CEC( $x$ ) variables and given as below, respectively



$$K_a = (x_m - x) / x \quad (2)$$

where  $x_m$  is the maximum CEC value at 100°C,  $x$  is the CEC remained after thermal treatment at any temperature, and  $x_m - x$  is the decrease in CEC by the same process.

- The basic thermodynamic relations should be valid for similar quantities described as arbitrary. The relation among some basic thermodynamic quantities is given as below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K \quad (3)$$

where,  $\Delta G^0$  is the change in Gibbs energy (free enthalpy),  $\Delta H^0$  is the change in enthalpy,  $\Delta S^0$  is the change in entropy,  $K$  is the equilibrium constant,  $T$  is the absolute temperature, and  $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  is the universal gas constant.

- Temperature dependence of the arbitrary and real thermodynamic functions may be different from each other, but their temperature derivatives or the slopes of the obtained straight lines could be the same.

*Calculations of thermodynamic quantities*

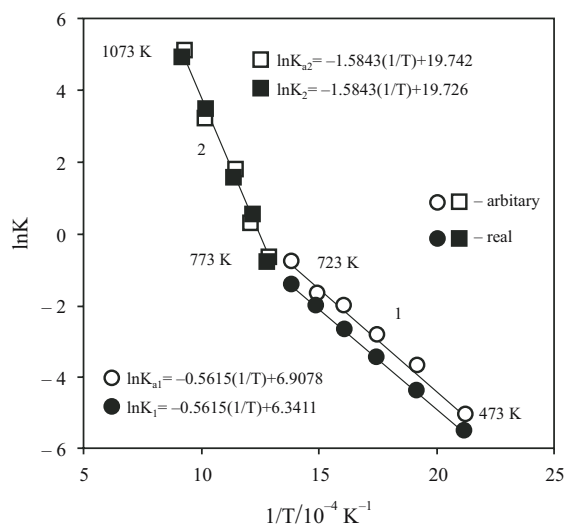
An arbitrary equilibrium constant ( $K_a$ ) and corresponding arbitrary change in Gibbs energy ( $\Delta G_a^0$ ) for each temperature are calculated from the Eqs (2) and (3), respectively. The van't Hoff graph of  $\ln K_a$  vs.  $1/T$ , and the graph of  $\Delta G_a^0$  vs.  $T$  were plotted by using the calculated values above, and given in Figs 3 and 4, respectively. As seen in these figures, there are two straight lines (1 and 2) having different slopes. First straight line (1) is for the deformation caused by the dehydration 200–450°C interval, and second straight one (2) is for the deformation caused by the dehydroxylation 500–800°C interval.

According to the assumption 5, the real enthalpy changes were calculated from the slopes of the straight lines 1 and 2 seen in Fig. 3 as  $\Delta H_1^0=47 \text{ kJ mol}^{-1}$  and  $\Delta H_2^0=132 \text{ kJ mol}^{-1}$  respectively. Also, the real entropy changes were calculated from the slopes of the straight lines 1 and 2 seen in Fig. 4 as  $\Delta S_1^0=53 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\Delta S_2^0=164 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. Hence, temperature dependence of each real change in Gibbs free energy may be written from Eq. (3) by using the real  $\Delta H^0$  and  $\Delta S^0$  values as follows:

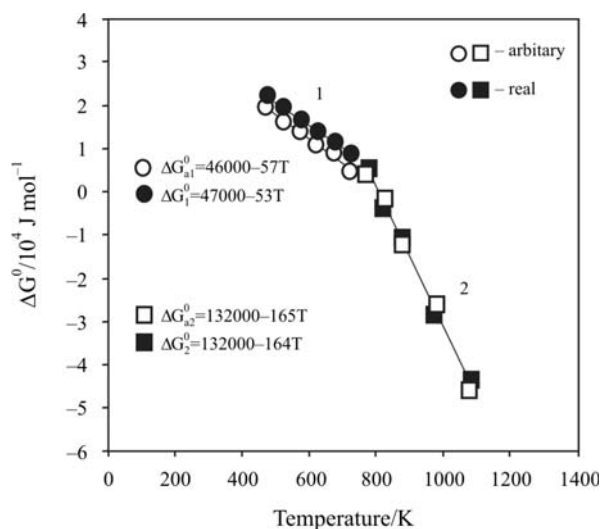
$$\Delta G_1^0 = 47000 - 53T, \text{ (200–450}^\circ\text{C)} \quad (4)$$

$$\Delta G_2^0 = 132000 - 164T, \text{ (500–800}^\circ\text{C)} \quad (5)$$

The  $\ln K-1/T$  and  $\Delta G^0-T$  plots were drawn again by using the calculated values given in Figs 3 and 4, respectively. Temperature dependence for each  $K$  and  $\Delta G^0$  is given in these figures. As seen in these figures, the arbitrary and real straight lines are coincided. These results show that the assumptions purposed for the indirect thermodynamics are satisfactory.



**Fig. 3** The arbitrary and real van't Hoff plots for the thermal deformation of smectite by the 1 – dehydration and 2 – dehydroxylation



**Fig. 4** The plots of the arbitrary and real free energy changes vs. temperature for the thermal deformation of smectite by the 1 – dehydration and 2 – dehydroxylation

The real change in Gibbs energy ( $\Delta G^0$ ) was calculated from the Eqs (4) and (5) at each temperature for steps 1 and 2. Also, the real equilibrium constant ( $K$ ) was calculated from the Eq. (3) by using the real  $\Delta G^0$  value at each temperature for same steps.

Since the  $\Delta H_1^0$ ,  $\Delta S_1^0$  and  $\Delta G_1^0$  values are close to the changes common in physical events, it is clear that the TOT (2:1) layers of smectite do not undergo a chemical change in structure up to 450°C. In contrast, as the  $\Delta H_2^0$ ,  $\Delta S_2^0$  and  $\Delta G_2^0$  values are close to the changes in chemical events, the TOT (2:1) layers of smectite undergo chemical deformation after 500°C.

## Conclusions

An indirect thermodynamic method has been proposed to investigate the thermal deformation of a smectite by using the cation exchange capacity measurements. This method is applicable to other minerals having a measurable parameter similar to CEC. The other measurable parameters changing with temperature such as density, porosity, surface area, hardness and shrinkage may be taken as the equilibrium variables instead of CEC. This method may be used to investigate the calcinations and sintering thermodynamics of ceramic materials.

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