

DYNAMIC AND CONTROLLED RATE THERMAL ANALYSIS OF ATTAPULGITE

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The thermal decomposition of the clay mineral attapulgite has been studied using a combination of dynamic and controlled rate thermal analysis. In the dynamic experiment two dehydration steps are observed over the 20–114 and 114–201°C temperature range. In the dynamic experiment three dehydroxylation steps are observed over the temperature ranges 201–337, 337–638 and 638–982°C. The CRTA technology enables the separation of the thermal decomposition steps. Calculations show the amount of water in the attapulgite mineral is variable. Dehydration in the CRTA experiment occurs as quasi-isothermal equilibria. Dehydroxylation occurs as a series of non-isothermal decomposition steps. CRTA technology offers better resolution and a more detailed interpretation of the decomposition processes of a clay mineral such as attapulgite via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal partial collapse of the layers of attapulgite as the attapulgite is converted to an anhydride.

Keywords: attapulgite, CRTA, palygorskites, sepiolite, thermal analysis, thermogravimetry

Introduction

Sepiolites, attapulgites and various forms of ‘Rocky mountain leather’ (also known as rocky mountain cork, mountain leather or mountain wood) all have a fibrous like morphology with a distinctive layered appearance [1–4]. Attapulgite has the structural formula $[(\text{OH}_2)_4(\text{Mg}, \text{Al}, \text{Fe})_5(\text{OH}) \cdot 2\text{Si}_8\text{O}_{20}] \cdot 4\text{H}_2\text{O}$ and sepiolite the formula $[(\text{OH}_2\text{Mg}_8(\text{OH}) \cdot 4\text{Si}_{12}\text{O}_{30}) \cdot 8\text{H}_2\text{O}$. The formulae are written as such to indicate the two types of water present, magnesium coordinated water and adsorbed water. The difference between the attapulgite and sepiolite formulae is that some substitution for Mg by Al and Fe(III) occurs for the attapulgite. Both sepiolite and attapulgite are chain minerals: attapulgite consists of two double chains of the pyroxene-type SiO_3^{2-} like amphibole $\text{Si}_4\text{O}_{11}^{6-}$ running parallel to the fibre axis. Unlike the amphiboles, the attapulgite units are connected to one another by shared oxygen atoms and not cations such as Ca or Mg. Sepiolite consists of three pyroxene-type chains instead of two as in attapulgite; the oxygens linking the chains together are doubly linked as opposed to the singly linked attapulgite oxygen atoms. The structure of these two minerals results in zeolite-like chan-

nels, which are approximately 3.7·6.0 and 5.6·11.0 Å wide, respectively. These channels may be filled with water or organic molecules. The water is partly arranged (ordered) in these channels and water molecules are also bound to the magnesium cations of the Mg (Al,Fe) brucite-like ribbon edges that border the channels running along the length of the crystals.

Because of their structural morphology, sepiolites and attapulgites have received considerable attention with regard to the adsorption of organics on the clay surfaces and to their use as support for catalysts [1, 5–11]. Sepiolites and attapulgites together with their adsorbed species or modified surfaces, have been studied using a number of techniques including X-ray diffraction [12–15]; infrared spectroscopy [3, 16–29]; Raman spectroscopy and scanning electron microscopy [14, 30–32]. A powder X-ray diffraction study of 52 samples having the mountain leather texture of a fibrous, matted intergrowth of asbestiform crystals, shows that 41 are either sepiolite or palygorskite (attapulgite), 7 were actinolite-tremolite, and 4 were chrysotile.

The dehydration and dehydroxylation of the palygorskite clays have been studied in detail by thermogravimetric techniques [33–35]. Differential

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thermal analysis (DTA) in combination with other techniques such as X-ray diffraction and Fourier Transform infrared spectroscopy (FTIR) proved most useful for the study of the dehydration process. It was found that dehydration of sepiolite and attapulgite take place in a series of four steps. Up to 200°C both hygroscopic and zeolitic water were lost. Between 250–450°C bound water was lost; more strongly bound water was lost in the temperature range 450–610°C; and coordinated water was lost in the temperature range 730–860°C. All of the dehydration steps were endothermic in DTA. For both minerals, the partial dehydration of bound H₂O in the ranges 250–610 and 210–550°C resulted in the formation of sepiolite anhydride and palygorskite anhydride, respectively. Dehydration of the bound H₂O in two steps was attributed to the difference in bonding position of H₂O in the structure of these minerals.

Thermal analysis using thermogravimetric techniques [36–54] enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined [42, 43, 55–59]. Thermoanalytical methods can provide a measure of the thermal stability of clays such as attapulgite and sepiolite. Controlled rate thermal analysis (CRTA) has proven extremely worthwhile in the study of the stability and thermal decomposition pathways of minerals and modified minerals such as mechanochemically activated kaolinite and intercalated kaolinites [45, 58, 60–65]. The application of CRTA technology to the study of the thermal stability of attapulgites has to the best of our knowledge never been reported.

In this work we report the thermal analysis using both dynamic thermal analysis and CRTA technology of attapulgite.

Experimental

Minerals

The clay minerals used in this research are (a) Source Clay Minerals Repository Standard Attapulgite PFI-1, (b) Attapulgite from Gadsen County Florida, USA. The clays were analysed by X-ray diffraction for phase purity and dried in a desiccator to remove adsorbed water before being submitted for thermal analysis. The clay minerals were ground to a fine powder of <0.5 micron particle size for thermal analysis.

Thermal analysis

Dynamic experiment

Thermal decomposition of the attapulgite mineral samples was carried out in a Derivatograph PC-type

thermoanalytical instrument (Hungarian Optical Works, Budapest, Hungary) capable of recording the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves simultaneously. The sample was heated in a ceramic crucible in static air atmosphere at a rate of 5°C min⁻¹.

Controlled rate thermal analysis experiment

Thermal decomposition of the intercalate was carried out in a derivatograph in a flowing air atmosphere (250 cm³ min⁻¹) at a pre-set, constant decomposition rate of 0.10 mg min⁻¹. Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 1°C min⁻¹. The samples were heated in an open ceramic crucible at a rate of 1°C min⁻¹. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage.

Results and discussion

Dynamic thermal analysis of attapulgite

The TG, DTG and DTA plots of the two selected attapulgite clay mineral samples are shown in Figs 1 and 2. In Fig. 1 four distinct DTG steps are observed at 92, 131, 249 and 434°C. In the DTA graph four separate endotherms are found at 98, 129, 245 and 438°C. These values correspond well with the values from the DTG curve. In Fig. 2 four distinct DTG steps are observed at 96, 128, 247 and 433°C. In the DTA graph four separate endotherms are found at 108, 132, 252 and 456°C. These values also correspond well with the values from the DTG curve. The values for the dynamic thermal analysis for the two attapulgite samples show no significant differences.

Four distinct mass losses are observed (Table 1). Two are ascribed to dehydration and two to dehydroxylation. The first step occurs at 92°C and is at-

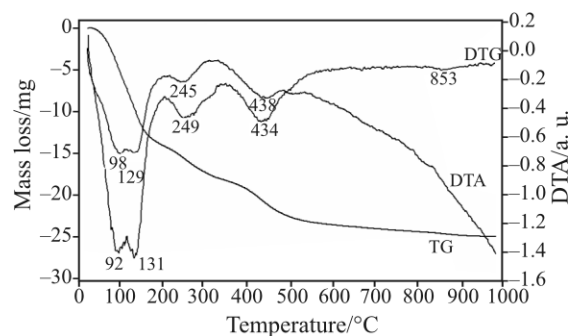


Fig. 1 The dynamic thermogravimetric and differential thermogravimetric analysis of attapulgite from Florida PFI-1

Table 1 Decomposition stages under dynamic conditions

Decomposition process	Attapulgitite, Florida Sample mass: 115.03 mg			Attapulgitite, Gadsen County, Florida Sample mass: 119.70 mg		
	Temp. range/°C	Mass loss/		Temp. range/°C	Mass loss/	
		mg	%		mg	%
Dehydration	20–114	7.5	6.5	21–113	7.3	6.1
Dehydration	114–201	6.6	5.7	113–194	6.9	5.8
Dehydroxylation	201–337	3.9	3.4	194–340	4.5	3.8
Dehydroxylation	337–638	5.6	4.9	340–605	5.4	4.5
Dehydroxylation	638–982	1.2	1.0	605–1000	1.4	1.2

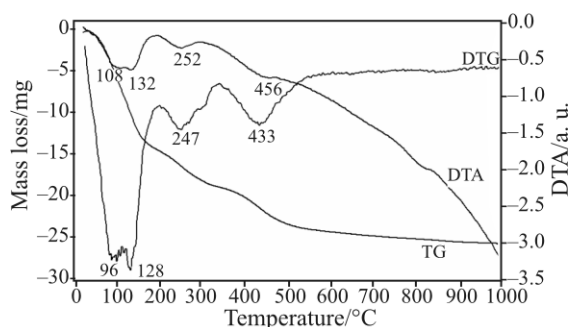
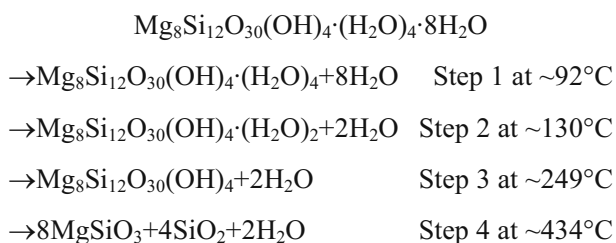


Fig. 2 The dynamic thermogravimetric and differential thermogravimetric analysis of attapulgitite from Gadsen County, Florida

tributed to the loss of adsorbed water (Fig. 1). There is a mass loss of 6.5% at this step. The second step is observed at 131°C. A mass loss of 5.7% is found for this step. The third mass loss step is complex with two overlapping mass loss steps observed at 249 and 434°C. Mass losses of 3.4 and 4.9% are observed. The final mass loss step is also complex and a mass loss of ~1.00% at 853°C is observed. Nagata *et al.* proposed a set of steps for the dehydration and dehydroxylation of a sepiolite. These steps correspond to (a) the loss of adsorbed water, (b) the loss of hydration water, (c) the loss of coordination water and (d) the loss of water through dehydroxylation. Such a scheme is represented by the following chemical equations:



Such a scheme is an apparent oversimplification as each of these steps may be subdivided into component mass loss steps. If one uses the formula (Mg₈Si₁₂O₃₀(OH)₄·(H₂O)₄·8H₂O) for attapulgitite then the theoretical mass loss for step 1 should be 11.0%. The % mass loss observed for the TG curve for attapulgitite was 11%. The theoretical mass loss for step 2 is 2.76% compared with the observed value of 3.3%. The third step theoretical mass loss also should be 2.76% and a value of 2.3% is observed. The final mass loss step should be 5.21%.

Controlled rate thermal analysis of attapulgitite

Controlled rate thermal analysis of attapulgitite

In order to better resolve the decomposition processes, controlled rate thermal analysis (CRTA) experiments were carried out as well in the same equipment using the CRTA control facility. In this case the decomposition of the mineral was carried out at a preset, constant, slow rate to provide time enough for the slow heat and mass transfer processes to occur. The

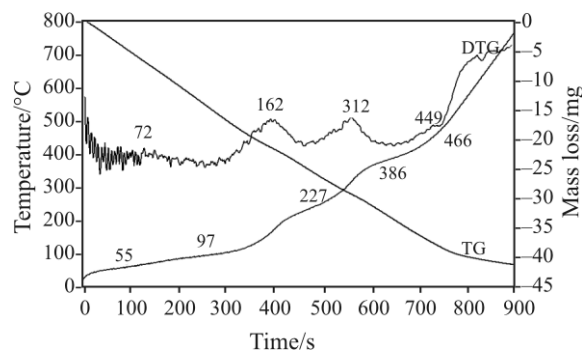


Fig. 3 The controlled rate thermal analysis of attapulgitite from Florida PFI-1

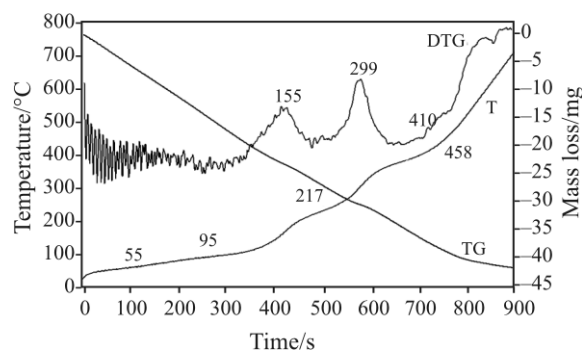


Fig. 4 The controlled rate thermal analysis of attapulgitite from Gadsen County, Florida

Table 2 Decomposition stages under CRTA conditions

Decomposition process	Attapulgit, Florida (sample mass: 236.78 mg)			Attapulgit, Gadsen County, Florida (sample mass: 234.80 mg)		
	Temp. range/°C	Mass loss/		Temp. range/°C	Mass loss/	
		mg	%		mg	%
Dehydration	23–73	8.1	3.4	23–73	9.9	4.2
	73–163	13.3	5.6	73–156	13.0	5.5
Dehydroxylation	163–312	7.8	3.3	156–299	7.4	3.2
	312–759	12.0	5.1	299–709	11.4	4.5

essence of the technique lies in that each sample particle shall be heated under identical conditions. With the slow and constant decomposition rate of 0.10 mg min^{-1} the decomposition is carried out under quasi-isothermal, quasi-equilibrium conditions. This is achieved by the control of the furnace temperature regulated by the DTG signal through the computer.

The controlled rate thermal analysis of the two attapulgite mineral samples is shown in Figs 3 and 4. The results of the CRTA analyses are reported in Table 2. The calculations of water content are shown in the appendix. The DTG and temperature plots show that two dehydration quasi-isothermal steps occur at 55 and 95°C followed by two non-isothermal at around 227, 386 and 449°C. These decomposition steps are ascribed to dehydroxylation of the attapulgite as detailed in the chemical reactions above. Some slight differences in the temperatures are observed between the two samples. Calculations using the results of the CRTA of the reference attapulgite show that 4.24 moles of water are lost in the two dehydration steps at 55 and 95°C. Calculations (see appendix) show that 1.55 moles are lost in the first step and 2.69 moles in the second step. The possible formulation of this attapulgite is $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_6 \cdot 4\text{H}_2\text{O}$. Calculations using the results of the CRTA for the second attapulgite sample show that 4.61 moles of water are lost in the two dehydration steps at 55 and 95°C. Calculations (see appendix) show that 2.00 moles are lost in the first step and 2.61 moles in the second step. The possible formulation of this second attapulgite is $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$. The CRTA experiment shows that the amount of water in the attapulgite minerals is variable.

Dehydroxylation occurs in a series of non-isothermal steps. For the first attapulgite sample 3.3% mass loss occurs over the 163–312°C temperature range and 5.1% over the 312–760°C temperature range. For the second attapulgite sample 3.4% mass loss occurs over the 156–299°C temperature range and 4.8% over the 299–710°C temperature range. The observation that the experimentally determined mass loss is less than that predicted is an indication that some dehydroxylation has

taken place in the previous dehydration steps with the evolution of the bound water [3, 66–70]. It has been found that sepiolite folds to the anhydride like form when about half the H_2O of coordination is removed, at <200°C in vacuum or at approximately 300°C in air [3, 69]. Removal of the remaining H_2O at 530°C under reduced pressure produces little further structural change. Infrared evidence suggests that partially dehydrated attapulgite is a folded structure with H_2O of coordination trapped in hexagonal holes [3, 69]. The remaining H_2O is lost, without significant structural change, at approximately 500°C under vacuum to give a true anhydride [3, 69].

Conclusions

The number of steps in the thermal analysis of attapulgite are greater compared with previous published results when using dynamic high resolution DTG techniques. The CRTA experiment enables the separation of mass losses for the dehydration steps of attapulgite minerals. Two dehydration steps are observed. These occur around 50–60°C, and 90 to 100°C. Two dehydroxylation steps are observed in the CRTA experiment. A low temperature mass loss at 160 to 310°C and a higher temperature mass loss above 300°C. Significant differences in the results as determined by the dynamic and CRTA experiment are observed.

CRTA technology offers better resolution and a more detailed interpretation of the decomposition processes of a clay mineral such as attapulgite via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal partial collapse of the layers of attapulgite as the attapulgite is converted to an anhydride, since in this cases a higher energy (higher temperature) is needed to drive out gaseous decomposition products through a decreasing space at a constant, pre-set rate. The CRTA experiment proves the thermal decomposition of

attapulgitic from different sources are almost identical. The CRTA technology offers a mechanism for the study of the thermal decomposition of minerals such as attapulgite.

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Appendix

Calculation of water content for attapulgite, Florida:

Composition: $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_6 \cdot x\text{H}_2\text{O}$

Removing water up to 162°C: 21.40 mg that is 1.188 mmol

Remaining dehydrated mineral up to 163°C: 215.38 mg that is 0.280 mmol

Molar mass of dehydrated mineral: 768.33 g mol⁻¹

Calculation of x:

$$\begin{aligned} 1 \text{ mol dehydrated mineral} - x \text{ mol H}_2\text{O} \\ 0.280 \text{ mol dehydrated mineral} - 1.188 \text{ mol H}_2\text{O} \\ x=4.24-4 \text{ mol} \end{aligned}$$

Formula: $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_6 \cdot 4\text{H}_2\text{O}$

Steps of water liberation according to the decomposition steps up to 162°C:

1. step:	1.55 mol
2. step:	2.69 mol

Calculation of water content for attapulgite, Gadsen County, Florida:

Composition: $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_6 \cdot x\text{H}_2\text{O}$

Removing water up to 155°C: 22.90 mg that is 1.271 mmol

Remaining dehydrated mineral up to 155°C: 211.9 mg that is 0.276 mmol

Molar mass of dehydrated mineral: 768.33 g mol⁻¹

Calculation of x:

$$\begin{aligned} 1 \text{ mol dehydrated mineral} - x \text{ mol H}_2\text{O} \\ 0.276 \text{ mol dehydrated mineral} - 1.271 \text{ mol H}_2\text{O} \\ x=4.61-5 \text{ mol} \end{aligned}$$

Formula: $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$

Steps of water liberation according to the decomposition steps up to 155°C:

1. step:	2.00 mol
2. step:	2.61 mol

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