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CONVENTIONAL AND CONTROLLED RATE THERMAL ANALYSIS OF NESQUEHONITE $Mg(HCO_3)(OH)\cdot 2(H_2O)$

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The understanding of the thermal stability of magnesium carbonates and the relative metastability of hydrous carbonates including hydromagnesite, artinite, nesquehonite, barringtonite and lansfordite is extremely important to the sequestration process for the removal of atmospheric CO_2.

The conventional thermal analysis of synthetic nesquehonite proves that dehydration takes place in two steps at 157, 179°C and decarbonation at 416 and 487°C. Controlled rate thermal analysis shows the first dehydration step is isothermal and the second quasi-isothermal at 108 and 145°C. In the CRTA experiment carbon dioxide is evolved at 376°C. CRTA technology offers better resolution and a more detailed interpretation of the decomposition processes of magnesium carbonates such as nesquehonite 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 nesquehonite structure.

Keywords: *CRTA, hydromagnesite, lansfordite, magnesite, nesquehonite, TA, TG*

Introduction

The thermoanalytical studies of basic carbonates such as nesquehonite and lansfordite and hydroxycarbonates such as hydrozincite and hydromagnesite are not new, the first reported studies were in 1910 [1–9]. A similar lack of recent studies is true of minerals such as hydroxyzincite and hydromagnesite [1–3, 5, 10–14]. There is a need to undertake a systematic study using the latest technology of carbonate and hydroxyl-carbonate minerals using thermo-analytical techniques including conventional and controlled rate thermal analysis. Very few thermo-analytical and spectroscopic studies of the hydroxy carbonates have been forthcoming and what studies that are available are not new. Few Raman studies of any note are available [15, 16]. To the best of the authors knowledge few recent thermo-analytical studies of hydromagnesite have been undertaken [1, 4], although differential thermal analysis of some related minerals has been published [12]. The decomposition of aurichalcite, hydrozincite and hydromagnesite may result in the formation of metal oxides or a mixture of metal oxides such as CuO and ZnO. Both these oxides may function as catalysts and photo-catalysts. The thermal activation of aurichalcite results in the formation of the oxide mixture, mixed at the molecular level and not at the particle level.

Recently thermogravimetric analysis has been applied to some complex mineral systems [17–41] and it is considered that TG-MS analysis may also be applicable to many carbonate minerals [37, 42–46]. The hydration-carbonation or hydration–and– carbonation reaction path in the $MgO–CO_2–H_2O$ system at ambient temperature and atmospheric CO_2 is of practical significance from the standpoint of carbon balance and the removal of green house gases from the atmosphere. A better understanding of the global masses of Mg and CO_2 and the thermal stability of the hydrated carbonates of magnesium will provide a practical understanding for carbon dioxide removal. From a practical point of view, the exact knowledge of the reaction path in $MgO– CO_2–H_2O$ system is of great significance to the performance of $Mg(OH)_2$ and related minerals for green house gas removal. The reaction path involving carbonation of brucite ($Mg(OH)_2$) is particularly complex, as Mg has a strong tendency to form a series of metastable hydrous carbonates. These metastable hydrous carbonates include hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$, or $Mg_4(CO_3)_3(OH)_2\cdot 3H_2O$), artinite ($Mg_2CO_3(OH)_2\cdot 3H_2O$), nesquehonite ($MgCO_3\cdot 3H_2O$), and lansfordite ($MgCO_3\cdot 5H_2O$).

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The free energy of formation for these hydroxy and hydrous carbonates differs and their formation will depend on the partial pressure of CO_2.

In this work we report the synthesis of one of these hydrous carbonate minerals namely nesquehonite and the thermal stability using conventional and controlled rate thermal analysis (CRTA) of synthetic nesquehonite.

Experimental

Synthesis of nesquehonite

The literature contains a number of methods for the synthesis of single phase nesquehonite and hydromagnesite. Various authors [6, 47–50] have discussed the effects of temperature and partial pressure of carbon dioxide pCO_2 on the stability of the synthetic products. Synthetic nesquehonite used in this study was synthesised by the wet chemical method which involved selective precipitation of each mineral by varying the carbonate buffering solution. A thermal stability study conducted by Lanas *et al.* [14] discussed the inherent difficulty associated with studying the $MgO–CaO–H_2O–CO_2$ system as there are multiple complex minerals which can form during the dolomitization process.

It was found that nesquehonite was preferentially precipitated from solution when equimolar amounts (0.5 M) $Mg(NO_3)_2$ and 0.5 HCO_3^- solutions were mixed drop wise over a period of 10 min at controlled reaction temperature of 45°C. The precipitate was then transferred to a centrifuge to be spun down. At this point it is interesting to note that the precipitate dissolved forming a clear solution. The liquor was left in the centrifuge tube for a week and a new precipitate was found to have formed producing large crystals. It is hypothesised that the initial precipitate was in fact $Mg(HCO_3)_2$ although subsequent experiments failed to trap the initial precipitate for analysis. The following reactions are envisaged:

$$Mg(NO_3)_2+2NaHCO_3 \rightarrow Mg(HCO_3)_2+2NaNO_3$$

$$Mg(HCO_3)_2+2H_2O \rightarrow MgCO_3 \cdot 3H_2O+CO_2$$

The synthesized mineral was characterised for phase specificity using XRD and chemical composition by EDX methods

Thermal analysis

Conventional experiment

Thermal decomposition of nesquehonite was carried out in a Derivatograph PC type thermoanalytical equipment (Hungarian Optical Works, Budapest, Hungary) capable of recording the TG, DTG and DTA curves simultaneously. The sample was heated in a ceramic crucible in static air atmosphere at a rate of 5°C min^{-1}. In order to determine the temperature at which evolved gases were liberated, a second experiment was undertaken using a second instrument. Thermal decomposition of the nesquehonite was also carried out using a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (60 cm^3 min^{-1}). Approximately 35 mg of sample underwent thermal analysis, with a heating rate of 5°C min^{-1}, and high resolution, to 1000°C. With the heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only water vapour, carbon dioxide and oxygen were analyzed.

Controlled rate thermal analysis experiment

Thermal decomposition of nesquehonite under CRTA conditions was carried out in the derivatograph. The samples were heated in static air in an open ceramic crucible at a pre-set, constant decomposition rate of 0.10 mg min^{-1}. (Below this threshold value the samples were heated under conventional conditions at a uniform 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

Conventional thermal analysis of nesquehonite

The conventional thermal analysis of synthetic nesquehonite is shown in Fig. 1. The results of the thermal decomposition are reported in Table 1. Nesquehonite has the simple formula ($MgCO_3 \cdot 3H_2O$). According to the webmineral data base the formula may also be written as $Mg(HCO_3)(OH) \cdot 2(H_2O)$ (see http://webmineral.com/data/Nesquehonite.shtml). In Fig. 1, two dehydration steps are observed at 157 and 179°C. The mass losses at these temperatures are 19.3 and 16.1%. This is a total mass loss due to dehydration of 35.4%. By using the formula $Mg(HCO_3)(OH) \cdot 2(H_2O)$ the total mass loss due to dehydration is 39.13%. The difference of 3.7% H_2O between the total theoretical and experimental values can be due to the possible departure from the ideal stoichiometry.

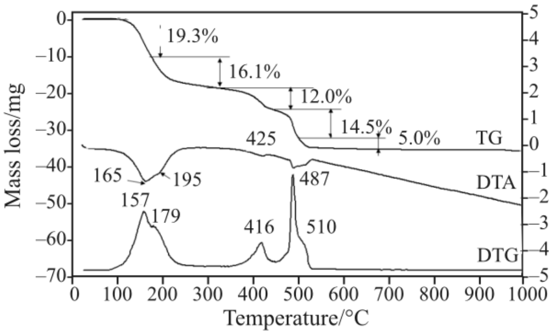

Fig. 1 Conventional thermal analysis of nesquehonite

In the DTA patterns two endotherms are observed at 165 and 195°C. According to our calculations, two moles of water are lost in two steps. Thus the dehydration steps may be written as

$$Mg(HCO_3)(OH)\cdot 2(H_2O)\rightarrow Mg(HCO_3)(OH)\cdot(H_2O)+$$
$$+H_2O \text{ at } 157°C$$

and

$$Mg(HCO_3)(OH)\cdot(H_2O)\rightarrow Mg(HCO_3)(OH)+$$
$$+H_2O \text{ at } 179°C$$

According to the DTA patterns of Beck [1] (page 995 of this reference), water of crystallisation is lost in two steps. The reaction begins at 140°C and is complete by 300°C. The dehydration steps as reported in Table 1 is in close agreement with the values of Beck [1].

A DTG peak is observed at 416°C. This peak is attributed to the loss of the third molecule of water according to the reaction:

$$Mg(HCO_3)(OH) \rightarrow MgCO_3 + H_2O$$

Table 1 Decomposition stages under conventional conditions

	Nesquehonite sample mass: 52.32 mg		
Decomp. process	Temp. range/°C	Mass loss/	
		mg	%
Dehydration	79–174	10.1	19.3
	174–307	8.4	16.1
Dehydroxylation and decarbonation	307–449	6.3	12.0
	449–501	7.6	14.5
	501–534	2.6	5.0

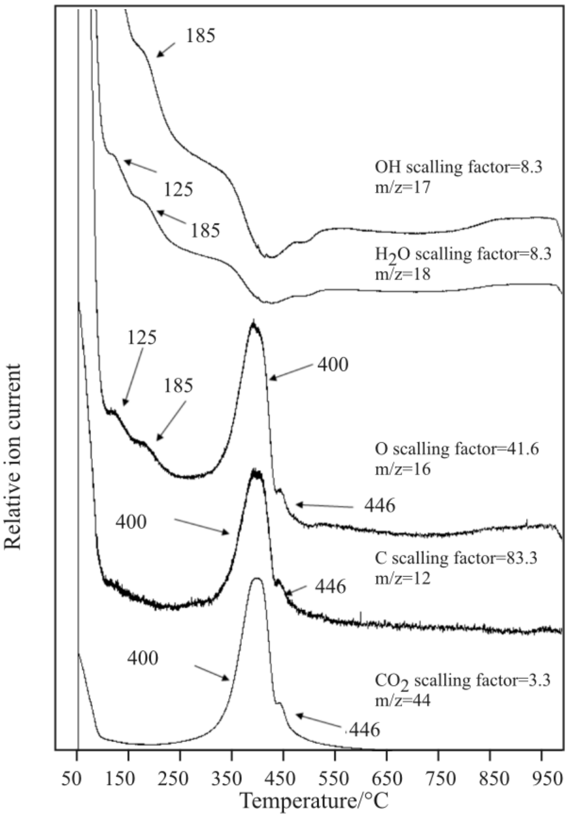

Fig. 2 Ion current curves for the evolved gases during the thermal decomposition of nesquehonite

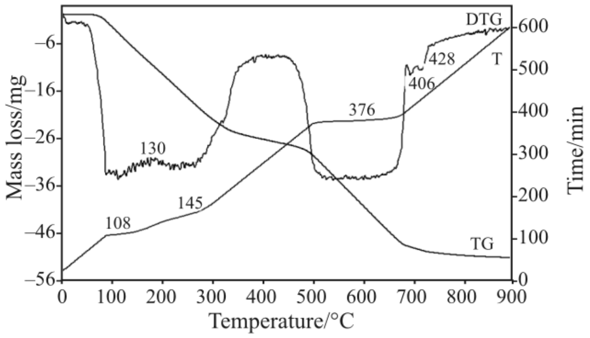

Fig. 3 Controlled rate thermal analysis of nesquehonite

The process begins at 307°C and is complete by 450°C. An endothermic peak in the DTA plot at 425°C is also observed. The theoretical mass loss due to CO_2 evolution is 31.88%. The observed mass loss at 487 and 510°C is 14.5 and 5.0% making a total of 19.5% which is less than the theoretical value. The assumption has been made that each of the thermal decomposition steps is solely due to dehydration or loss of CO_2. In fact this may not be the case and some CO_2 may be evolved when dehydration occurs. The ion current curves (Fig. 2) show CO_2 is lost over a temperature range from 350 to 550°C. Decarbonation of the dehydrated mineral takes place in three steps at 416, 487 and 510°C as shown by the DTG curve. The observed mass loss (31.5%) is in perfect agreement with the theoretical figure of 31.9%.

$$MgCO_3\rightarrow MgO+CO_2$$

In the DTA pattern three endotherms can be observed corresponding to the DTG peaks. Dissimilarly to the statement of Davis more than 100 years ago reporting that a third water was lost with CO_2 [51] no water was identified by mass spectrometry in the 350–550°C range.

Beck reported a second endothermic step at 425°C in the DTA patterns which is in good agreement with our results from the DTG pattern.

A sharp DTG peak at 487°C is observed which is attributed to the loss of carbonate from the thermally decomposing nesquehonite according to the reaction:

$$MgCO_3 \rightarrow MgO + CO_2$$

In the DTA patterns an endotherm at 485°C is observed. Our results differ at this point from the work of Beck [1] who reported that decarbonation took place at 480°C reaching a doublet at 535 and 585°C and is completed by 620°C. An additional DTG peak is observed at 510°C. Ion current curves for evolved gases indicate that this peak is attributable to oxygen loss (Fig. 2). Davis in a reference more than 100 years old reported that using synthetic nesquehonite that the third molecule of water was lost with CO_2. A hydrous calcium substituted magnesium carbonate from Spanish playa lake sediments was shown to have a formula of $((Mg_{0.92},Ca_{0.08})CO_3 \cdot 3H_2O)$ [52]. This mineral is close to the formula of nesquehonite. The authors reported the DTA and TG patterns for this mineral. Two endotherms were found at 455 and 630°C but endotherms at ~160 and ~380°C may be observed. No DTG peaks were reported by the authors; however steps in the TG curves may be observed at ~180, 405 and 500°C [52]. It is also interesting that minerals such as nesquehonite were used in antiquity [53].

Controlled rate thermal analysis of nesquehonite

The controlled rate thermal analysis of nesquehonite is shown in Fig. 3. The decomposition of nesquehonite under CRTA conditions are reported in Table 2. Figure 3 shows the TG and DTG curves obtained under CRTA conditions together with the change in temperature with experiment time. Two separate dehydration stages are observed at 108 and 145°C. The first step indicates an isothermal while the second one a quasi-isothermal process. The decomposition of the carbonate takes place in an isothermal process at 376°C. A small mass loss step between 400 and 450°C resulting in the liberation of 3.4% CO_2 can be due to the decomposition of a more crystalline (therefore thermally more stable) part of the carbonate mineral. The observed mass loss of 33.7% is in good agreement with the theoretical value (31.9%).

Table 2 Decomposition stages under CRTA conditions

	Nesquehonite sample mass: 73.54 mg		
Decomp. process	Temp. range/°C	Mass loss/	
		mg	%
Isothermal dehydration	63–129	10.7	14.5
Non-isothermal dehydration	129–282	15.5	21.1
Decarbonation and dehydration	282–400	22.3	30.3
	400–418	0.6	0.8
	418–600	1.9	2.6

Sequestration of green house gases

In order to understand the potential sequestration of green house gases through reaction with magnesium minerals it is important to have fundamental knowledge of the reactions of $Mg(OH)_2$ and MgO with CO_2. The following reaction is envisaged:

$$MgO + CO_2 \rightarrow MgCO_3$$

and

$$MgO + CO_2 + H_2O \rightarrow Mg(OH)(HCO_3) \cdot 2H_2O$$

(nesquehonite)

It is important to understand the stability of such minerals both in terms of temperature and partial pressure of the CO_2 and in the presence of other green house gases. The hydration–carbonation or hydration–and–carbonation reaction path in the CO_2–MgO–H_2O system at ambient temperature and atmospheric CO_2 is of practical significance from the standpoint of carbon balance and the removal of green house gases from the atmosphere. A better understanding of the global masses of Mg and CO_2 and the thermal stability of the hydrated carbonates of magnesium provide a practical understanding for carbon dioxide removal. From an experimental point of view, the exact knowledge of the reaction path in MgO–CO_2–H_2O system is of great significance to the performance of $Mg(OH)_2$ and related minerals for green house gas removal. The reaction path involving carbonation of brucite ($Mg(OH)_2$) is particularly complex, as Mg has a strong tendency to form a series of metastable hydrous carbonates. These metastable hydrous carbonates include hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, or $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$), artinite ($Mg_2CO_3(OH)_2 \cdot 3H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), and lansfordite ($MgCO_3 \cdot 5H_2O$). The free energy of formation for these hydroxy and hydrous carbonates differs and their formation will depend on the partial pressure of CO_2. In this research we have presented some concepts with respect to the thermal stability of nesquehonite, a mineral which will at least potentially be formed upon the reaction of MgO and CO_2.

Conclusions

The hydration-carbonation or hydration–and–carbonation reaction path in the $MgO–CO_2–H_2O$ system at ambient temperature and atmospheric CO_2 is of environmental significance from the standpoint of carbon balance and the removal of green house gases from the atmosphere. The understanding of the thermal stability of the carbonates of magnesium and the relative metastability of hydrous carbonates including hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$, or $Mg_4(CO_3)_3(OH)_2\cdot 3H_2O$), artinite ($Mg_2CO_3(OH)_2\cdot 3H_2O$), nesquehonite ($MgCO_3\cdot 3H_2O$), and lansfordite ($MgCO_3\cdot 5H_2O$) is extremely important to the sequestration process for the removal of atmospheric CO_2.

CRTA technology offers better resolution and a more detailed interpretation of the decomposition processes of magnesium carbonate minerals 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 nesquehonite structure, since in this case 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 technology offers a mechanism for the study of the thermal decomposition of minerals such as nesquehonite. With this technique the temperatures of decomposition can be standardized thereby providing the opportunity of comparison for the thermal behaviour of various minerals.

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