

DTA AND FT-IR ANALYSIS OF THE REHYDRATION OF BASIC MAGNESIUM CARBONATE

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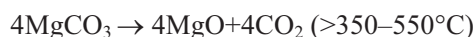
Abstract

The rehydration characteristics of a commercially produced hydromagnesite and two basic magnesium carbonates synthetically produced from $\text{Mg}(\text{OH})_2$, are presented. The products were dehydrated and dehydroxylated at 325°C before rehydration was attempted. DTA and FT-IR were used to follow the structural changes that occurred during the rehydration processes. The results obtained for the commercially and synthetically produced hydromagnesite products indicated that the original symmetry of the groups was reclaimed during rehydration. This was not observed for the synthetically produced unidentified basic magnesium carbonate product. This investigation provides insight into the rehydration characteristics of a select group of basic magnesium carbonates.

Keywords: basic magnesium carbonates, DTA, FT-IR, hydromagnesite, rehydration

Introduction

The thermal decomposition of hydromagnesite, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is known to proceed via three steps. This includes dehydration (removal of water of crystallisation), dehydroxylation (decomposition of $\text{Mg}(\text{OH})_2$ to MgO) and decarbonation (decomposition of MgCO_3 to MgO) [1]. These processes can be summarised as follow:



Various approaches have been followed in order to gain knowledge into these processes. This includes work done by Rajeswara Rao *et al.* [2] regarding the kinetics governing the thermal decomposition of hydromagnesite. Sawada *et al.* [3] investigated the thermal decomposition of hydromagnesite under different partial pressures of carbon dioxide. Choudhary *et al.* [1] showed that the preparation conditions of the basic magnesium carbonates influence its thermal decomposition. The origin of the exothermic peak in the thermal decomposition of basic magnesium carbonate has

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also been investigated [4]. There seemed to be a lack of information regarding the rehydration characteristics of the basic magnesium carbonates.

The aim of this study was to investigate the rehydration of a select group of basic magnesium carbonates after the products have been dehydrated and dehydroxylated. The rehydration characteristics of two synthetically produced basic magnesium carbonates were investigated and compared to a commercially produced hydromagnesite. The synthetically produced basic magnesium carbonate products were synthesised from $\text{Mg}(\text{OH})_2$ as described in previous work [5]. This in short entailed sparging CO_2 through a $\text{Mg}(\text{OH})_2$ suspension at ambient temperature. The solid product was divided in half after filtration and dried at 80 and 120°C, which resulted in the formation of an unidentified basic magnesium carbonate and hydromagnesite, respectively.

The rehydration characteristics were investigated using differential thermal analysis (DTA) and Fourier transform infrared spectroscopy (FT-IR). TG and DTA have been used extensively in studying the thermal decomposition of the basic magnesium carbonates [1, 4–6]. Infrared characterisation of the basic magnesium carbonates has also been used successfully in providing valuable structural information [3, 6–8]. The changes observed during DTA are correlated to the changes observed in the IR spectra and vice versa.

This investigation provides insight into the structural changes that characterise the rehydration of a select group of basic magnesium carbonates.

Experimental

Thermogravimetric analysis

Thermogravimetric and calorimetric analyses were performed on a Netzsch STA 409 simultaneous TG-DTA instrument. Sample sizes varied between 12 and 14 mg. A heating rate of $10^\circ\text{C min}^{-1}$ was used in an air atmosphere. All data were obtained using platinum crucibles. DTA peak maxima were used and compared to each other, as sample sizes and conditions were kept as constant as possible.

Infrared analysis

Transmission spectra were recorded with a Bruker® 113 FTIR spectrometer in the mid-infrared range. All spectra were obtained from KBr discs containing approximately 1 mg of sample and 100 mg of KBr. The sample chamber was evacuated ($P=170$ mbar) during the recordings to minimise any effects caused by water vapour and carbon dioxide. The resolution was 2 cm^{-1} and 32 scans were signal-averaged in each interferogram.

X-ray diffraction analysis

X-ray powder diffraction analyses were performed on a Siemens D501 diffractometer using CuK_α radiation. The PDF-2 database from ICDD volume 1–45 was used to analyse the data.

Rehydration experiments

The basic magnesium carbonate products under investigation are a commercially produced hydromagnesite (CP from Unilab[®], Saarchem (Pty) Ltd, South Africa) and two basic magnesium carbonates synthetically produced from $Mg(OH)_2$ [5]. The basic magnesium carbonate products were dehydrated and dehydroxylated by heating at 325°C for 2.5 h. The treated products were then placed in a sealed humidity cabinet with a saturated water vapour atmosphere. At various time intervals, a sample was taken from the rehydrating product for DTA and FT-IR analysis and the remaining sample returned to the cabinet for the duration of the investigation.

Results and discussion

The discussion on the rehydration of the basic magnesium carbonate products will be structured in three parts. The DTA and FT-IR characteristics of the various products will be discussed for the various stages investigated namely before dehydration, directly after dehydration (0 h rehydration) and during rehydration. The commercially produced hydromagnesite product will be referred to as the commercial product. The synthetically produced hydromagnesite product will be referred to as the 120°C product and the synthetically produced unidentified basic magnesium carbonate as the 80°C product.

Commercial and 120°C products (hydromagnesite)

The DTA and FT-IR results corresponding to the various stages of dehydration and rehydration are presented in Fig. 1 for the commercial hydromagnesite product and in

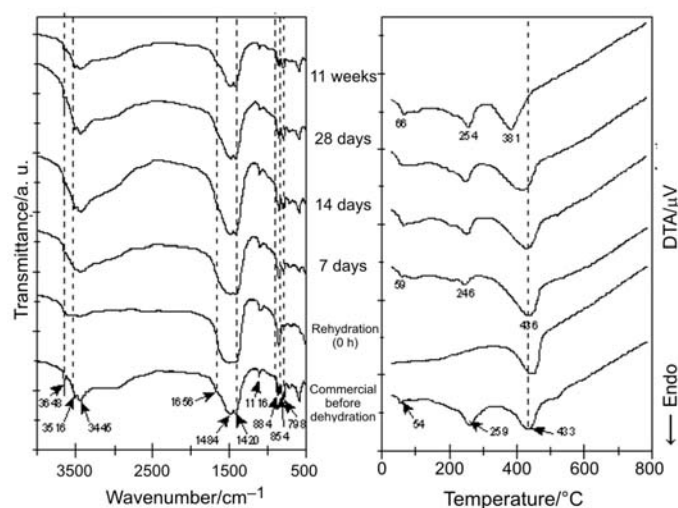


Fig. 1 FT-IR and DTA dehydration and rehydration results for the commercial hydromagnesite product

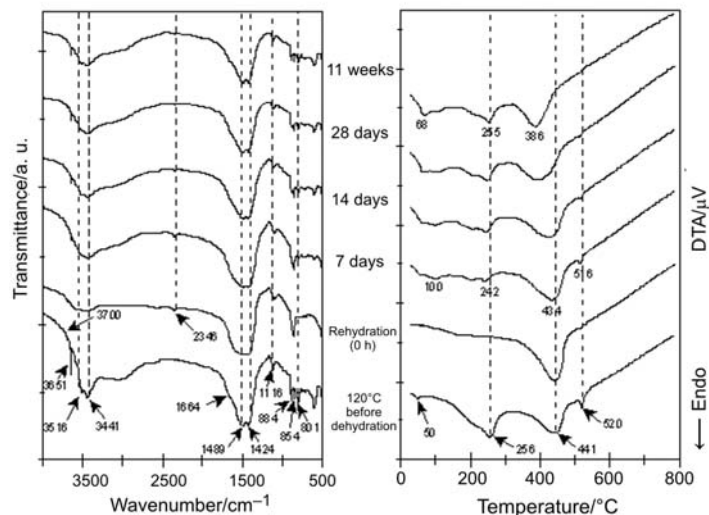


Fig. 2 FT-IR and DTA dehydration and rehydration results for the 120°C hydromagnesite product

Fig. 2 for the 120°C product. The results for the commercial and 120°C products will be discussed together since these two products are essentially the same.

Before dehydration

Before discussing the IR and DTA results for hydromagnesite it is necessary to take note of the characteristic IR bands and DTA peaks that can be associated with this specific compound. By observing these bands closely it will be possible to identify any changes resulting from the dehydration and rehydration processes. The CO_3^{2-} ν_3 asymmetric stretching vibrations are observed as a strong band split in two at $\sim 1420\text{--}1480\text{ cm}^{-1}$ [3]. This is a characteristic of the bicarbonate and shows that the carbonate ion in the hydromagnesite exists as bicarbonate [8]. The three absorption bands at $\sim 800\text{ cm}^{-1}$ (strongest), 850 and 880 cm^{-1} are assigned to the CO_3^{2-} bending vibrations [3, 6]. A band at $\sim 1120\text{ cm}^{-1}$ is assigned to the CO_3^{2-} ν_1 symmetric stretching vibration [3, 6]. The DTA peaks corresponding to decarbonation are at ~ 433 and 520°C . An almost free O–H vibration gives rise to a sharp band at $\sim 3650\text{ cm}^{-1}$ [6, 7]. This band can be correlated to the DTA peak at $\sim 259^\circ\text{C}$ (dehydroxylation). Bands resulting from water of crystallisation are observed at ~ 3510 and 3450 cm^{-1} [6, 7]. These bands can be associated with the DTA peak corresponding to the dehydration step at $\sim 54^\circ\text{C}$. The H_2O bending vibration band at $\sim 1650\text{ cm}^{-1}$ is very weak and appears only as a faint shoulder on the side of the CO_3^{2-} stretching band [7].

The only difference between the commercial and 120°C products was the presence of a small band at $\sim 3700\text{ cm}^{-1}$ in the IR spectrum of the 120°C product. This band was attributed to the anti-symmetrical OH stretching vibration of the lattice hy-

droxide corresponding to $\text{Mg}(\text{OH})_2$. This band is possibly an indication that a small amount of $\text{Mg}(\text{OH})_2$ remained unreacted. A similar observation was made from the IR spectrum of the 80°C product.

Directly after dehydration

It is expected that the H_2O and hydroxyl groups would be removed from the crystal lattice during dehydration and dehydroxylation. This was confirmed by the absence of the IR band corresponding to the water of crystallisation at ~ 3510 and 3450 cm^{-1} and the absence of the DTA peak at $\sim 54^\circ\text{C}$ at 0 h rehydration. The sharp O–H vibration band at $\sim 3650\text{ cm}^{-1}$ also disappeared, corresponding to the absence of the DTA

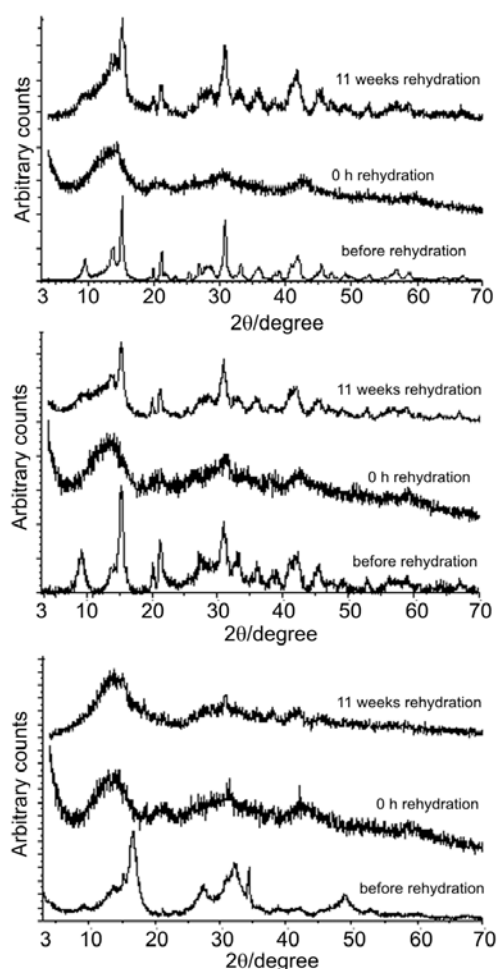


Fig. 3 XRD patterns of commercial hydromagnesite; a – 120°C hydromagnesite; b – 80°C unidentified basic magnesium carbonate; c – during the various stages of rehydration

peak at $\sim 259^\circ\text{C}$. Only one of the three absorption bands at $\sim 850\text{ cm}^{-1}$ was retained after dehydration, which suggested an increase in symmetry in the carbonate radical [3]. This change in symmetry was ascribed to the absence of the H_2O and hydroxyl groups that inadvertently influenced the coordination of the carbonate groups. The split band at $\sim 1450\text{ cm}^{-1}$ changed into a single absorption band. The change from a split band into a single broader band was associated with the change from crystalline to amorphous phase during dehydration. This was confirmed by the XRD results given in Fig. 3a for the commercial product and in Fig. 3b for the 120°C product.

During rehydration

During the initial stages of rehydration, corresponding to the first 7 days of rehydration, water vapour is mainly taken up as bulk water. This was evident from the development of a broad IR band between ~ 3510 and 3450 cm^{-1} as well as the appearance of the corresponding DTA peak at $\sim 100^\circ\text{C}$. The development of a sharp band at $\sim 3650\text{ cm}^{-1}$ and the appearance of the corresponding DTA peak at $\sim 246^\circ\text{C}$ during the first 7 days, was also taken as an indication of the uptake of hydroxyl groups into the hydromagnesite crystal lattice. As the H_2O and hydroxyl groups re-coordinated within the crystal lattice, the symmetry of the carbonate radicals were inadvertently influenced. The single CO_3^{2-} bending vibration at $\sim 850\text{ cm}^{-1}$ expressed this change in symmetry as the single band, at 0 h rehydration, gradually split to form the original three bands after 11 weeks of rehydration. The single band at $\sim 1450\text{ cm}^{-1}$ also split into two bands at ~ 1420 – 1480 cm^{-1} , as well as becoming progressively narrower as the amorphous structure converted back to the crystalline phase during the 11-week period. It would seem for both the hydromagnesite products that the original orientation and vibrations of the molecules were reclaimed during rehydration. The XRD results confirmed the conversion from amorphous to the original hydromagnesite crystalline phase during rehydration for both products (Fig. 3a and b).

The only noticeable difference between the rehydration of the commercial product and 120°C product, was the appearance of a relatively small band at $\sim 2346\text{ cm}^{-1}$ in the IR spectrum of the 120°C product. This phenomenon will be discussed at the dehydration of the 80°C product. This band gradually disappeared as rehydration progressed.

80°C product (unidentified basic magnesium carbonate)

The DTA and FT-IR results corresponding to the various stages of dehydration and rehydration are presented in Fig. 4 for the 80°C product.

Before dehydration

The IR spectrum and DTA results for the 80°C product indicated several similarities and differences compared to the hydromagnesite products. The band split in two at ~ 1420 – 1480 cm^{-1} was similar to the CO_3^{2-} ν_3 asymmetric stretching vibration observed for hydromagnesite. This band was broader for the 80°C product, which was indicative of its amorphous structure as seen in the XRD (Fig. 3c). The three bands at

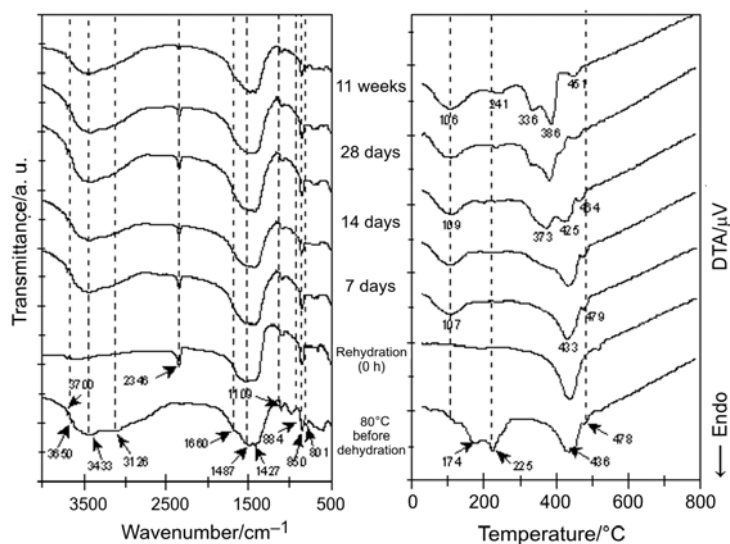


Fig. 4 FT-IR and DTA dehydration and rehydration results for the 80°C unidentified basic magnesium carbonate product

~ 800 , 850 cm^{-1} (strongest) and 880 cm^{-1} corresponded to the CO_3^{2-} bending vibrations although the intensity ratio of these bands differed from those observed for hydromagnesite. The band at $\sim 1110\text{ cm}^{-1}$ was assigned to the CO_3^{2-} ν_1 symmetric stretching vibration. The similarities between the carbonate vibrations of the 80°C product and the hydromagnesite products were also reflected in the position of the DTA peak at $\sim 436^\circ\text{C}$ for the 80°C product. This corresponded to the decarbonation step above 350°C for the hydromagnesite products.

It is suspected that the 80°C product contains mainly water of crystallisation and to a lesser extent hydroxyl groups. This was deduced from the DTA results where the peaks at 174 and 225°C should correspond to water of crystallisation, which is expected to be given off below 250°C . This was confirmed by the absence of a dehydroxylation step between 250 and 350°C in the DTA. The IR spectrum also confirmed this assumption when the bands at ~ 3510 and 3450 cm^{-1} , assigned to water of crystallisation, overshadow the band at 3650 cm^{-1} , that was associated with an almost free O–H vibration. The band at 3650 cm^{-1} was not nearly as intense as observed for the commercial and 120°C products. The very broad band around 3500 cm^{-1} could be indicative of different types of water of crystallisation as well as corresponding to the amorphous structure of the compound.

Directly after dehydration

After dehydration the absence of water of crystallisation is expected. This was confirmed in the IR spectrum due to the absence of the corresponding band around

3500 cm^{-1} and the double DTA peak around 200°C at 0 h rehydration. Both the IR and DTA results at 0 h rehydration for the dehydrated and dehydroxylated 80°C product was almost identical to that of the dehydrated and dehydroxylated hydromagnesite products. The only noticeable difference was the appearance of a very sharp band at 2346 cm^{-1} in the IR spectrum of the 80°C product. This band was more intense than in the IR spectrum of the 120°C product (Fig. 2). The band at 2346 cm^{-1} could be assigned to either a CO_2 inclusion or a terminal CO_2 , as it corresponds to the position of the ν_3 fundamental of CO_2 [9]. Prolonged heating of the product at 325°C did not result in the disappearance of this band. A more detailed analysis of the spectra will be necessary to make a more accurate assignment of this band (which is out of scope of the present study).

During rehydration

The only changes observed during rehydration as water vapour was taken up as bulk water, was the appearance of the IR bands between 3510 and 3450 cm^{-1} which coincided with the uptake of water of crystallisation. This was also observed as a DTA peak at ~100°C. The band that appeared at 2346 cm^{-1} disappeared as rehydration progressed but to a lesser extent than that observed for the 120°C product.

The changes during rehydration were more evident from the DTA results. During rehydration the peak at ~436°C developed a shoulder at 14 days and by 21 days two distinct peaks were noticeable at 373 and 425°C. By 11 weeks this peak shifted to ~386°C with a shoulder at 336°C. During peak shifting, no changes could be observed in the IR spectra. The DTA changes were associated with a weakening of the carbonate bonds as rehydration progressed.

Conclusions

The investigation into the rehydration characteristics of a commercially and synthetically produced hydromagnesite product and a synthetically produced unidentified basic magnesium carbonate, gave insight into the structural changes that take place during rehydration of the dehydrated and dehydroxylated products. It was evident from the results that the hydromagnesite products seemed to regain the original symmetry of the various groups during an 11-week rehydration period in a water vapour saturated atmosphere at ambient temperature. The unidentified product did not seem to regain its original symmetry. The combined use of DTA and FT-IR made it possible to identify the changes taking place by correlating the results.

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