

The Thermal Decomposition of Huntite and Hydromagnesite - A Review

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Abstract

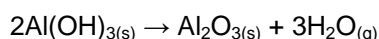
Naturally occurring mixtures of hydromagnesite and huntite are important industrial minerals. Their endothermic decomposition over a specific temperature range, releasing water and carbon dioxide, has led to such mixtures being successfully used as fire retardants, often replacing aluminium hydroxide or magnesium hydroxide. The current understanding of the structure and thermal decomposition mechanism of both minerals and their combination in natural mixtures is reviewed. The crystalline structure of both minerals has been fully characterised. The thermal decomposition of huntite has been characterised and is relatively simple. However, the thermal decomposition mechanism of hydromagnesite is sensitive to many factors including rate of heating and the composition of the atmosphere. The partial pressure of carbon dioxide significantly affects the decomposition mechanism of hydromagnesite causing magnesium carbonate to crystallise and decompose at a higher temperature instead of decomposing directly to magnesium oxide.

Keywords: hydromagnesite, huntite, fire, flame, retardant, mineral

This review critically examines the sometimes conflicting reports in the published literature. It draws together current knowledge of the structure and thermal decomposition of hydromagnesite and huntite, in order to provide an insight into the thermal behaviour of mixtures of these minerals and to optimise their selection and applications.

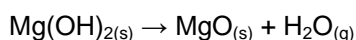
1. Industrial use of Mineral Fillers as Fire Retardant Additives

The largest group of mineral fire retardants are metal hydroxides. Their endothermic decomposition and associated release of inert gasses or water vapour, above the processing temperature but below the thermal decomposition temperature of polymers suppresses the ignition, while the accumulation of a solid inert residue on the surface of the burning polymer reduces the heat release rate. Aluminium hydroxide (ATH) and magnesium hydroxide are the most widely used[1]. Globally aluminium hydroxide is the highest tonnage fire retardant[2,3]. It decomposes according to the following reaction:



The endothermic loss of water resulting from the thermal decomposition of ATH has been variously reported[3-5] between 1170 and 1300 Jg⁻¹. The decomposition starts at about 180 – 200°C[5] depending on the particle size and physical form.

Magnesium hydroxide is used less widely than ATH. It decomposes through a similar endothermic mechanism to ATH, giving off water.



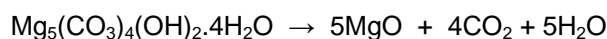
The endotherm for this reaction is quoted at values between 1244 to 1450 Jg⁻¹ by various authors[3,5-7]. It starts to decompose at about 300 – 330°C giving off water[5].

Although ATH and magnesium hydroxide are the most well known mineral fire retardants, Rothon[5] has identified a number of minerals (Table 1) that could be of potential benefit in polymers. Each decomposes endothermically with the evolution of either carbon dioxide, water or both. Of these minerals, hydromagnesite is the one that has probably seen most commercial interest. Hydromagnesite is naturally occurring in mixtures with huntite. Its onset of decomposition is at a slightly higher temperature than that of ATH making it suitable for polymers where ATH has been traditionally used, as well as in polymers where ATH becomes unsuitable due to higher processing temperatures.

Mineral	Approximate onset of Decomposition (°C)
Nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$)	70 – 100
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	60 – 130
Magnesium phosphate octahydrate ($\text{Mg}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$)	140 – 150
Aluminium hydroxide ($\text{Al}(\text{OH})_3$)	180 – 200
Hydromagnesite ($\text{Mg}_5[\text{CO}_3]_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$)	220 – 240
Dawsonite ($\text{NaAl}(\text{OH})_2\text{CO}_3$)	240 – 260
Magnesium hydroxide ($\text{Mg}(\text{OH})_2$)	300 – 320
Magnesium carbonate subhydrate ($\text{MgO} \cdot \text{CO}_2[0.96]\text{H}_2\text{O}[0.3]$)	340 – 350
Bohemite ($\text{AlO}(\text{OH})$)	340 – 350
Calcium hydroxide ($\text{Ca}(\text{OH})_2$)	430 – 450

Table 1: Minerals with potential fire retardant benefits, and their decomposition temperatures[5]

Hydromagnesite has been shown[8-14] to decompose endothermically releasing water and carbon dioxide over a temperature range of approximately 220°C to 550°C.



This endothermic decomposition and release of inert gases gives hydromagnesite its fire retardant properties.

Huntite also decomposes endothermically[15-18] releasing carbon dioxide over a temperature range of approximately 450°C to 800°C.



While this is too hot to coincide with major polymer decomposition and fuel production stages occurring around ignition, its platy morphology reinforces the formation of a thermally protective barrier layer which may reduce the rate of burning.

The structure of these minerals and their thermal decomposition will be discussed in greater detail in the main body of this review.

2. Sources of Hydromagnesite and Huntite

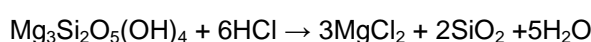
Hydromagnesite is a naturally occurring mineral and has been found in a number of locations around the world, it is the third most common[19] carbonate found in caves, after calcite and aragonite. Commercial extraction of hydromagnesite is not from caves, as there are locations where larger quantities occur at the surface, in mixtures with another carbonate mineral, huntite. Huntite is rarer than hydromagnesite, although it is also found in caves[20] as flowstone.

Georgiades[21] reported some of the history of one such deposit of mixed hydromagnesite and huntite in Greece. It had been known by local people as a source of material for whitewashing their houses for many centuries. Then in the mid 20th century it began to be used as a filler for shoe soles. It was ground using the local granite mills designed for wheat. Georgiades started investigating commercial exploitation of the minerals in 1978 and commenced worldwide sales in 1986. The Greek deposit is still operated commercially,

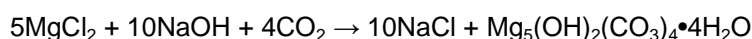
although the world's largest known reserves are in Turkey, operated commercially by Minelco. Stamatakis[22] has carried out some evaluation on a source of hydromagnesite in British Columbia[23,24] and concluded that it is composed mainly of hydromagnesite with minor amounts of magnesite but no huntite. The whiteness and decomposition properties are reported to be similar to commercially mined minerals from Greece, leading to the conclusion that this source of hydromagnesite might be suitable for use as a fire retardant.

Since hydromagnesite is a carbonate, it has been proposed that its production could be used to convert the greenhouse gas carbon dioxide into a solid carbonate. A slurry of magnesium hydroxide can be converted[25] into hydromagnesite by bubbling carbon dioxide through the slurry.

A method for the conversion of serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) into hydromagnesite has been investigated[26] as a way of trapping carbon dioxide and preventing its accumulation in the atmosphere. The process involves production of magnesium chloride from serpentine through the following reaction.



The magnesium chloride is then converted to hydromagnesite in the presence of sodium hydroxide and carbon dioxide.



These studies are primarily driven by the desire to trap carbon dioxide in a stable form. However, the suitability of both synthetic and natural hydromagnesite as a fire retardant for polymers could improve the cost effectiveness of the plan and lead to a future commercial source of hydromagnesite. There has also been interest in the literature[25,27-31] in synthetic hydromagnesite as a fire retardant.

3. Morphology and Thermal Decomposition of Hydromagnesite and Huntite

Naturally occurring huntite particles have a fine highly platy structure as shown in the electron micrographs (Figure 1 and Figure 2) produced by the present authors. Samples were gold coated and examined using a Carl Zeiss (Leo) 1530VP FEGSEM. Many of the individual particles have a diameter of 1 micron or less and thicknesses in the nanometer range.

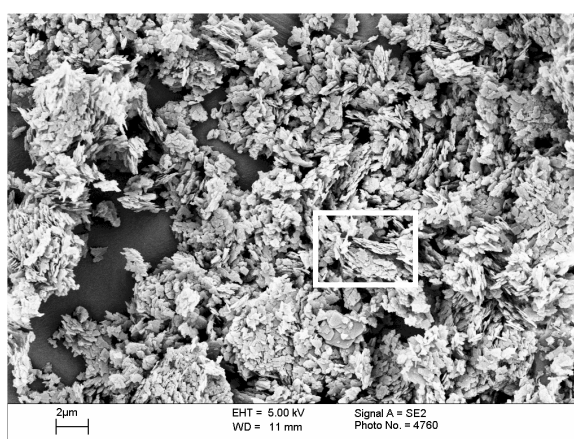


Figure 1: Huntite particles

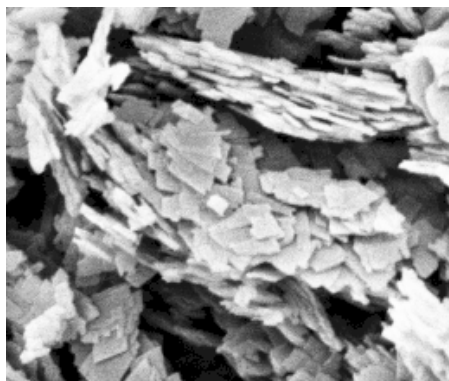


Figure 2: Enlarged section taken from the boxed area in Figure 1

Figure 3 (again produced by the present authors) shows a natural mixture of hydromagnesite and huntite where the larger hydromagnesite particles can be seen interspersed with smaller platy huntite particles. The enlarged section shown in Figure 4 clearly shows the more blocky nature of larger particles which often have diameters greater than 1 micron.

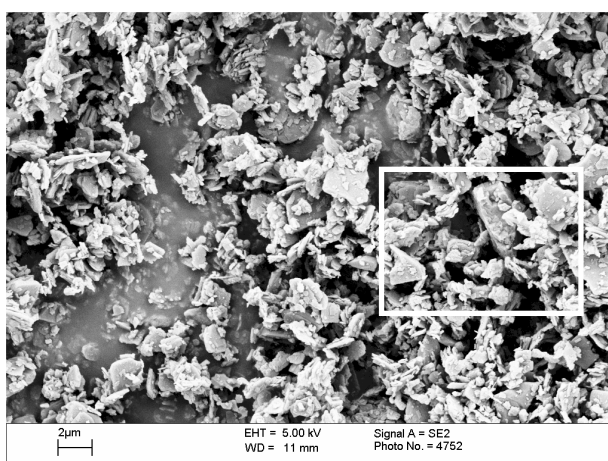


Figure 3: A mixture of hydromagnesite and huntite particles

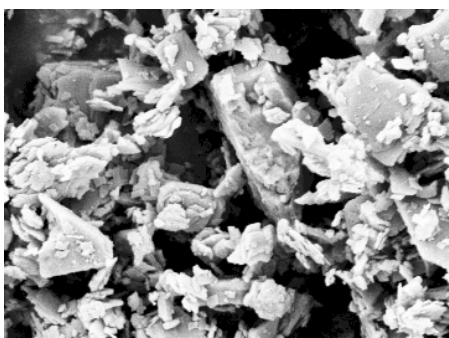
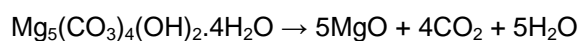


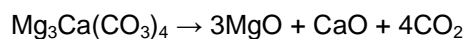
Figure 4: Enlarged section taken from the boxed area in Figure 3

Hydromagnesite and huntite decompose through the following endothermic reactions although there has been much discussion about the exact mechanism.

Hydromagnesite[8,10-14,26,32-34]



Huntite[15-18]



Typical thermogravimetric analysis (TGA), and derivative mass loss curves, using a T A Instruments Q5000 at a heating rate of $10^\circ\text{C min}^{-1}$ in air, have been measured by the present authors for natural hydromagnesite, natural huntite and a commercially available mixture of hydromagnesite and huntite supplied by Minelco under the UltraCarb trade name. The results are shown in Figure 5, Figure 6 and Figure 7 respectively.

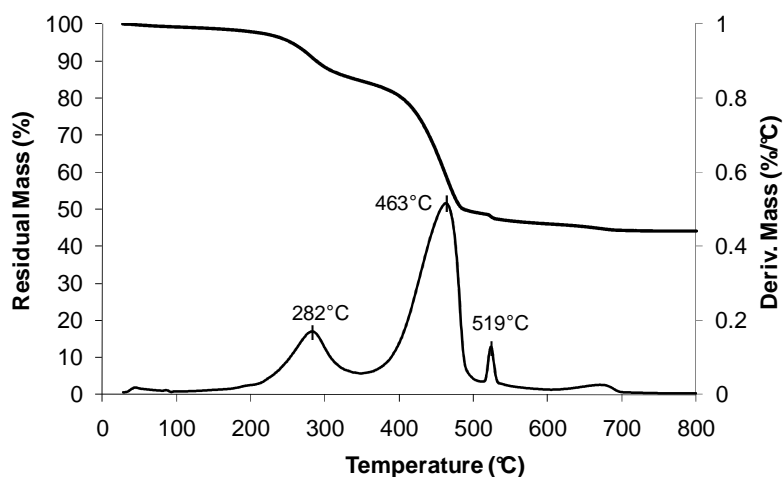


Figure 5: TGA profile of natural hydromagnesite

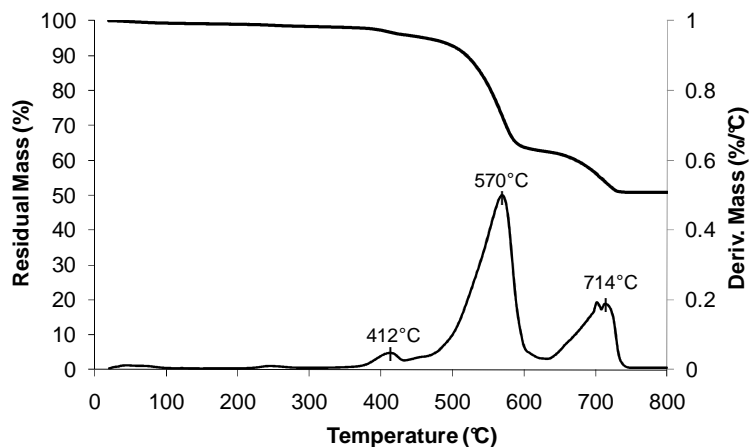


Figure 6: TGA profile of natural huntite

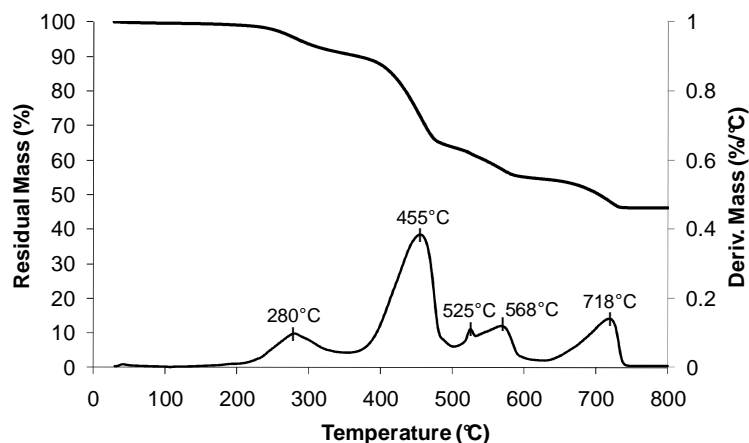


Figure 7: TGA profile of an approximately 60:40 mixture of natural hydromagnesite and huntite (UltraCarb)

Decomposition of hydromagnesite begins to occur at about 220°C and progresses through two major mass losses. Huntite begins to decompose at about 450°C and again progresses through two major mass losses. The mixture of hydromagnesite and huntite provides a broad decomposition range starting at about 220°C and being complete by about 740°C. During these decomposition reactions approximately 54% of the original mass of the mixture of hydromagnesite and huntite is released as carbon dioxide and water.

Figure 8 shows differential scanning calorimetry (DSC) measurement, made by the present authors, using a Rheometric Scientifics DSC1500, under a nitrogen atmosphere, with a heating rate of 10°C min⁻¹. A mixture of hydromagnesite and huntite shows that each of the decompositions measured by TGA is associated with an endotherm. The total heat of decomposition of the mixture is approximately -990 Jg⁻¹. This figure will vary depending on the ratio of the two minerals.

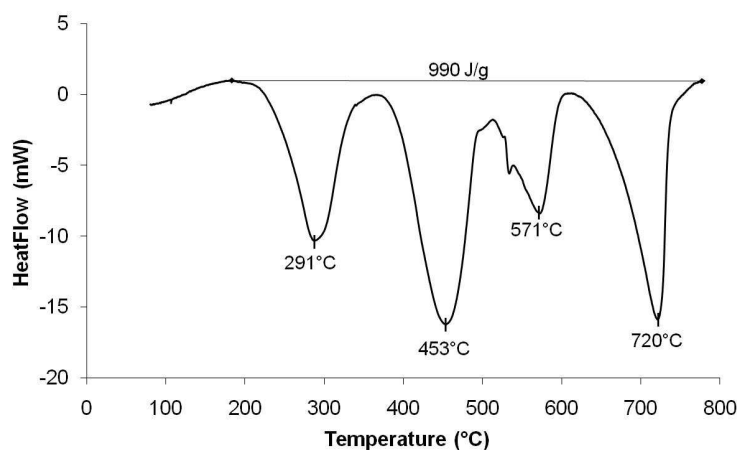
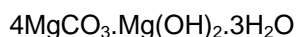


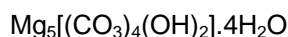
Figure 8: DSC profile of a mixture of natural hydromagnesite and huntite (UltraCarb)

4. Chemical Formula and Crystal Structure of Hydromagnesite

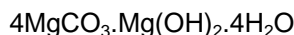
There is some variation in the chemical formula reported for hydromagnesite. Rotheron inadvertently illustrates this in his well regarded book[35] on particulate filled polymer composites. The following formula is shown in one chapter[36] by Hancock and Rotheron:



while in a later chapter[5], by Rotheron alone, the following formula is given. This formula is also given by Frost[27] and Winchell[37].



This formula would have equivalent composition to:



Therefore the amount of water of crystallisation differs, 4 moles are shown in the formula given by Frost[27] and Winchell[37] compared to only 3 moles in formula reported by Hancock and Rotheron[36].

In the 1970's Todor[9] also made the point that in various mineralogical handbooks two formulae are given, one with three water molecules and one with four.

Botha[25] introduces a third variation observing that hydromagnesite is a hydrated basic magnesium carbonate that can be synthesised in two forms, referred to as light and heavy magnesium carbonate with 4 and 5 water molecules respectively, adding a third variation.

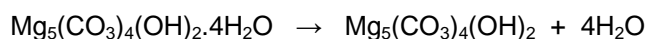
In 1972 Robie reported[38] that the geometry of the hydromagnesite unit cell was still in question with some authors[39] taking $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ as the correct form while others[37] considered it to be $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Robie's own measurements using specific gravity, chemical and x-ray analysis lead him to the conclusion that the correct formula for a sample of hydromagnesite from Hindubagh, Pakistan contained four water molecules. A further sample of hydromagnesite from Soghan, Iran, analysed by Bariand[40] in 1973 confirmed that the formula contained 4 water molecules in agreement with Robie[38], Winchell[37], and with Todor's[9] findings from thermal analysis. This now appears to be accepted and is the formula given by the Mineralogical Society of America in their Handbook of Mineralogy[19].

Various studies[41-46] have been made on the crystalline structure of hydromagnesite. Murdoch[43] concludes that it is a monoclinic crystal with a pseudo-orthorhombic structure. Akao[46] first published a crystal structure of hydromagnesite in 1974. It was determined using three dimensional X-ray data. The structure was shown to be based on a three dimensional framework of MgO_6 octahedra with the magnesium atom surrounded by the six oxygen atoms. The octahedra share oxygen atoms with the surrounding octahedra forming a 3 dimensional structure. The octahedra consist of two distinct structures. The first contains a magnesium atom surrounded by four oxygen atoms from carbonate ions, the fifth from a hydroxyl ion and the sixth from a water molecule. The second structure contains four carbonate ions and two hydroxyl ions. The strong C-O bonds of the carbonate ion reinforce the crystal by forming a triangular structure with three oxygen atoms from three different octahedra. In a subsequent publication[45] in 1977 Akao further developed understanding of the structure by determining in greater detail the positions of the remaining water molecules and the hydroxyl group. The hydroxyl group was shown to be shared between three MgO_6 octahedra and does not take part in any hydrogen bonding, while the water molecules are located at unshared corners of the MgO_6 octahedron and form a network of hydrogen bonds. The water molecules are arranged so that the oxygen atoms are tetrahedrally surrounded by two hydrogen atoms, one magnesium atom and one hydrogen from a neighbouring water molecule. This hydrogen atom from the neighbouring water molecule forms a hydrogen bond, causing the water molecules to form a chain. The chain consists of one hydrogen atom in each water molecule forming a hydrogen bond to its neighbouring water molecule and the other hydrogen atom forming a hydrogen bond with oxygen in the carbonate groups. The three dimensional structures has been characterised in the excellent works of Akao[45,46] where detailed tables of interatomic distances, bond angles, diagrams of the crystal structures and in depth discussion and comment is given.

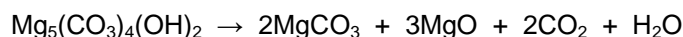
5. Endothermic Decomposition of Hydromagnesite

In the 1950's Beck [8] published information on the decomposition characteristics of a range of carbonate minerals including natural hydromagnesite from California. Beck quoted the chemical formula as $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. He noted that the hydromagnesite went through a series of endothermic decompositions releasing water and carbon dioxide and published DTA curves to accompany his observations.

Todor[9] published one of the earliest attempts to characterise the decomposition mechanism of hydromagnesite. Between 210°C and 395°C, the four water molecules are released.



Immediately following the loss of the four water molecules, between 395°C and 460°C, the loss of a carbon dioxide molecule occurs, followed by a reorganisation of the crystal structure. Todor does not give any detail on what this reorganisation involves. Between 460°C and 515°C a fifth molecule of water is released due to the decomposition of the hydroxide group and a further carbon dioxide molecule is released.



Finally over the temperature range of 515°C to 640°C a further two carbon dioxide molecules are released to leave a magnesium oxide residue.



Todor notes that the complicated decomposition mechanism may have led to some of the confusion over the actual chemical structure of hydromagnesite. However this precise mechanism and order of events is not in agreement with that of more recent work, as discussed below.

Padeste[33] showed that hydromagnesite decomposes through different mechanisms depending on the surrounding atmosphere. In the absence of carbon dioxide only two decomposition stages were observed; the loss of the crystalline water, followed by the combined dehydroxylation and decarbonation. However, under carbon dioxide the dehydroxylation and decarbonation were thought to occur separately, giving three steps.

In the late 1970's Sawada published a number of papers[10-14] investigating in detail the decomposition of hydromagnesite. These investigations included the effect of different gaseous atmospheres at varying partial pressures on the decomposition of hydromagnesite. He confirmed that under a nitrogen atmosphere the decomposition of hydromagnesite occurs through only two steps. Increasing the partial pressure of carbon dioxide was found to strongly influence the decomposition[10], separating the single loss of carbon dioxide between 350°C and 500°C into three distinct losses at 350°C – 500°C, 500°C – 520°C and 530°C – 650°C. The first and third losses of carbon dioxide were found to be endothermic, while the middle loss was exothermic. This effect was also observed on increasing the heating rate. Low heating rates gave only one decarbonation step which split into two and which were then separated by a third sharp exothermic decomposition at even higher heating rates, presumably due to the local increase in the partial pressure of carbon dioxide in the bulk of the solid.

Further study[11] under helium also showed dehydration below 300°C followed by a single decarbonation step between 300°C and 500°C, while XRD analysis showed an amorphous structure, with no indication of magnesium carbonate crystals. Above 500°C, magnesium oxide was detected by XRD with the peaks becoming sharper and stronger at higher temperatures. When the same decomposition was carried out under helium and carbon dioxide ($P_{\text{CO}_2}=0.5$ atm) the dehydration below 300°C was unaffected. Samples examined using XRD after the occurrence of the exotherm at about 520°C showed the presence of crystalline magnesium carbonate. It is therefore concluded that under conditions of high partial pressure of carbon dioxide, or high heating rates, exothermic crystallisation of

magnesium carbonate occurs at about 520°C. The magnesium carbonate then decomposes through decarbonation to magnesium oxide, between 530°C and 650°C. This led Sawada to propose two types of decomposition for hydromagnesite[12]

Type I: $P_{\text{CO}_2} < 0.1 \text{ atm}$ - The amorphous carbonate formed after dehydration decomposes directly to magnesium oxide.

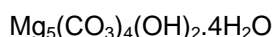
Type II: $P_{\text{CO}_2} \sim 1 \text{ atm}$ - The amorphous carbonate formed after dehydration partially decarbonates followed by exothermic crystallisation of magnesium carbonate at about 520°C. The magnesium carbonate then itself decarbonates to magnesium oxide between about 530°C and 650°C.

Having investigated the effects of carbon dioxide partial pressures at atmospheric pressure Sawada went on to investigate the decomposition of hydromagnesite under high pressure atmospheres[12]. Increasing pressures of nitrogen, argon, and carbon dioxide had no effect on the dehydration temperature up to 50 atm. Increasing pressures of argon, and nitrogen had minimal effect on the temperature of the exothermic crystallisation of magnesium carbonate and subsequent decarbonation. Increasing pressures of carbon dioxide had a significant effect. The temperature of the exothermic crystallisation of magnesium carbonate was linearly reduced by about 30°C as the pressure was increased from 1 to 50 atm, while the peak of decomposition of the resultant magnesium carbonate increased to just less than 700°C. At pressures of carbon dioxide above about 10 atm a third decomposition mechanism was identified. This was given the classification of Type III by Sawada, in which a second exotherm occurred at a slightly lower temperature than the Type II exotherm. An intermediate phase is formed before the occurrence of the Type II exotherm and the formation of crystalline magnesium carbonate.

These differing mechanisms have implications for the decomposition mechanism of hydromagnesite in polymer compounds for two reasons. First, the heating rate in a fire situation is likely to be high and the self generated carbon dioxide atmosphere will both contribute to the formation of the crystalline magnesium carbonate and associated higher decomposition temperature of the Type II decomposition mechanism. Second, in a hydromagnesite-polymer composite the local partial pressure of carbon dioxide during hydromagnesite decomposition is likely to be much higher than atmospheric pressure due to the tortuous route from the surface of the hydromagnesite crystal to the polymer-gas interface on the surface.

6. Comparison of Synthetic Hydromagnesite with Naturally Occurring Blends of Hydromagnesite and Huntite.

More recently Haurie et al.[29] studied the use of synthetic hydromagnesite with the following chemical formula:



It had a total decomposition endotherm of 800 Jg^{-1} associated with the loss of carbon dioxide and water. Decomposition studies using TGA/DTA at $10^\circ\text{C min}^{-1}$ in air showed that it decomposed in three steps as follows:

200–250°C release of water of crystallisation

380–450°C release of water from decomposition of the hydroxides

510–550°C release of carbon dioxide from decomposition of the carbonate

The three decomposition stages detected in the synthetic hydromagnesite were also detected in mixtures of natural hydromagnesite and huntite (UltraCarb) although the temperatures varied slightly. In addition two peaks at 540–600°C and 725–780°C due to decomposition of huntite were observed.

The synthesis and three step decomposition of hydromagnesite is also discussed by Botha[25]. The second study[32] discusses the decomposition of hydromagnesite and then goes on to investigate the re-hydration of hydromagnesite that has been dehydrated and dehydroxylated at 325°C. It was found that over an 11 week period the dehydrated hydromagnesite reverted back to its original form. During the first 7 days water was taken up by physical surface absorption and the reappearance of hydroxyl groups in the crystal lattice was also observed. These observations were confirmed with FTIR and the appearance of DTA peaks at about 100°C and 246°C. Over the 11 week period FTIR analysis showed water molecules integrating into the crystal lattice. Changes in the carbonate FTIR spectra showed that there was interaction between these groups and the water molecules as they realigned themselves into the crystal structure. This may well have been due to hydrogen bonding of the water molecules to the carbonate groups as discussed by Akao[45].

One work[27] differs from most others in the decomposition temperatures reported. Frost reports that a 5°C min⁻¹ heating rate gives decomposition temperatures of 135, 184, 412 and 474°C for hydromagnesite that he synthesised. The first two decompositions at 135 and 184°C are attributed to loss of water of crystallisation in two steps, each giving a loss of two water molecules. The third decomposition at 412°C is attributed to dehydroxylation. Decarbonation is said to occur at 412°C and 474°C. These conclusions are all drawn through comparisons of theoretical mass losses compared to the mass losses measured using TGA, no analysis of the gases emitted during the decomposition appears to have been made. Comparing with other authors' work[8,25,29,30,32] the first two decompositions seem to occur at very low temperatures. Frost comments on this, referring to the fact that Beck[8] found decomposition temperatures between 275 and 325°C for loss of water, and loss of carbon dioxide at 485°C and again at 565 – 600°C. Frost appears to question the validity of Beck's results at this stage, stating that "the results of Beck are so significantly different that the measurement is open to question". The difference in the higher temperature decompositions appears to arise from the fact that Frost did not find the exotherm that Beck had reported. However several workers[10-14,33,47] have published work showing the conditions needed for the exotherm to occur. One of these conditions being a heating rate of greater than 18°C min⁻¹. It is therefore unsurprising that no exotherm was seen by Frost at heating rates of 5°C min⁻¹. Beck does not state what heating rate he used, however the strong exotherm that was detected suggests it was fairly fast.

Frost[27] also used controlled rate thermal analysis to study the decomposition of this sample of synthetic hydromagnesite. This method involved using a variable heating rate, up to a maximum of 1°C min⁻¹, in order to maintain a constant decomposition rate of 0.1mg min⁻¹. These very slow heating rates showed that the sample went through five stages of decomposition with mass losses at 100°C and 145°C being attributed to dehydration. Dehydroxylation was shown to occur at 203°C followed by isothermal loss of carbon dioxide at 370°C. At 409°C a second brief isothermal was measured, Frost suggests this may be due to the recrystallisation of magnesium oxide as suggested by Beck[8]. Comparison of these results with those achieved at a fixed 5°C min⁻¹ clearly illustrates how the decomposition of hydromagnesite is affected by the rate of heating. There is no one true decomposition mechanism for the mineral and no "correct" method for measuring the decomposition, but a number of mechanisms depending on the test conditions.

Frost's work was carried out using synthetic hydromagnesite produced in his own laboratory. He reported that the hydromagnesite produced was characterised for phase specificity using XRD and chemical composition using EDX although details of these analysis are not shown. Perhaps, as the TGA decomposition temperatures suggest, the product produced was not true hydromagnesite. Frost's own calculations based on measured mass losses leads him to conclude (in an appendix not discussed within the text) that the formula for the hydromagnesite that he had synthesised was Mg₅(CO₃)₄(OH)₂·2H₂O. This may well explain the disagreement between the decomposition temperatures reported in the work and that of other authors. Clearly the material that he synthesised was not true hydromagnesite as it did not contain enough water. As the work of Botha[32] showed the process of hydration can take some weeks at ambient conditions and would certainly influence the crystal structure[45,46] since the water molecules form a network of hydrogen bonding with the carbonate ions. This

oversight has to throw doubt on the validity of any comparisons made between this work and that of previous authors.

7. Exothermic Event in the Decomposition of Hydromagnesite

The overall decomposition of hydromagnesite is endothermic, enhancing the fire retardant action of the mineral. However under some conditions an exothermic event has been recorded in hydromagnesite at a little over 500°C. This has led to some discussion about its source and mechanism. Some researchers appear to have missed it completely while others have devoted entire papers to it. It is clear that the event is highly dependant on test conditions which explains why there are differing reports as to its importance and mechanism. The appearance of an exotherm during the thermal decomposition of minerals used as fire retardants is not unique to hydromagnesite. Magnesium hydroxide has also been reported[48] to show an exotherm at about 507°C. This is due to crystallisation of cubic magnesium oxide from the hexagonal magnesium hydroxide crystals after dehydroxylation.

The present authors' own work has confirmed the presence of an exotherm within the decomposition of hydromagnesite and its dependence on heating rate. Figure 9 and Figure 10 show only a very slight exotherm at about 520°C when a heating rate of 10°C min⁻¹ was used. At 20°C min⁻¹ the exotherm becomes much larger and is followed by the appearance of an endotherm between 520°C and 590°C which was not observed at a heating rate of 10°C min⁻¹.

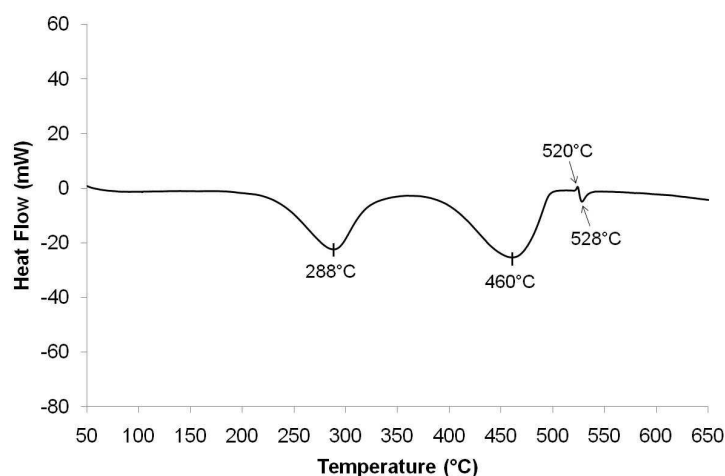


Figure 9: Decomposition of hydromagnesite measured by DSC at 10°C min⁻¹ in nitrogen

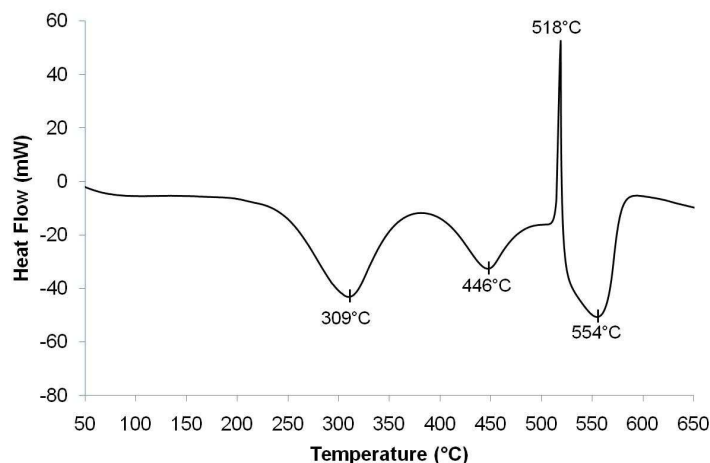


Figure 10: Decomposition of hydromagnesite measured by DSC at $20^{\circ}\text{C min}^{-1}$ in nitrogen

In Beck's[8] work from the 1950's, comparing the decomposition of a quantity of carbonate minerals using differential thermal analysis, an exothermic event in the decomposition of hydromagnesite was reported. This exotherm was reported to result from '*the formation of amorphous (?) MgO which inverts to cubic MgO at 510°C*'. The question mark in parenthesis suggests that Beck was not sure whether the magnesium oxide was actually amorphous at this stage.

In the early 1970's Todor[9] made the observation that an exotherm could be detected at a range of temperatures between 385°C and 460°C . Most other researchers, as discussed below, are in agreement that the exotherm occurs between about 510°C and 530°C which is consistent with Figure 10. However, Todor gives no details of the test conditions that gave this wide temperature range, so it is difficult to comment on their validity.

Further investigation in the 1970's by Sawada[10] confirms that an exothermic event occurs under certain specific conditions. The conditions favouring the exotherm include a high partial pressure of carbon dioxide, dense packing of the sample and a high heating rate. The exotherm was not seen at a heating rate of $10^{\circ}\text{C min}^{-1}$ but was seen at $20^{\circ}\text{C min}^{-1}$. In a later paper again by Sawada[14] further investigation into the exotherm confirms that it is due to the crystallisation of magnesium carbonate from the amorphous phase.

Padeste's work [33] from 1991 gives a detailed analysis of the decomposition of hydromagnesite under nitrogen and carbon dioxide atmospheres. Under nitrogen only two decomposition stages are observed in hydromagnesite, under carbon dioxide the second decomposition stage resolves itself into two separate stages separated by an exotherm. It is reported that the exotherm is caused by the crystallisation of magnesium carbonate after the loss of the hydroxide group. X-ray diffraction was used to confirm that this crystallisation occurred.

More recently, in 2001, Khan[47] carried out some investigation into the exothermic peak in the decomposition of hydromagnesite. This work again confirmed the presence of the exotherm under certain conditions. DTA analysis revealed, in a nitrogen atmosphere, that no exotherm was observed for heating rates of less than $18^{\circ}\text{C min}^{-1}$ but at $18.5^{\circ}\text{C min}^{-1}$ or faster an exotherm was seen at about 525°C . The size of the exotherm increased as the heating rate was increased above $18.5^{\circ}\text{C min}^{-1}$. The magnitude of the exotherm was reported to increase and also occur at a lower heating rate as the sample size was increased. Khan also investigated the effect of a carbon dioxide atmosphere, this gas caused the exotherm to be observed at much lower heating rates and with smaller sample sizes. Although Sawada[10] did not report any exotherm in a nitrogen atmosphere, his conclusion that carbon dioxide and high heating rates are required is consistent with this work. Khan also suggests that the exotherm is due to mechanical stress within the crystal structure caused by the release of carbon dioxide which becomes trapped. This trapped gas is then suddenly released resulting

in a small 'explosion within the sample'. The mechanical breakdown of the crystallite and the release of heat energy associated with the explosive release of the carbon dioxide is given as the cause of the exotherm. This theory is based on the fact that a sudden mass loss is associated with the exotherm and that electron microscopy shows that the magnesium oxide residue appears more "fluffy and dispersed" in samples that have been through the exothermic decomposition than those that are decomposed without the exothermic event. Such sudden eruptions, especially close to ignition temperatures, could extinguish early flaming increasing the ignition resistance of polymers using hydromagnesite compounds as fire retardant additives.

Clearly an exothermic event does occur during the decomposition of hydromagnesite under certain conditions but at least two different theories about its origin have been proposed. Sawada's work[10-14] is the most detailed and appears the most reliable. Therefore the explanation of the exotherm being due to the crystallization of magnesium carbonate seems a likely explanation. Sawada attributes the sudden mass loss to a sudden increase in the rate of decarbonation, caused by the exotherm. This theory is also consistent with the data presented in Figure 9 and Figure 10. This data clearly shows the presence of an exotherm at about 520°C which is dependant on heating rate when measured in air. The appearance of an endotherm between 520°C and 590°C is consistent with the subsequent decomposition of crystalline magnesium carbonate following its exothermic crystallisation at 520°C.

Inglethorpe[49] carried out one of the more recent investigations into the decomposition of hydromagnesite and huntite. Following a review of the work of earlier researchers and his own investigations he concluded that the decomposition of hydromagnesite contains four stages as follows:

- 1) endothermic loss of water of crystallisation
- 2) endothermic dehydroxylation and formation of amorphous magnesium carbonate
- 3) exothermic crystallisation of magnesium carbonate
- 4) endothermic decarbonation of magnesium carbonate

This scheme provides a good summary of the findings of all other researchers.

In none of these studies was the effect of the exothermic event on fire retardancy studied. In fact Inglethorpe[49] is the only researcher to comment on the fact that the exotherm could have a detrimental effect on fire retardant properties. However, as can be seen from Figure 10 the heat emitted by the exotherm (which is proportional to the area under the curve) is small in comparison to the total heat absorbed by the endothermic decomposition of hydromagnesite. All of these studies were carried out on the mineral alone, not on polymer compound containing the minerals. The existence of the exothermic event occurring in a burning polymer containing hydromagnesite has not been reported. Inglethorpe is the only researcher to comment on this, suggesting that such a detrimental effect is only likely in polymer compounds with high loading levels of the minerals. In the case of commercially available mixtures of hydromagnesite and huntite, the temperature range of the endothermic decomposition of the huntite overlaps the hydromagnesite exotherm. This will remove some of the heat generated by the crystallisation of the magnesium carbonate. This effect can be seen in Figure 8, the exotherm is present as a slight discontinuity in the curve at about 530°C but the endotherm of the huntite outweighs the exotherm of the hydromagnesite.

8. Influence of Particle Size, Milling and Surface Coating on the Decomposition Mechanism

In much of the work discussed no information is given on the particle size of the mineral powders. This could have an influence on the decomposition due to thermal conduction within the particles and may explain some of the differences in decomposition temperatures and mechanisms reported at apparently similar test conditions. Haurie[30] has carried out some studies into the effect of particle size reduction through different milling processes on the thermal decomposition characteristics of synthetic hydromagnesite. It was found that

mechanical milling methods could cause an increase in the decomposition rate between 400°C and 500°C and reduce the exothermic crystallisation of magnesium carbonate. This was suggested to result from the milling action causing defects in the crystal lattice resulting in the early release of carbon dioxide. Particle size reduction using an air jet mill did not cause significant changes in the decomposition profile of the hydromagnesite. Haurie makes the comment that these changes could influence the fire retardant efficiency of the synthetic hydromagnesite but that further work is needed to investigate this.

Earlier work by Haurie[28] showed that coating of synthetic hydromagnesite with stearic acid, which is frequently used as compatibiliser to aid dispersion of the filler within a polymer, also has an effect on the decomposition of the mineral. Levels of 3% and above influence the decomposition in the region of 350–450°C causing a faster rate of decomposition. A similar effect has been reported for magnesium hydroxide[36] where stearate coating has been shown to increase the rate of decomposition, suggesting that the acid protonates the hydroxide with the release of water. Haurie states that the TGA tests were carried out under an oxygen atmosphere at a heating rate of 10°C min⁻¹. The decomposition profile for the uncoated hydromagnesite shows the same distinctive three step decomposition reported by Sawada[12] as Type II decomposition, even though the test was carried out under oxygen with a low heating rate. As the stearic acid coating level was increased to 4.5% the decomposition profile as measured by TGA gradually became more like the Sawada's Type I decomposition. The rate and magnitude of the decomposition between about 350 – 450°C increased and the magnitude of the decomposition above 480°C correspondingly decreased. Haurie shows that X-Ray diffraction shows a stronger, more defined magnesium oxide peak when hydromagnesite coated with 4.5% stearic acid is heated at 400°C for one hour, compared to an uncoated sample. This indicates a higher degree of crystallinity in the magnesium oxide. No attempt to determine the phase changes in terms of formation and decomposition of a crystalline magnesium carbonate during the decomposition were made. However, taking into account Sawada's detailed work[10-13] it would appear that the stearic acid could be preventing the formation of crystalline magnesium carbonate, causing the hydromagnesite to decompose directly to magnesium oxide. A similar effect on the decomposition profile was also seen by Haurie[30] when hydromagnesite was mechanically ground to smaller particle sizes. The method used for coating the stearic acid was a heated high speed mixer. It is possible that similar stresses resulting in defects are being introduced into the crystal structure through the mechanical action of coating the filler, as they are during mechanical grinding.

9. Structure and Decomposition of Huntite

The earliest reference to huntite is a paper by George Faust[16] from 1953 in which the discovery of a new mineral in Nevada was announced. Faust acknowledges that the mineral probably had been discovered previously but had been misidentified as impure magnesite by W. E. Ford in 1917. Faust announced that the new mineral was to be named huntite in honour of his former teacher, Walter F. Hunt, Professor of Petrology at the University of Michigan from 1922 until 1933 and editor of *American Mineralogist* for 35 years[50]. Faust carried out DTA analysis of the newly discovered mineral, huntite, discovering that it went through endothermic decompositions at 644°C and 901°C, these decompositions were attributed to the dissociation of MgCO₃ and CaCO₃ respectively. It was also shown by chemical analysis that the chemical formula for huntite was Mg₃Ca(CO₃)₄.

The crystal structure of huntite is somewhat simpler than hydromagnesite. In 1962 Graf and Bradley[51] described it as an ordered rhombohedral double carbonate, similar to a deformed face centred cube. The calcium atom is located at the origin with three magnesium atoms at the face centres and three carbonate groups at the edge centres, the final carbonate group is located at the body centre. For detailed information regarding the crystal structure of huntite, including tables of d spacings, structural factors, interatomic distances and structural diagrams, the reader should refer to Graf and Bradley's work[51].

In 1966, a white powder was discovered on the wreck of a Roman ship. Barbieri[17] carried out an analysis on the powder identifying it as huntite. DTA analysis confirmed that it went

through two endothermic decompositions, one at 650°C and one at 910°C, much the same as the findings of Faust. Barbieri also went into some detail trying to determine whether the huntite had formed from some other mineral such as magnesite due to being submerged in sea water for many years. Their chemical analysis concluded that it was most likely that the huntite was in its original form and that therefore the Romans were in fact trading huntite. The fact that huntite was used in the ancient world is confirmed by Riederer[52] in a paper indentifying pigments used by the ancient Egyptians. A bowl that had been excavated in Nubia and accurately dated to 1600BC was analysed and it was shown that huntite was used as a white pigment. It therefore seems reasonable that the Roman ship (dated to the 3rd century AD) may well have been trading huntite as part of its cargo. There is also evidence[53] that huntite was used as a white pigment in Cambodian manuscripts from the 18th and 19th centuries.

Ozao and Otsuka[15] stated in 1985 that a detailed study of the decomposition of huntite had not yet been carried out. They went on to describe their work in this area, confirming the previously known decompositions shown by Faust[16] and Barbieri[17]. Ozao's DTA curves, measured in a carbon dioxide atmosphere, of mechanical mixtures of magnesite (MgCO₃) and calcite (CaCO₃) were shown to be clearly different to those of huntite (Mg₃Ca[CO₃]₄). The distinctive peaks associated with the decomposition of the magnesium carbonate and the calcium carbonate were present in the huntite but they occurred at slightly lower temperatures. This indicates that huntite is not a simple mechanical mixture of the two minerals. XRD analysis showed that at about 620°C huntite has decomposed to leave poorly crystallised magnesium oxide and "magnesian calcite". This is illustrated by Ozao as follows:



n gradually reduces from 0.2 to 0.05 over the temperature range 620°C to 790°C.

The magnesian calcite gradually decomposes to form further magnesium oxide as the temperature increases to about 790°C and over the same temperature range the magnesium oxide crystallises to leave magnesium oxide and calcite. The remaining magnesian calcite then decomposes to leave magnesium oxide and calcium oxide at about 900°C. Illustrated by Ozao as follows:



$n < 0.05$

More recently Kangal & Guney[18] made some investigations on Turkish huntite. They quote huntite as having a two stage decomposition at 602°C and 622°C, and a further decomposition at 829°C but make no measurements of what these decompositions correspond to in terms of chemical decomposition.

10. Decomposition of a Natural Mixture of Hydromagnesite and Huntite.

Figure 11 shows how the decomposition of hydromagnesite and huntite compares to calculated theoretical mass losses.

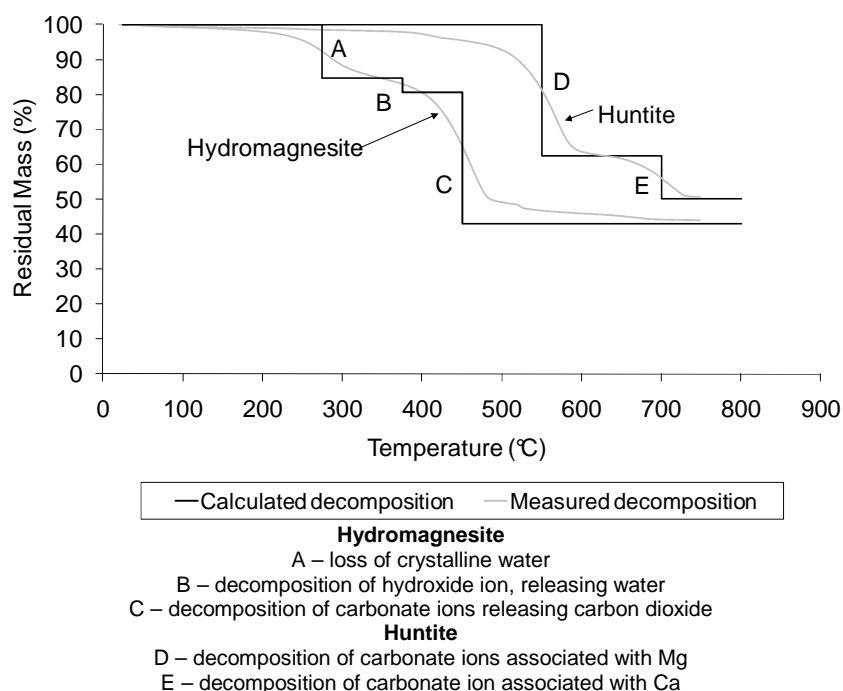
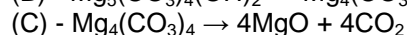
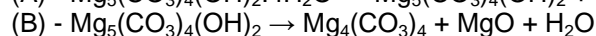
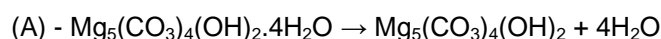


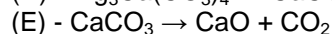
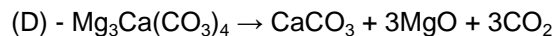
Figure 11: Decomposition of hydromagnesite and huntite compared to the calculated theoretical mass losses

There are three decomposition steps associated with the decomposition of hydromagnesite which are marked in Figure 11 as A, B, and C.



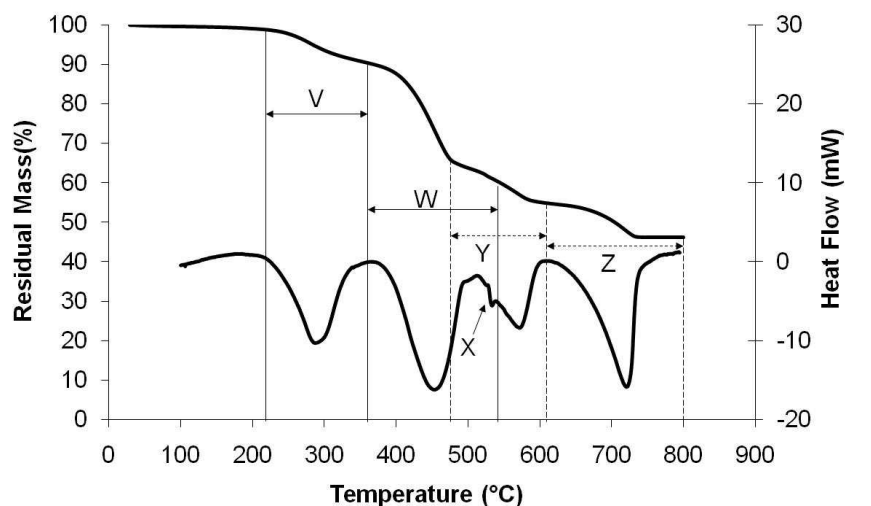
These three steps are associated with cumulative mass losses of 15.45%, 19.31% and 57.08% respectively. It can be seen in Figure 11 that these calculated mass losses correspond quite closely to the mass losses measured for hydromagnesite by TGA.

Huntite has two steps associated with its decomposition; these are marked as D and E in Figure 11.



These two steps are associated with cumulative mass losses of 37.5% and 50.0% respectively. Again, the calculated mass losses correspond quite closely to the mass losses measure for huntite by TGA.

Figure 12 summarises the decomposition mechanisms discussed above, and in the previous sections, in relation to the decomposition of UltraCarb; a natural mixture of hydromagnesite and huntite. The data shown in Figure 12 was measured by the present authors, in air at a heating rate of $10^\circ\text{C min}^{-1}$. At this heating rate only a minimal amount of crystallisation of magnesium carbonate is expected to occur during the decomposition.



- V – Loss of water from hydromagnesite approx. 220°C – 350°C
 W – Loss of carbon dioxide from hydromagnesite approx. 350°C-550°C
 X – Exothermic crystallisation of magnesium carbonate
 Y – Initial loss of carbon dioxide from huntite
 Z – Secondary loss of carbon dioxide from huntite

Figure 12: TGA and DSC decomposition of an approximately 60:40 natural mixture of hydromagnesite and huntite

An initial mass loss and associated endotherm (V) between the temperatures of 220°C and 350°C is due to the loss of crystalline water from the hydromagnesite. This is followed by a second step in mass loss. In Figure 11 it is clear that this mass loss, associated with the loss of carbon dioxide from the hydromagnesite, is not complete until about 540°C (W). It, therefore, overlaps with the initial mass loss associated with loss of carbon dioxide from the huntite (Y). The loss of the hydroxyl group from hydromagnesite as water is not detected as a separate mass loss in Figure 12. However, it was reported by Haurie[29] that this loss of water occurs between 380°C and 450°C which would mean that it occurs in the lower half of region W in Figure 12. This region also covers the temperature range where carbon dioxide is being lost from the hydromagnesite. At about 520°C a slight discontinuity is seen in the DSC graph (X). This is the temperature at which the exothermic crystallisation of magnesium carbonate has been reported. The heating rate used for this measurement was 10°C min⁻¹ which is why the exotherm is very small, indicating that there is only very minimal crystallisation of magnesium carbonate. It also occurs in the temperature range (Y) at which huntite is endothermically decomposing. Figure 11 shows that above 520°C there is a continued slow loss in mass from hydromagnesite up to about 700°C which is probably slow degradation of the small amount of crystalline magnesium carbonate.

Figure 11 shows that huntite begins to decompose rapidly at about 470°C. This loss in mass with its associated endotherm is complete at about 610°C. The decomposition over this temperature range (Y) is due to the loss of carbon dioxide from the carbonate groups associated with the magnesium ions. A final mass loss and endotherm (Z) between 610°C and 800°C is due to a final loss of carbon dioxide resulting from the decomposition of the carbonate groups associated with the calcium ions.

At 800°C the hydromagnesite has decomposed to leave a magnesium oxide residue and the huntite has decomposed to leave a mixture of calcium oxide and magnesium oxide.

11. Implications for the Suitability of Mixtures of Hydromagnesite and Huntite as Fire Retardant Additives

It is generally accepted[54-56] that for metal hydroxides to act as effective fire retardant additives in polymer composites the decomposition temperature of the polymer must be closely matched by the endothermic decomposition temperature of the metal hydroxide. The rate of polymer decomposition is therefore slowed because of the heat absorbed by the decomposing metal hydroxide and the released water dilutes the flammable polymer decomposition products. The metal oxide residue also acts as a thermal barrier to further decomposition of the underlying polymer.

A mixture of hydromagnesite and huntite meets all of the above requirements and compared to the commonly used metal hydroxides may well provide some further benefits. The initial decomposition temperature of hydromagnesite has been shown[8-14,33] to be about 220°C compared to 180 – 200°C for ATH[5]. This gives it the advantage of being able to withstand higher processing temperatures meaning that it is suitable for polymers with higher melt temperatures such as polypropylene where ATH cannot be used.

When used as a fire retardant additive the rate of temperature increase that hydromagnesite will experience within a burning polymer is likely to be well in excess of the $18.5^{\circ}\text{Cmin}^{-1}$ that Khan[47] found to be the point at which crystallisation of magnesium carbonate occurs. The hydromagnesite particles will also be held in a self generated carbon dioxide atmosphere, which will also contribute to the decomposition mechanism becoming close to that described by Sawada[12] as type II decomposition. These effects mean that, within a polymer composite, hydromagnesite will be likely to follow the mechanism of releasing water at about 220°C, followed by partial decomposition of the carbonate ions up to 520°C and creation of a high partial pressure of carbon dioxide around the particles. Following the crystallisation of magnesium carbonate the final release of carbon dioxide will occur up to 600°C. This gives hydromagnesite a wide decomposition range making it suitable for reducing flammability of a wider range of polymers.

Initially huntite may appear to have a decomposition temperature that is too high for fire retardancy in polymers. However it is feasible that it may provide some benefit in high temperature polymers such as polyetheretherketone (PEEK). Studies of the decomposition mechanisms[57] of this polymer show that it does not begin to decompose until 575°C. PEEK's melting point of 343°C makes both aluminium hydroxide and magnesium hydroxide unsuitable. Huntite's initial decomposition temperature of about 400°C and endothermic release of carbon dioxide up to 750°C makes it an interesting possible additive for this polymer. Of course only pure huntite would be suitable, any hydromagnesite present would decompose during melt processing.

In mixtures with hydromagnesite, huntite's platy morphology may provide a barrier to the transport of combustible decomposition products to the flame. It may also enhance mechanical reinforcement of carbonaceous or inorganic char. Once formed into a char layer huntite will also provide additional protection to the underlying polymer through further endothermic decomposition in response to high external heat fluxes. These functions will not be provided by magnesium hydroxide or aluminium hydroxide due to their complete decomposition at lower temperatures.

12. Conclusions

The chemical composition and crystalline structure of huntite has been well defined. Its endothermic decomposition through evolution of carbon dioxide to leave a mixed residue of magnesium oxide and calcium oxide has been well characterised.

There has been some difference in opinion over the chemical structure of naturally occurring hydromagnesite. This may have arisen from the fact that it is possible to synthesise several chemicals of very similar chemical structure but with varying amounts of water present. However it seems that the accepted geological definition of hydromagnesite is

$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Synthetic hydrated basic magnesium carbonate has the same structure and can be produced in two forms known as “light” and “heavy” corresponding to structures that contain 4 water molecules (as in the natural form) or 5 water molecules. The formula containing 3 water molecules may be due to inaccurate analysis. However, other hydrated hydroxy carbonates are closely related to hydromagnesite in terms of chemical formula and stoichiometry. In cases where analysis was made on the basis of DTA or TGA alone the samples may not have been pure hydromagnesite leading to some of the differences in results.

The decomposition of hydromagnesite is influenced by a number of factors, including heating rate and composition of the atmosphere. High heating rates or partial pressures of carbon dioxide causes the decomposition to progress through an exothermic crystallisation of magnesium carbonate after water has been lost from the structure. This causes the carbonate ions to decompose at a higher temperature than they do in the absence of carbon dioxide. At higher heating rates the carbon dioxide generated by the decomposition of the carbonate ions has less time to disperse, encouraging the crystallisation of the remaining magnesium carbonate. In mixtures of hydromagnesite with huntite the endothermic decomposition of the huntite overlaps with the exothermic event in the hydromagnesite reducing the overall effect of the exotherm. There is no single decomposition mechanism for hydromagnesite, and the commonly held belief that slower heating rates give more accurate thermal analysis results does not hold true for this mineral since higher heating rates are needed in order to study the exothermic crystallisation of magnesium carbonate. The main commercial use of hydromagnesite is as a fire retardant, therefore understanding of the decomposition mechanism at high heating rates is more important for this application than at slow heating rates or controlled rates of decomposition.

In comparison to the well known metal hydrate fire retardants, the decomposition mechanism and morphology of mixtures of hydromagnesite and huntite should provide several advantages. Hydromagnesite starts to decompose at a higher temperature than aluminium hydroxide meaning that it can be used in polymers with higher processing temperatures. The wide endothermic decomposition range of a mixture of hydromagnesite and huntite means that it provides cooling over a wider temperature range than either aluminium hydroxide or magnesium hydroxide. The platy morphology of the huntite may provide a barrier to the transport of combustible decomposition products to the flame. They could also reinforce the char layer and provide further protection to the underlying polymer by endothermically decomposing in response to high external heat fluxes. Huntite alone may be of benefit to polymers such as PEEK where the polymer's high melt and decomposition temperatures mean that aluminium hydroxide, or magnesium hydroxide would be unsuitable.

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