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1 A Review of The Structure and Thermal Decomposition of Hydromagnesite and Huntite

2
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8
9

10 Abstract

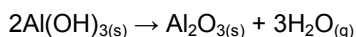
11
12 Naturally occurring mixtures of hydromagnesite and huntite are important industrial minerals.
13 Their endothermic decomposition over a specific temperature range, releasing water and
14 carbon dioxide, has lead to such mixtures being successfully used as fire retardants, often
15 replacing aluminium hydroxide or magnesium hydroxide. The current understanding of the
16 structure and thermal decomposition mechanism of both minerals and their combination in
17 natural mixtures is reviewed. The crystalline structure of both minerals has been fully
18 characterised. The thermal decomposition of huntite has been characterised and is relatively
19 simple. However, the thermal decomposition mechanism of hydromagnesite is sensitive to
20 many factors including rate of heating and the composition of the atmosphere. The partial
21 pressure of carbon dioxide significantly affects the decomposition mechanism of
22 hydromagnesite causing magnesium carbonate to crystallise and decompose at a higher
23 temperature instead of decomposing directly to magnesium oxide.
24

25 Keywords: hydromagnesite, huntite, fire, flame, retardant, mineral
26
27

28 This review critically examines the sometimes conflicting reports in the published literature. It
29 draws together current knowledge of the structure and thermal decomposition of
30 hydromagnesite and huntite, in order to provide an insight into the thermal behaviour of
31 mixtures of these minerals and to optimise their selection and applications.
32

33 1. Industrial use of Mineral Fillers as Fire Retardant Additives

34
35
36 The largest group of mineral fire retardants are metal hydroxides. Their endothermic
37 decomposition and associated release of inert gasses or water vapour, above the processing
38 temperature but below the thermal decomposition temperature of polymers suppresses the
39 ignition, while the accumulation of a solid inert residue on the surface of the burning polymer
40 reduces the heat release rate. Aluminium hydroxide (ATH) and magnesium hydroxide are the
41 most widely used[1]. Globally aluminium hydroxide is the highest tonnage fire retardant[2,3]. It
42 decomposes according to the following reaction:
43



45
46 The endothermic loss of water resulting from the thermal decomposition of ATH has been
47 variously reported[3-5] between 1170 and 1300 Jg⁻¹. The decomposition starts at about 180 –
48 200°C[5] depending on the particle size and physical form.
49

50 Magnesium hydroxide is used less widely than ATH. It decomposes through a similar
51 endothermic mechanism to ATH, giving off water.
52



54
55 The endotherm for this reaction is quoted at values between 1244 to 1450 Jg⁻¹ by various
56 authors[3,5-7]. It starts to decompose at about 300 – 330°C giving off water[5].
57
58

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

10 Mineral	11 Approximate onset of 12 Decomposition (°C)
13 Nesquehonite (MgCO ₃ ·3H ₂ O)	70 – 100
14 Gypsum (CaSO ₄ ·2H ₂ O)	60 – 130
15 Magnesium phosphate octahydrate (Mg ₃ [PO ₄] ₂ ·8H ₂ O)	140 – 150
16 Aluminium hydroxide (Al(OH) ₃)	180 – 200
17 Hydromagnesite (Mg ₅ [CO ₃] ₄ [OH] ₂ ·4H ₂ O)	220 – 240
18 Dawsonite (NaAl(OH) ₂ CO ₃)	240 – 260
19 Magnesium hydroxide (Mg(OH) ₂)	300 – 320
20 Magnesium carbonate subhydrate (MgO·CO _{2(0.96)} ·H ₂ O _(0.3))	340 – 350
21 Bohemite (AlO(OH))	340 – 350
22 Calcium hydroxide (Ca(OH) ₂)	430 – 450

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

25
 26
 27 Hydromagnesite has been shown[8-14] to decompose endothermically releasing water and
 28 carbon dioxide over a temperature range of approximately 220°C to 550°C.



31
 32 This endothermic decomposition and release of inert gases gives hydromagnesite its fire
 33 retardant properties.

34
 35 Huntite also decomposes endothermically[15-18] releasing carbon dioxide over a temperature
 36 range of approximately 450°C to 800°C.



38
 39 While this is too hot to coincide with major polymer decomposition and fuel production stages
 40 occurring around ignition, its platy morphology reinforces the formation of a thermally
 41 protective barrier layer which may reduce the rate of burning.

42
 43 The structure of these minerals and their thermal decomposition will be discussed in greater
 44 detail in the main body of this review.

45 46 47 **2. Sources of Hydromagnesite and Huntite**

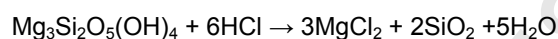
48
 49 Hydromagnesite is a naturally occurring mineral and has been found in a number of locations
 50 around the world, it is the third most common[19] carbonate found in caves, after calcite and
 51 aragonite. Commercial extraction of hydromagnesite is not from caves, as there are locations
 52 where larger quantities occur at the surface, in mixtures with another carbonate mineral,
 53 huntite. Huntite is rarer than hydromagnesite, although it is also found in caves[20] as
 54 flowstone.

55
 56 Georgiades[21] reported some of the history of one such deposit of mixed hydromagnesite
 57 and huntite in Greece. It had been known by local people as a source of material for
 58 whitewashing their houses for many centuries. Then in the mid 20th century it began to be
 59 used as a filler for shoe soles. It was ground using the local granite mills designed for wheat.
 60 Georgiades started investigating commercial exploitation of the minerals in 1978 and
 61 commenced worldwide sales in 1986. The Greek deposit is still operated commercially,

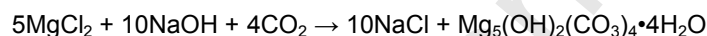
1 although the world's largest known reserves are in Turkey, operated commercially by Minelco.
 2 Stamatakis[22] has carried out some evaluation on a source of hydromagnesite in British
 3 Columbia[23,24] and concluded that it is composed mainly of hydromagnesite with minor
 4 amounts of magnesite but no huntite. The whiteness and decomposition properties are
 5 reported to be similar to commercially mined minerals from Greece, leading to the conclusion
 6 that this source of hydromagnesite might be suitable for use as a fire retardant.
 7

8 Since hydromagnesite is a carbonate, it has been proposed that its production could be used
 9 to convert the greenhouse gas carbon dioxide into a solid carbonate. A slurry of magnesium
 10 hydroxide can be converted[25] into hydromagnesite by bubbling carbon dioxide through the
 11 slurry.
 12

13 A method for the conversion of serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) into hydromagnesite has been
 14 investigated[26] as a way of trapping carbon dioxide and preventing its accumulation in the
 15 atmosphere. The process involves production of magnesium chloride from serpentine through
 16 the following reaction.
 17



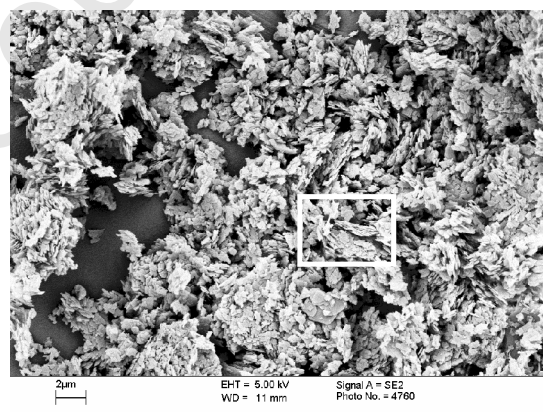
19
 20 The magnesium chloride is then converted to hydromagnesite in the presence of sodium
 21 hydroxide and carbon dioxide.
 22



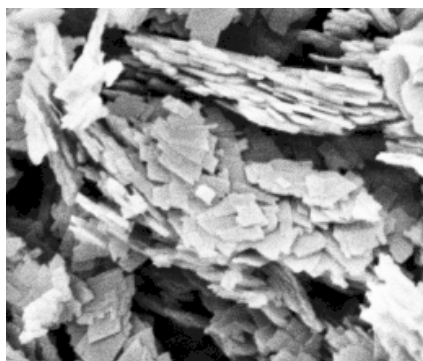
24
 25 These studies are primarily driven by the desire to trap carbon dioxide in a stable form.
 26 However, the suitability of both synthetic and natural hydromagnesite as a fire retardant for
 27 polymers could improve the cost effectiveness of the plan and lead to a future commercial
 28 source of hydromagnesite. There has also been interest in the literature[25,27-31] in synthetic
 29 hydromagnesite as a fire retardant.
 30

31 **3. Morphology and Thermal Decomposition of Hydromagnesite and Huntite**

32
 33 Naturally occurring huntite particles have a fine highly platy structure as shown in the electron
 34 micrographs (Figure 1 and Figure 2) produced by the present authors. Samples were gold
 35 coated and examined using a Carl Zeiss (Leo) 1530VP FEGSEM. Many of the individual
 36 particles have a diameter of 1 micron or less and thicknesses in the nanometer range.
 37



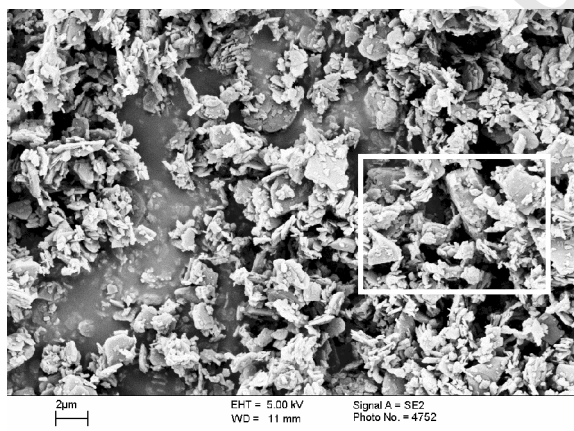
38
 39
 40 **Figure 1: Huntite particles**
 41



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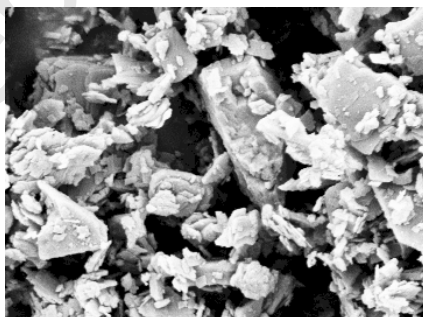
Figure 2: Enlarged section taken from the boxed area in Figure 1

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.



10
11
12

Figure 3: A mixture of hydromagnesite and huntite particles

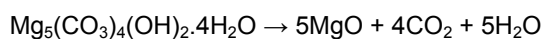


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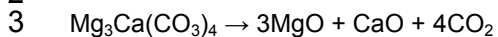
Figure 4: Enlarged section taken from the boxed area in Figure 3

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

20
21 Hydromagnesite[8,10-14,26,32-34]

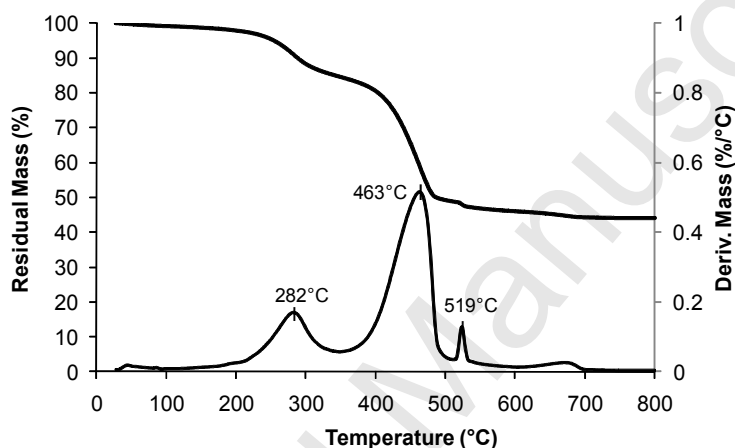


1 Huntite[15-18]



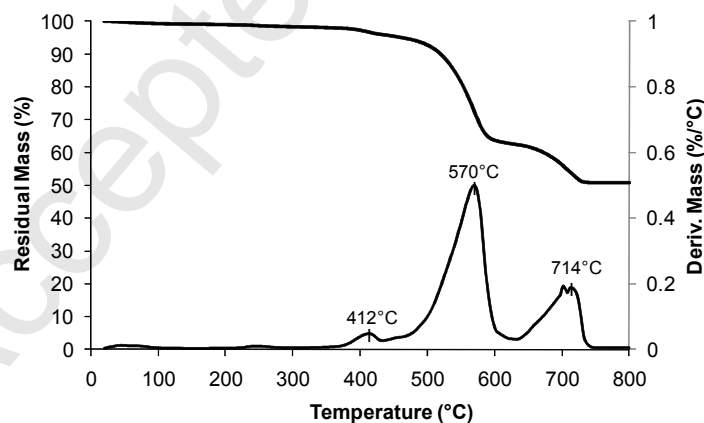
3
4
5 Typical thermogravimetric analysis (TGA), and derivative mass loss curves, using a T A
6 Instruments Q5000 at a heating rate of $10^\circ\text{C min}^{-1}$ in air, have been measured by the present
7 authors for natural hydromagnesite, natural huntite and a commercially available mixture of
8 hydromagnesite and huntite supplied by Minelco under the UltraCarb trade name. The results
9 are shown in Figure 5, Figure 6 and Figure 7 respectively.

10
11
12
13



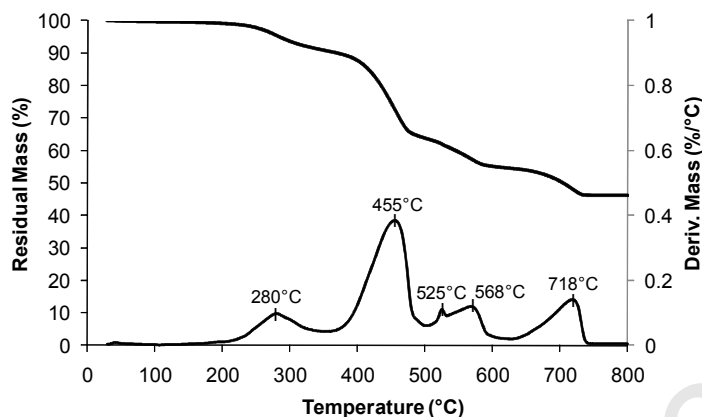
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Figure 5: TGA profile of natural hydromagnesite



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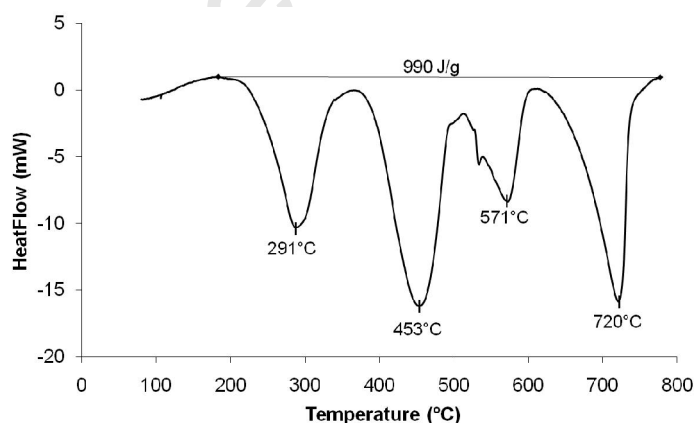
Figure 6: TGA profile of natural huntite



1
2
3 **Figure 7: TGA profile of an approximately 60:40 mixture of natural hydromagnesite and**
4 **huntite (UltraCarb)**

5
6 Decomposition of hydromagnesite begins to occur at about 220°C and progresses through
7 two major mass losses. Huntite begins to decompose at about 450°C and again progresses
8 through two major mass losses. The mixture of hydromagnesite and huntite provides a broad
9 decomposition range starting at about 220°C and being complete by about 740°C. During
10 these decomposition reactions approximately 54% of the original mass of the mixture of
11 hydromagnesite and huntite is released as carbon dioxide and water.

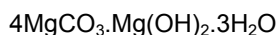
12
13 Figure 8 shows differential scanning calorimetry (DSC) measurement, made by the present
14 authors, using a Rheometric Scientifics DSC1500, under a nitrogen atmosphere, with a
15 heating rate of 10°C min⁻¹. A mixture of hydromagnesite and huntite shows that each of the
16 decompositions measured by TGA is associated with an endotherm. The total heat of
17 decomposition of the mixture is approximately -990 Jg⁻¹. This figure will vary depending on
18 the ratio of the two minerals.
19



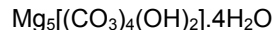
20
21 **Figure 8: DSC profile of a mixture of natural hydromagnesite and huntite (UltraCarb)**
22
23
24

25 **4. Chemical Formula and Crystal Structure of Hydromagnesite**

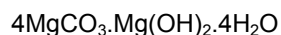
26
27 There is some variation in the chemical formula reported for hydromagnesite. Rothon
28 inadvertently illustrates this in his well regarded book[35] on particulate filled polymer
29 composites. The following formula is shown in one chapter[36] by Hancock and Rothon:



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



4
 5
 6 This formula would have equivalent composition to:



8
 9
 10 Therefore the amount of water of crystallisation differs, 4 moles are shown in the formula
 11 given by Frost[27] and Winchell[37] compared to only 3 moles in formula reported by Hancock
 12 and Rotheron[36].

13
 14 In the 1970's Todor[9] also made the point that in various mineralogical handbooks two
 15 formulae are given, one with three water molecules and one with four.

16
 17 Botha[25] introduces a third variation observing that hydromagnesite is a hydrated basic
 18 magnesium carbonate that can be synthesised in two forms, referred to as light and heavy
 19 magnesium carbonate with 4 and 5 water molecules respectively, adding a third variation.

20
 21 In 1972 Robie reported[38] that the geometry of the hydromagnesite unit cell was still in
 22 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
 23 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
 24 specific gravity, chemical and x-ray analysis lead him to the conclusion that the correct
 25 formula for a sample of hydromagnesite from Hindubagh, Pakistan contained four water
 26 molecules. A further sample of hydromagnesite from Soghan, Iran, analysed by Bariand[40] in
 27 1973 confirmed that the formula contained 4 water molecules in agreement with Robie[38],
 28 Winchell[37], and with Todor's[9] findings from thermal analysis. This now appears to be
 29 accepted and is the formula given by the Mineralogical Society of America in their Handbook
 30 of Mineralogy[19].

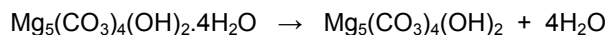
31
 32 Various studies[41-46] have been made on the crystalline structure of hydromagnesite.
 33 Murdoch[43] concludes that it is a monoclinic crystal with a pseudo-orthorhombic structure.
 34 Akao[46] first published a crystal structure of hydromagnesite in 1974. It was determined
 35 using three dimensional X-ray data. The structure was shown to be based on a three
 36 dimensional framework of MgO_6 octahedra with the magnesium atom surrounded by the six
 37 oxygen atoms. The octahedra share oxygen atoms with the surrounding octahedra forming a
 38 3 dimensional structure. The octahedra consist of two distinct structures. The first contains a
 39 magnesium atom surrounded by four oxygen atoms from carbonate ions, the fifth from a
 40 hydroxyl ion and the sixth from a water molecule. The second structure contains four
 41 carbonate ions and two hydroxyl ions. The strong C-O bonds of the carbonate ion reinforce
 42 the crystal by forming a triangular structure with three oxygen atoms from three different
 43 octahedra. In a subsequent publication[45] in 1977 Akao further developed understanding of
 44 the structure by determining in greater detail the positions of the remaining water molecules
 45 and the hydroxyl group. The hydroxyl group was shown to be shared between three MgO_6
 46 octahedra and does not take part in any hydrogen bonding, while the water molecules are
 47 located at unshared corners of the MgO_6 octahedron and form a network of hydrogen bonds.
 48 The water molecules are arranged so that the oxygen atoms are tetrahedrally surrounded by
 49 two hydrogen atoms, one magnesium atom and one hydrogen from a neighbouring water
 50 molecule. This hydrogen atom from the neighbouring water molecule forms a hydrogen bond,
 51 causing the water molecules to form a chain. The chain consists of one hydrogen atom in
 52 each water molecule forming a hydrogen bond to its neighbouring water molecule and the
 53 other hydrogen atom forming a hydrogen bond with oxygen in the carbonate groups. The
 54 three dimensional structures has been characterised in the excellent works of Akao[45,46]
 55 where detailed tables of interatomic distances, bond angles, diagrams of the crystal structures
 56 and in depth discussion and comment is given.

58 **5. Endothermic Decomposition of Hydromagnesite**

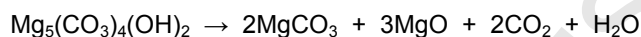
59

1 In the 1950's Beck [8] published information on the decomposition characteristics of a range
 2 of carbonate minerals including natural hydromagnesite from California. Beck quoted the
 3 chemical formula as $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$. He noted that the hydromagnesite went through
 4 a series of endothermic decompositions releasing water and carbon dioxide and published
 5 DTA curves to accompany his observations.

6
 7 Todor[9] published one of the earliest attempts to characterise the decomposition mechanism
 8 of hydromagnesite. Between 210°C and 395°C, the four water molecules are released.



11 Immediately following the loss of the four water molecules, between 395°C and 460°C, the
 12 loss of a carbon dioxide molecule occurs, followed by a reorganisation of the crystal structure.
 13 Todor does not give any detail on what this reorganisation involves. Between 460°C and
 14 515°C a fifth molecule of water is released due to the decomposition of the hydroxide group
 15 and a further carbon dioxide molecule is released.



17
 18 Finally over the temperature range of 515°C to 640°C a further two carbon dioxide molecules
 19 are released to leave a magnesium oxide residue.



21
 22 Todor notes that the complicated decomposition mechanism may have lead to some of the
 23 confusion over the actual chemical structure of hydromagnesite. However this precise
 24 mechanism and order of events is not in agreement with that of more recent work, as
 25 discussed below.

26
 27 Padeste[33] showed that hydromagnesite decomposes through different mechanisms
 28 depending on the surrounding atmosphere. In the absence of carbon dioxide only two
 29 decomposition stages were observed; the loss of the crystalline water, followed by the
 30 combined dehydroxylation and decarbonation. However, under carbon dioxide the
 31 dehydroxylation and decarbonation were thought to occur separately, giving three steps.

32
 33 In the late 1970's Sawada published a number of papers[10-14] investigating in detail the
 34 decomposition of hydromagnesite. These investigations included the effect of different
 35 gaseous atmospheres at varying partial pressures on the decomposition of hydromagnesite.
 36 He confirmed that under a nitrogen atmosphere the decomposition of hydromagnesite occurs
 37 through only two steps. Increasing the partial pressure of carbon dioxide was found to
 38 strongly influence the decomposition[10], separating the single loss of carbon dioxide
 39 between 350°C and 500°C into three distinct losses at 350°C – 500°C, 500°C – 520°C and
 40 530°C – 650°C. The first and third losses of carbon dioxide were found to be endothermic,
 41 while the middle loss was exothermic. This effect was also observed on increasing the
 42 heating rate. Low heating rates gave only one decarbonation step which split into two and
 43 which were then separated by a third sharp exothermic decomposition at even higher heating
 44 rates, presumably due to the local increase in the partial pressure of carbon dioxide in the
 45 bulk of the solid.

46
 47 Further study[11] under helium also showed dehydration below 300°C followed by a single
 48 decarbonation step between 300°C and 500°C, while XRD analysis showed an amorphous
 49 structure, with no indication of magnesium carbonate crystals. Above 500°C, magnesium
 50 oxide was detected by XRD with the peaks becoming sharper and stronger at higher
 51 temperatures. When the same decomposition was carried out under helium and carbon
 52 dioxide ($P_{CO_2}=0.5$ atm) the dehydration below 300°C was unaffected. Samples examined
 53 using XRD after the occurrence of the exotherm at about 520°C showed the presence of
 54 crystalline magnesium carbonate. It is therefore concluded that under conditions of high
 55 partial pressure of carbon dioxide, or high heating rates, exothermic crystallisation of
 56 magnesium carbonate occurs at about 520°C. The magnesium carbonate then decomposes
 57
 58
 59

1 through decarbonation to magnesium oxide, between 530°C and 650°C. This led Sawada to
 2 propose two types of decomposition for hydromagnesite[12]
 3

4 Type I: $P_{\text{CO}_2} < 0.1$ atm - The amorphous carbonate formed after dehydration decomposes
 5 directly to magnesium oxide.
 6

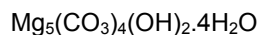
7 Type II: $P_{\text{CO}_2} \sim 1$ atm – The amorphous carbonate formed after dehydration partially
 8 decarbonates followed by exothermic crystallisation of magnesium carbonate at about 520°C.
 9 The magnesium carbonate then itself decarbonates to magnesium oxide between about
 10 530°C and 650°C.
 11

12 Having investigated the effects of carbon dioxide partial pressures at atmospheric pressure
 13 Sawada went on to investigate the decomposition of hydromagnesite under high pressure
 14 atmospheres[12]. Increasing pressures of nitrogen, argon, and carbon dioxide had no effect
 15 on the dehydration temperature up to 50 atm. Increasing pressures of argon, and nitrogen
 16 had minimal effect on the temperature of the exothermic crystallisation of magnesium
 17 carbonate and subsequent decarbonation. Increasing pressures of carbon dioxide had a
 18 significant effect. The temperature of the exothermic crystallisation of magnesium carbonate
 19 was linearly reduced by about 30°C as the pressure was increased from 1 to 50 atm, while
 20 the peak of decomposition of the resultant magnesium carbonate increased to just less than
 21 700°C. At pressures of carbon dioxide above about 10 atm a third decomposition mechanism
 22 was identified. This was given the classification of Type III by Sawada, in which a second
 23 exotherm occurred at a slightly lower temperature than the Type II exotherm. An intermediate
 24 phase is formed before the occurrence of the Type II exotherm and the formation of
 25 crystalline magnesium carbonate.
 26

27 These differing mechanisms have implications for the decomposition mechanism of
 28 hydromagnesite in polymer compounds for two reasons. First, the heating rate in a fire
 29 situation is likely to be high and the self generated carbon dioxide atmosphere will both
 30 contribute to the formation of the crystalline magnesium carbonate and associated higher
 31 decomposition temperature of the Type II decomposition mechanism. Second, in a
 32 hydromagnesite-polymer composite the local partial pressure of carbon dioxide during
 33 hydromagnesite decomposition is likely to be much higher than atmospheric pressure due to
 34 the tortuous route from the surface of the hydromagnesite crystal to the polymer–gas
 35 interface on the surface.
 36
 37

38 **6. Comparison of Synthetic Hydromagnesite with Naturally Occurring Blends of** 39 **Hydromagnesite and Huntite.**

40 More recently Haurie et al.[29] studied the use of synthetic hydromagnesite with the following
 41 chemical formula:
 42



44 It had a total decomposition endotherm of 800 Jg⁻¹ associated with the loss of carbon dioxide
 45 and water. Decomposition studies using TGA/DTA at 10°C min⁻¹ in air showed that it
 46 decomposed in three steps as follows:
 47
 48

- 49 200–250°C release of water of crystallisation
- 50 380–450°C release of water from decomposition of the hydroxides
- 51 510–550°C release of carbon dioxide from decomposition of the carbonate
- 52
- 53

54 The three decomposition stages detected in the synthetic hydromagnesite were also detected
 55 in mixtures of natural hydromagnesite and huntite (UltraCarb) although the temperatures
 56 varied slightly. In addition two peaks at 540–600°C and 725–780°C due to decomposition of
 57 huntite were observed.
 58

59 The synthesis and three step decomposition of hydromagnesite is also discussed by
 60 Botha[25]. The second study[32] discusses the decomposition of hydromagnesite and then

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

12 One work[27] differs from most others in the decomposition temperatures reported. Frost
13 reports that a 5°C min⁻¹ heating rate gives decomposition temperatures of 135, 184, 412 and
14 474°C for hydromagnesite that he synthesised. The first two decompositions at 135 and
15 184°C are attributed to loss of water of crystallisation in two steps, each giving a loss of two
16 water molecules. The third decomposition at 412°C is attributed to dehydroxylation.
17 Decarbonation is said to occur at 412°C and 474°C. These conclusions are all drawn through
18 comparisons of theoretical mass losses compared to the mass losses measured using TGA,
19 no analysis of the gases emitted during the decomposition appears to have been made.
20 Comparing with other authors' work[8,25,29,30,32] the first two decompositions seem to
21 occur at very low temperatures. Frost comments on this, referring to the fact that Beck[8]
22 found decomposition temperatures between 275 and 325°C for loss of water, and loss of
23 carbon dioxide at 485°C and again at 565 – 600°C. Frost appears to question the validity of
24 Beck's results at this stage, stating that "the results of Beck are so significantly different that
25 the measurement is open to question". The difference in the higher temperature
26 decompositions appears to arise from the fact that Frost did not find the exotherm that Beck
27 had reported. However several workers[10-14,33,47] have published work showing the
28 conditions needed for the exotherm to occur. One of these conditions being a heating rate of
29 greater than 18°C min⁻¹. It is therefore unsurprising that no exotherm was seen by Frost at
30 heating rates of 5°C min⁻¹. Beck does not state what heating rate he used, however the strong
31 exotherm that was detected suggests it was fairly fast.
32

33 Frost[27] also used controlled rate thermal analysis to study the decomposition of this sample
34 of synthetic hydromagnesite. This method involved using a variable heating rate, up to a
35 maximum of 1 °C min⁻¹, in order to maintain a constant decomposition rate of 0.1mg min⁻¹.
36 These very slow heating rates showed that the sample went through five stages of
37 decomposition with mass losses at 100°C and 145°C being attributed to dehydration.
38 Dehydroxylation was shown to occur at 203°C followed by isothermal loss of carbon dioxide
39 at 370°C. At 409°C a second brief isothermal was measured, Frost suggests this may be due
40 to the recrystallisation of magnesium oxide as suggested by Beck[8]. Comparison of these
41 results with those achieved at a fixed 5°C min⁻¹ clearly illustrates how the decomposition of
42 hydromagnesite is affected by the rate of heating. There is no one true decomposition
43 mechanism for the mineral and no "correct" method for measuring the decomposition, but a
44 number of mechanisms depending on the test conditions.
45

46 Frost's work was carried out using synthetic hydromagnesite produced in his own laboratory.
47 He reported that the hydromagnesite produced was characterised for phase specificity using
48 XRD and chemical composition using EDX although details of these analysis are not shown.
49 Perhaps, as the TGA decomposition temperatures suggest, the product produced was not
50 true hydromagnesite. Frost's own calculations based on measured mass losses leads him to
51 conclude (in an appendix not discussed within the text) that the formula for the
52 hydromagnesite that he had synthesised was Mg₅(CO₃)₄(OH)₂.2H₂O. This may well explain
53 the disagreement between the decomposition temperatures reported in the work and that of
54 other authors. Clearly the material that he synthesised was not true hydromagnesite as it did
55 not contain enough water. As the work of Botha[32] showed the process of hydration can take
56 some weeks at ambient conditions and would certainly influence the crystal structure[45,46]
57 since the water molecules form a network of hydrogen bonding with the carbonate ions. This
58 oversight has to throw doubt on the validity of any comparisons made between this work and
59 that of previous authors.
60

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.

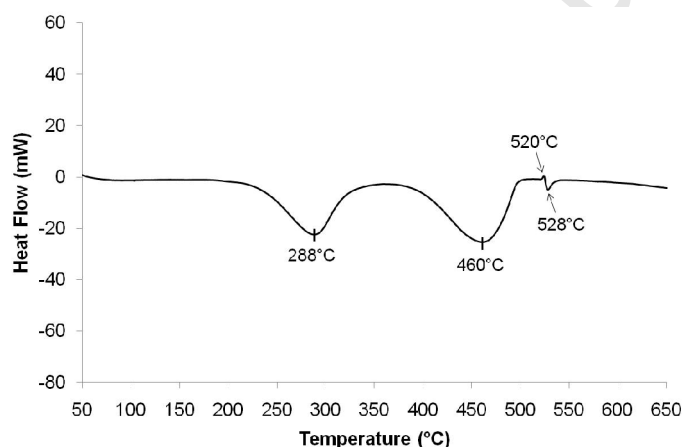


Figure 9: Decomposition of hydromagnesite measured by DSC at 10°C min⁻¹ in air

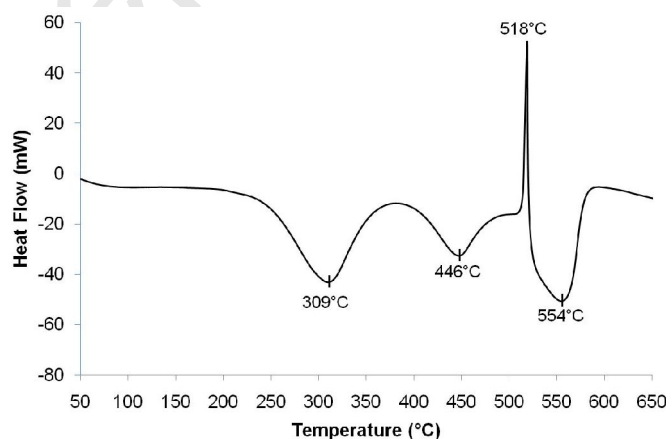


Figure 10: Decomposition of hydromagnesite measured by DSC at 20°C min⁻¹ in air

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

1 hydromagnesite was reported. This exotherm was reported to result from '*the formation of*
2 *amorphous (?) MgO which inverts to cubic MgO at 510°C*'. The question mark in parenthesis
3 suggests that Beck was not sure whether the magnesium oxide was actually amorphous at
4 this stage.

5
6 In the early 1970's Todor[9] made the observation that an exotherm could be detected at a
7 range of temperatures between 385°C and 460°C. Most other researchers, as discussed
8 below, are in agreement that the exotherm occurs between about 510°C and 530°C which is
9 consistent with Figure 10. However, Todor gives no details of the test conditions that gave
10 this wide temperature range, so it is difficult to comment on their validity.

11
12 Further investigation in the 1970's by Sawada[10] confirms that an exothermic event occurs
13 under certain specific conditions. The conditions favouring the exotherm include a high partial
14 pressure of carbon dioxide, dense packing of the sample and a high heating rate. The
15 exotherm was not seen at a heating rate of 10°C min⁻¹ but was seen at 20°C min⁻¹. In a later
16 paper again by Sawada[14] further investigation into the exotherm confirms that it is due to
17 the crystallisation of magnesium carbonate from the amorphous phase.

18
19 Padeste's work [33] from 1991 gives a detailed analysis of the decomposition of
20 hydromagnesite under nitrogen and carbon dioxide atmospheres. Under nitrogen only two
21 decomposition stages are observed in hydromagnesite, under carbon dioxide the second
22 decomposition stage resolves itself into two separate stages separated by an exotherm. It is
23 reported that the exotherm is caused by the crystallisation of magnesium carbonate after the
24 loss of the hydroxide group. X-ray diffraction was used to confirm that this crystallisation
25 occurred.

26
27 More recently, in 2001, Khan[47] carried out some investigation into the exothermic peak in
28 the decomposition of hydromagnesite. This work again confirmed the presence of the
29 exotherm under certain conditions. DTA analysis revealed, in a nitrogen atmosphere, that no
30 exotherm was observed for heating rates of less than 18°C min⁻¹ but at 18.5°C min⁻¹ or faster
31 an exotherm was seen at about 525°C. The size of the exotherm increased as the heating
32 rate was increased above 18.5°C min⁻¹. The magnitude of the exotherm was reported to
33 increase and also occur at a lower heating rate as the sample size was increased. Khan also
34 investigated the effect of a carbon dioxide atmosphere, this gas caused the exotherm to be
35 observed at much lower heating rates and with smaller sample sizes. Although Sawada[10]
36 did not report any exotherm in a nitrogen atmosphere, his conclusion that carbon dioxide and
37 high heating rates are required is consistent with this work. Khan also suggests that the
38 exotherm is due to mechanical stress within the crystal structure caused by the release of
39 carbon dioxide which becomes trapped. This trapped gas is then suddenly released resulting
40 in a small 'explosion within the sample'. The mechanical breakdown of the crystallite and the
41 release of heat energy associated with the explosive release of the carbon dioxide is given as
42 the cause of the exotherm. This theory is based on the fact that a sudden mass loss is
43 associated with the exotherm and that electron microscopy shows that the magnesium oxide
44 residue appears more "fluffy and dispersed" in samples that have been through the
45 exothermic decomposition than those that are decomposed without the exothermic event.
46 Such sudden eruptions, especially close to ignition temperatures, could extinguish early
47 flaming increasing the ignition resistance of polymers using hydromagnesite compounds as
48 fire retardant additives.

49
50 Clearly an exothermic event does occur during the decomposition of hydromagnesite under
51 certain conditions but at least two different theories about its origin have been proposed.
52 Sawada's work[10-14] is the most detailed and appears the most reliable. Therefore the
53 explanation of the exotherm being due to the crystallization of magnesium carbonate seems a
54 likely explanation. Sawada attributes the sudden mass loss to a sudden increase in the rate of
55 decarbonation, caused by the exotherm. This theory is also consistent with the data
56 presented in Figure 9 and Figure 10. This data clearly shows the presence of an exotherm at
57 about 520°C which is dependant on heating rate when measured in air. The appearance of
58 an endotherm between 520°C and 590°C is consistent with the subsequent decomposition of
59 crystalline magnesium carbonate following its exothermic crystallisation at 520°C.

60

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

- 5
- 6 1) endothermic loss of water of crystallisation
- 7 2) endothermic dehydroxylation and formation of amorphous magnesium
8 carbonate
- 9 3) exothermic crystallisation of magnesium carbonate
- 10 4) endothermic decarbonation of magnesium carbonate
- 11

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

13
14 In none of these studies was the effect of the exothermic event on fire retardancy studied. In
15 fact Inglethorpe[49] is the only researcher to comment on the fact that the exotherm could
16 have a detrimental effect on fire retardant properties. However, as can be seen from Figure
17 10 the heat emitted by the exotherm (which is proportional to the area under the curve) is
18 small in comparison to the total heat absorbed by the endothermic decomposition of
19 hydromagnesite. All of these studies were carried out on the mineral alone, not on polymer
20 compound containing the minerals. The existence of the exothermic event occurring in a
21 burning polymer containing hydromagnesite has not been reported. Inglethorpe is the only
22 researcher to comment on this, suggesting that such a detrimental effect is only likely in
23 polymer compounds with high loading levels of the minerals. In the case of commercially
24 available mixtures of hydromagnesite and huntite, the temperature range of the endothermic
25 decomposition of the huntite overlaps the hydromagnesite exotherm. This will remove some
26 of the heat generated by the crystallisation of the magnesium carbonate. This effect can be
27 seen in Figure 8, the exotherm is present as a slight discontinuity in the curve at about 530°C
28 but the endotherm of the huntite outweighs the exotherm of the hydromagnesite.

31 **8. Influence of Particle Size, Milling and Surface Coating on the Decomposition** 32 **Mechanism**

33
34 In much of the work discussed no information is given on the particle size of the mineral
35 powders. This could have an influence on the decomposition due to thermal conduction within
36 the particles and may explain some of the differences in decomposition temperatures and
37 mechanisms reported at apparently similar test conditions. Haurie[30] has carried out some
38 studies into the effect of particle size reduction through different milling processes on the
39 thermal decomposition characteristics of synthetic hydromagnesite. It was found that
40 mechanical milling methods could cause an increase in the decomposition rate between
41 400°C and 500°C and reduce the exothermic crystallisation of magnesium carbonate. This
42 was suggested to result from the milling action causing defects in the crystal lattice resulting
43 in the early release of carbon dioxide. Particle size reduction using an air jet mill did not cause
44 significant changes in the decomposition profile of the hydromagnesite. Haurie makes the
45 comment that these changes could influence the fire retardant efficiency of the synthetic
46 hydromagnesite but that further work is needed to investigate this.

47
48 Earlier work by Haurie[28] showed that coating of synthetic hydromagnesite with stearic acid,
49 which is frequently used as compatibiliser to aid dispersion of the filler within a polymer, also
50 has an effect on the decomposition of the mineral. Levels of 3% and above influence the
51 decomposition in the region of 350–450°C causing a faster rate of decomposition. A similar
52 effect has been reported for magnesium hydroxide[36] where stearate coating has been
53 shown to increase the rate of decomposition, suggesting that the acid protonates the
54 hydroxide with the release of water. Haurie states that the TGA tests were carried out under
55 an oxygen atmosphere at a heating rate of 10°C min⁻¹. The decomposition profile for the
56 uncoated hydromagnesite shows the same distinctive three step decomposition reported by
57 Sawada[12] as Type II decomposition, even though the test was carried out under oxygen
58 with a low heating rate. As the stearic acid coating level was increased to 4.5% the
59 decomposition profile as measured by TGA gradually became more like the Sawada's Type I
60 decomposition. The rate and magnitude of the decomposition between about 350 – 450°C

1 increased and the magnitude of the decomposition above 480°C correspondingly decreased.
2 Haurie shows that X-Ray diffraction shows a stronger, more defined magnesium oxide peak
3 when hydromagnesite coated with 4.5% stearic acid is heated at 400°C for one hour,
4 compared to an uncoated sample. This indicates a higher degree of crystallinity in the
5 magnesium oxide. No attempt to determine the phase changes in terms of formation and
6 decomposition of a crystalline magnesium carbonate during the decomposition were made.
7 However, taking into account Sawada's detailed work[10-13] it would appear that the stearic
8 acid could be preventing the formation of crystalline magnesium carbonate, causing the
9 hydromagnesite to decompose directly to magnesium oxide. A similar effect on the
10 decomposition profile was also seen by Haurie[30] when hydromagnesite was mechanically
11 ground to smaller particle sizes. The method used for coating the stearic acid was a heated
12 high speed mixer. It is possible that similar stresses resulting in defects are being introduced
13 into the crystal structure through the mechanical action of coating the filler, as they are during
14 mechanical grinding.

15 16 17 **9. Structure and Decomposition of Huntite**

18
19 The earliest reference to huntite is a paper by George Faust[16] from 1953 in which the
20 discovery of a new mineral in Nevada was announced. Faust acknowledges that the mineral
21 probably had been discovered previously but had been misidentified as impure magnesite by
22 W. E. Ford in 1917. Faust announced that the new mineral was to be named huntite in honour
23 of his former teacher, Walter F. Hunt, Professor of Petrology at the University of Michigan
24 from 1922 until 1933 and editor of American Mineralogist for 35 years[50]. Faust carried out
25 DTA analysis of the newly discovered mineral, huntite, discovering that it went through
26 endothermic decompositions at 644°C and 901°C, these decompositions were attributed to
27 the dissociation of $MgCO_3$ and $CaCO_3$ respectively. It was also shown by chemical analysis
28 that the chemical formula for huntite was $Mg_3Ca(CO_3)_4$.

29
30 The crystal structure of huntite is somewhat simpler than hydromagnesite. In 1962 Graf and
31 Bradley[51] described it as an ordered rhombohedral double carbonate, similar to a deformed
32 face centred cube. The calcium atom is located at the origin with three magnesium atoms at
33 the face centres and three carbonate groups at the edge centres, the final carbonate group is
34 located at the body centre. For detailed information regarding the crystal structure of huntite,
35 including tables of d spacings, structural factors, interatomic distances and structural
36 diagrams, the reader should refer to Graf and Bradley's work[51].

37
38 In 1966, a white powder was discovered on the wreck of a Roman ship. Barbieri[17] carried
39 out an analysis on the powder identifying it as huntite. DTA analysis confirmed that it went
40 through two endothermic decompositions, one at 650°C and one at 910°C, much the same as
41 the findings of Faust. Barbieri also went into some detail trying to determine whether the
42 huntite had formed from some other mineral such as magnesite due to being submerged in
43 sea water for many years. Their chemical analysis concluded that it was most likely that the
44 huntite was in its original form and that therefore the Romans were in fact trading huntite. The
45 fact that huntite was used in the ancient world is confirmed by Riederer[52] in a paper
46 indentifying pigments used by the ancient Egyptians. A bowl that had been excavated in
47 Nubia and accurately dated to 1600BC was analysed and it was shown that huntite was used
48 as a white pigment. It therefore seems reasonable that the Roman ship (dated to the 3rd
49 century AD) may well have been trading huntite as part of its cargo. There is also
50 evidence[53] that huntite was used as a white pigment in Cambodian manuscripts from the
51 18th and 19th centuries.

52
53 Ozao and Otsuka[15] stated in 1985 that a detailed study of the decomposition of huntite had
54 not yet been carried out. They went on to describe their work in this area, confirming the
55 previously known decompositions shown by Faust[16] and Barbieri[17]. Ozao's DTA curves,
56 measured in a carbon dioxide atmosphere, of mechanical mixtures of magnesite ($MgCO_3$)
57 and calcite ($CaCO_3$) were shown to be clearly different to those of huntite ($Mg_3Ca(CO_3)_4$). The
58 distinctive peaks associated with the decomposition of the magnesium carbonate and the
59 calcium carbonate were present in the huntite but they occurred at slightly lower
60 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.

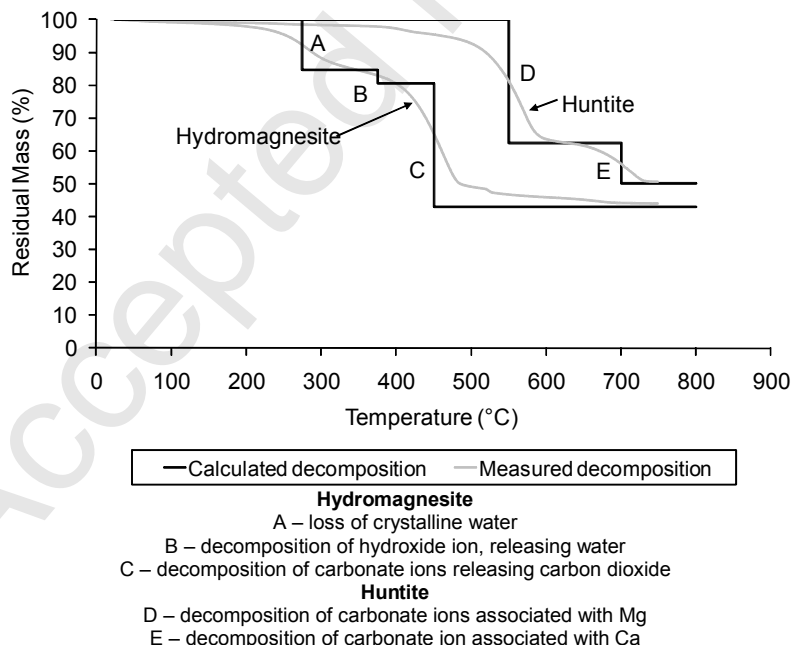
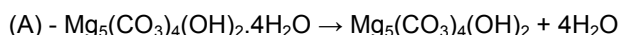
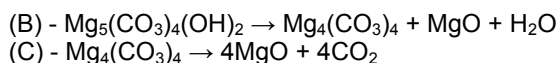


Figure 11: Decomposition of hydromagnesite and huntite compared to the calculated theoretical mass losses

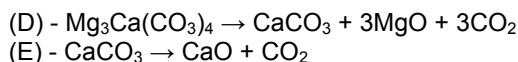
There are three decomposition steps associated with the decomposition of hydromagnesite which are marked in Figure 11 as A, B, and C.





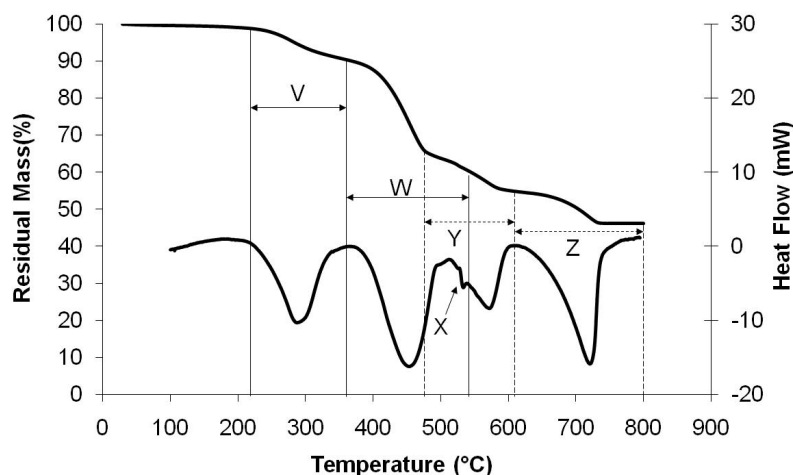
3
 4 These three steps are associated with cumulative mass losses of 15.45%, 19.31% and
 5 57.08% respectively. It can be seen in Figure 11 that these calculated mass losses
 6 correspond quite closely to the mass losses measured for hydromagnesite by TGA.

7
 8 Huntite has two steps associated with its decomposition; these are marked as D and E in
 9 Figure 11.



12
 13 These two steps are associated with cumulative mass losses of 37.5% and 50.0%
 14 respectively. Again, the calculated mass losses correspond quite closely to the mass losses
 15 measure for huntite by TGA.

16
 17 Figure 12 summarises the decomposition mechanisms discussed above, and in the previous
 18 sections, in relation to the decomposition of UltraCarb; a natural mixture of hydromagnesite
 19 and huntite. The data shown in Figure 12 was measured by the present authors, in air at a
 20 heating rate of $10^\circ\text{C min}^{-1}$. At this heating rate only a minimal amount of crystallisation of
 21 magnesium carbonate is expected to occur during the decomposition.
 22
 23
 24



25 V – Loss of water from hydromagnesite approx. $220^\circ\text{C} - 350^\circ\text{C}$
 26 W – Loss of carbon dioxide from hydromagnesite approx. $350^\circ\text{C} - 550^\circ\text{C}$
 27 X – Exothermic crystallisation of magnesium carbonate
 28 Y – Initial loss of carbon dioxide from huntite
 29 Z – Secondary loss of carbon dioxide from huntite
 30
 31
 32

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

35
 36
 37 An initial mass loss and associated endotherm (V) between the temperatures of 220°C and
 38 350°C is due to the loss of crystalline water from the hydromagnesite. This is followed by a
 39 second step in mass loss. In Figure 11 it is clear that this mass loss, associated with the loss
 40 of carbon dioxide from the hydromagnesite, is not complete until about 540°C (W). It,
 41 therefore, overlaps with the initial mass loss associated with loss of carbon dioxide from the
 42 huntite (Y). The loss of the hydroxyl group from hydromagnesite as water is not detected as a
 43 separate mass loss in Figure 12. However, it was reported by Haurie[29] that this loss of
 44 water occurs between 380°C and 450°C which would mean that it occurs in the lower half of
 45 region W in Figure 12. This region also covers the temperature range where carbon dioxide is

1 being lost from the hydromagnesite. At about 520°C a slight discontinuity is seen in the DSC
2 graph (X). This is the temperature at which the exothermic crystallisation of magnesium
3 carbonate has been reported. The heating rate used for this measurement was 10°C min⁻¹
4 which is why the exotherm is very small, indicating that there is only very minimal
5 crystallisation of magnesium carbonate. It also occurs in the temperature range (Y) at which
6 huntite is endothermically decomposing. Figure 11 shows that above 520°C there is a
7 continued slow loss in mass from hydromagnesite up to about 700°C which is probably slow
8 degradation of the small amount of crystalline magnesium carbonate.

9
10 Figure 11 shows that huntite begins to decompose rapidly at about 470°C. This loss in mass
11 with its associated endotherm is complete at about 610°C. The decomposition over this
12 temperature range (Y) is due to the loss of carbon dioxide from the carbonate groups
13 associated with the magnesium ions. A final mass loss and endotherm (Z) between 610°C
14 and 800°C is due to a final loss of carbon dioxide resulting from the decomposition of the
15 carbonate groups associated with the calcium ions.

16
17 At 800°C the hydromagnesite has decomposed to leave a magnesium oxide residue and the
18 huntite has decomposed to leave a mixture of calcium oxide and magnesium oxide.

19 20 21 **11. Implications for the Suitability of Mixtures of Hydromagnesite and Huntite as** 22 **Fire Retardant Additives**

23
24 It is generally accepted[54-56] that for metal hydroxides to act as effective fire retardant
25 additives in polymer composites the decomposition temperature of the polymer must be
26 closely matched by the endothermic decomposition temperature of the metal hydroxide. The
27 rate of polymer decomposition is therefore slowed because of the heat absorbed by the
28 decomposing metal hydroxide and the released water dilutes the flammable polymer
29 decomposition products. The metal oxide residue also acts as a thermal barrier to further
30 decomposition of the underlying polymer.

31
32 A mixture of hydromagnesite and huntite meets all of the above requirements and compared
33 to the commonly used metal hydroxides may well provide some further benefits. The initial
34 decomposition temperature of hydromagnesite has been shown[8-14,33] to be about 220°C
35 compared to 180 – 200°C for ATH[5]. This gives it the advantage of being able to withstand
36 higher processing temperatures meaning that it is suitable for polymers with higher melt
37 temperatures such as polypropylene where ATH cannot be used.

38
39 When used as a fire retardant additive the rate of temperature increase that hydromagnesite
40 will experience within a burning polymer is likely to be well in excess of the 18.5°Cmin⁻¹ that
41 Khan[47] found to be the point at which crystallisation of magnesium carbonate occurs. The
42 hydromagnesite particles will also be held in a self generated carbon dioxide atmosphere,
43 which will also contribute to the decomposition mechanism becoming close to that described
44 by Sawada[12] as type II decomposition. These effects mean that, within a polymer
45 composite, hydromagnesite will be likely to follow the mechanism of releasing water at about
46 220°C, followed by partial decomposition of the carbonate ions up to 520°C and creation of a
47 high partial pressure of carbon dioxide around the particles. Following the crystallisation of
48 magnesium carbonate the final release of carbon dioxide will occur up to 600°C. This gives
49 hydromagnesite a wide decomposition range making it suitable for reducing flammability of a
50 wider range of polymers.

51
52 Initially huntite may appear to have a decomposition temperature that is too high for fire
53 retardancy in polymers. However it is feasible that it may provide some benefit in high
54 temperature polymers such as polyetheretherketone (PEEK). Studies of the decomposition
55 mechanisms[57] of this polymer show that it does not begin to decompose until 575°C.
56 PEEK's melting point of 343°C makes both aluminium hydroxide and magnesium hydroxide
57 unsuitable. Huntite's initial decomposition temperature of about 400°C and endothermic
58 release of carbon dioxide up to 750°C makes it an interesting possible additive for this
59 polymer. Of course only pure huntite would be suitable, any hydromagnesite present would
60 decompose during melt processing.

1
2 In mixtures with hydromagnesite, huntite's platy morphology may provide a barrier to the
3 transport of combustible decomposition products to the flame. It may also enhance
4 mechanical reinforcement of carbonaceous or inorganic char. Once formed into a char layer
5 huntite will also provide additional protection to the underlying polymer through further
6 endothermic decomposition in response to high external heat fluxes. These functions will not
7 be provided by magnesium hydroxide or aluminium hydroxide due to their complete
8 decomposition at lower temperatures.
9

10 **12. Conclusions**

11
12 The chemical composition and crystalline structure of huntite has been well defined. Its
13 endothermic decomposition through evolution of carbon dioxide to leave a mixed residue of
14 magnesium oxide and calcium oxide has been well characterised.
15
16

17 There has been some difference in opinion over the chemical structure of naturally occurring
18 hydromagnesite. This may have arisen from the fact that it is possible to synthesise several
19 chemicals of very similar chemical structure but with varying amounts of water present.
20 However it seems that the accepted geological definition of hydromagnesite is
21 $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. Synthetic hydrated basic magnesium carbonate has the same
22 structure and can be produced in two forms known as "light" and "heavy" corresponding to
23 structures that contain 4 water molecules (as in the natural form) or 5 water molecules. The
24 formula containing 3 water molecules may be due to inaccurate analysis. However, other
25 hydrated hydroxy carbonates are closely related to hydromagnesite in terms of chemical
26 formula and stoichiometry. In cases where analysis was made on the basis of DTA or TGA
27 alone the samples may not have been pure hydromagnesite leading to some of the
28 differences in results.
29

30 The decomposition of hydromagnesite is influenced by a number of factors, including heating
31 rate and composition of the atmosphere. High heating rates or partial pressures of carbon
32 dioxide causes the decomposition to progress through an exothermic crystallisation of
33 magnesium carbonate after water has been lost from the structure. This causes the carbonate
34 ions to decompose at a higher temperature than they do in the absence of carbon dioxide. At
35 higher heating rates the carbon dioxide generated by the decomposition of the carbonate ions
36 has less time to disperse, encouraging the crystallisation of the remaining magnesium
37 carbonate. In mixtures of hydromagnesite with huntite the endothermic decomposition of the
38 huntite overlaps with the exothermic event in the hydromagnesite reducing the overall effect
39 of the exotherm. There is no single decomposition mechanism for hydromagnesite, and the
40 commonly held belief that slower heating rates give more accurate thermal analysis results
41 does not hold true for this mineral since higher heating rates are needed in order to study the
42 exothermic crystallisation of magnesium carbonate. The main commercial use of
43 hydromagnesite is as a fire retardant, therefore understanding of the decomposition
44 mechanism at high heating rates is more important for this application than at slow heating
45 rates or controlled rates of decomposition.
46

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