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# The Fire Retardant Effects of Huntite in Natural Mixtures with Hydromagnesite

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## Abstract

The fire retardant effects of natural mixtures of huntite and hydromagnesite have been investigated. As well as being entirely natural these mixtures of minerals can be considered "greener" and more environmentally friendly, in their production methods, than alternatives such as aluminium hydroxide and magnesium hydroxide. It has been shown that the release of water and carbon dioxide from hydromagnesite helps to increase the time to ignition and peak heat release in cone calorimeter testing. Huntite has been shown to decrease the average rate of heat release and increase the strength of the residue. Electron microscopy has shown that the huntite particles maintain their platy morphology during combustion in the cone calorimeter. The morphology of these particles helps to reduce the rate of heat release by slowing the release of flammable decomposition products to the flame. The platy shape of the huntite particles increases the strength of the residue containing higher proportions of this mineral. Huntite is shown to play an active part in improving fire retardancy when used in a mixture with hydromagnesite, giving performance for typical mixtures comparable to those of aluminium hydroxide.

## Introduction

This paper forms the final part in a recent series of papers by the current authors highlighting the thermal decomposition and fire retardant behaviour of natural mixtures of huntite and hydromagnesite[1-4]. Mixtures of huntite and hydromagnesite form naturally and are commercially mined and processed as an alternative to the commonly used mineral filler fire retardants, aluminium hydroxide (ATH) and magnesium hydroxide (MDH). It has been argued that such mixtures are a 'greener', more environmentally friendly alternative to these more widely used fire retardants because of a cleaner, less energy intensive production process.

ATH is produced from bauxite using the Bayer process[5] which involves dissolving bauxite ore in concentrated sodium hydroxide at temperatures up to 270°C. After separation of the remaining solids (red mud), the aluminium oxide is precipitated from the solution. The red mud is a highly alkaline, toxic product. The conventional way of disposing of the red mud is to collect it in artificial lakes held back by a dam where the mud naturally dries. Once the lake is full and dried it can be sealed and buried. However, if storage of the mud is not carefully managed the consequences can be dire, as illustrated by the 2010 accident in Hungary[6], resulting in contamination of land and waterways.

Natural magnesium hydroxide exists in the form of brucite and is commercially exploited as a fire retardant. However, the most common form of magnesium hydroxide is precipitated from sea water or brine through reaction of magnesium chloride in the brine with lime or dolomitic lime[7].

Production methods for both ATH and magnesium hydroxide involve the use of a mined mineral (bauxite, lime) followed by a chemical process, and in the case of ATH, the storage and disposal problems of the red mud. Commercially exploited natural reserves of mixed huntite and hydromagnesite are very pure and do not need chemical processing or precipitation of the final product. This makes production of fine particle size mixtures of huntite and hydromagnesite much less energy intensive. The only by product is a small quantity of dolomite, $MgCa(CO_3)_2$, a mineral closely related to huntite, $Mg_3Ca(CO_3)_4$. Dolomite is a very white mineral that occurs naturally in the mixture and is removed during the grinding process. It finds industrial application due to its high brightness in surface coatings.

Previous authors have discussed the decomposition of huntite[1,3,4,8-11] and hydromagnesite[1,3,4,8,12-24]. Natural hydromagnesite particles have a blocky morphology[1,2] and once processed the majority of the particles are usually between 1 and 10 µm in diameter depending on the processing. It has the following chemical formula[25] and thermally decomposes[1,3], between about 220°C and 550°C in two stages, initially releasing water then carbon dioxide, leaving a solid residue of magnesium oxide.

$$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O \rightarrow 5MgO + 4CO_2 + 5H_2O$$

Huntite particles have a platy morphology[1,2] and the particles are usually about 1 µm or less in diameter, much smaller than hydromagnesite particles. It has the following chemical formula[26] and thermally decomposes[1,3], between about 450°C and 750°C in two stages, releasing only carbon dioxide, leaving a solid residue of magnesium oxide and calcium oxide.

$$Mg_3Ca(CO_3)_4 \rightarrow 3MgO + CaO + 4CO_2$$

The thermal decomposition of mixtures of these minerals through endothermic release of carbon dioxide and water has led to several studies showing their potential applications, including fire retardant additives for polymer compounds[2,4,27-46], controlling burning rates in cigarettes[47,48], and as a potential material for fighting forest fires[49-53]. Due to its high decomposition temperature it has been suggested[40,41,43] that huntite has little more influence than an inert diluent filler in terms of fire retardancy. It has been argued by the current authors[2] that the evidence in the literature does not back up this assertion. Details of recent work, presented here, demonstrates that huntite contributes significantly to the fire retardant properties of polymer compounds, filled with mixtures of huntite and hydromagnesite, in ways that had perhaps not been considered previously.

## Experimental

### Materials

Mixtures of huntite and hydromagnesite with different ratios of the two minerals were supplied by Minelco Ltd. The samples are labelled throughout this work according to the ratio of the two minerals. For example HU43HM50 signifies that the sample contained a mixture of the minerals in the ratio: 43% huntite and 50% hydromagnesite. The remaining percentage comprises of closely related minerals such as dolomite. It therefore follows that the labels HU24HM67, HU93HM5, and HM100 indicate ratios of 24%:67% and 93%:5% huntite:hydromagnesite, and HM100 indicates pure hydromagnesite.

Also used in this work were:

Natural calcium carbonate supplied by Minelco under the name MicroCarb ST10H
Aluminium hydroxide supplied by Nabaltec under the name Apyral AP40
Magnesium hydroxide supplied by Martinswerk under the name Magnifin H5A

The following polymer formulation (Table 1) was chosen as a typical, general purpose, halogen free compound found in the wire and cable industry. It has been used throughout this study to investigate the effects of huntite and hydromagnesite.

| **Tradename** | **Supplier** | **Description** | **Quantity (phr)** |
|---|---|---|---|
| Escorene UL00328 | Exxon | Ethylene vinyl acetate (28%) | 55 |
| Exact 8201 | ExxonMobil | Polyolefin elastomer | 30 |
| Fusabond MB226D | DuPont | Maleic anhydride grafted polyethylene | 10 |
| Borealis BS2581 | Borealis | High density polyethylene | 5 |
| Irganox 1010 | Ciba (BASF) | phenolic antioxidant | 1 |
| Mineral filler | various | metal hydroxide / carbonate | 160 |
| | | **Total** | **261** |

**Table 1: Typical wire and cable formulation**

## Methods

### *Compound preparation*

Compounds were mixed using a two roll mill with a roll temperature of 140°C, and roll speeds of 15 and 20 rpm. This was followed by compression moulding of plaques 6 mm in thickness at a temperature of 180°C for cone calorimeter testing and plaques of 3mm thickness for limiting oxygen index testing.

### *Limiting oxygen index – BS EN ISO 4589-2:1999*

A Stanton Redcroft oxygen index instrument was used with a total gas flow rate of 18 l min$^{-1}$. Samples of 10 mm x 125 mm x 3 mm were cut from compression moulded plaques.

### *Cone calorimeter – ISO 5660*

A Fire Testing Technologies (FTT) cone calorimeter was used with a heat flux of 50 kW m$^{-2}$. Sample size was 100 mm x 100 mm x 6 mm. Results were completed in triplicate and the average values presented.

### *Thermogravimetric analysis (TGA)*

A TA Instruments Q5000IR thermogravimetric analyser was used. Tests were carried using a heating rate of 10°Cmin$^{-1}$ in air with a gas flow rate of 50 ml min$^{-1}$. Samples sizes of approximately 10 mg were used.

### *Scanning Electron Microscopy (SEM)*

Electron microscopy was carried out using a LEO Gemini field emission gun scanning electron microscope (FEGSEM). Samples were mounted on a metallic stub and gold coated.

## Effect of huntite and hydromagnesite on limiting oxygen index measurements

The effect of the ratio of the two minerals, huntite and hydromagnesite, on limiting oxygen index has been studied. Kirschbaum reported[41] that increasing the proportion of hydromagnesite in a mixture of huntite and hydromagnesite from 0% up to 40% of the total by mass increases the oxygen index of the polymer compound in which the mixture is used. He also reported that increasing the proportion of hydromagnesite any further has no further significant benefit in terms of increased oxygen index. Table 2 shows the results of oxygen index testing on compounds made to the formulation shown in Table 1, these results follow the trend described by Kirschbaum. There is only a small increase in the oxygen index as the proportion of hydromagnesite in the mixture is increased from 50 – 100%, but there is a much more significant effect as the hydromagnesite proportion is increased from 5 to 50%.

| Sample | Oxygen Index |
|---|---|
| HU93HM5 | 24.5 |
| HU43HM50 | 28.0 |
| HU41HM57 | 29.0 |
| HU24HM67 | 29.5 |
| HM100 | 29.5 |
| ATH | 30.0 |

**Table 2: Effect of huntite/hydromagnesite ratio on limiting oxygen index**

The fact that the oxygen index value of an ATH filled compound (Table 2) is very similar to that the compounds filled with mixtures of huntite and hydromagnesite (with hydromagnesite content greater than 50%) suggests that huntite must be having some fire retardant effect. If huntite has little or no active fire retardant effect (as suggested by some authors[35,40,41,43]) then hydromagnesite must be almost twice as effective as ATH. The EVA compound containing HU43HM50 contains only half the quantity of hydromagnesite as there is ATH in the ATH filled compound but the LOI value is only 2 percentage points lower. Clearly hydromagnesite is no more effective than ATH because the compound containing HM100 has an LOI of 29.5% as compared to 30.0% for the ATH filled compound. Therefore, the huntite portion of the mixture of huntite and hydromagnesite must be providing some kind of fire retardant action that has not been previously identified.

## Effect of mineral ratios on combustion in the cone calorimeter

Averages of three repeat tests in the cone calorimeter (at a heat flux of 50 kW $m^{-2}$) of EVA compounds filled with calcium carbonate, hydromagnesite, ATH and MDH are shown in Figure 1. The heat release rate curves for the hydromagnesite, ATH and MDH filled compounds are characteristic of char or residue forming materials. When a char forms it slows the combustion of the underlying polymer leading to a decrease in heat release rate, following an initial peak, as the fire progresses through the polymer compound. The initial peak in rate of heat release on ignition is believed to result from the ignition of acetic acid[54] released during the early decomposition stages of the EVA.

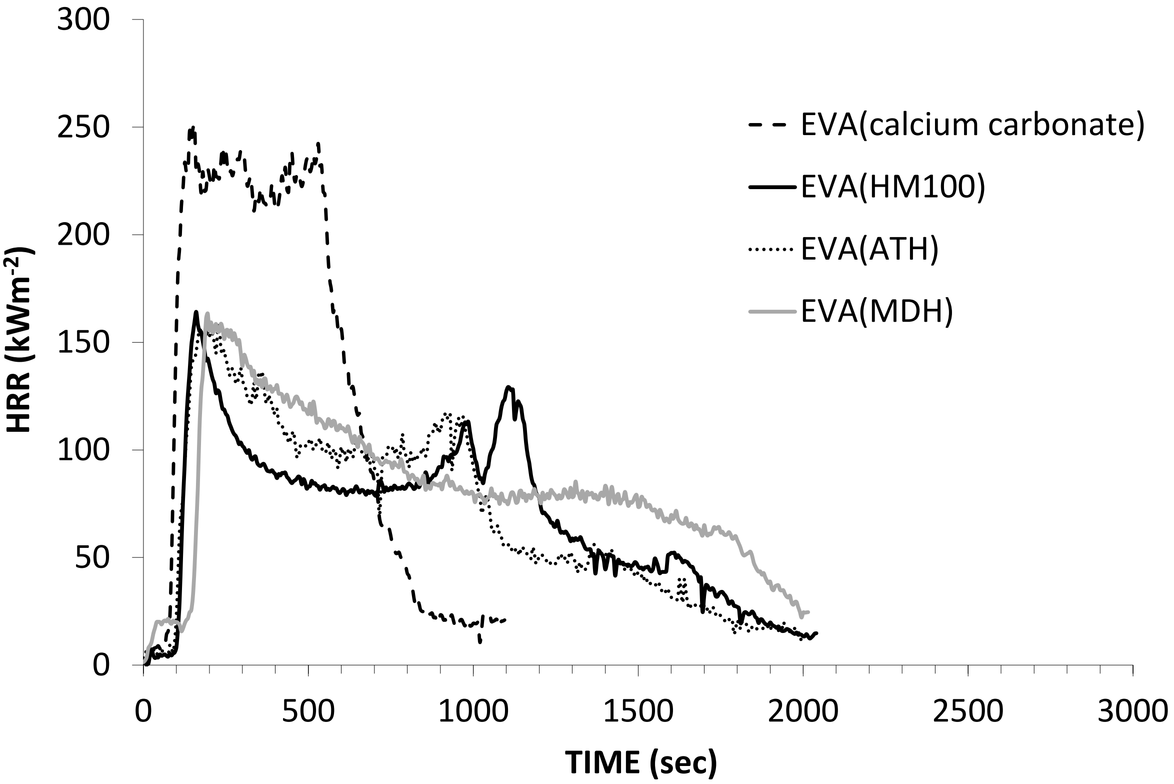

**Figure 1: Comparison of the effect of hydromagnesite, ATH, MDH, and calcium carbonate on the rate of heat release**

Clearly the calcium carbonate filled compound has a high, steady, rate of heat release and a short burning time as would be expected for a compound containing no active fire retardant additive. Replacement of calcium carbonate with ATH, MDH or hydromagnesite reduced the rate of heat release over the entire burning period and increased the duration of burning. The hydromagnesite filled compound behaves in a very similar manner to the ATH filled compound, both show an initial peak in rate of heat release followed by a second fairly sharp peak associated with movement and collapse of the residue. The MDH filled compound has a low steady rate of heat release initially greater than that of the hydromagnesite filled compound, however it did not show the second peak of heat release because the residue did not expand and collapse like the ATH and hydromagnesite filled compounds.

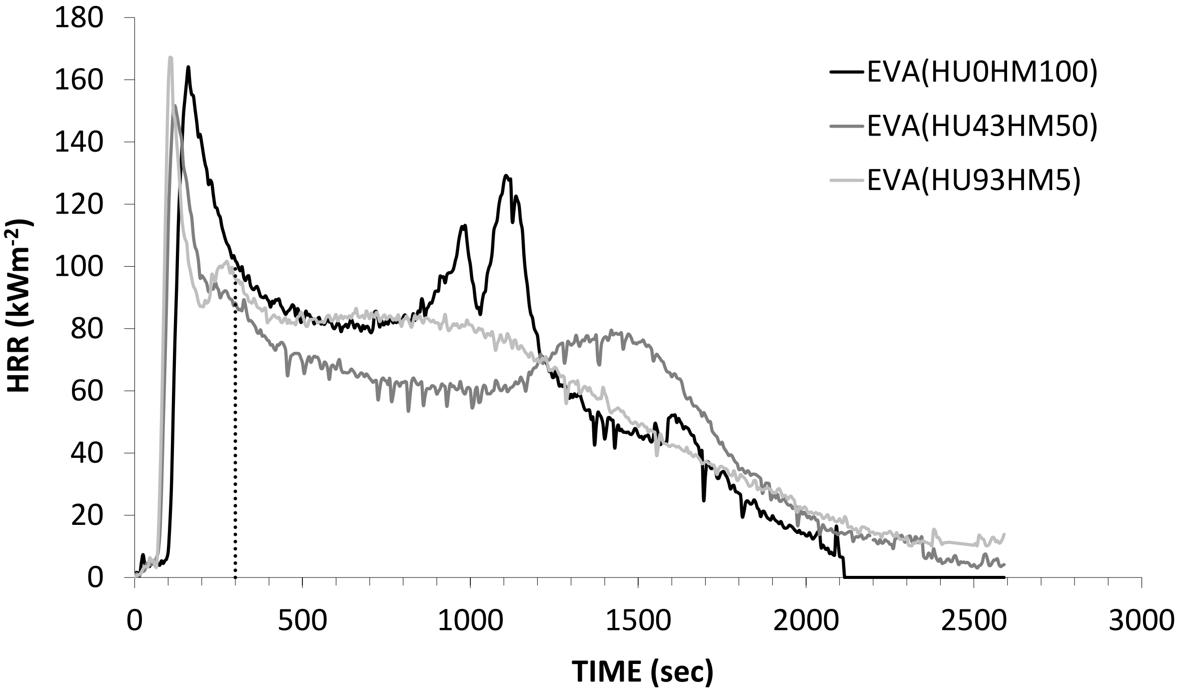

Figure 2: Effect of huntite:hydromagnesite ratio on the rate of heat release

Figure 2 shows the effect of the ratio of huntite to hydromagnesite on the rate of heat release. Each sample shows an initial peak in rate of heat release on ignition due to the ignition of acetic acid[54], as previously described for the samples shown in Figure 1. This peak is followed by a declining rate of heat release dependant on the ratio of huntite to hydromagnesite. The initial peak occurs when the build-up of combustible volatiles above the decomposing sample ignites. This excess of volatiles quickly burns off and the heat release rate becomes steadier as decomposition of the polymer feeds a constant rate of fuel to the flame. However, the area under each peak from 0 – 300 seconds shows that the sample containing 100% hydromagnesite gives the greatest heat release rate in the critical initial phase of burning. The heat release rate then decreases to a steadier value, before a second peak is observed prior to the final decline in heat release and extinction of the flame. The second peak is reduced as the ratio of huntite in the mixture is increased. It was observed that larger hydromagnesite contents produced a much less physically robust residue that had a tendency to move and collapse in the later stages of burning. This movement and collapse of the residue is linked to the second peak in heat release rate. As the residue collapses it exposes flammable material trapped beneath the residue causing the rate of heat release to increase. Compounds containing a higher proportion of huntite formed a more stable and stronger residue, preventing the sudden heat release as the structure collapses; instead there was a steady release of volatiles through gaps between the particles that form the residue. Therefore huntite is providing physical reinforcement of the residue in the later stages of burning as well as reducing the rate of heat release in the initial stages. Huntite is providing a definite contribution to the fire retardant effect of this mixture of minerals.

Table 3 summarises the key data from the cone calorimeter for six compounds containing different ratios of huntite and hydromagnesite in comparison to ATH, MDH, and calcium carbonate filled compounds.

| Sample Reference | Time to ignition | Peak HRR | Average HRR | Time to flame out |
|---|---|---|---|---|
| | (sec) | (kW m$^{-2}$) | (kW m$^{-2}$) | (sec) |
| | | | | |
| HM100 | 101 | 168 | 89 | 1883 |
| HU24HM67 | 93 | 162 | 73 | 1702 |
| HU41HM57 | 88 | 168 | 71 | 2175 |
| HU43HM50 | 81 | 154 | 56 | 2253 |
| HU93HM5 | 78 | 174 | 67 | 2359 |
| | | | | |
| MDH | 115 | 163 | 88 | 2088 |
| ATH | 98 | 169 | 84 | 2007 |
| Calcium carbonate | 81 | 256 | 133 | 1067 |

**Table 3: Summary of cone calorimeter results for EVA filled with calcium carbonate, ATH, MDH, and different ratios of huntite and hydromagnesite at 50kW m$^{-2}$**

There is a trend of increasing time to ignition with increasing hydromagnesite content. This is probably due to the endothermic decomposition of hydromagnesite near the surface of the sample in the early stages. As the heat flux is applied to the sample, the first response of hydromagnesite is to release water vapour endothermically. This will delay the ignition time by cooling the sample and therefore reducing the rate of emission of flammable decomposition products from the polymer. Once the bubbles of water vapour break through the surface of the polymer it also has the effect of diluting the gas phase with water vapour increasing the amount of time needed for these vapours to reach the concentration required for ignition to occur. Following bubble formation, a carbonaceous skin formed on the surface of the sample. In each case the skin broke immediately before or upon ignition of the sample. This is a very similar to the observation made by McGarry et al[54] that during the decomposition of EVA, in a TGA instrument or tube furnace, a protective skin forms which then breaks down to allow combustion of the underlying material.

The time to ignition for the ATH filled compound is similar to the times measured for the samples containing higher proportions of hydromagnesite. This suggests that the mechanisms of ATH and hydromagnesite are similar, and that the endothermic release of water has an effect on increasing time to ignition. The MDH filled compound has a longer time to ignition than either the hydromagnesite or the ATH filled compound. MDH has a higher decomposition temperature (about 330 °C) compared to ATH (about 180 °C) or hydromagnesite (about 220°C). It is possible that this delayed reaction accounts for the longer time to ignition since is corresponds more closely with the decomposition temperature of EVA (about 300 °C)[54].

The carbonaceous skin appeared to be very coherent across the whole surface. The fact that it is so coherent is probably what leads to its break down. It traps water vapour and polymer decomposition products beneath it until it is no longer strong enough to withstand the pressure being exerted by these vapours. At that point the skin splits releasing decomposition vapours which immediately ignite.

The calcium carbonate filled sample gave a time to ignition similar to that of the compounds containing higher levels of huntite. Since calcium carbonate does not decompose until temperatures in excess of 600°C[55] it can be considered inert during the initial stage of the fire. Its only function is as a diluent reducing the amount of combustible polymer within the test piece. The similar time to ignition to the huntite filled sample suggests that during ignition, huntite, which begins to decompose at about 450°C, also acts only as a diluent filler.

The effect of the ratio of huntite to hydromagnesite shows a trend towards reducing peak rate of heat release with increasing hydromagnesite content. The peak in heat release rate immediately follows ignition, as shown in Figure 2. It is caused when the build up of flammable gases above the sample ignites. Therefore the observation that higher proportions of hydromagnesite reduce the peak heat release rate is consistent with the idea that the endothermic release of water vapour from the hydromagnesite is the controlling factor in the initial stages of ignition and combustion. The ATH filled compound (Table 3) shows a similar peak in heat release rate to the compounds containing higher hydromagnesite content; again this suggests the similar mechanism of ATH and hydromagnesite. The calcium carbonate filled compound (Table 3) shows a much higher peak in heat release rate than any of the blends of huntite and hydromagnesite, including the compounds containing very high proportions of huntite. It is interesting to note that the average heat release rate over the duration of the test is reduced with increasing huntite content. Therefore the hydromagnesite portion of the blend is having the largest positive effect in the initial stages of ignition, but the huntite portion must be having an effect in the later stages, reducing the average heat release rate.

Huntite does not begin to thermally decompose until about 450°C, this is above the temperature at which most of the polymer has decomposed, which has led some researchers[40,41,43] to conclude that huntite is simply an inert filler in terms of fire retardancy. However, given the fact that it appears to be having an effect on the average rate of heat release this notion needs reconsideration. In order to determine the stage of decomposition that the huntite and hydromagnesite reached during combustion in cone calorimeter testing, the ash residue was investigated using TGA at a heating rate of 10°C $min^{-1}$ in air.

Figure 3 shows the thermal decomposition, measured by TGA, of the ash residue obtained from the EVA compound containing a mixture of huntite and hydromagnesite compared to the thermal decomposition of the mixture of the two minerals alone. The thermal decomposition of the mineral powder shows the characteristic mass loss profile of the decomposition of hydromagnesite[1,3], releasing water at about 275°C and carbon dioxide at about 430°C, followed by the decomposition of huntite[1,3], releasing carbon dioxide at about 555°C and 690°C.

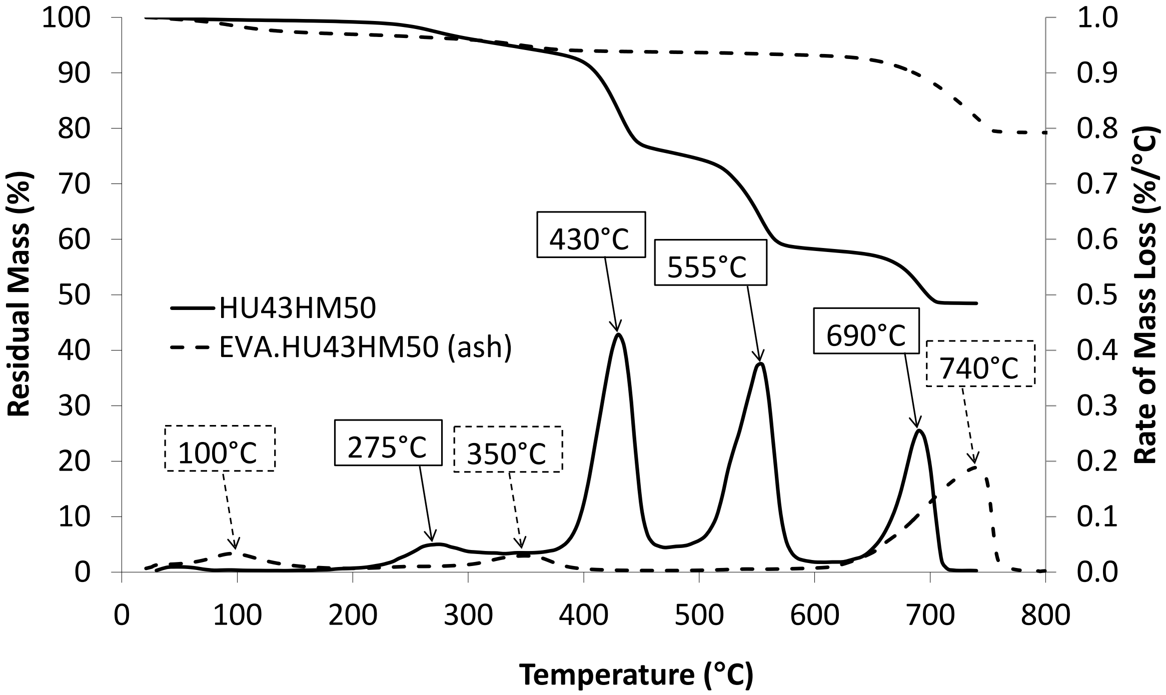

**Figure 3: Thermal decomposition by TGA of HU43HM50 (blend) in comparison with ash residue obtained from EVA.HU43HM50**

The residue sample shows a small mass loss at around 100°C which is probably associated with moisture absorbed from the atmosphere in the time between combustion of the compound and testing of the residue. It also shows another small mass loss at about 350°C. This mass loss does not match with either of the mass losses associated with hydromagnesite. The magnesium oxide residue remaining after the decomposition of hydromagnesite is likely to react with water from the atmosphere to form magnesium hydroxide, the temperature at which this mass loss occurs is consistent with the decomposition of this product. It also shows that all of the major mass losses associated with the decomposition of hydromagnesite and huntite below 600°C are no longer present. The only mass loss remaining is the higher temperature loss from huntite above 600°C. This has shifted to a higher temperature, probably due to rearrangement of the crystal structure after the partial decomposition of the huntite. The greater percentage mass loss of the residue arises because it has already lost most of the water and carbon dioxide contained in the HU43HM50 material. Therefore, during combustion under a 50 kW m$^{-2}$ heat flux in the cone calorimeter, hydromagnesite contributes to fire retardancy through complete decomposition, endothermically releasing water and carbon dioxide, while huntite partially decomposes endothermically releasing carbon dioxide.

In the cone calorimeter the test is carried out on horizontally mounted flat plaques of material subjected to a heat flux from above. Therefore any non-combustible residue will remain in place. As the polymer compound burns and the hydromagnesite decomposes, a layer of magnesium oxide and huntite will form. It has been shown[56] that at 50kW m$^{-2}$ heat flux from a cone calorimeter will raise the surface temperature of a ceramic plate, placed where the sample sits, to about 610°C. This temperature is in excess of the initial decomposition temperature of huntite and therefore some decomposition of this mineral is expected. Even though all of the polymeric material may have decomposed in the upper layers of the sample, the endothermically decomposing huntite will still absorb heat and reduce heat transfer to the underlying polymer. The carbon dioxide released from this decomposition will also dilute the flammable volatiles feeding into the flame from the underlying polymer. This effect will work particularly well in the cone calorimeter due to the fixed radiant heat flux and the horizontal orientation of the samples. However, it is also likely to have an effect in real fire situations where the heat flux is high, either due to the flame above the material or other radiant heat within the area of the material.

From these observations it seems clear that hydromagnesite has a role to play in the initial stages of the fire, its decomposition at lower temperatures helps to increase the time to ignition and peak heat release rate. However, huntite's higher decomposition temperature has a positive effect in the later stages of the fire by reducing the average rate of heat release over longer periods and extending the time to extinction, thereby slowing the burning of the compound after ignition has taken place.

## Analysis of the ash residue from the cone calorimeter

In order to more fully explain some of the results that have been observed, particularly in relation to the part that huntite plays in fire retardancy, some analysis of the ash residue is necessary. Visually the ash residue (Figure 4) remaining after combustion of the polymeric components of the compounds was complete was very different depending on the huntite/hydromagnesite ratio.

**(A) EVA.HU93HM5** **(B) EVA.HU43HM50**

**(C) EVA.HU24HM67** **(D) EVA.HM100**

**Figure 4: Ash from the cone test of samples containing blends of huntite and hydromagnesite**

The ratio of huntite to hydromagnesite has several noticeable effects:

1. The colour of the ash. Higher hydromagnesite content leads to progressively greyer and eventually black residue indicating that there is more carbon present. Almost pure huntite gives a very white ash indicating that there is very little residual carbon.
2. All the samples clearly show inorganic remains of the skin formed by the decomposition of EVA[54,57] during the initial stages of combustion. This is particularly evident in the compounds containing higher huntite content.
3. The sample containing almost pure huntite shows very little breakage of the skin. Higher hydromagnesite content shows progressively more breakage of the skin and deeper 'cracks' within the sample corresponding to the breaks in the skin. This suggests that when the skin remains intact it provides protection to the material beneath. Where the skin breaks this protection is lost allowing faster degradation of the material below leading to the 'cracks' within the body of the sample. This is similar to the behaviour of wood in the cone calorimeter, where cracks in the char expose fresh fuel deeper in the sample[56].

Figure 5 shows cross sections through the inorganic residue taken from the cone calorimeter.

**EVA.HU93HM5**

**EVA.HU43HM50**

**EVA.HU24HM67**

**EVA.HM100**

**Figure 5: Section through ash of samples containing blends of huntite and hydromagnesite**

Again there are several observations that can be made:

1. The samples all contain bubbles. Higher huntite content samples contained a larger number of small bubbles, while the higher hydromagnesite content samples contained a smaller number of larger bubbles.
2. The colour differences seen on the surface of the residue samples is present throughout the thickness of the sample. Higher huntite gives a whiter residue, while higher hydromagnesite gives blacker residue.
3. Higher huntite content in the samples leads to a thicker residue. The original sample thickness was 6mm. It is therefore clear that the samples containing high levels of huntite

have approximately doubled in thickness. The sample containing pure hydromagnesite does not appear to have increased in thickness at all.

4. The strength of the residue is very dependent on the huntite content. The sample containing the highest huntite content was strong enough to easily handle without breaking the residue. The sample containing the highest level of hydromagnesite was very weak. This sample could not be handled without disintegration, although the photograph of EVA.HM100 in Figure 5 is an accurate representation of the thickness.

The final observation that the residue became stronger as the huntite content increased was more difficult to quantify. There are no standard test methods for measuring the strength of the residue from the cone calorimeter. In many cases the residue from a cone calorimeter test is very weak and loses its integrity simply from the vibrations caused by removing the sample from the holder. In a crude attempt to quantify the strength of the residues a series of samples were removed very carefully from the sample holder after combustion was completed and the residue had cooled. A circular plastic petri dish of 87mm diameter was placed centrally onto the residue and weights were manually added to the dish until the residue collapsed. The recorded weights to cause collapse of the ash are shown in Table 4 and an estimate of the compressive strength in N $m^{-2}$ has been calculated.

| Ratio of huntite:hydromagnesite | Weight to cause collapse | Approximate compressive strength (N $m^{-2}$) | Notes |
|---|---|---|---|
| EVA(HM100) | 25g | 40 | Difficult to handle without breakage |
| EVA(HU25HM75) | 50g | 80 | Difficult to handle without breakage |
| EVA(HU50HM50) | 75g | 120 | Handleable with care |
| EVA(HU75HM25) | 140g | 230 | Easily handleable |
| EVA(ATH) | 30g | 50 | Difficult to handle without breakage |

**Table 4: Strength of residues from the cone calorimeter**

The rate of heat release data, presented in Table 3, suggest that the hydromagnesite had an effect in the initial stages of the fire, increasing time to ignition, and reducing the peak rate of heat release, while the huntite content appeared to reduce the rate of heat release in the later stages of combustion and extend the time of burning. It is clear the huntite is promoting the formation of a thicker more stable residue which insulates and protects the underlying material more efficiently than the thinner, weaker residue of the compounds that contain a higher proportion of hydromagnesite.

## Microscopic analysis of the residue

Figure 6 - Figure 8 show low magnification electron microscope images of cross sections of the residues containing varying ratios of huntite and hydromagnesite. In each case it is clear that the bubbles formed during decomposition and combustion of the polymer have been preserved in the inorganic residue.

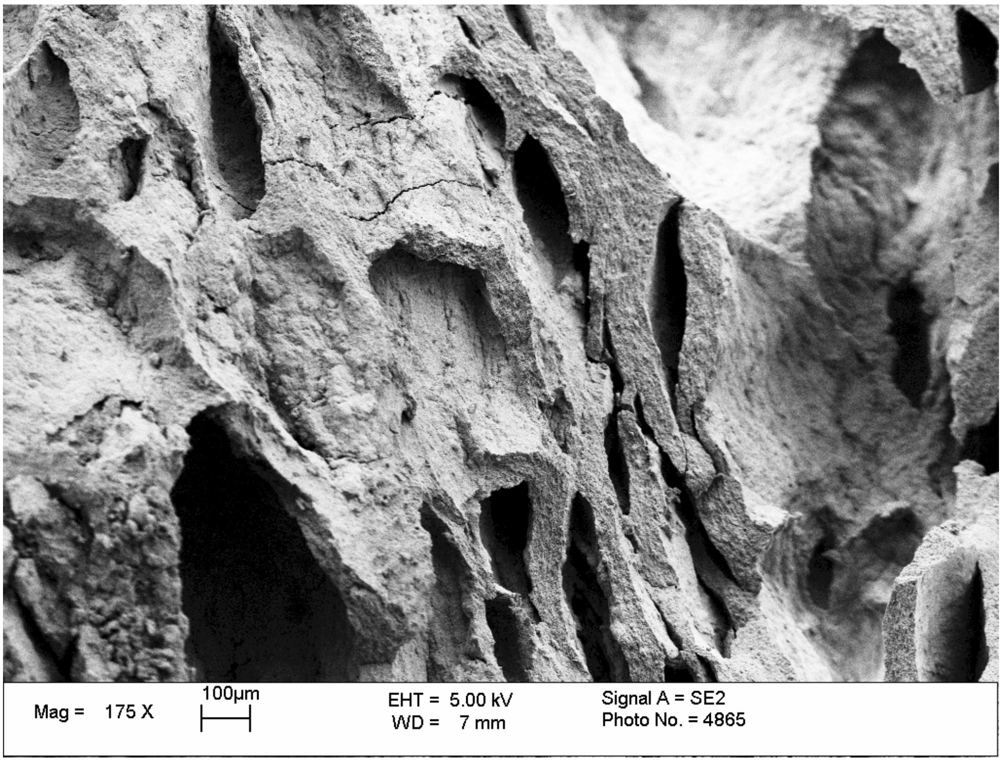

Figure 6: HU93HM5 Ash Residue

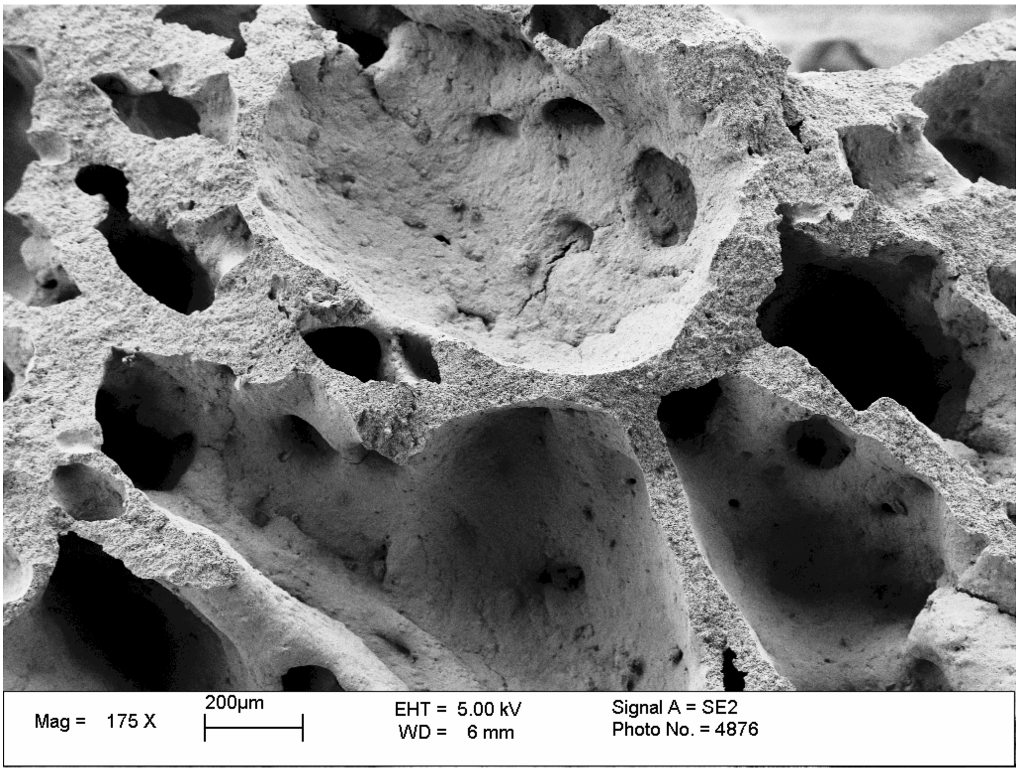

Figure 7: HU43HM50 Ash Residue

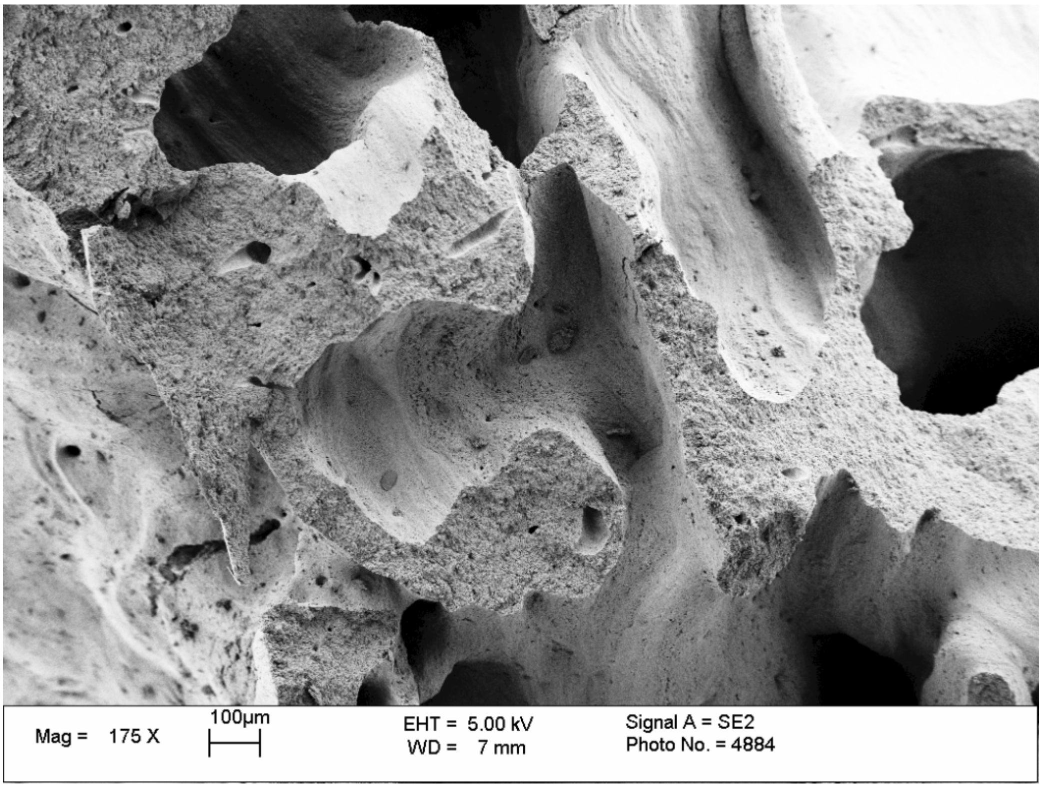

Figure 8:HU24HM67 Ash Residue

Figure 9 shows a magnified cross section of part of a bubble wall in Figure 6. It can be seen that the platy huntite particles in the HU93HM5 filled compound have aligned themselves parallel to one another almost completely. This alignment of the particles around the walls of the bubbles explains the strength of the huntite residue. The particles reinforce the bubble wall when the polymer is still present, then as the polymer decomposes it leaves a randomly arranged, overlapping and interlocking, structure of platy particles of reasonable strength.

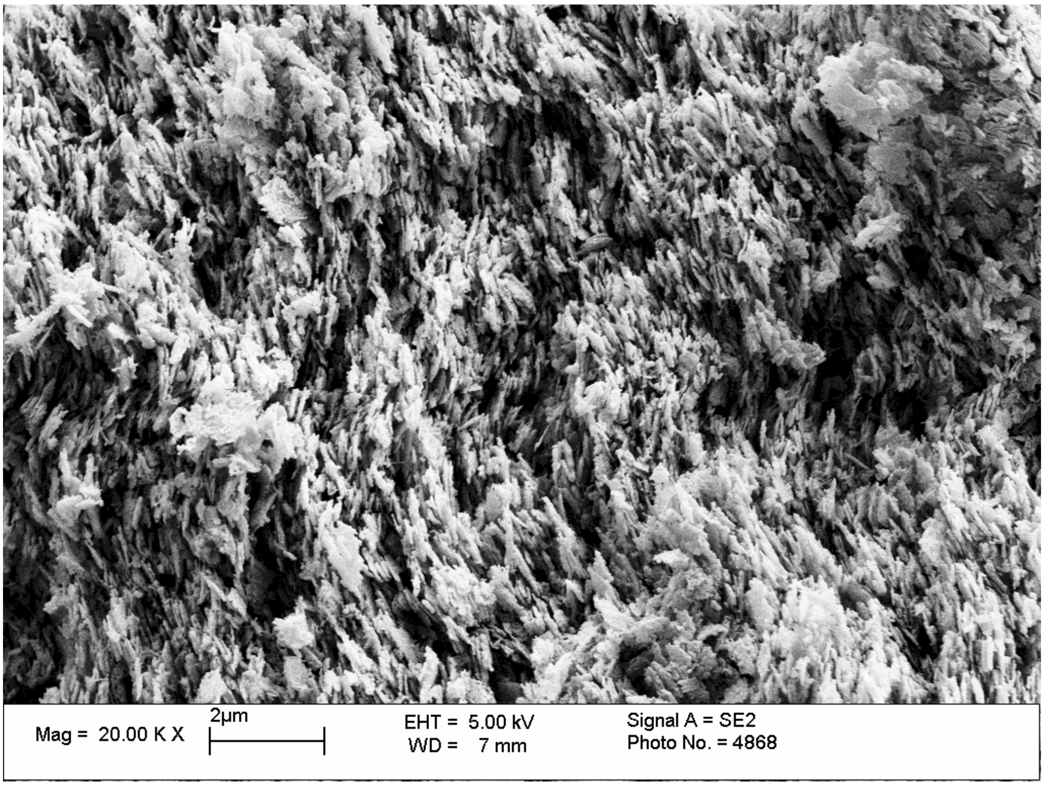

**Figure 9: Cross section of bubble wall (HU93HM5)**

This alignment and overlapping of the particles will help to reduce the rate at which combustible organic decomposition products can migrate to the surface, and therefore to the flame, by creating a tortuous route that the fuel vapours must follow. This will starve the flame by restricting the supply of fuel, therefore reducing the severity of the fire. The arrangement may also act as an improved radiation shield compared to a more random arrangement of particles. This observation of the physical structure of the residue fits with the measurement showing that increased ratios of huntite in a mixture with hydromagnesite gave lower heat release rates in the cone calorimeter.

Figure 10 shows the internal surface of a bubble within the residue of the HU93HM5 sample. The huntite particles can be seen positioned parallel to the surface of the bubble. This arrangement of the particles again confirms the reinforcing nature of the huntite decomposition product on the bubble and also its ability to hinder the escape of decomposition gases from the bubble. It is clear that the huntite particles have maintained their platy shape even after combustion of the polymer. However, it can be seen that although the particles have maintained their shape they are no longer solid due to the loss of carbon dioxide during thermal decomposition. Instead they have the appearance of a porous network. This small degree of porosity may be optimum in terms of fire retardancy. Impervious barriers result in a pressure build up and structural collapse, strong permeable structures lead to low heat release rates.

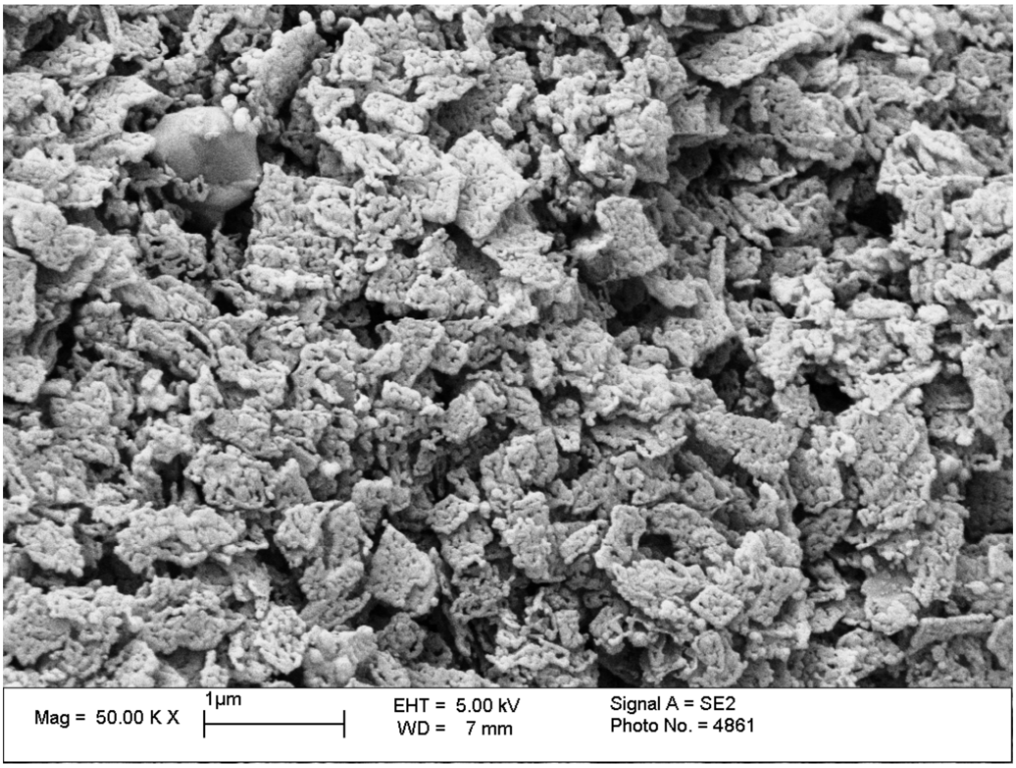

**Figure 10:Internal surface of bubble (HU93HM5)**

Figure 11 shows that when a mixture of huntite and hydromagnesite is used in the compound the huntite particles still maintain their shape and align themselves parallel to the surface of the bubble. However, they are interspersed with smaller bead like structures which must originate from the decomposition of the hydromagnesite particles.

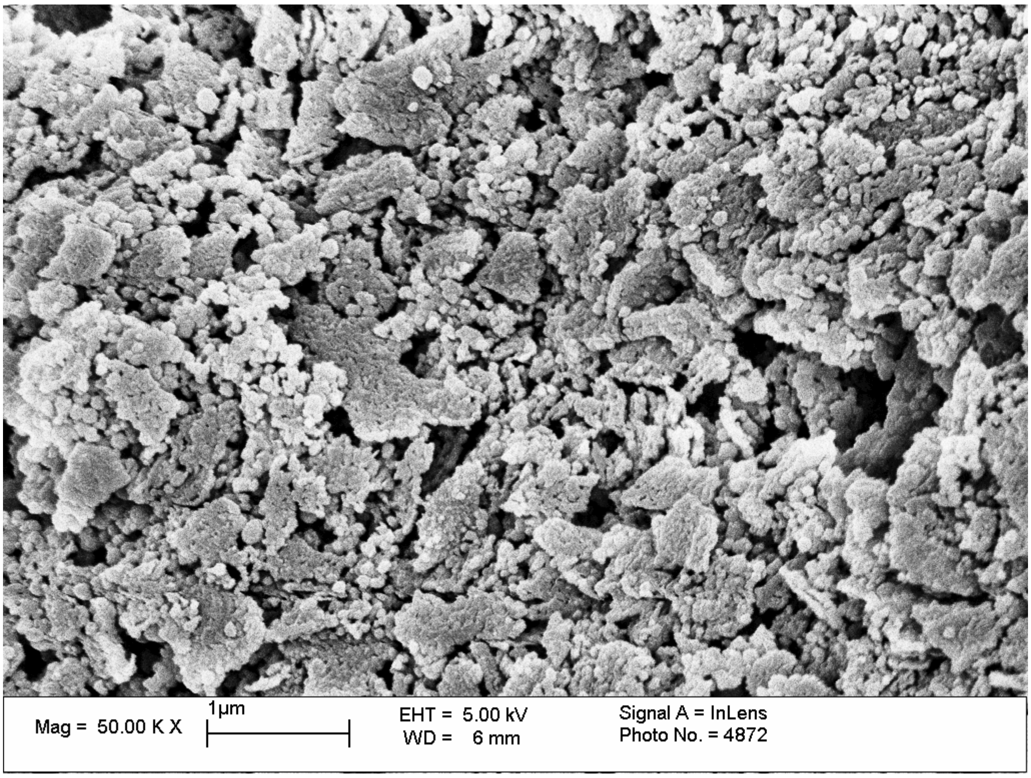

**Figure 11:Internal surface of bubble (HU43HM50)**

Figure 12 shows the internal surface of a bubble within the residue of the compound that contained HM100. The structure of the hydromagnesite decomposition product can be seen in more detail. The internal surface of the bubble consists entirely of the bead like structures, of less than 100 nm in diameter, formed from the hydromagnesite. Clearly this kind of structure will not offer as much strength or hinder the escape of decomposition gases as effectively as the residue containing the overlapping platelets of the huntite decomposition product.

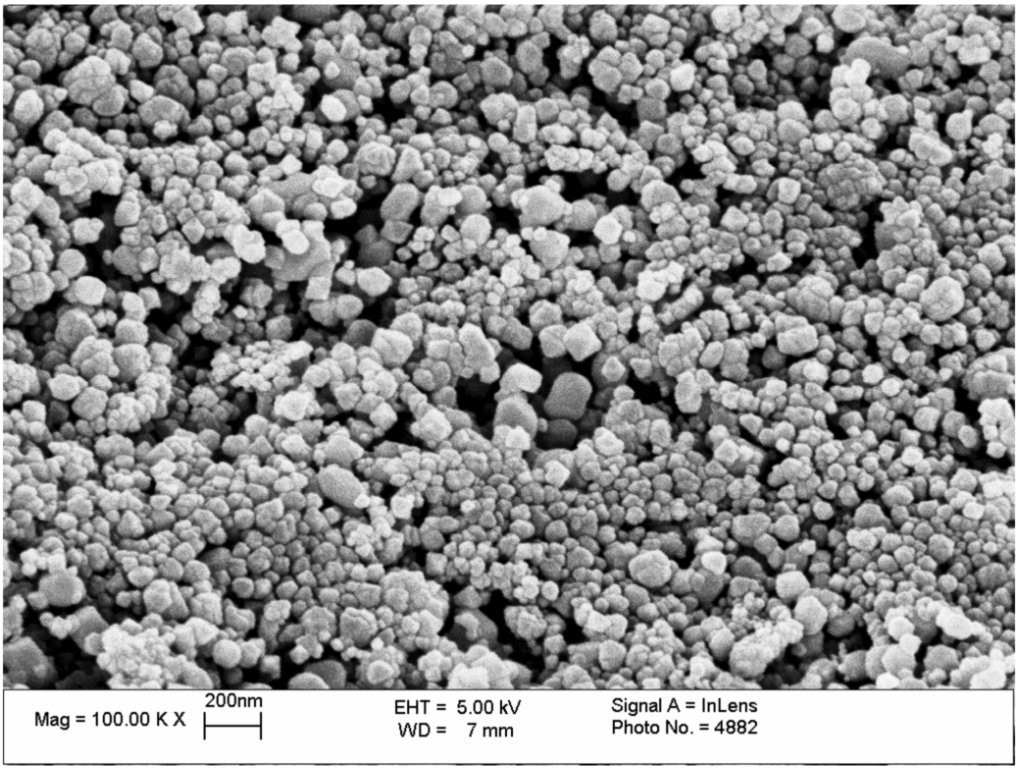

**Figure 12: Internal surface of bubble (HU24HM67)**

## Conclusions

The endothermic decomposition of hydromagnesite coincides with the temperature range at which polymers such as ethylene vinyl acetate and polyethylene thermally decompose. This is a good indicator that hydromagnesite has potential to perform well as a fire retardant. Huntite decomposes between about 450°C and 750°C, a temperature range where most of the polymer has completely volatilised. This suggests that the fire retardant mechanism of huntite is not simply the endothermic release of inert diluent vapour typical of other mineral fillers, since it has been shown that mixtures of huntite and hydromagnesite perform similarly to aluminium hydroxide in measurements involving cone calorimetry. Huntite certainly has much greater effect than an inert diluent filler.

Electron microscope images of the inorganic residue show that hydromagnesite decomposes to almost spherical particles of about 100 nm in diameter. Partially decomposed huntite particles maintain a plate-like structure. Additionally, the partially decomposed huntite particles align themselves around the boundaries of the bubbles formed within the polymer during decomposition of the hydromagnesite and the polymer itself. This alignment physically reinforces the residue, making it stronger and also provides a barrier, making escape of the combustible gases from the condensed phase to the flame more difficult.

This combined evidence shows that the endothermic release of water and carbon dioxide from hydromagnesite at temperatures between 220°C and 500°C helps to reduce the initial peak of heat release and increase the time to ignition. It shows that the partial decomposition of huntite at temperatures between 450°C and 600°C helps to reduce the rate of heat release during the later stages of combustion by providing a physical barrier, slowing the release of combustible gases to the flame. The additional heat absorbed during the endothermic, partial decomposition, of huntite also reduces the heat transferred to the underlying polymer and further dilutes the gas phase with non-combustible carbon dioxide. The platy huntite particles also help to physically stabilise the residue during the later stages of combustion forming a strong insulating barrier to the underlying polymer.

In summary the fire retardant action of mixtures of huntite and hydromagnesite comes from a combination of the actions of the two minerals.

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