Institution: University of Central Lancashire (UCLan)

Unit of Assessment: 13 Electrical and Electronic Engineering, Metallurgy and Materials

Title of case study:

Mechanistic research supports the transition to environment friendly fire retardant

1. Summary of the impact (indicative maximum 100 words)

Our research provided the evidence to persuade companies to develop fire retardant formulations based on naturally occurring mixtures of hydromagnesite and huntite (HMH) that were more effective, cheaper, and greener than the market leader, aluminium hydroxide (ATH). Before the research started, in 2005, annual global sales of HMH as a fire retardant were less than XXX 000 tonnes. By 2012, sales had already doubled to XXX 000 tonnes (£XXX M) and continue to grow. LKAB minerals supply over 90% of the global market in HMH, and as a result of UCLan's fire retardant research, expect HMH to replace at least 25% of fine grade ATH within 5 years (increasing HMH sales to £XXX M). Not only is HMH a more effective fire retardant, it does not have the environmental problems associated with ATH.

2. Underpinning research (indicative maximum 500 words)

From 2000 to 2006 **Hull's** fire group, now at UCLan, had undertaken detailed research in the mechanism of the world's best-selling fire retardant, aluminium hydroxide (colloquially, but incorrectly, referred to as alumina trihydrate, or ATH). In 2007, the fire group moved to UCLan, and continued to build on this important work, supported by the €2 M PredfireNano project. In 2008, this led to Minelco (now LKAB Minerals) seconding one of their staff (Hollingbery) to undertake a PhD at UCLan to investigate the fire retardant behaviour of hydromagnesite and huntite (HMH) mixtures.

Our detailed research explained why the established understanding of the fire retardant mechanism of mineral fillers was incorrect, and showed that naturally occurring mixtures of hydromagnesite and huntite (HMH) were more effective than the market leader, ATH. Hitherto, HMH had been reported as an unsuitable alternative to ATH, based on a flawed understanding of HMH's fire retardant mechanism[*†]. Two critical reviews of the literature highlighted, first, the conflicting accounts of the mechanisms of thermal decomposition of HMH mixtures [1], and second, the major misconceptions regarding their fire retardant behaviour [2]. While these reviews clarified a number of issues, they identified clear gaps in our understanding of the thermal decomposition and fire retardant behaviour of HMH.

In parallel to this work, a UCLan funded PhD student (Witkowski) modelled the fundamental mechanisms of thermal decomposition and fire retardant behaviour, using an energy-balance model of fire retardant effects caused by the decomposition of various mineral fillers. This allowed the four fire retardancy contributions (heat capacity of the filler; decomposition endotherm; heat capacity of the volatiles; and heat capacity of the residue) to be quantified. Moreover, their effects

[*] Kirschbaum G. Minerals on fire: flame retardants look to mineral solutions. Ind Mineral; 2001:61-7.

[†] Morgan AB, Cogen JM, Opperman RS, Harris JD. The effectiveness of magnesium carbonate-based flame retardants for poly(ethylene-co-vinyl acetate) and poly(ethylene-co-ethyl acrylate). Fire Mater 2007;31:387-410.

in standard flammability assessments such as the limiting oxygen index (LOI), UL 94 and cone calorimeter were estimated. The purpose of the model was to separate the known and quantifiable effects of mineral filler fire retardants from other, less-known factors. The failure of the model to predict the superior fire retardant performance of HMH demonstrated the importance of these other factors.

This led to two detailed experimental studies. The first investigated the interaction between the decomposition of the combination of the two minerals and the influence of the decomposition product carbon dioxide, which could not escape when fillers were compounded into a polymer [3]. The second focused on the fire retardant behaviour [4]. This paper conclusively showed:

(i) that the platy nature of the huntite component of the mixture was responsible for stabilisation of the protective residue around the bulk of the polymer;
(ii) the inadequacy of the LOI test to predict burning behaviour;
(iii) the superiority of HMH mixtures over the market leader, ATH.

A further investigation reconciled the differences between the simple model and the actual fire retardant behaviour [5], showing how the cone calorimeter failed to respond to the large decomposition endotherm, the conversion of acetic acid to acetone on the surface of the filler, and the subsequent delay in heat release rate.

3. References to the research (showing downloads from UCLan's institutional repository - Clok)
*Best indicates quality of the research

[1] *L.A. Hollingbery and T.R. Hull, *The Thermal Decomposition of Huntite and Hydromagnesite - A Review,* Thermochimica Acta, 509, 1-11, (2010), (downloaded 1139 times).

[2] *L.A. Hollingbery and T.R. Hull, *Fire Retardant Behaviour of Huntite and Hydromagnesite - A Review,* Polymer Degradation and Stability 95, 2213-2225, 2010, (downloaded 1432 times in Aug 2012-Jul 2013).

[3] *T. R. Hull, A. Witkowski, L. Hollingbery, *Fire retardant action of mineral fillers,* Polymer Degradation and Stability, 96, 1462-1469, 2011, (downloaded 618 times in Aug 2012-Jul 2013).

[4] L.A.Hollingbery, T.R.Hull, *The Thermal Decomposition of Huntite and Hydromagnesite,* Thermochimica Acta, **528**, 45-52, (2012). (downloaded 140 times in Aug 2012-Jul 2013)

[5] L.A.Hollingbery, T.R.Hull, *The Fire Retardant Effects of Huntite in Natural Mixtures with Hydromagnesite.* Polymer Degradation and Stability, **97**, 504-512, (2012), (downloaded 178 times in Aug 2012-Jul 2013)

[6] A. Witkowski, L. Hollingbery and T. R. Hull, *Fire Retardancy of Mineral Fillers in EVA Copolymers* Fire and Polymers VI: New Advances in Flame Retardant Chemistry and Science, ACS Symposium Series, Vol. 1118, Chapter 7, pp 97–111, Oxford University Press, 2012. (not available for download)

Fire retardants are a major class of industrial products with global sales exceeding $5 billion dollars. Fire retardant formulation and development is multidisciplinary and not immediately accessible to generic chemists, physicists, engineers or polymer scientists. This leads to a very compact research community (globally around 500 scientists) where the best research is published in specific journals, read within the community, rather than those of generally higher impact. For example a paper by Schartel and **Hull** on cone calorimetry in Fire and Materials in 2007 has been cited 179 times although at the time of publication the journal had an impact factor of 0.87. Research quality does not correlate to journal impact factor in this field.

Funding
Feb 2005-Dec 2008 Awarded €300 k from European Union (as part of €2M Predfire Nano

	Project) to predict fire behaviour of nanocomposite materials.
April 2008-July 2011	Application of naturally occurring huntite and hydromagnesite to fire retardancy, Minelco Ltd., (PhD studentship).
July 2008-Dec 2011	Modelling polymer decomposition and fire retardant behaviour, UCLan (PhD studentship)

4. Details of the impact (indicative maximum 750 words)

This important research has had an impact in 3 ways:

1) *large increase in sales of HMH;*
2) *Encouraged the use of a more effective, and cleaner fire retardant;*
3) *Provided an example of a safe, environment-friendly fire retardant, to counter the "green" arguments for an outright ban (maintaining fire safety and avoiding pollution from fires).*

The growth of the plastics industry in the 1960s and 1970s led to a sharp increase in fire deaths. Fire retardants were added to plastics for use in high risk applications. Most of these were very stable brominated compounds which are easy to use, provided they are compatible with the host polymer, and at loadings of around 10 % they will meet the flammability requirements. Unfortunately they leach out of products and have subsequently been found to be persistent, bioaccumulative and toxic (PBT). The fire retardant community has been searching for replacements, while parts of the "green" lobby have been calling for a global ban on all fire retardants. In general, halogen-free fire retardants based on phosphorus, nitrogen or mineral fillers are much more polymer specific, and therefore require greater time and investment to optimise product formulations. Once a formulation has been optimised, approved and certified, any further changes must overcome large barriers. HP estimate that replacement of a single substance in a product formulation costs $5-10 M (H. Wendschlag; FRPM, Lille 2013). In the case of HMH, merely knowing it had fire retardancy potential was not enough to persuade customers to investigate it further; the claims and counterclaims in the literature needed to be addressed and the mechanism understood, to explain why the good results were not artefacts. An independent academic study from UCLan's leading fire research group provided the credible evidence base to support results produced in-house at LKAB. This was necessary to encourage innovation, including costly changes in formulation. To hasten the progress, drafts of the papers were provided to the company sales team, prior to formal publication. In addition, two important points needed to be made in respect of the perceived problems of fire retardants. The first, that many of fire retardants had no connection with the PBT problems of halogenated fire retardants, and the second that there were significant differences within the halogen-free group of fire retardants. Like aluminium metal, ATH requires very large amounts of energy during manufacture, and produces an equal mass of highly alkaline toxic red sludge (which flooded an area of Hungary in 2010, resulting in 10 deaths), whereas HMH production involves low energy processes of mining, sieving and grinding. As a plenary speaker at the Brominated Flame Retardants Symposium in Kyoto (BFR 2010, an academic conference of environmental scientists concerned about the widespread distribution and harmful effects of brominated flame retardants), **Hull** shared the platform with professors from Amsterdam Free University,Berkeley, Boston, Kyoto and Stockholm where he was able to highlight these important distinctions. Soon afterwards, Wikipedia's pages on "flame retardants" and "fire retardants" described HMH as a key example of an environment friendly fire retardant. Direct links to CloK, UCLan's online repository have resulted in thousands of downloads of these key research papers (see section 3). The final obstacle was the need for LKAB to increase production - there is no point in persuading customers to undertake the costly process of formulation development using a product which is in short supply. Armed with the mechanistic understanding, technology was selected to optimise particle size distribution, platyness and mixture ratios. This involved LKAB investing several million dollars in new plant in Turkey and the UK, tripling capacity to 60,000 tonnes per year. This confidence in the continued shift from ATH (the market for the fine grade of ATH alone is $250 M per annum) is the most concrete indicator of the significant impact of this research. The greater fire safety and environmental benefits are much harder to quantify.

Beneficiaries and nature of impact

LKAB Minerals are the primary beneficiaries of this research, through significant increase in sales volume. However LKAB's product is their customers' raw material, offering superior FR performance and better environmental ratings. Therefore, where the use of HMH results in a market lead for product, this is of far greater value than the cost of the raw materials. For example in the halogen-free cable industry (a rapidly growing area of the European market) XXX [cable compounder] have gone into production with a superior ethylene-copolymer HMH formulation. Unlike the alternatives, the platy huntite slows down the burning rate, through formation of a resilient residue, allowing the cable to meet Euroclass B2. The use of a naturally occurring raw material, requiring minimal processing has obvious environmental advantages, both in energy usage and clean manufacture (especially when compared with the toxic red mud generated as part of ATH production). Combined with the improvements in fire safety, society is the ultimate beneficiary in having access to a greener, safer product.

Key dates relating to impact

2007	Prof Hull appointed to UCLan
	Minelco decision to fund PhD studentship at UCLan in fire retardancy
2008	Hollingbery and Witkowski start PhD studentships
2008-09	Experimental investigation of thermal decomposition of HMH mixtures
2010	Experimental investigation of flammability behaviour of HMH in comparison to hydromagnesite, ATH and magnesium hydroxide (MDH) etc.
	Numerical modelling of fire retardant effects of mineral fillers.
	Publication of references [1] and [2]
2011	Further investigation of HMH/ATH/MDH fire retardant mechanisms
	Publication of references [3] and [4]
2012	Publication of references [3] and [4]
20XX	LKAB decision to triple production capacity of HMH
August 2013	Finalisation of current impact case study
20YY	LKAB's new plant fully operational

5. Sources to corroborate the impact (indicative maximum of 10 references)

CONTACT 1: Mr Ian Yates, Team Leader (Flame Retardants), LKAB Minerals GMBH.

CONTACT 2: Mr James Robinson, Senior Engineer, Applications and Standards, Wire and Cable Division, Borealis Polymers NV.

SP Report 2005:45, Fire-LCA Model: Cable case study II – NHXMH and NHMH cable, pages 65-68 http://www-v2.sp.se/publ/user/default.aspx?lang=eng#6135

How toxic is Hungary's red sludge? http://www.bbc.co.uk/news/world-europe-11492387