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Alkaline earth silicate wools – A new generation of high temperature insulation

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ABSTRACT

Intensive study of the natural asbestiform minerals that cause human diseases, and the consequent understanding of their hazardous characteristics, has enabled the development of manufactured fibres whose physical and/or chemical properties, in particular as they relate to biopersistence, have been adjusted to minimize possible harm to health. A strong driver for the development of new high temperature insulation materials was the perception of the toxicity of refractory ceramic fibres (RCF) and their classification in the EU as a category 2 carcinogen under Directive 67/548/EEC. Such classification carries with it the requirement for substitution by less hazardous materials. This paper focuses on the development of alkaline earth silicate (AES) wools as a new class of high temperature insulation with the capability of such substitution in a number of applications. These wools have only a low potential to cause harm because they do not persist in lung tissue once deposited, and have produced minimal effects in experimental test systems. AES wools are increasingly being used in a wide range of high temperature applications.

1. Introduction

Until the dangers associated with the use of asbestos were fully realized, it was very widely used in thermal (and other) insulation applications, both industrial and domestic. As asbestos usage subsequently declined, the use of manmade fibrous materials, both organic and inorganic (such as rock wool and glass wool; see text box) increased, sometimes as so-called ‘asbestos substitutes’ but mostly in new applications.

However, precisely because of their fibrous form, which they share with the asbestos minerals, these manmade materials also attracted concern regarding possible health effects. As a consequence, a number of experimental studies were performed over the years that, together with mechanistic studies on asbestos, have provided invaluable information about both the nature of the hazard and the intrinsic properties of fibres that might explain their effects. This in turn has led to the development of man-made vitreous fibres whose physical and/or chemical properties have been adjusted to minimize their possible harm to health.

A strong driver for the development of new fibres/wools suited for high temperature insulation was concern about the toxicity of refractory ceramic fibres (RCF), used for very high temperature insulation applications. Following a series of experiments carried out at the Research and Consulting Company, Geneva (RCC), RCFs and some other glass wools were subsequently classified by the EU as category 2 carcinogens under Directive 67/548/EEC. Such a classification carries with it the requirement for substitution by less hazardous materials or systems.

The purpose of this paper is to investigate and explain how the concepts of biopersistence and bioaccumulation are fundamental to an understanding of fibre toxicity, and how less hazardous mineral fibres can, and have been, developed. It includes a review of how high-temperature insulating wools are currently classified and regulated, and a history of the development and testing of one particular family of man-made vitreous fibres, the alkaline earth silicate (AES) wools.

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Nomenclature for man-made inorganic fibres

Some of the names given to synthetic inorganic fibrous materials reflect the ingredients used in their manufacture rather than their chemical composition. Such names include rock or stone wool, slag wool, glass wool, glass fibres, fiberglass and refractory ceramic fibres (RCF; originally made from calcined kaolin).

Various groupings of these materials have been described:

- Man-made Vitreous Fibres (MMVF) are by definition glasses and include glass fibres/wools, rock/stone wools, slag wools, RCF (alumino-silicate glass wools; ASW) and the alkaline earth silicate glass (AES) wools. There are no clear definitions of most of these classes of material; the exceptions are the AES wools, which are defined by CAS registration number 436083-99-7, and RCF (ASW), defined by CAS number 142844-00-6.
- Man-made Mineral Fibres (MMMF) comprise any inorganic fibre - including the MMVF above - and also crystalline fibres (e.g., polycrystalline wools; PCW) and sometimes, but not always, acicular crystals or whiskers such as silicon carbide or boron nitride.
- 'Mineral wools' is a term used in the USA (and also in some IARC publications) as a collective term for rock and slag wools, but in other settings it may be synonymous with ''mineral fibres'' or MMMF.

2. Principles of fibre toxicity and the key role of biopersistence

There is little or no evidence in humans of disease arising from exposure to manmade mineral fibres, but experimental studies with a wide range of fibrous materials and the differences observed between the effects of the different natural asbestos minerals led to the conclusion that the dangers from fibres are largely determined by what have been called the "three D's"; that is:

Dose – or, as commonly used, cumulative exposure
Dimension – the size (length, diameter) of inhaled fibres which determines both access to the respiratory tract (respirability) and biological activity
Durability – the ability of a fibre to persist once deposited, now known as ''biopersistence''

These should not be regarded as independent variables as they all affect ''dose'' in the sense of the amount of material in the target tissue, either as an instantaneous value or integrated over time.

The principles of fibre toxicology are well described elsewhere; e.g. Hesterberg and Hart (2001), Maxim et al. (2006), Bernstein (2007). A recent review article by Donaldson and Seaton (2012) provides an interesting account of the history of the toxicology of inhaled particles, explaining the development of the present understanding of the relationship between fibre characteristics and pathogenicity.

Observations on asbestos form the major part of the evidence for relating fibre persistence and health effects in humans. The asbestiform minerals are very heterogeneous and differences between the properties of the different types of asbestos and their propensity to cause disease has provided convincing evidence for the effect of biopersistence on pathogenicity; studies have clearly indicated that amphiboles are both more biopersistent and more pathogenic than serpentine (chrysotile) asbestos (e.g. see Wagner and Skidmore, 1965; Davis et al., 1978; Davis, 1989; Case et al., 1997; McDonald et al., 1997; McDonald, 1998). The conclusion that less biopersistent fibres are less hazardous has also been demonstrated for a number of man-made vitreous fibres in studies by Hesterberg et al. (1998) and Miller et al. (1999) for example, and is reflected in the findings of an IARC Working Party (IARC, 2002) and the conclusions of Hesterberg et al. (2012) on the safe manufacture and use of glass fibre. The central role of biopersistence in fibre toxicology is also supported by more recent studies on a polymer (Donaldson, 2009) and carbon nanotubes (Donaldson et al., 2010), for example.

The idea that biopersistence is a fundamental correlate of fibre pathogenicity is coherent with the assessment of other classes of toxic substances where those with long residence times in the body are considered more likely to be dangerous. This is especially so where the substance arrives faster than it can be eliminated and thus accumulates.

Further, there is no reason to believe that fibre effects should be exempt from Paracelsus' axiom – central to toxicology – that ''it is the dose that makes the poison''. The relationship between fibre accumulation and clearance has been modelled (see Fig. 1; Moolgavkar et al., 2001a) and related to calculations of human risk (Moolgavkar et al., 2001b, and Turim and Brown, 2003) for fibres with different rates of clearance from the lung. This shows, as might be expected, that the dose to the target tissue increases with the ability to persist and hence accumulate. The more fibres there are in contact with potential tissue targets – and, importantly, the longer they remain – the greater the chance of a reaction, or reactions, leading to disease.

The importance of fibre length in the pathogenicity of mineral fibres has been demonstrated in numerous experiments, both injection studies and inhalation experiments (e.g. Stanton et al., 1977; Pott, 1978; Davis et al., 1978, 1986; Davis and Jones, 1988; Davis, 1989), with longer fibres being demonstrably more active than shorter fibres (Dodson et al., 2003). Reanalysis of Davis' results by Berman et al. (1995) led to the suggestion that fibres >40 μm long were some 500 times more potent than short fibres. Bernstein (2007) concluded that 20 μm represents an appropriate 'cut-off' between short fibres and more pathogenic long fibres, and this is often the critical length referred to in studies of fibre toxicity.

While studies on asbestos clearance confirmed the expectation that short fibres are cleared from the lungs faster than long fibres (Roggli and Brody, 1984; Roggli et al., 1987), this is not the case for long man-made vitreous fibres as these break transversely - hence

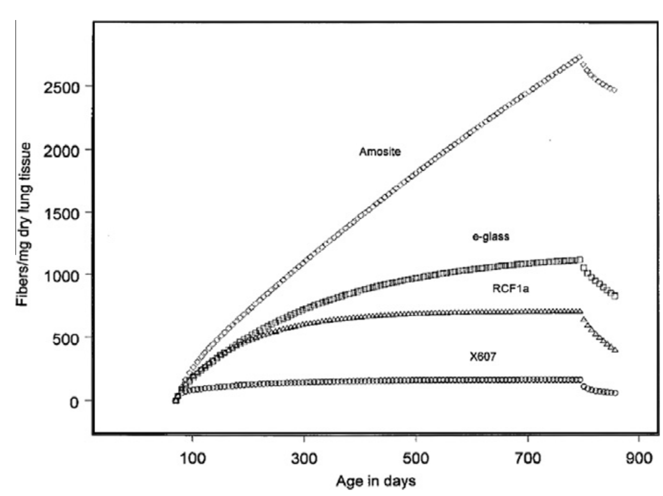

Fig. 1. Fibre content of lung tissue (burden) for a number of fibre types with different abilities to persist as a function of age for rats exposed under the assumption that 12 fibres/mg of lung was deposited each day of exposure (from Moolgavkar et al., 2001a). Note: X607 is a type of AES wool.