FILE NAME: Refractories (REF)

DATE: 1987 Apr

DOC#: REF007

DOCUMENT DESCRIPTION: Journal Article - The Identification and Control of Health Hazards

GLASS TECHNOLOGY, 1987 (April); 28(2): 69-73.

IA 7479
Code 36 38 52 53 90 82

The identification and control of health hazards*

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The health hazards caused by refractories containing silica and asbestos are discussed together with problems from other refractories and man made mineral fibres. The disposal of material contaminated during the life of the furnace is also considered.

Legislation and standards are examined and methods of controlling these hazards now and in the future are discussed.

Refractories are defined in the Oxford English Dictionary as 'substances specially resistant to heat, corrosion, etc.' and have been an essential part of glassmaking for centuries. Their impact on the environment, both the internal factory environment in their manufacture and use and the external environment in the disposal of waste materials, is the subject of this paper which reviews the various types of refractory materials, the possible hazards to health associated with them, and the controlled use of these materials to prevent or minimise these hazards.

Traditionally, the refractory materials used in glassmaking have been based on aluminosilicate minerals ranging from materials having a high alumina content such as silimanite and mullite, through a considerable variety of clays, to siliceous materials which, in the extreme case of silica brick, consist essentially of free silica. Whilst all these materials can and do produce dust during their production, during their working and handling in furnace construction, repair, and demolition, and during their final disposal from site, it is essential to understand that it is the composition and particle size of the dust that are the two critical parameters influencing the extent and severity of the industrial diseases associated with them.

During the present century, other refractory materials have found a place in furnace design and construction. They have included fibrous asbestos minerals and more recently man made fibres, zircon based materials, and refractories containing magnesite and chrome. In addition, the contamination of refractory materials with the residues of the combustion of fossil fuels used in heating the furnace (especially vanadium pentoxide from certain heavy fuel oils) and with batch materials often carried over from the tank itself into the associated system of flues and regenerators can present toxid hazards (e.g. from lead, arsenic, etc.) whenever deposits of contaminants are disturbed.

Silicosis

The major occupational disease which has been associated with refractory materials, probably since antiquity, is silicosis, an insidious pulmonary disease contracted by the inhalation of free silica dust of respirable size, usually in relatively small quantities over a long (i.e. several years) period of time.

Silica dust in the particle size range 0·5 to 5 μm diameter produces nodular lesions of fibrous tissue in the deep lung. These nodules aggregate to form massive fibrotic lesions with the involvement of emphysema as a result of fibrous contraction and distortion. Disturbance of the lung function with a reduction in vital capacity results in difficult and shallow breathing on exertion and progressively increases in severity, eventually leading to death from heart failure. In the past, tuberculosis has been a very common complication.

The disease is not due to mechanical lung damage by sharp particles. Other hard dusts, e.g. corundum (alumina) and carborundum (silicon carbide), which are commonly part of the atmospheric pollution of the workplace are relatively inert in the lungs. Neither can the disease be attributed simply to the chemical solubility of silica, but rather it is believed to be an immunological reaction with the lung tissue.

Why is the size range 0·5 to 5 μm so important? The human body is capable of inhaling dust particles up to 20 μm diameter. Particles with greater diameters than this tend to have high settling velocities and are not retained in the workplace environment for long periods. Particles between 5 and 20 μm, whilst inhaled,

*Presented at the Society's symposium on refractories and the environment held in the Ardsley Moat House Hotel on 15 October 1986.

are prevented from reaching the alveolar regions of the lung by being impacted on the walls of the bronchial tree and subsequently removed from the lung as phlegm as the result of cilliary action in the bronchii. A further body defence mechanism is the engulfing of dust particles by phagocytes (scavenger cells) in the lung. Particles less than 0·5 μm diameter tend to be exhaled from the lung without deposition.

The aluminosilicate group of refractories vary in their free silica content. The highly aluminous mullites and sillimanites contain little or no free silica, their silica content being completely bound with alumina as aluminium silicates which do not cause silicosis.

The greatest silicosis hazard is from highly siliceous material such as silica brick and refractories made from ball clays and grogs mixed with silica flour. The latter material requires a very high degree of control in its use. In addition, some aluminosilicate refractories when subjected to the constant high temperature of the glass manufacturing campaign can undergo conversion to free silica and hence can present an increased hazard in repair and demolition work.

Whilst the usual form of silica encountered in refractory materials is crystalline α-quartz, the two high temperature forms of silica, tridymite and cristobalite, can be present in quantity in refractories, especially those having been subjected to furnace use. Both tridymite and cristobalite are regarded as being more active in the aetiology of silicosis than is α-quartz.

The amorphous forms of silica are generally much less active than the crystalline forms, although diatomaceous earth can reform to cristobalite on straight or flux calcining.

Generally silicates as opposed to free silica do not have a permanent adverse effect on the body. Glass dust, alumina dust, and many other silicates (e.g. aluminium, calcium, and zirconium) have not been shown to be hazardous in the same way as free silica, although it should be said that all these dusts can cause irritation in the upper respiratory tract and should be regarded as nuisance dusts with an obligation on their control. Asbestos dust, however, is a most hazardous silicate material.

Asbestos

The second most important agent for occupational disease in the refractories and glass industries is asbestos. Asbestos is the generic name for a number of fibrous silicate minerals, the most important commercially being chrysolite (white asbestos), a fibrous form of serpentine, and two fibrous amphiboles, crocidolite (blue asbestos) and amosite (brown asbestos). They have been used extensively in the past as insulation blocks, boards, textile drapes, sprayed coatings, and trowel applied cements around furnaces, lehrs, etc. In recent years their use has greatly diminished. Both amosite and crocidolite are now effectively banned from importation but can still be present in quantity in older furnace areas.

There are three principal hazards to health from asbestos.

Asbestosis

This is a form of pneumoconiosis resulting in fibrosis of the lung. It is similar to silicosis in that it is an insidious long term disease progressing in severity, dependent on the amount of asbestos to which the individual has been exposed and the length of exposure to the dust. Asbestos fibres can remain in the lung for long periods and the fibrosis continues to develop for many years after exposure stops. Lung function gradually decreases, especially if the development of chronic obstructive lung disease from tobacco smoke occurs, and symptoms may be aggravated and death hastened.

Lung cancer

This is really carcinoma of the bronchus and is indistinguishable from other bronchial cancers caused by cigarette smoking. Asbestos apparently exerts its effect synergistically with tobacco smoke and it is believed that there is a strong interaction, so that the chance of a smoker exposed to asbestos contracting lung cancer is much greater than that of a nonsmoker exposed to asbestos or a smoker not exposed to asbestos. The disease has a long latent period, which can be in excess of 20 years, and in common with other occupational cancers, as opposed to other lung diseases such as pneumoconiosis, has no known dose/response relationship. Hence it is necessary to control the inhalation of asbestos dust to the lowest reasonably practicable levels.

Mesothelioma

Mesotheliomas of the pleura or peritoneum are extremely rare cancers which have been associated with exposure to asbestos dust. They have an extremely long latency. The delay between first exposure and effect is longer for mesothelioma than most other cancers and is seldom less than 15 years and often greater than 40 to 50 years.

The relationship of asbestos with mesothelioma differs in several ways from its relationship with lung cancer. It is largely unaffected by smoking habits and appears to be more dependent on the type of asbestos, the amphibole types crocidolite and amosite being thought to be the most active agents. However, in common with other occupational cancers, there is no accepted dose/response level.

Man made mineral fibres

The knowledge of the hazard to health of respirable asbestos fibres has caused industry to look for safer alternative materials. A wide range of man made fibrous materials is now available for thermal insulation, ranging from relatively low temperature materials such as glass and rock fibres to higher temperature resistant materials based on ceramic fibres, e.g. aluminosilicate, calcium silicate, alumina–zirconia, and silica.

Research workers in the early 1970s, ostensibly looking for the mechanism of the induction of cancer by asbestos, carried out experiments involving the implantation of glass and other natural and synthetic fibres in the pleural cavities of animals and this led to the development of tumours similar to the mesothelioma caused in man by asbestos. The conclusion of this work was that carcinogenicity is more closely related to the morphology of the fibres than to differences in mineralogical composition.

These studies have attracted interest in the possible health hazards of inhaling the respirable fraction of man made mineral fibre materials and the American and European glass fibre manufacturers have both instigated independently conducted research programmes to evaluate the long term health hazards in the manufacture and use of such products. Animal experiments designed to test their carcinogenic and fibrogenic potential when fibres are inhaled have shown that, in general, insulation, reinforcement, and textile fibres made to a diameter of several micrometres do not cause lung cancer, pulmonary fibrosis, or mesothelioma and that glass fibres are far more soluble in the lungs than is asbestos and are not retained for lengthy periods.

Epidemiological studies undertaken by the International Cancer Research Institute in Lyons have included observations on large groups of workers employed in the European mineral fibre industry. No excess in overall mortality rate from mesothelioma tumours was found in these studies nor was there an overall excess of cancer of the lung. However, the studies did indicate a small excess of lung cancer in small groups of workers some 30 years or more after first exposure but with no association of the increased mortality with either the intensity or the duration of exposure to the fibres. Hence it is possible for the increase in mortality to be related to other occupational factors, e.g. use of asbestos, or to nonoccupational exposure, e.g. smoking.

The status of some ceramic fibres has similarly been under investigation by animal studies. Preliminary results from the USA have recently indicated that one single case of mesothelioma occurred in the inhalation studies of hamsters. In addition, the continued exposure of these fibres to very high temperatures, as in their use in insulating blankets on the external surfaces of furnace and regenerator structures, results in the formation of crystalline silica (cristobalite) which, if inhaled over a long period of time, can result in fibrosis of the human lung.

As a precautionary measure, one of the manufacturers of ceramic fibres in the USA has issued warning labels with their products indicating the possible cancer hazard and the hazard from crystalline silica.

Other refractories

The hazard to health from most other refractories, e.g., zirconia or magnesia based, is not believed to be significant. However, the use of refractories containing chrome may present health risks. Chromium in refractories is normally present in the trivalent state chromium III. However, it is postulated that the reaction of batch raw materials carried into regenerator stacks could result in the formation of hexavalent chromium compounds, chromium VI, especially calcium and sodium chromates, which are thought to be more toxic in terms of carcinogenicity and mutagenicity than chromium III compounds.

Some health effects of chromium, such as chrome ulcers, contact dermatitis, and sensitisation, have been known for many years and are more common where hexavalent chromium compounds are used. Chrome ulceration is a particular hazard of chromium plating and anodising where acid sodium dichromate is used as the electrolyte. The International Agency for Research on Cancer (IARC) Monograph Vol. 23 evaluates the carcinogenic potential of chromium compounds as follows:

> 'There is sufficient evidence for the carcinogenicity of calcium chromate and some relatively insoluble chromium VI compounds (sintered calcium chromate, lead chromate, strontium chromate, sintered chromium trioxide and zinc chromate) in rats. There is limited evidence for the carcinogenicity of lead chromate VI oxide and cobalt chromium alloy in rats.
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> 'The data were inadequate for the evaluation of the carcinogenicity of other chromium VI compounds and of chromium III compounds.
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> 'There is sufficient evidence of respiratory carcinogenicity in men occupationally exposed during chromate production. Data on lung cancer risk in other chromium associated occupations and for cancer at other sites are insufficient. The epidemiological data do not allow an evaluation of the relative contributions to carcinogenic risk of metallic chromium, chromium III and chromium VI or of soluble versus insoluble chromium compounds.'

Clearly, the occurrence of chromates and sintered oxides in used chrome refractories is a possibility. Also, whilst hexavalent chromium compounds are most clearly implicated, the IARC monograph does not absolve chromium III compounds, but merely states that the data available are inadequate for evaluation. However, it does seem reasonable to assume the major hazard is presented by the presence of hexavalent chrome compounds and, therefore, total chromium content (e.g. of used refractories) may not be a good guide to the magnitude of the risk to health. Furthermore, the Health and Safety Executive's Occupational Exposure Limits for chromium compounds are 0·5 mg/m^3 for other than hexavalent materials and 0·05 mg/m^3 for hexavalent.

A specialised type of refractory based on beryllium ceramic materials is capable of having a very high toxicity when absorbed into the human body.

Contamination of refractory materials

The most common contaminants associated with glassmaking refractory materials originate from the batch composition and the fuel used to heat the furnace. In soda-lime-silica glass compositions, the raw materials do not present significant health problems but in other glass compositions, the elements having a potential health hazard include lead in crystal glasses, lead and barium in optical glasses, arsenic and antimony, which are often added to the batch in minor quantities as fining agents, and selenium which is used as a decolorising agent in container ware and to give bronze tints in flat glass manufacture.

Other potentially toxic heavy metals, e.g. cobalt, nickel, and cadmium, are used as colorants in various glasses, silver is used in photochromic glasses, and fluorides are used to produce opal glasses.

All of these batch additives can contaminate the refractory materials of the tank, regenerator system, and flues and arsenic and selenium compounds, being particularly volatile, can be deposited in flues and stacks remote from the furnace.

The furnace is usually fired by either natural gas or petroleum oils. Natural gas from the North Sea is essentially free of toxic contaminants as are the low viscosity gas oils used to fire some furnaces. The heavy fuel oils, of viscosity around 2000 seconds, can contain significant amounts of sulphur and vanadium, dependent on their origin. Venezuelan crudes are notoriously high in vanadium compounds which, on deposition as vanadium pentoxide in the flues and regenerator system, can be a health hazard during furnace repair, demolition, and disposal. Vanadium pentoxide dust or fume when inhaled has a toxic action on the respiratory system causing attacks of acute bronchitis involving soreness and tightness of the chest with wheezing and a dry cough; more serious complications, including pneumonia, have been reported. The acid nature of the pentoxide causes irritation of the skin and eyes and a characteristic effect of vanadium absorption is the greenish-black discoloration of the tongue.

Legislation and standards

The hazards to health of refractory materials have been known for many years and have, in the case of manufacture and use, been subject to the provisions of the Factories Act 1961, particularly Section 63—Removal of Dust or Fumes. Specific regulations and orders for safety, health, and welfare in miscellaneous industries also apply (viz. The Asbestos Regulations 1969, Clayworks (Welfare) Special Regulations 1948, The Pottery (Health & Welfare) Special Regulations 1950, and The Refractory Materials Regulations 1931) together with the far reaching provisions of the Health and Safety at Work Act 1974, an enabling Act which provides a framework for more specific regulations on particular hazards and will eventually provide for the progressive repeal of existing statutory provisions made under the Factories Act.

Regulations, together with Approved Codes of Practice and Guidance Notes, have subsequently been produced for asbestos, lead, control of dusty processes, etc. An important HSE Guidance Note is EH40 *Occupational exposure limits*, which is updated each year. It lists both control limits (those contained in regulations etc.) and recommended limits which are advisory, limit values being given for both full shift (8 hour time weighted average) and short term (10 minute) exposures.

The external environment involving the disposal of wastes is covered by The Control of Pollution (Special Wastes) Regulations 1980 and the provisions of the Packaging and Labelling of Dangerous Substances Regulations also apply here. Special waste is that which it is considered 'is or may be so dangerous or difficult to dispose of that special provision is required for its disposal', It is quite clear from the regulations that special waste is waste that has the potential to cause acute harm or injury to persons directly exposed to it. The schedule to the Special Wastes Regulations does not include refractory materials directly but does include the following categories of substances that may well be present in a consignment of refractory waste: acids and alkalis, antimony and its compounds, arsenic compounds, asbestos (all chemical forms), barium compounds, beryllium and its compounds, boron compounds, cadmium and its compounds, hexavelent chromium compounds, lead compounds, nickel and its compounds, selenium and its compounds, vanadium compounds, and silver compounds.

The criteria to be used in deciding whether a particular waste should be treated as special waste are:

1. is it dangerous to life in that
   - (a) either a single dose of not more than 5 cm^3 would be likely to cause death or serious tissue damage if ingested by a child of 20 kg body weight
   - (b) or exposure to it for 15 minutes or less would be likely to cause serious damage to human tissue by inhalation, skin contact, or eye contact
2. has it a flash point of 21°C or less
3. is it a medicinal product as defined by the Medicinal Act 1968.

The assessment procedure for a particular waste involves establishing whether or not it contains substances in the schedule and whether or not they comply with the above provisions for toxicity, corrosivity, and flammability. Should the provisions apply, then, before waste is removed from the premises at which it is produced, a procedure of making out consignment notes for each load or skip of waste is required. This involves the producer of the waste, the carrier of the waste, and the waste disposal authorities for both the area in which the waste is produced and the area where the waste will be deposited. Registers of consignments are required to be kept and in some cases local authorities may lay down additional regulations for the disposal of specific substances.

Labelling of consignments of special waste must conform to the requirements of the Classification, Packaging and Labelling of Dangerous Substances Regulations 1984.

Control of hazards

There are several ways of controlling a dust hazard, not all of them equally effective; if in doubt, seek professional advice from an occupational hygienist or an environmental engineer. Ideally, one should consider the control of a dust hazard at the design stage of a manufacturing process. A manager should ask himself (and his colleagues) the following questions: is the material necessary, can it be stored safely, what is its toxicity (or other hazard), can the plant handle the material, is the material recoverable, can waste products be disposed of safely, and what are the likely impurities (e.g. free silica content of an otherwise nuisance dust)?

More frequently, one has to consider dust control in an existing process when it becomes obvious that the degree of control needs to be increased. On an existing plant this is often difficult and usually expensive to achieve if for no other reason that the plant is not productive and profitable whilst down for modification.

The most effective method of control is to substitute a safe material for a hazardous one. There have been several examples of the replacement of highly siliceous materials in the history of occupational health. The use of artificial bonded abrasive wheels for sandstone wheels, the prohibition of sand blasting, and the substitution of alumina for powdered flint as a parting medium in the firing of pottery ware have all significantly reduced or eliminated silicosis in industry. We are presently witnessing the replacement of asbestos products as refractory materials and this process must continue whenever materials are judged to be sufficiently hazardous, such as being carcinogenic, for the risk of serious disease to be so high as to make the material totally unacceptable.

Segregation of the hazardous material from the workforce is a control method which deserves more attention than it has so far received. The classic example is in the control of highly radioactive substances but the principles can equally apply to non-radioactive dust hazards. Segregation, which includes the enclosure of plant which emits dust, can be by distance e.g. remote control, by time, e.g. maintenance work segregated from production work, or by age and sex.

Ventilation is a common method of control. My own experience of over 25 years in occupational hygiene is that the principles of ventilation in respect of sources of toxic dust emissions are still misunderstood by plant designers and as a result, effective capture is not always achieved.

Wet methods of control are useful when working refractories, dust emissions in wet cutting operations being significantly lower than in dry cutting; once dust has become airborne, wet methods of control are useless.

Personal protection has a place in dust control, but not as a primary method in lieu of engineering control. In short term maintenance jobs, however, the dust hazard can be effectively minimised by the use of approved respiratory protection, selected with a clear knowledge of the likely airborne dust concentrations expected.

Several of these control methods can be extended into the field of waste disposal, particularly segregation and enclosure during transport and disposal. Wetting of wastes may also be beneficial in reducing airborne contamination.

The future

There will inevitably be increased pressure to further protection of the environment, both working and external, from hazardous substances.

Proposed UK and EEC legislation is aimed at more comprehensive control of these environments, a good example being the proposed Control of Substances Hazardous to Health Regulations. These regulations, if enacted, will require the assessments of all industrial processes involving many hundreds of hazardous substances, monitoring of the working environment to determine levels of action, and a range of control measures to keep airborne concentrations of contaminants below recommended limits and at as low a level as is reasonably practicable.

There is already in some parts of the country a shortage of suitable holes in the ground for the disposal of toxic wastes and of course no one wants waste dumped in their own neighbourhood.

There will be further restrictions on the disposal of toxic waste, especially those considered to be carcinogenic. Also, there is a strong movement for the recycling of wastes, which, in many ways, makes good economic sense but involves increased handling of hazardous materials with an increased risk to some people, albeit with a reduced risk to the general population.

Likewise the concepts of converting highly dangerous soluble wastes, e.g. some radioactive wastes or dusty wastes such as asbestos, into relatively insoluble glasses for permanent disposal by burial will be extended.

The refractories industry will undoubtedly be faced with these pressures and should be now considering how to reconcile the need for environmental protection with the economics of running a successful and profitable business.

Glass in high speed transport*

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Windscreens employed in various forms of high speed transport invariably involve a high degree of complex engineering. Most often the windscreen will be designed to withstand a substantial high energy impact. Thus, for instance, a civil aircraft windscreen is tested, usually, to withstand the impact of a 4 lb bird travelling at 450 mph. Similarly, a locomotive windscreen will be expected to withstand the impact, for instance, of a brake shoe thrown from a locomotive travelling in the opposite direction. Apart from these most demanding dynamic requirements, windscreens also need to meet high standards of optical performance and must be reliable in use.

*Presented at the Society's symposium on 'Exploiting glass's potential' held in the Peebles Hotel Hydro, Scotland, on 12 and 13 June 1986.