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INVESTIGATION OF THE THERMAL MODIFICATION OF ASBESTOS WASTES FOR POTENTIAL USE IN CERAMIC FORMULATION

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Preliminary research has been carried out on the thermal modification of chrysotile asbestos. Destruction of the tubular structure of asbestos was achieved by calcination at 1000°C. In order to characterize the changes accompanying thermal modification both natural asbestos and calcined asbestos were subjected to thermogravimetric and differential thermal analysis, X-ray analysis and examination by scanning electron microscopy. The possibility of utilization of the calcined asbestos in the presence of a phosphate binder for the manufacture of refractory materials has been demonstrated.

Keywords: *asbestos, DTA, phosphate bonding, refractories, SEM, thermal modification, XRD*

Introduction

Asbestos is a commercial term applied to a group of fibrous silicate minerals that have desirable properties such as high tensile strength, heat and fire resistance, heat, electrical and sound insulation, and resistance to chemical and biological attack. Asbestos minerals are divided into two groups, serpentines and amphiboles, depending upon structure. The serpentines have a sheet structure and the amphiboles have a double chain structure. Within these groups there are six principal asbestos minerals [1–3].

Serpentines are hydrous magnesium silicates that occur in three polymorphs: antigorite, lizardite and chrysotile. Chrysotile, the only fibrous member, is the most commercially important variety accounting for over 90% of the world production of asbestos. The chemical composition of chrysotile asbestos may be represented as: $Mg_3(Si_2O_5)(OH)_4$ or $3MgO\cdot 2SiO_2\cdot 2H_2O$. The crystalline structure of chrysotile asbestos consist of two layers of chemicals: a brucite layer and a tetrahedral layer. Due to the differing chemical and physical characteristics of the two materials these fibers tend to curl into hollow tubes. Chrysotile fibers may range from 10 to 12 cm long and can occur as aggregates of long, thin and elastic elementary fibers, so called fibrils. Chrysotile is also known as ‘white asbestos’ [1, 3].

Amphiboles are silicates of magnesium, iron, calcium, sodium and aluminium such as amosite, crocidolite, tremolite, actinolite and anthophyllite. Amphibole fibers tend to be straight and splintery. About 5–10% of world production is of the amosite (brown asbestos) and crocidolite (blue asbestos) variety of asbestos. Tremolite, actinolite and anthophyllite are rare and of no economic importance [3].

Asbestos encompasses a diverse family of fibers with differing physico-chemical identities and pathogenicities. Exposure to asbestos has been causally linked to the development of lung and pleural diseases including lung cancer, asbestosis and mesothelioma [4]. All forms of asbestos are carcinogenic, although crocidolite seems to be two to four times more potent than chrysotile in its capacity to induce mesothelioma. All forms of asbestos have the some capacity to cause cancer of the lung [5].

Most experimentalists in the asbestos field today would acknowledge that the length of the fiber is an important determinant of biological activity. Fibers with lengths well below 5 μm are considered ‘inert’ while those exhibiting lengths just below this value exhibit markedly less activity than their counterparts of greater length when tested in the same system [6]. It is known from [3] that the most carcinogenic fibers have been reported to be longer than 8 μm and less the 1.5 μm in diameter. The longer, thinner fibers seem to be more dangerous than shorter ones. These longer, thinner fibers are also more valuable.

Carcinogenic activity of asbestos was the reason for including it in a list of seriously hazardous materials. Up to that time asbestos had been used for many years on a very large scale. There are over 3000 different types of commercial products containing varying concentrations of asbestos depending on ultimate usage. Asbestos products still popular in developing countries include construction products

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such as roofing and siding shingles, asbestos cement pipes, and materials used in stoves, vinyl carpets and floor tiles. There are also other products used in sound proofing (lecture theatres), thermal insulation (e.g. hot water and steam pipe) and fire proofing (e.g. in bank vaults), adhesives, filers, brake shoe and clutch linings, and several textile products [7]. A tendency to limit the use of asbestos appeared in Poland several years ago. As a consequence of legislation and technological activities, questions dealing with the production, exploitation, storage of asbestos as well as the management of asbestos waste heave lead to asbestos products being regulated [8]. At present there is one method of disposing of asbestos containing products. Asbestos products and asbestos wastes are packed into polyethylene foil bags and then the bags are stored in special stockyards designated for dangerous wastes [9–11]. There has also been a suggestion to insert asbestos-containing products in inoperative mining works [12]. However, such procedure does not represent a final solution for the problem of disposal of asbestos wastes. Because of this research directed forward a practical utilization of asbestos wastes has been conducted. The law on asbestos wastes recycling is obligatory in UE countries – the methods developed for the use of asbestos wastes must, as a primary consideration priority, for the destruction the fibrous structure of asbestos [13].

A method has been patented in USA, in which modification of asbestos products consists of dissolving products in acids, for instance in sulphuric acid or in various organic acids [14, 15]. In order to obtain solidification of the post-reaction mixture and to obtain building material, pozzolanic material, lime or hydrated lime to increase the mixture pH up to value of approx. 7 is added. As a result of neutralization calcium sulfate is formed. The method may be used for building materials already in place to remove the asbestos fibers contained therein.

The next method [16] consists of treatment with acid in the presence of fluoride ions (ammonium fluoride). The acid hydrolyses the magnesium oxide units in the asbestos while the fluoride ions attack the interleaved silica layers in the crystal structure of asbestos, thereby destroying the fibrous nature of asbestos.

A new method elaborated in [17] consists in the digestion of the asbestos wastes in a strongly acidic environment of the phosphoric acid with such a concentration of hydrogen ions that it assures maintaining all the originating phosphates in the soluble form. Thus, all phosphates, mainly calcium and magnesium ones, can easily be separated from the solid residue and processed to other products. After the neutralization with calcium hydroxide or calcium carbonate the solution can be processed to fodder phosphates or to phosphate fertilizers [18].

Once of the patents [19] presents processing asbestos with a concentrated solution of NaOH in a reactor – autoclave at the temperature of 175–200°C and under the pressure of 0.3 to 1.0 MPa. The waste obtained after the decomposition may be utilized for the production of cement.

Other suggested methods to render harmless toxic asbestos materials are: mechanochemical treatment [20], vitrification [21, 22] as well as thermal treatment [23–26].

This paper contains results from some preliminary research on the thermal modification of chrysotile asbestos. The focus of this work was the destruction of characteristic tubular structure of chrysotile by means of thermal decomposition, which leads to elimination of its carcinogenic activity. Data exists to show that chrysotile asbestos does not retain its mineral properties, or biological activity, at temperatures far below the olivine transformation point [6].

The aim of the first stage of the study was the examination of physical changes and chemical reactions proceeding at temperatures up to 1000°C for asbestos fibers. The aim of the second stage was an examination of the possibilities for using the calcined asbestos for the manufacture of refractories that were chemically bonded with phosphate binder.

Experimental

The subject of examination was chrysotile asbestos of P-3-50 type (long-fibres asbestos) that is supplied to the chlorine industry. This asbestos was subjected to X-ray analysis as well as differential thermal analysis (DTA) and thermogravimetry (TG). Its microstructure was examined as well. Then, to check the usability of asbestos as a raw material for the manufacture of refractories, asbestos was subjected to initial calcination at a temperature 1000°C over two hours. The phase composition of the product obtained was determined using X-ray analysis and changes in its microstructure were determined by means of SEM.

The X-ray phase analysis of examined samples was accomplished using a XRD-3003 TT type X-ray diffractometer [(Seifert), CuK_α radiation and Ni filter]. Diffraction patterns were analysed using the JCPDS PDF-2 powder diffraction data base [27].

DTA and TG was carried out using a Paulik–Paulik–Erdey (MOM, Hungary) type derivatograph within the range of temperature 20–1000°C. The mass of sample was 500 mg. The reference material was alumina. The heating rate was 10 K min^{-1}.

The microstructure of samples was examined by scanning electron microscopy, SEM (Tesla BS 340, Czech Republic). Microscope observations were made after coating the samples surface with a thin layer of gold.

Asbestos calcined at 1000°C was subjected to short-time (5 min) homogenisation in a laboratory vibration mill and then to sieve analysis. Dry press body was prepared by adding water (10 mass%) as well as a phosphate–aluminium–chromium binder in an amount of 15 mass% (Glifos C of density 1.57 g cm^{-3}). The calcined asbestos was wetted with water and stored for 24 h in a tight container to obtain good homogenisation. Then it was mixed with phosphate binder and granulated through a sieve of mesh 0.8 mm. Cylinder samples of 30 mm in diameter and about 30 mm in height were pressed in a steel die by means of hydraulic press at a pressure of 100 MPa. Samples were dried at a temperature 150°C and then baked at temperatures of 600 and 1200°C (time at those temperatures was 4 h). Before and after thermal treatment the cylinder dimensions were measured in order to determine the linear shrinkage. The baked samples were subjected to an absorbability test, as well as open porosity and apparent density tests using the Archimedes method. Compressive strength was also evaluated.

Results and discussion

DTA, TG and DTG curves for chrysotile asbestos are presented in Fig. 1, whereas its X-ray diffraction pattern is shown in Fig. 2. Figure 3 presents the X-ray diffraction pattern of asbestos calcined at temperature 1000°C. The microstructure of chrysotile asbestos as well as that of them the product of calcination is presented in Fig. 4. The particle-size distribution of calcined asbestos is provided in Table 1. The physical properties of test forsterite products bonded with phosphate binder are presented in Table 2.

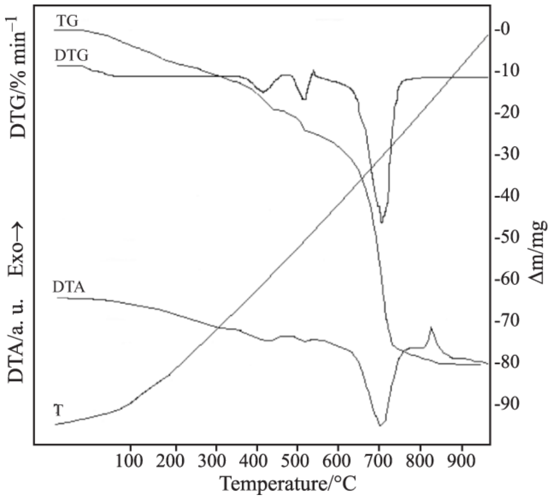

Fig. 1 DTA, TG and DTG curves for chrysotile asbestos

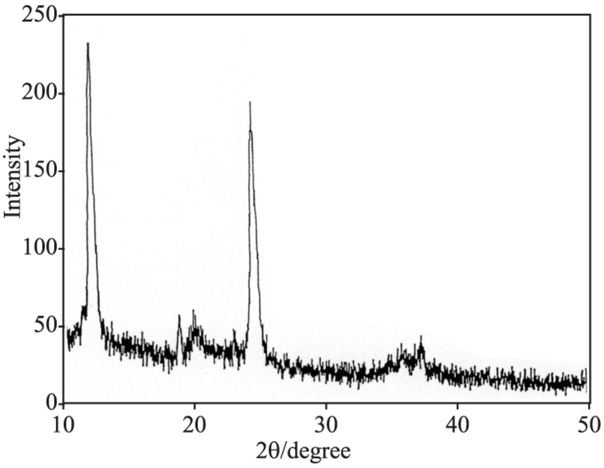

Fig. 2 XRD profile of chrysotile asbestos

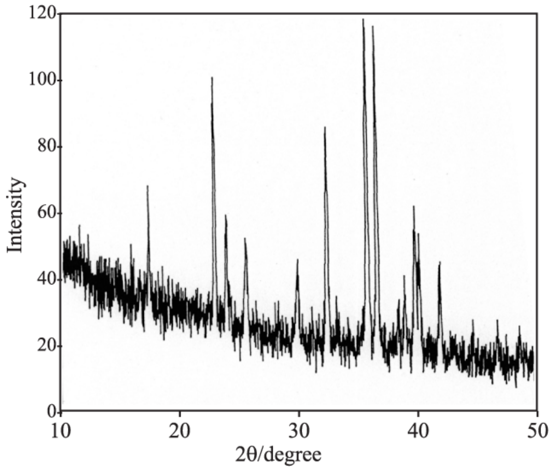

Fig. 3 XRD profile of chrysotile asbestos calcined at a temperature of 1000°C (forsterite)

Heating of chrysotile induces profound change in the mineral. It is known [2] that chrysotile, during heating up to about 400°C, gradually loses water absorbed on the surface or inside tubular crystals (interpacket water). Thermal analysis of natural chrysotile asbestos (Fig. 1) indicates a gradual loss of structural water. Some 2.5% of the structural water is lost in the temperature range 150–500°C. Within the range of temperature from 600 to 800°C chrysotile loses its chemically combined water (dehydroxylation of the brucite layer) that can be denoted by DTA which displays a characteristic strong endothermic peak with a minimum at 710°C. This represents the complete breakdown of the mineral structure and creation of an amorphous mixture of magnesia and silica, which mineralogists have dubbed serpentine anhydride [28]. The mechanism by which water is driven from chrysotile is thought to be donor-acceptor in character. The donor regions of the mineral supply cations and oxygen to the acceptor regions where they react with protons to form water [6].

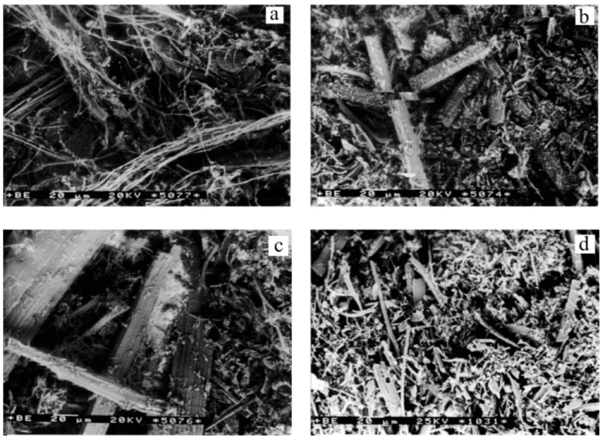

Fig. 4 Microphotograph (SEM) of chrysotile asbestos: a – natural; b, c – after heating at 1000°C, transformation into forsterite and d – after heating at 1000°C and homogenisation in a laboratory vibrating mill

Table 1 Particle-size distribution for calcined asbestos

Fraction / μm	Contents of fractions/mass%
>1.25	–
1.25–0.8	0.5
0.8–0.63	1.0
0.63–0.25	5.3
0.25–0.125	27.0
0.125–0.08	12.5
<0.08	53.7

At temperatures above 800°C, forsterite is created from chrysotile decomposition products [29]. Crystallization of the forsterite is observed by DTA as an exothermic peak of $T_{\max}$~840°C (Fig. 1). Many investigations consider only the olivine transformation temperature as the point at which chrysotile is converted to a biologically inactive substance [6]. The presence of forsterite has been confirmed by X-ray analysis of calcined asbestos (Fig. 3). Forsterite Mg_2SiO_4 is an orthosilicate, which has no fibrous structure and which displays high melting temperature (1890°C). The natural mineral is used to manufacture forsterite refractories [30].

Natural chrysotile asbestos exists as an intertwined mixture of a large quantity of very thin fibres and a smaller amount of fibre of lesser quality (Fig. 4a). As a result of calcination at 1000°C both long and short fibres are converted into strips of forsterite of various size (Figs 4b and c). Homogenization in a vibration mill generated material of more uniform size (Fig. 4d, Table 1).

Shaped samples prepared from calcined asbestos (forsterite), after drying at 150°C are characterized by high open porosity, above 36%. This exceeds significantly the values usually obtained for forsterite refractories. The samples baked at 600°C display slightly lower open porosity (Table 2). The compressive strength of samples after drying at 150°C or after baking at 600°C is comparable and in both cases is approximately 20 MPa. Shrinkage for these samples is low, i.e., it does not exceed 3%. Increasing the baking temperature up to 1200°C decreases the open porosity of samples up to approximately 12% and increases very distinctly the apparent density as well as the compressive strength, which exceeds 50 MPa. At the same time significant shrinkage of the samples occurs. Thus products do not display acceptable volume stability at high temperature.

In order to obtain products of open porosity not exceeding 25% – as a result of thermal treatment at low temperatures (not exceeding 600°C) – it would be advisable to select the optimum particle-size distribution of dry press body for the preparation of samples. In practice, three size grades of solid raw material, namely: fine, average and coarse may be used. Experience has shown that the best arrangement of grain in the product, and as a consequence the least porosity can be achieved where there is a small content of grains of average size in the dry press body for instance: 40% of fine grains (0–1 mm), 10% of average grains (1–2 mm) as well as 50% of coarse grains (2–4 mm) [31]. During the process of manufacturing forsterite refractories from natural raw materials (olivine, dunite, serpentinite) a mixture of 40–60% of forsterite clinker (1–3 mm) as well as flour of forsterite and magnesite is used. To use calcined chrysotile asbestos as a raw material it would be advisable to separate coarse and average grain size or to add a coarse grain modifier (for instance waste from the manufacture of magnesite or magnesite-chromite refractory materials).

On the basis of preliminary results presented here it may be suggested that initially calcined asbestos can be used as one of raw materials for a conventional ceramic industry, i.e., to manufacture sintered products.

Table 2 Physical properties of test forsterite products

Temperature of formation/°C	Linear shrinkage/ %	Absorbability/ %	Open porosity/ %	Apparent density/ g cm^{-3}	Compressive strength/MPa
150	<3	19.7	37.0	1.90	20
600	<3	18.2	35.3	1.94	22
1200	12.7	4.5	12.1	2.72	58

Conclusions

Within the range of temperature from 600 to 800°C chrysotile completely dehydroxylates to form a serpentine anhydride, a material void of structure and absent of chrysotile properties. The olivine (forsterite) transformation occurs at about 840°C. As a result of chrysotile asbestos calcinations at a temperature 1000°C its microstructure changes fundamentally, i.e., chrysotile fibres are converted into forsterite strips. This is a highly refractory material free from carcinogenic properties. Strength examination using shaped samples made of calcined asbestos support its usability for the manufacture of forsterite refractories. After addition of phosphate binder to shaped samples dried at 150°C their compressive strength reach 20 MPa. Forsterite refractories made of natural raw materials (no phosphate binder), after baking at 1500°C show compressive strength from 55 up to 65 MPa. Material of compressive strength of 60 MPa may be obtained using lower baking temperature, e.g., 1200°C. Selection of raw material of proper grain size should permit the formation of products of open porosity not exceeding 25% after baking at low temperatures.

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