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Study on the thermal decomposition of chrysotile asbestos

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Abstract This article reports the possibility of detoxification of chrysotile asbestos through a low temperature heating and grinding treatment. The effect of thermal treatment at different temperatures in the range from 500 to 725 °C for 3 h on raw natural asbestos was characterized by thermal analysis, X-ray diffraction, and scanning electron microscopy. It was found that an isothermal treatment at 650 °C caused the complete dehydroxylation of chrysotile $Mg_3Si_2O_5(OH)_4$. Transformation of the dehydroxylated phase to forsterite Mg_2SiO_4 was obtained by heat treatment in the range 650–725 °C. The study of microstructure changes of heated asbestos show the destruction of characteristic fibers of chrysotile and formation of strips of forsterite. It is easily milled to pulverulent-shape material by mechanical milling in vibratory mill.

Keywords Chrysotile asbestos · Grinding · Low temperature treatment · SEM · Thermal analysis · XRD

Introduction

The asbestos minerals have been used for a number of applications due to their excellent physical properties that include non-flammability, high tensile strength, heat and electrical insulation, and resistance to chemical and biological attack. They were widely used as component of building materials such as insulations, acoustic and thermal sprays, pipe and boiler wraps, plasters paints, flooring products, roofing materials, and cementitious products [1–4].

The word “asbestos” refers to several types of fibrous minerals. There are many different types of asbestos fibers which are divided into two main categories: amphibole and serpentine asbestos. The group of serpentine includes only chrysotile $Mg_3Si_2O_5(OH)_4$. Others belong to group of amphiboles; they are crocidolite, amosite, tremolite, antophylite, and actinolite. Chrysotile (white asbestos), crocidolite (blue asbestos), and amosite (brown asbestos) have the largest industrial applications [1, 5, 6]. The evidence concerning the asbestos carcinogenicity began to be demonstrated increasingly since the sixties of the twentieth century. The first ban on use of the material started in eighties. Asbestos is considered to be extremely hazardous for people, causes lung diseases such as asbestosis or lung cancer [1, 5–11]. The most dangerous are fibers which have an aspect ratio equal to or greater than 3:1 and a length equal to or greater than 5 μm.

A tendency to limit the use of asbestos appeared in Poland several years ago. At the present time, there is one method of depositing asbestos-containing products. Asbestos products and asbestos wastes are packed into polyethylene foil bags and stored in special stockyards designated for dangerous wastes [2, 3].

However, such procedure does not represent a final solution for the problem of disposal of asbestos wastes.

Methods of rendering asbestos and the asbestos containing materials harmless

In UEs countries the law of the asbestos wastes recycling is obligatory in order to reduce their hazardous influence on environment.

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Technical literature presents a number of ways, mainly the patented ones that concern the utilization and neutralization of asbestos and the asbestos products. Most literature reports, concerning both the basic research as well as the application one, concern the chemical treatment of the waste, where the compounds from serpentine and amphiboles group are decomposed using strong bases and inorganic as well as the organic acids [12].

One of the patents 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 MPa to 1.0 MPa. Depending on the nature of the asbestos treated, various solid materials will be obtained. In the case of amphiboles, a ferrate (complex iron hydroxide) precipitate will be obtained which can be adopted as a function of its utilization, in particular as flocculent for heavy metals in industrial effluents or in hydrometallurgical solutions. In the case of other types of asbestos, like chrysotiles, the precipitates will be, for example, mixed into a cement-based composition or introduced as adjuvants into refractory materials [13].

A lot of literature reports concern the destruction of asbestos using strong inorganic acids (for example sulfuric acid) and various organic acids [14–17]. The next method [18] consists of treatment with acid in the presence of the fluorine ions. The secondary products of utilization, emitted in a solid form, are then utilized as fillers in the production of the fireproof materials.

A new method elaborated in [12] consists in the dissolution of the asbestos wastes in a strongly acidic environment of the phosphoric acid. After the neutralization with calcium hydroxide or calcium carbonate the solution can be processed to phosphate fodders or to phosphate fertilizers and silica, which will be examined in respect to its potential application as an active material or a filler in the building and the plastic industries.

The mechanochemical process applied to the asbestos-containing waste is able to transform asbestos in an amorphous material, with a complete modification of its fibrous morphology. In [19] a high-speed mil was used to simulate the operating conditions of a mechanochemical reactor. According to [20, 21] the structure disorder of the clay minerals increased by grinding. It was observed that grinding caused a decrease of the temperature at which the structure bound OH group released.

Other suggested methods to render harmless toxic asbestos materials are vitrification [22, 23] as well as thermal treatment and recycling in the clinker burning process and traditional ceramics (refractories and building materials) [24–31].

In this article chrysotile asbestos was studied in order to investigate the structural changes caused by its thermal treatment and the ability to grinding of calcined samples.

Experimental

The samples of chrysotile asbestos, each having a mass of 100 g, were heated up from 500 to 725 °C and were thermally treated by maintaining at each temperature for 3 h in a box furnace. A vibratory mill carried out the grinding of the samples for 30 min. For comparison, raw chrysotile asbestos was also grinding, but longer time of grinding (120 min) was applied.

The raw and thermally treated chrysotile asbestos were studied by differential thermal analysis (DTA), thermogravimetric analysis (TG/DTG), X-ray diffraction (XRD), as well as scanning electron microscopy (SEM).

DTA, TG, and DTG curves were recorded using an MOM type derivatograph (Hungary). 500 mg of sample was placed in a corundum crucible and was heated from 20 to 1,000 °C at a heating rate of 10 K min^{-1}, using α-Al_2O_3 as an inert material.

X-ray powder diffraction patterns were obtained using a Seifert 3003 TT diffractometer operating at 40 kV and 30 mA with Ni-filtered Cu K_α radiation at intervals 0.02°. Step time of 2 s per interval was used.

SEM micrographs were obtained by using TESLA scanning electron microscope, model BS 340. Observations were made after coating the samples surfaces with a thin layer of gold.

Results and discussion

Study of asbestos by XRD method

X-ray diffraction study showed that the main mineral constituent of the raw asbestos is a well-crystallized chrysotile, as indicated by the characteristic narrow and intense two major diffraction peaks at $d_{002} = 7.3$ Å and $d_{004} = 3.64$ Å (Fig. 1).

Heating of chrysotile asbestos causes structural and textural changes connected to the dehydroxylation process. So,

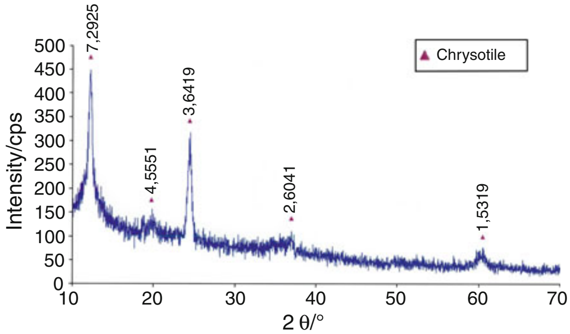

Fig. 1 XRD diagram of natural chrysotile asbestos

- there is not any significant change in the XRD pattern of the heated sample up to 500 °C.
- after heating the raw material up to 600 °C for 3 h (Fig. 2), the intensity of the peaks at 7.3 Å and 3.64 Å is slightly decreased and new weak peaks at d = 2.77 Å, 2.51 Å, 2.46 Å, and 1.75 Å appear due to formation of forsterite (Mg_2SiO_4) as a new crystalline phase, according to [32].

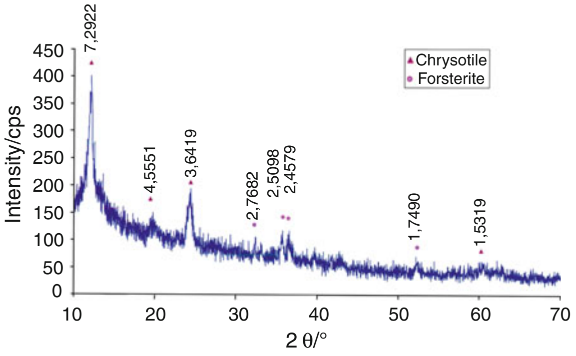

Fig. 2 XRD diagram of chrysotile asbestos calcined at a temperature of 600 °C

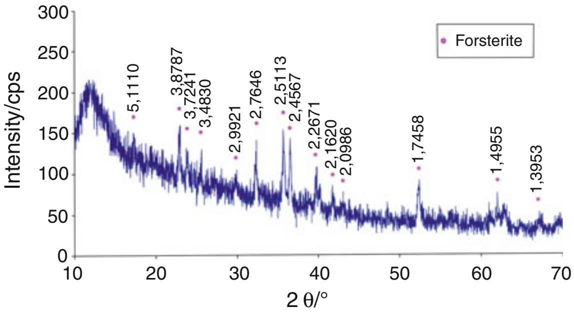

Fig. 3 XRD diagram of chrysotile asbestos calcined at a temperature of 650 °C

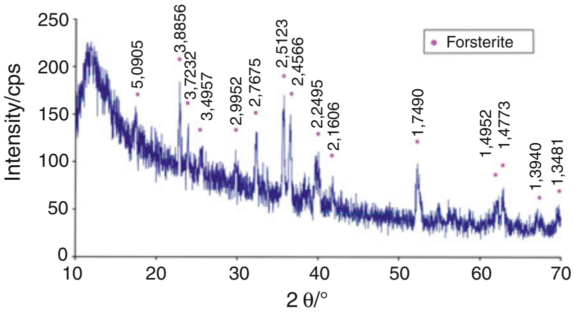

Fig. 4 XRD diagram of chrysotile asbestos calcined at a temperature of 725 °C

- when the sample is heated up to 650 °C, the peaks at 7.3 Å and 3.64 Å are disappeared (Fig. 3) indicating the total destruction of chrysotile.
- after heating of the sample up to 725 °C, the strong peaks of forsterite appear (Fig. 4).

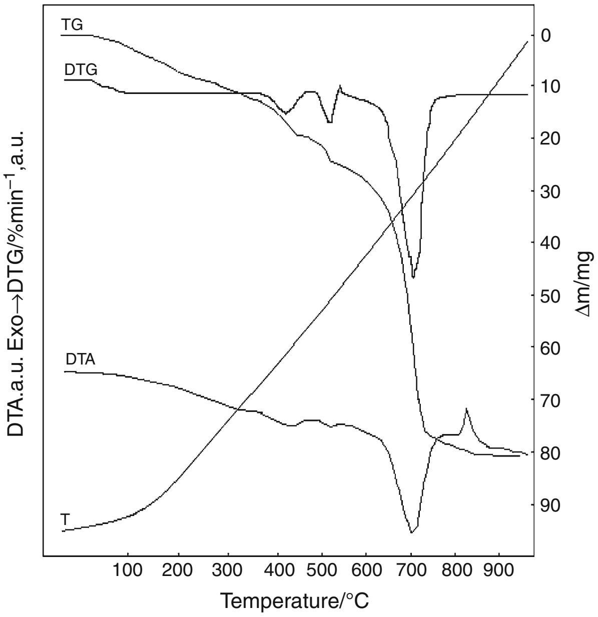

Fig. 5 DTA, TG, and DTG curves of raw natural chrysotile asbestos

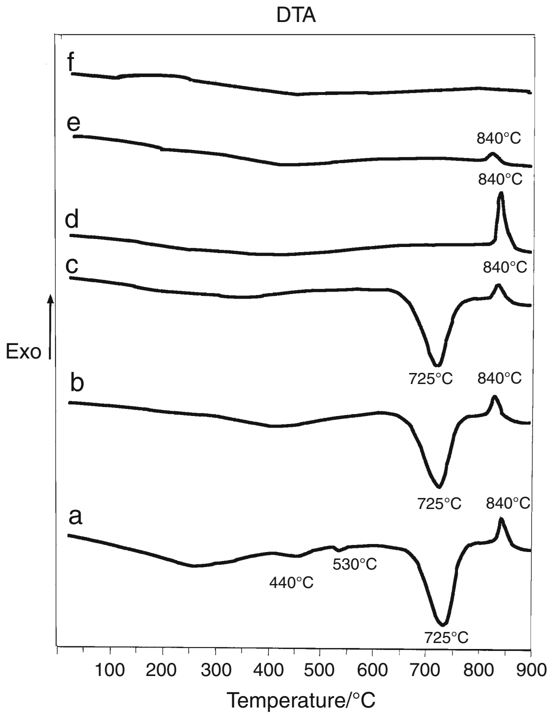

Fig. 6 DTA curves of raw chrysotile asbestos (*a*) and thermally treated: (*b*) 500 °C, (*c*) 600 °C, (*d*) 650 °C, (*e*) 700 °C, (*f*) 725 °C

Study of asbestos by thermal analysis

DTA, TG, and DTG curves of the natural chrysotile asbestos are given in the Fig. 5. In the temperature range 60–500 °C minor endothermic mass losses are observed due to the dehydration of hygroscopic and zeolite water. A peak at ~400 °C on DTG curve may be related to the decomposition of brucite present in minor amount.

The major endothermic mass loss between 600 and 800 °C with the maximum rate at 725 °C is caused by dehydration of chemically bound water (dehydroxylation of the octahedrically coordinated hydroxyl groups of chrysotile $Mg_3Si_2O_5(OH)_4$). According to [11] this marks complete breakdown of the mineral structure and creation of an amorphous mixture of silica and magnesia, which mineralogists have dubbed "serpentine anhydride." The exothermic peak at ~840 °C on DTA curve without mass loss corresponds to crystallization of the dehydroxylated phase and the formation of forsterite Mg_2SiO_4 [33, 34]. According to [34] the amorphous dehydroxylate of chrysotile is unstable, and forsterite is the first observed reaction product. Perraki and Orfanoudaki [35] show that the exothermic peak at ~850 °C in the DTA curve corresponds to recrystallization of the dehydroxylated phase and the formation of enstatite $MgSiO_3$. This result was confirmed by Pérez-Maqueda et al. [36], i.e., formation of enstatite was characterized by an exothermal effect at 830 °C.

The above transformations are represented by the following chemical reactions:

$$Mg_3Si_2O_5(OH)_4 \rightarrow Mg_3Si_2O_7 + 2\,H_2O$$

$$Mg_3Si_2O_7 \rightarrow Mg_2SiO_4 + Mg_2SiO_3$$

Like forsterite, enstatite has a very high melting point [37].

The results of the DTA of raw and thermally treated asbestos are reported in Fig. 6. At 650 °C the structural water has been completely removed and chrysotile mineral no longer exists. However, crystallization of the forsterite during calcination for 3 h in a furnace is not completed. There is indication that exothermic peak at ~840 °C on DTA (Fig. 6d). As the temperature increases up to 700 °C, the area of the peak of crystallization decreases (Fig. 6e), which shows advancement of forsterite crystallization during thermal treatment in the furnace. Crystallization of the forsterite is completed as a result of calcination sample of asbestos at the temperature 725 °C in the furnace for 3 h. Testify for that absence of crystallization peak on DTA (Fig. 6f).

Literature data show that cytotoxicity of chrysotile toward human fibroblasts, red blood cells, and bovine

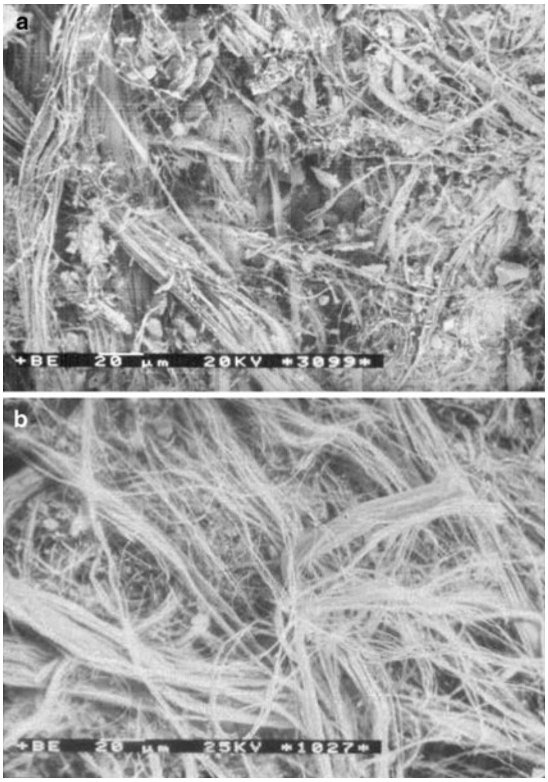

Fig. 7 SEM micrographs of chrysotile asbestos: **a** raw natural, ×1,000 and **b** after grinding, ×1,000

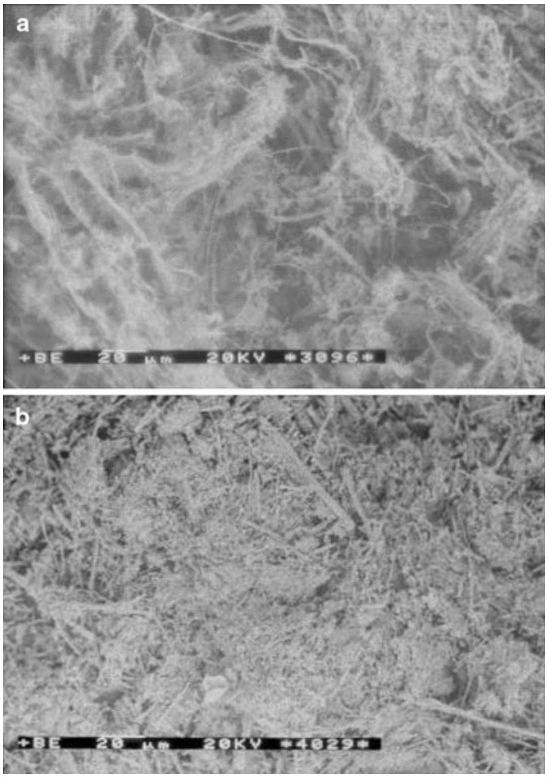

Fig. 8 SEM micrographs of chrysotile asbestos samples after heating at 500 °C: **a** unground, ×1,000 and **b** ground sample, ×1,000

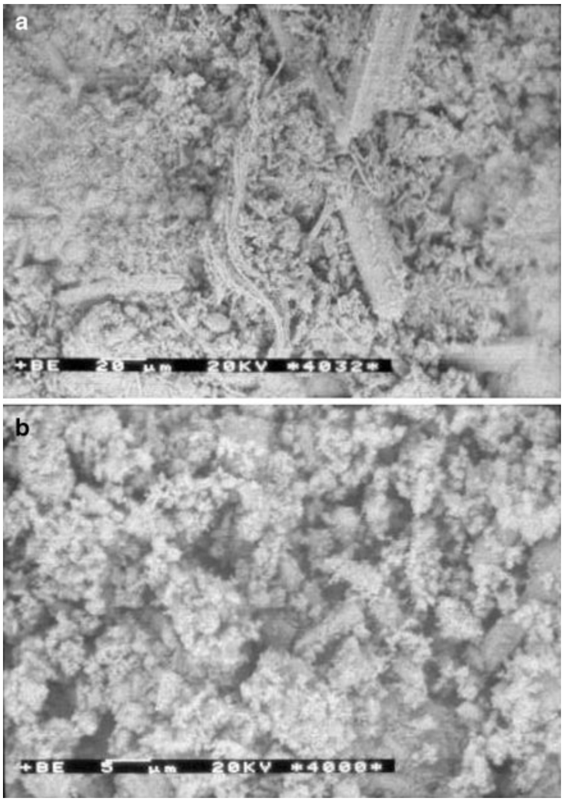

Fig. 9 SEM micrographs of thermally treated chrysotile asbestos samples: **a** 600 °C, ground sample, ×1,000 and **b** 650 °C, ground sample, ×4,000

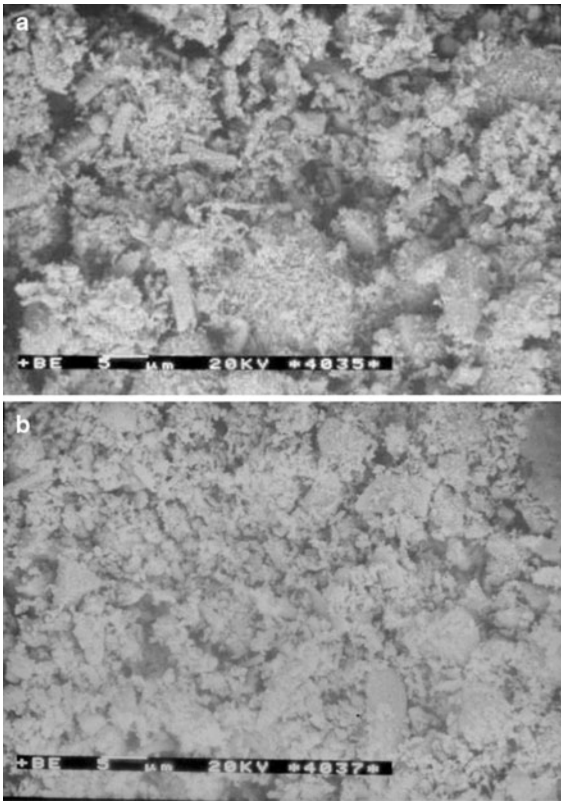

Fig. 10 SEM micrographs of thermally treated chrysotile asbestos samples: **a** 700 °C, ground sample, ×4,000 and **b** 725 °C, ground sample, ×4,000

alveolar macrophages was decreased by calcination at low temperature [34]. According to [38] this is due to a significant lowering of the capacity to trigger free radical generation, which is consistent with a dehydroxylation reaction. Hence, to reduce the hazard of chrysotile asbestos, an isothermal treatment at 650 °C for at least 3 h should result in a satisfactory yield of decomposition of chrysotile. Complete transformation of the dehydroxylated phase to forsterite is obtained by calcination at temperatures ≥725 °C for 3 h.

Study of asbestos by SEM

The SEM image of the raw natural chrysotile asbestos (Fig. 7a) shows the typical bundles of long chrysotile fibers. Grinding of asbestos in a vibratory mill does not destroy characteristic tubular structure of chrysotile (Fig. 7b).

Microstructure of asbestos after heating at 500 °C (Fig. 8a) is similar to raw asbestos; its fibrous structure remains unbroken; however, compact bundles got loose. It was found that after grinding compact bundles disintegrate on single fibers, often broken (Fig. 8b). In sample calcined in temperature of 600 °C after grinding single, broken fibers of chrysotile were still present (Fig. 9a).

Sample calcined at 650 °C and milled was fine-grained, fibrous of chrysotile are not evident (Fig. 9b). Similar SEM image was obtained for sample calcined at the temperature of 700 °C (Fig. 10a). Sample which was heating to 725 °C (Fig. 10b) after grinding consists small grains <2 μm next to strips of forsterite of size up to 10 μm (Fig. 11a) or sometimes larger (Fig. 11b).

Conclusions

The effect of thermal treatment in the range 500–725 °C on raw natural chrysotile asbestos was characterized of DTA, XRD, and SEM. It was observed that an isothermal treatment at 650 °C for at least 3 h caused the complete dehydroxylation of chrysotile $Mg_3Si_2O_5(OH)_4$. Transformation of the dehydroxylated phase to forsterite Mg_2SiO_4 was obtained by heat treatment in the range 650–725 °C. In addition, it is easily milled to pulverulent-shape material by mechanical milling. These results have practical

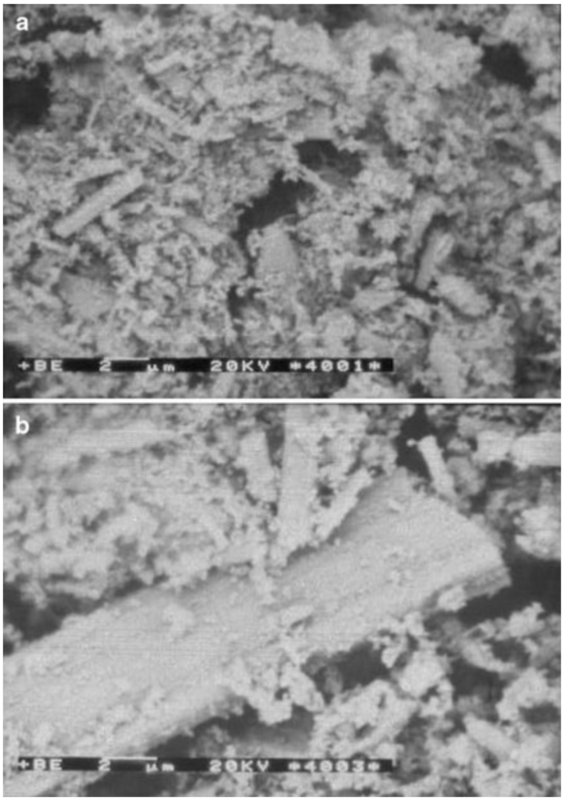

Fig. 11 SEM micrographs of chrysotile asbestos sample after heating at 725 °C and grinding: **a** ×10,000 and **b** ×12,000

implications for the design of the treatment plants and control of the firing processes of asbestos-containing materials.

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