Physicochemical Problems of Mineral Processing, 35 (2001), 83-90
Fizykochemiczne Problemy Mineralurgii, 35 (2001) 83-90

Ludwik DOMKA*, Lubomira DOMKA**, Maciej KOZAK**

UTILISATION OF ASBESTOS WASTES

Received March 5, 2001; reviewed and accepted May 15, 2001

The fibrous structure of asbestos, the ubiquitous material in the environment and exhibiting multiple applications, has proven to constitute hazards for human health. For this reason at present utilisation of asbestos has to be stopped, its resources have to be neutralised and reutilised in a safe way. In this paper we shall present studies on asbestos utilisation with the use of selected fluxes in order to alter its fibrous character but preserving fire resistance of the new material.

Key words: asbestos, utilisation, structural change

INTRODUCTION

Asbestos belongs to the dangerous air-polluting agents, ranked third in importance in the list of global scale environment-polluting substances in the Report of the Rome Club on The Limits to Development (World Health Organisation, 1986). The common name of asbestos (from the Greek, asbestos = unextinguished, undestroyable) includes natural silicates of the serpentinite and amphibole groups. The first group include chrysolite ($3MgO \cdot 2SiO_2 \cdot 2H_2O$) while the other contains actinolite ($2CaO \cdot 4MgO \cdot FeO \cdot 8SiO_2 \cdot H_2O$), tremolite ($2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$), crockidolite ($Na_2O \cdot Fe_2O_3 \cdot 3FeO \cdot 8SiO_2 \cdot H_2O$), antophyllite ($7MgO \cdot 8SiO_2 \cdot H_2O$) and amosite ($5.5FeO \cdot 1.5MgO \cdot 8SiO_2 \cdot H_2O$). All the mentioned varieties differ in respect to physical and chemical traits, which reflects both the type of deposite and conditions which prevailed when the asbestos was formed.

---

* Technological Centre, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań.
Asbestos Handler Certificate (04713) New York and (10254) State of New Jersey Department of Labor Office of Asbestos Control and Licensing.

** Department of Environmental Education, Adam Mickiewicz University, Słowackiego 20, 60-823 Poznań.

*** Department of Macromolecular Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań.

Apart from its fibrous structure, all asbestos varieties exhibit extensive resistance to physical forces, mechanical strength, high resistance to tearing, temperature changes and to action of corrosive substances. They exhibit low electrical conductance, high elasticity, specific sorptive and isolating properties. Due to these properties, asbestos finds multiple applications. Its presence can be noted in over 3,000 industrial products (Domka et al 2000; Wachowski and Domka 2000).

In the human environment, asbestos originates, first of all, from:

- natural deposits, from which asbestos is washed off with the outflowing waters (asbestos impurities are encountered in exploited deposits of coal, copper ores, construction stones, etc);
- asbestos processing (e.g., in mines, industrial works, wastes formed in the course of production of articles containing the fibrous material);
- utilised asbestos products (asbestos dust is released to air during corrosion of asbestos-cement or eternit panels, upon abrasion of brake and gear box discs, from heating, ventilation, air-conditioning appliances, from house elevations and isolation).

The mineral fibres may penetrate human organism through the respiratory tract, alimentary tract or through the injured skin. The first of the penetration pathways has received the greatest attention. The stable, chemically resistant fibres of the mineral puncture walls of pulmonary alveoli, lead to inflammatory conditions, tissue hyperplasia and to further, life-threatening conditions. Together with the asbestos fibrils, the organism may be penetrated by fibre surface-adsorbed hazardous aromatic hydrocarbons (e.g., benzo(a)pyrene). Human populations exposed to asbestos manifested numerous clinical signs/symptoms, radiological alterations, impoverished pulmonary function, appraised by the pulmonary function tests. The resulting diseases include asbestosis, lung cancer, pleural or peritoneal mesothelioma, laryngeal tumours and other. The risk of severe disturbances linked to the long-term exposure to asbestos dust corresponds to the size and morphology of incorporated fibrils. Fibres of more than 5 μm in length and of a diameter below 3 μm (according to the norm ISO DP10312, 1995; ISO 13794, 1997; ASTM, 1990) are thought to carry the highest potential to induce malignant tumours in humans and animals. In view of the health and life hazards associated with asbestos exposure, in 1970s many countries have implemented very restrictive regulations, which reduce contact of the material with humans. In the countries regulations have been introduced which forbid utilisation of the fibrous materials. For a long time, air pollution monitoring has been conducted and methods are used to eliminate asbestos-containing materials (mainly using the wet technique with addition of surfactants) by dismantling them, securing all safety precautions, removing them from rooms, installations (central heating, ventilation).

The removed asbestos wastes are secured in such a way as to prevent emission of mineral dusts and fibres to the environment. The so called solid wastes contain below 20% asbestos, strongly fixed in the material. The wastes manifest higher volume density (exceeding 1,000 kg/m^3) and, due to higher mechanical strength, they present lower risk of asbestos fibre emission, which used to accompany mechanical processing. Product defined as soft asbestos products contain over 20% asbestos and are regarded to be particularly dangerous for health and, as such, they should be removed and utilised in an alternate way. Solid wastes are packed in polyethylene foil of at least 0.2 mm in thickness while the soft wastes, such as asbestos dust or loose asbestos are placed in bags made of a similar foil, hermetically sealed at an elevated temperature or using an appropriate glue. Following the packing, fibrous aerosol content has to be established in the air. The collected waste material should be placed in depositories adjusted for the purpose. Asbestos wastes should be covered by 20 cm thick layer of soil or an inert material. After filling an appropriate chamber, it is additionally covered by HDPE geomembrane of at least 1.5 mm in thickness, which is overlaid by 2 m soil layer.

A new, chemical technique for asbestos utilisation at the site of its manifestation is worth attention, patented and marketed by the American company, Grace (Grace Construction 1999). The applied DMA (Digestion Material for Asbestos) product is based on phosphoric acid, supplemented with fluoride catalyser and surfactants, which induce foaming of the mixture (Mastalski 1999). In order to identify the surfaces subjected to DMA action, a pigment was additionally introduced to the preparation. Surfactant content assures that the deeper layers of the treated material are penetrated and appropriately wetted. The preparation was found to react with chrysotile asbestos and to abolish its fibrous structure while preserving the required characters, like fire-proof property of the new material. Chrysotile asbestos contains alternate layers of silicate and magnesium, oriented according to a cylindrical geometry, which under effect of DMA active component become split. Application of the technique may, to a certain extent, restrict the need for exchange of asbestos-containing elements to new elements which do not contain asbestos. Moreover, the costs associated with utilisation of asbestos wastes and with isolation of the renovated site are lowered (Grace Construction 1999).

In Poland, the health hazards associated with asbestos are particularly grave. Much later than in other countries, the act of 19 June, 1997 (Dz.U. No.101, pos.928), which abolished the use of asbestos-containing products, established the deadline for production of asbestos-cement items at 28 September, 1998. Legal regulations have been worked out which control application and utilisation of asbestos-containing products. In the decision of 17 June, 1998 (Dz.U. No.79, pos.513), the Minister of Labour and of Social Policies established the highest permissible levels and intensities of health-hazardous agents in a work environment. In our country, asbestos-associated hazards are very severe and solution of the problems will probably take several years. For example, in the Szczucin community the total volume of asbestos wastes with the earth masses polluted with the mineral is appraised at 1 million m^3. Volatile asbestos dusts, originating from destruction or modernisation of buildings constructed of asbestos materials, will continue to present a hazardous source for a long time (Dołegowski, Janczała 1999). In such a situation, the search and design of effective asbestos utilisation techniques is an important and a currently urgent goal. We have attempted to approach the problem in this presentation.

EXPERIMENTAL

The studies were performed on asbestos samples mixed with selected flux. The samples were subjected to elevated temperatures. The zero (standard) sample consisted of asbestos which contained over 95% chrysotile. The asbestos decomposition reaction was conducted in various experimental conditions. The temperature of the reaction varied between 50 °C to 500 °C, and the reaction time was 2 to 3 h. Asbestos samples were mixed with selected fluxes, introduced in excess, at the molar ratio of 1.5:1. Two series of experiments were performed.

In the first series, the agents which degraded asbestos structure included the following fluxes: NaF, NH_4F, $Na_2B_4O_7.10H_2O$, H_3BO_3, H_3PO_4+NH_4F. The samples were subjected to the temperature of 500 °C in a muffle furnace.

In the other series of experiments, 4% flux solutions and mineral acids were used, known for their catalytic affect of reactions which take place upon structural alterations in the studied fibrous mineral. In the series, extensively mixed samples in the modifying reagent solutions were left for 24 h at room temperature. Then, the solutions were paper-filtered and the residue on the filter was dried at around 100 °C. The obtained residue was subjected to a structural analysis. Before microscopic analysis, some of the samples were additionally roasted at 300 °C.

Morphology of samples was examined by scanning electron microscopy (SEM-515, Philips). The powdered sample, intended for the studies, was dispersed in t-butanol and, following sedimentation on a microscope holder, it was coated with gold using ionisation chamber. The typical magnification ratio was 100-200.

Some asbestos samples were also examined by powder X-ray diffraction analysis using a modified HZG-3 powder diffractometer and CuKa radiation (λ=1.54178 Å). The source of X-ray was X-ray tube mounted on TUR M62 generator operated at 30 kV and 30 mA. Diffraction test were conducted within the t angle of 5-45, at the scanning rate 0.05 °/s. The identification took advantage of the POWDER data base

RESULTS

Results of morphological analysis of asbestos samples, fused with selected fluxes, are presented in SEM microphotographs (Figs. 1 to 6). As compared to the standard sample (Fig. 1), fusing of asbestos with sodium fluoride (at 500 °C, Fig. 2) or with boric acid (at 300 °C, Fig. 3) proved least effective: the fibrous structure of asbestos remained practically unaltered, large chrysotile fibres were seen, of few hundred μm in length and few to more than ten μm in diameter. Also the fine, particularly dangerous fibres of few to more than ten μm in length and less than 1 μm in diameter remained unchanged. Somewhat better effects were obtained with asbestos samples fused with borax at 300 °C (Fig. 4). Analysis of morphology of such a sample demonstrated a clearly reduced fine fibrous fraction of asbestos. The best effects were noted for asbestos fused at 500 °C for 2 and 3 h with borax (Fig. 5) or ammonium fluoride (Fig. 6). The respective SEM microphotograph demonstrated none or sporadic only fine or long asbestos fibres.

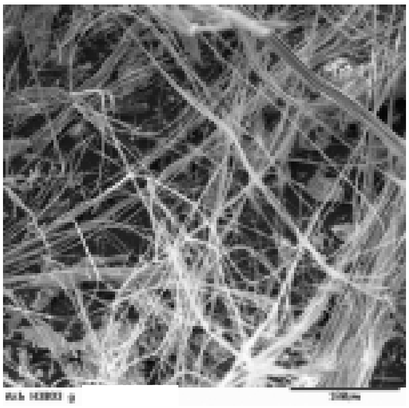

Fig 1. Asbestos (chrysotile) - standard

Fig 2. Asbestos fused with NaF (500 ºC, 2h)

Fig 3. Asbestos fused with H_3BO_3 (300 ºC, 2h)

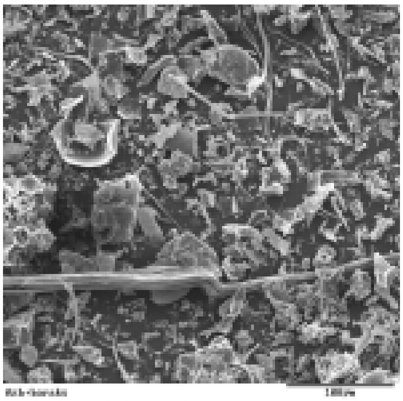

Fig 4. Asbestos fused with borax (300 ºC, 2h)

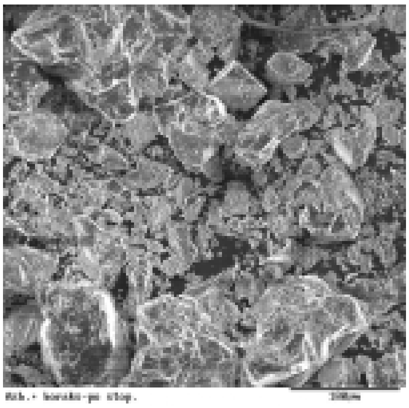

Fig 5. Asbestos fused with borax
(500 ºC, 2h)

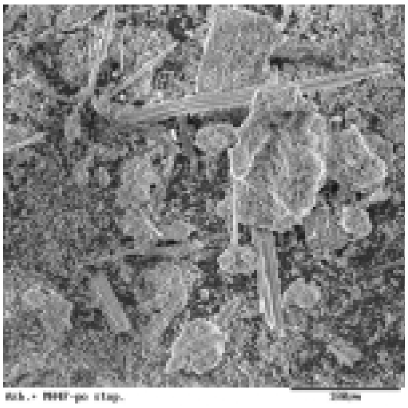

Fig 6. Asbestos fused with NH_4F
(500 ºC, 2h)

Results of microstructure analysis and those on morphology of asbestos samples subjected to degradation in 4% solution of NaF, NH_4F, H_3BO_3 are presented in Figs 7. In most of the samples subjected to degradation process in solution, only weak effects of the modifying agents on asbestos structure could be detected. Both the asbestos fibre structure and content of individual size fractions remained unchanged. The situation did not change when the additional stage of roasting the dried samples was introduced.

The most extensive degradation of asbestos fibrous structure was observed using H_3PO_4 and NH_4F mixture (at the molar ratio of 2:2, respectively, per 3 moles of asbestos). The so degraded sample showed a fully amorphous structure even when no roasting stage was used. (Fig. 8).

The samples of asbestos fused with borax and those fused with phosphoric acid and ammonium fluoride, which showed the most desirable morphology, suggesting transition from the stratified to amorphic structure, were subjected to diffraction studies. The recorded powder diffractograms were compared with the standard data, listed in ASTM files 22-1162, 25-645 and 31-808, characterising diffractive parameters of chrysotile. The course of diffractogram lines and the absence of diffractive peaks comparable of the standard peaks pointed to complete degradation of chrysotile asbestos structure and to amorphic structure of the samples.

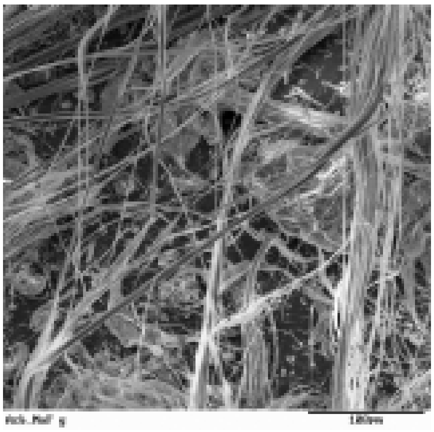

Fig 7. Asbestos after degradation process in solution (NaF)

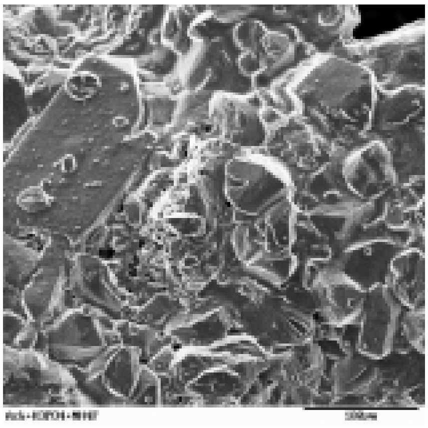

Fig 8. Asbestos after degradation process in solution (NH_4F and H_3PO_4)

CONCLUSIONS

In the conducted series of experiments, effects of selected fluxes were demonstrated on alteration of chrysotile asbestos structure from a fibrous to amorphic one. In asbestos samples with flux supplementation the desired effect was obtained upon roasting at 700 °C, at lower temperatures the structure was only partially degraded.

Alterations of asbestos structure in samples subjected to action of flux solutions was negligible but was complete in samples subjected to action of a mixture of the flux (NH_4F) and phosphoric acid.

REFERENCES

WORLD HEALTH ORGANISATION, (1986), *Environmental Health Criteria 53, Asbestos and other natural fibres*, WHO Press, Geneva.

DOMKA L., KOZAK M., KOZAK A. (2000), *Unieszkodliwianie odpadów azbestowych*. Materiały Ogólnopolskiej Konferencji Szkoleniowej *Unieszkodliwianie i utylizacja komunalnych odpadów niebezpiecznych*. Wisła 11-13 IV 2000", pp. 143-156, Abrys.

WACHOWSKI L., DOMKA L. (2000) *Sources and effects of asbestos and other mineral fibres presence in ambient air*. Pol. J. Environ. Stud. **9(6)**, 443-454.

DOŁĘGOWSKI B., JANCZAŁA S. (1999), *Bhp przy pracy z azbestem,* Gdańsk.

MASTALSKI J. (1999), *Wyroby zawierające azbest - bezpieczne użytkowanie i usuwanie*. Biuletyn Instytutu Gospodarki Odpadami **2**, 3-7.

GRACE CONSTRUCTION PRODUCTS (1999), *DMA^{TM} - Digestion material for asbestos - product information*.

ISO DP10312, (1995) *Ambient air determination of asbestos fibres - direct transfer transmission electron microscopy method*. International Standards Organisation.

ISO 13794, (1997) *Ambient air determination of asbestos fibres - indirect transfer transmission electron microscopy method*. International Standards Organisation.

ASTM, American Society for Testing Materials, (1990), *Standard method for testing for asbestos containing materials by polarized light microscopy*.

Domka L., Domka L., Kozak M., *Utylizacja odpadów azbestowych*. Fizykochemiczne Problemy Mineralurgii, 35, 2001, 83-90 (w jęz. ang.).

Włóknista struktura azbestu, mającego wiele różnorodnych zastosowań co wiąże się z jego wszechobecnością w środowisku, okazała się zagrożeniem dla zdrowia człowieka. W związku z tym obecnie, ważnym problemem jest wycofywanie azbestu z użytkowania, unieszkodliwianie go i utylizacja. W niniejszym opracowaniu zaprezentowano badania nad utylizacją azbestu przy wykorzystaniu wybranych topników celem zmiany jego struktury włóknistej przy zachowaniu cech ognioodporności nowego materiału. Próbkę wzorcową stanowił chryzotyl. Jako topniki zastosowano związki znane z katalitycznego wpływu na przebieg zachodzących reakcji przy zmianie minerału. Były to: NaF, NH_4F, $Na_2B_4O_7.10H_2O$, H_3BO_3, H_3PO_4+NH_4F. Najlepszy wynik w postaci zmiany struktury uzyskano dla prób azbestu stapianego w temperaturze 500 ºC w ciągu 2 i 3 godzin z boraksem, kwasem fosforowym oraz mieszaniną kwasu fosforowego i fluorku amonu. Dokumentują to mikrofotografie SEM.