Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Chemical elimination of the harmful properties of asbestos from military facilities

Adam Pawełczyk [a,*], František Božek [b], Kazimierz Grabas [c], Jacek Chęcmanowski [a]

[a] Wroclaw University of Technology, Faculty of Chemistry, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
[b] University of Defense, Kounicova 65, 662 10 Brno, Czech Republic
[c] Wroclaw University of Technology, Faculty of Environmental Engineering, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

ARTICLE INFO

Article history:
Received 19 March 2016
Revised 29 November 2016
Accepted 29 November 2016
Available online xxxx

Keywords:
Asbestos
Military waste disposal
Health hazard
X-ray analysis

ABSTRACT

This work presents research on the neutralization of asbestos banned from military use and its conversion to usable products. The studies showed that asbestos can be decomposed by the use of phosphoric acid. The process proved very effective when the phosphoric acid concentration was 30%, the temperature was 90 °C and the reaction time 60 min. Contrary to the common asbestos treatment method that consists of landfilling, the proposed process ensures elimination of the harmful properties of this waste material and its transformation into inert substances. The obtained products include calcium phosphate, magnesium phosphate and silica. Chemical, microscopic and X-ray analyses proved that the products are free of harmful fibers and can be, in particular, utilized for fertilizers production. The obtained results may contribute to development of an asbestos utilization technique that fits well into the European waste policy, regulated by the EU waste management law.

1. Introduction

Asbestos is a common name for a group of minerals belonging to serpentine and amphibole silicates. They mainly include hydrated calcium, magnesium and sodium silicates. In the first half of the 20th century, due to military interests, asbestos was recognized as a strategic material and because of its efficiency and low cost, it was used extensively until the 1970s. It was widely used wherever fireproofing and effective heat insulation was needed. Such requirements were imposed on military vehicles, submarines, warships, aircrafts, shelters, ambulances and buildings. The most common asbestos-containing construction elements used in army equipment were sealing and abrasive products, such as brake blocks, textile products, gaskets, fireproof mats and coverings, firewalls, fire proof clothing, fire-extinguishing blankets, filters, pipes and hydroinsulation. The aircraft carrier Clemenceau, for example, carried 700 tons of asbestos between her decks (Wainwright, 2009). Fig. 1 presents typical fireproof pipe coverings in a Swedish submarine.

In the 1960s, the first evidence concerning asbestos carcinogenicity began to emerge. It was reported that fibers embedded in lung tissue over time caused serious changes in the lungs (Pawełczyk and Božek, 2015). As a result of long time exposure, mesothelioma, lung cancer, and asbestosis may occur.

The first ban on the use of asbestos materials started in the 1980s. European members (EU) members had been obliged to limit the application of asbestos since 1991. Nowadays, all EU member states have banned the use and production of asbestos-containing materials. At the same time, other countries have developed programs aimed at exposure reduction and abatement of environmental contamination from asbestos.

For the past 30 years, asbestos has been removed, but not eliminated; it has been simply bagged, tagged and stored in landfills. This creates significant liability for the maintenance of such facilities and leads to unlimited costs for the responsible parties. A search for effective ways to dispose of asbestos-containing materials used in the military, construction, public utilities and transport was triggered by the introduction of Directive 89/106/EEC, relating to construction products in EU countries (EEC, 1988).

A lot of asbestos disposal methods can be found in the literature. The proposed ideas include, among others, collection of the waste asbestos in specially constructed storage yards, cementation of the wastes, covering the asbestos constructions on site with protective measures preventing the fibers from being released into the environment, etc. Other solutions are based on thermal destruction of the asbestos structures. There are also chemical methods of

* Corresponding author.
E-mail addresses: adam.pawelczyk@pwr.edu.pl (A. Pawełczyk), frantisek.bozek@unob.cz (F. Božek), kazimierz.grabas@pwr.edu.pl (K. Grabas), jacek.checmanowski@pwr.edu.pl (J. Chęcmanowski).

http://dx.doi.org/10.1016/j.wasman.2016.11.041
0956-053X/

Fig. 1. Asbestos heat insulation in a retired Swedish submarine (photo by Adam Pawełczyk).

asbestos neutralization using aggressive agents capable of destroying harmful fibers.

So far, the most popular method is storing asbestos waste in especially prepared landfills. Such a solution is very disputable because the area of the storing dumps loses any utility value and requires constant expenditure of money for its supervision and maintenance. Nevertheless, in Poland and many other countries, storing is the only method of asbestos waste treatment allowed by the law.

In the United States, other methods of asbestos risk abatement have gained a lot of popularity. These methods consist in coating the asbestos elements installed in the existing buildings, without taking them down. The construction elements are painted or sealed or covered with a non-asbestos product. The coverings increase asbestos mechanical strength and resistance against erosion. Most often urethane, latex, preparations containing powdered metal, etc. are used to achieve the desired result. Some preparations intended for asbestos treatment on site are capable of transforming this material into a product containing less than 1% by weight of chrysotile asbestos (Pritchett, 1997; Mirick and Forrister, 1993; Block, 1998). A significant fault of this method is the limited life of the insulating materials that preserve the asbestos products against erosion.

Several authors reported thermal neutralization in special furnaces, hearth ovens, plasma torches or microwave ovens (Witek et al., 2012; ATON, 2016; Domka et al., 2007; Block, 1998; Debailleul, 2002; Mirick and Forrister, 1993; Pritchett, 1997; Trefler et al., 2003, 2004; Zaremba et al., 2010, 2011; Kusiorowski et al., 2013; Pawlikowski et al., 2013; Sakamoto, 2014). Among these methods, thermal treatment of asbestos waste mixed with supplementary materials that decrease the melting temperature of the mixture is reported. After grinding to a grain range from 10 μm to 500 μm, the obtained material is introduced into the tunnel or rotary kiln and gradually subjected to a temperature in the range from 1000 °C to 1500 °C, for 15 to 45 min. The process results in material completely devoid of asbestos fibers (Kashimura et al., 2014). Treatment of asbestos within 30 min at 900 °C completely destroys the fibers. This suggestion was confirmed in large-scale tests, at a rate of 2 tons/day. The large-scale equipment comprised three units: a microwave rotary furnace (2.45 GHz, 0.6–10 kW) for asbestos cement waste, a rotary furnace for wood waste to provide additional energy, and an exhaust gas filter.

Zaremba et al. (2010) reported the possibility of detoxification of asbestos through low temperature heating and grinding. It has been found that chrysotile can be transformed to a mixture of non-hazardous silicate phases as a result of thermal treatment at temperatures higher than 600 °C. Other inertization techniques found in the literature propose melting and subsequent solidification (Osada et al., 2013) or amorphisation by mechanochemical treatment (Colangelo et al., 2011).

Numerous studies in the literature report on the chemical treatment of asbestos. It consists in treatment of the compounds included in the serpentine and amphiboles group with aggressive agents such as bases, inorganic and organic acids often involving the addition of fluorine compounds. Among the first researchers who tried to use chemical treatment for asbestos waste inertization were Hyatt et al. (1982). They used hydrochloric acid for fiber breakdown. According to Kiyoji and Toshiya (2009), sulfuric acid could also be an effective agent to destroy the fiber structures.

Sugama et al. (1998) investigated a fluorosulfonic acid (FSO_3H) aqueous solution for decomposing chrysotile asbestos fibers. The process is determined by the establishment of the equilibrium in aqueous medium, $FSO_3H + H_2O = HF + H_2SO_4$. Sulfuric acid, derived from FSO_3H aqueous solution, reacts with the outer $Mg(OH)_2$ layers of the tubular scroll-like fibers of chrysotile. Once the breakdown of $Mg(OH)_2$ layers is initiated, the diffusion of FSO_3H-derived HF into the silicious layers promotes the breakage of Si-O-Si. Asbestos can also be treated with a mixture of H_2SO_4 and HF. Fluoride compounds are also used in a process reported by Nocito (2014). In this method, proprietary chemicals are used to chemically and physically destroy the structure of the asbestos fiber. The method is based upon the reaction of fluorides in the reagent identified as "ABCOV-C" with the silicon in the asbestos crystals to destroy the physical structure of the mineral.

Brown (2006) proposed in-situ treatment of the asbestos materials containing chrysotile using a polycarboxylic acid such as oxalic acid. The agent converts the asbestos to a non-asbestos material. Additional sulfuric acid may be introduced to assist in conversion of the asbestos to a non-asbestos form. Turci et al. (2008), similarly to Brown, proposed asbestos decomposition with oxalic acid, but the chemical process is additionally assisted by a vigorous acoustic cavitation in a "cavitating tube" operating at 19.2 kHz and 150 W. Such a treatment is referred to as a sonochemical process.

Other authors studied mechanochemical processing of chrysotile asbestos. In this method, mechanochemical treatment of asbestos wastes is carried out in a mill of a rotating speed of 250 rpm. Under the effect of aggressive mechanical impact chrysotile, asbestos tends to be in the amorphous phase after 4 min, while amphiboles are transformed in 8–12 min (Plescia et al., 2003). A similar mechanochemical process was applied by Inoue et al. (2007). They confirmed that the needle crystals of chrysotile asbestos transform to amorphous state after grinding, using a planetary ball mill. The product could be remade into useful materials after mixing them with water, compacting and keeping it under humid conditions. In these conditions, stable hydrates are formed, which could be useful as new raw materials for cement-like products.

Chou (1989) proposed digestion of the asbestos with sulfuric acid. The reaction proceeds according to the following chemical equation:

$$Mg_3(Si_2O_5)(OH)_4 + 3H_2SO_4 \rightarrow 3MgSO_4 + 2SiO_2 + 5H_2O$$

The asbestos decomposition rate is limited by the rate of chemical agents' and products' transport inside narrow canals formed by unreactive silica layers. As a result, the magnesium compounds cannot be completely removed from the silicate structure. A com-

Please cite this article in press as: Pawełczyk, A., et al. Chemical elimination of the harmful properties of asbestos from military facilities. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.11.041