



Chemical elimination of the harmful properties of asbestos from military facilities



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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.

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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

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

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; Treffer 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 $^{\circ}\text{C}$ to 1500 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$. 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).

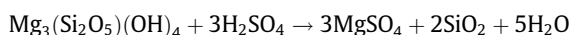
Numerous studies in the literature report on the chemical treatment of asbestos. It consists in treatment of the compounds included in the serpentine and amphiboles group with aggressive agents such as bases, inorganic and organic acids often involving the addition of fluorine compounds. Among the first 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, $\text{FSO}_3\text{H} + \text{H}_2\text{O} = \text{HF} + \text{H}_2\text{SO}_4$. Sulfuric acid, derived from FSO_3H aqueous solution, reacts with the outer $\text{Mg}(\text{OH})_2$ layers of the tubular scroll-like fibers of chrysotile. Once the breakdown of $\text{Mg}(\text{OH})_2$ 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:



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-

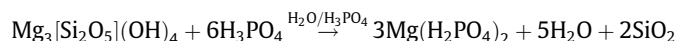
bination of strong acids with HF is capable of decomposing the chrysotile fibers, but applying such an aggressive agent involves high risk to the environment.

One of the patents (Mirick, 1991) presents a method of neutralization of construction materials containing chrysotile asbestos with the use of mixture of organic acids, ammonium fluoride or alkaline metals fluorides. In Debailleul (2002), a method was presented, which applies a concentrated solution of NaOH in a reactor-autoclave at the temperature of 175–200 °C and under the pressure of 0.3–1.0 MPa. The waste obtained after the decomposition may be utilized for the production of cement.

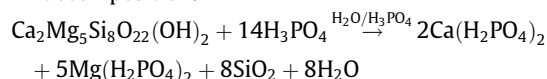
Despite the variety of advantages, all of the above mentioned methods have defects that make them highly difficult to implement on a larger scale. They usually involve making secondary waste materials. Using strong acids and fluorine agents may be dangerous and requires adopting specifically dedicated corrosion resistant materials. In turn, thermal methods are characterized by high energy consumption, which means that this method is very expensive. As regards landfilling, it requires construction of storage sites, which creates a significant liability for the maintenance of such facilities and leads to unlimited costs for the responsible parties.

In this study, asbestos waste processing relies upon dissolution of the waste materials with phosphoric acid solution, using a two-stage reaction system involving phosphoric acid for asbestos decomposition. Compared with the above mentioned inertization methods, the application of phosphoric acid has a great advantage because instead of secondary waste or materials of little use, calcium and magnesium phosphates are produced (Pawełczyk and Szczygieł, 2009). Both of these compounds can be used as components of fertilizers or fodder phosphates. The simplified chemical equations of decomposition of selected serpentine and amphibole asbestos, by means of phosphoric acid, are presented below.

– serpentine asbestos—clinocrysotile decomposition:



– amphibole asbestos—tremolite (Leake et al., 1997) decomposition:



This work involves studies on the destruction of asbestos waste materials from the demolition of military equipment and construction collected from an army unit in south Poland. The aim of the study is to examine whether the obtained decomposition products are free of asbestos fibers so that they could be safely used in further applications.

2. Materials and methods

Materials for the experiments included asbestos sealing cord samples from combat infantry vehicles withdrawn from the army and asbestos-cement board (eternit) samples received from the demolition of military storage facilities. All the samples were kindly supplied by a waste disposal company that executed its contract for the army. The original materials, as well as the products obtained after the chemical treatment of the wastes, were thoroughly examined using chemical and microscopic methods, followed by X-ray analysis.

Chemical analyses were carried out using ICP spectroscopy. The samples, prior to analysis, were prepared according to own procedure of the authors, based on literature data. No standard methods are available for chemical analysis of asbestos. The asbestos sample

preparation combines thermal treatment at 800 °C and chemical digestion with aqua regia. The melting agent used was sodium carbonate. This agent is effective for various materials for example for siliceous samples, alumino-silicates and asbestos (Dulski, 1996). The melting agent decreases temperature of asbestos thermal destruction. The sample is mixed with sodium carbonate in proportion 8:1 (sodium carbonate to asbestos) and heated, slowly at the beginning, then more intensively, for 45 min. During thermal decomposition sodium carbonate reacts with asbestos. Thus, the decomposition temperature can be reduced significantly. Similar procedures aiming at reducing asbestos decomposition temperature are presented in (Kowalczyk, 1998; Schüller et al., 1993; Mason, 1992). After melting in platinum crucibles the sample was digested for 30 min with aqua regia. ICP-MS spectrometer Elan 9000 Perkin Elmer was used for determination of the sample composition.

Silica was analyzed using the gravimetric method (ISO, 2008). For analyzing K, P and Ca procedures available in the literature were used (Minczewski and Marczenko, 2001; Tadeo, 2008; Namieśnik, 2000; Hermanowicz et al., 1999). Relative errors for these methods were 0.8%, 0.59% and 0.62%, respectively.

Apart from the chemical examinations, microscopic investigations were carried out with respect to the respirable fibers present in the solids. The tests were accomplished using a Quanta scanning electron microscope (FEI Company, USA). The samples, prior to microscopic investigations, were not subjected to special treatment. There was no need to coat them with any preparations.

The semi-qualitative microscopic analysis of the decomposition products was carried out using phase-contrast optical microscope, ZEISS, Germany, without image registration, according to the adopted procedure presented in (PS, 1988). The Walton and Beckett graticule was used for counting fibrous structures. The circle in the graticule was divided into four by two diametrical scaled lines. A fiber observed in the counting field underwent dimensional assessment (length and diameter was estimated). For this purpose, fibers longer than 5 μm and thinner than 3 μm were taken into account.

Identification of the qualitative composition of the asbestos and the obtained products was carried out on the basis of X-ray diffraction analysis. An X-ray diffractometer, ULTIMA IV (Rigaku-Denki), was used for phase detection. A filtered copper lamp, CuK_α at 40 kV/40 mA, was applied in the examinations. The measurements were carried out within the Bragg angle range of 5–90° with steps of 0.02° in the 2θ scale. The obtained data were then processed using Inorganic Crystal Structure Database (ICSD).

Tests of the chemical decomposition of the asbestos waste materials were carried out using solutions of concentrated raw phosphoric acid received from an industrial plant. Composition of the concentrated phosphoric acid was as follows: P₂O₅ 49.26, SO₄²⁻ 3.4, Pb < 0.5, Cr 650, Cd 6.7, Cu 1.7, Ni 5.9, Zn 441, Mg 786, Fe 10670, Mn 414, As < 0.1, Hg < 0.3. P₂O₅ and SO₄²⁻ are given in %, the other components in ppm.

Prior to the decomposition, the asbestos samples were wet ground in a vibration mill, so that the obtained grains were less than 0.315 mm in diameter. The water to solid mass ratio amounted to 0.3:1 during the size reduction. After drying, the samples, 50 g each, were put into a three-neck glass flasks equipped with agitators and thermostats. Next, they were treated with phosphoric acid. The applied phosphoric acid concentration, reaction times and temperature are given in the subsequent Sections 3.2 and 3.4. The contents of the flasks were continuously agitated and the vapors refluxed by means of condensers attached to the tops of the flasks.

After decomposition, the resulting suspensions were filtered, the sediments rinsed with water, and dried. The obtained products

were scrutinized for any sign of the presence of asbestos using chemical, microscopic and X-ray examinations.

3. Results

Comprehensive chemical, microscopic and X-ray examinations of the waste asbestos materials and the obtained decomposition products made it possible to assess to what extent the primary materials had undergone structural transformations that might eliminate their harmful properties.

3.1. Chemical physical analyses of the starting materials

Results of the chemical analyses and physical measurements of asbestos and asbestos-cement materials are shown in Tables 1 and 2. Table 1 presents chemical analyses of the primary asbestos waste materials, namely, the sealing cord and asbestos-cement products.

The results of thermal treatment of the asbestos and asbestos-cement samples are shown in Table 2.

Based on the chemical analyses, the contents of the cement used for the manufacturing of the asbestos-cement boards were determined. It amounted to 65% of the total board mass. Differences between both eternit materials result from two different cement types used as raw materials in the eternit production process.

3.2. Chemical inertization of the asbestos waste

3.2.1. Single stage treatment

In the single-stage neutralization tests, asbestos cord and asbestos-cement flat board samples were treated for 60 min with phosphoric acid of concentration 30% in terms of P_2O_5 at the temperature of 90 °C. The stoichiometric proportion of the acid in relation to $CaO + MgO + Fe_2O_3 + Al_2O_3$ in the materials was applied. It means that per 50.0 g of asbestos cord and asbestos-cement flat board 73.8 g and 90.7 g of phosphoric acid in term of 100% H_3PO_4 was used, respectively.

After the treatment, some solid residue was obtained. The separated sediment was rinsed with water, then dried and analyzed. The liquid phase was also examined. The weight measurements demonstrated that the initial sample of 50.0 g was reduced to 15.6 g after the chemical treatment. The remaining part passed in ionic form to the liquid phase. The solid remnants may include new products as well as undecomposed waste material. Therefore detailed examinations of the products were necessary to confirm if phosphoric acid could be a medium for such waste destruction. In the case of the flat asbestos-cement the initial sample mass was reduced to 9.4 g.

Table 1

Results of the chemical analyses of asbestos and asbestos-cement flat and corrugated board samples.

Component		Asbestos cord	Asbestos-cement flat board	Asbestos-cement corrugated board
CaO	%	1.24	41.3	41.0
MgO	%	27.9	5.34	5.41
SiO ₂	%	32.4	21.6	20.4
K ₂ O	%	5.99	0.29	0.14
Na ₂ O	%	0.04	0.21	0.12
Al ₂ O ₃	%	1.68	4.02	3.85
Fe ₂ O ₃	%	3.55	2.72	2.89
Cu	mg/kg	13.2	18.1	18.8
Zn	mg/kg	106	346	183
Pb	mg/kg	14.7	23.4	35.8
Ni	mg/kg	100	96.0	214
Cd	mg/kg	1.7	10.2	3.8
Cr	mg/kg	716	69.8	109

Table 2

Loss of mass on heating the asbestos cord and flat and corrugated asbestos-cement boards (%).

Measurement type	Value		
	Asbestos cord	Asbestos-cement flat board	Asbestos-cement corrugated board
Drying loss at temp. 110 °C	0.10	0.03	0.48
Calcination loss up to 400 °C	4.10	24.10	19.72
Calcination loss up to 900 °C	25.23	26.81	26.01

Table 3 shows the analyses of the liquid and solid products obtained in the process of asbestos cord and asbestos-cement decomposition. The obtained data proved that magnesium passes almost as a whole into the filtrate. This might be proof that asbestos underwent destruction and was not found in the solid phase.

The acidic post-decomposition liquid phase contains mainly phosphate anions, magnesium and calcium cations, as well as other ions characteristic of serpentine group minerals. Evidence for asbestos destruction should be provided by the microscopic studies.

3.2.2. Repeated chemical treatment

Although about 92% of the asbestos waste material undergoes destruction during its chemical treatment, important concerns arise from the morphology of the remaining solid. It is not clear if the elongated structures are safe. Therefore, we propose an additional process—that is, a secondary treatment of this solid material. In the second processing stage, the material was treated again with phosphoric acid of the concentration 30% at 90 °C up to 120 min, with constant stirring. To promote the aggressive conditions of the chemical reaction, a surplus of 20% of the acid stoichiometric amount was applied in relation to $CaO + MgO + Fe_2O_3 + Al_2O_3$ in the material. The liquid to solid ratio in the reaction slurry was maintained at 3:1 by the addition of water. After the treatment, the resulting suspension was separated, the solid phase rinsed with water, dried and then treated with aqua regia. In such conditions, the fibrous magnesium silicate minerals that could potentially be present in this material should be decomposed and easily analyzed. The presence of magnesium compounds in the solid might be evidence of incomplete destruction of asbestos.

In order to test whether the fibrous structures had been decomposed, chemical analyses of the obtained solid residues were carried out. A complete decomposition of the asbestos structures should result in the release of magnesium ions to the liquid phase. The analyses demonstrated that the undecomposed remnants

Table 3

Concentration of individual components in the filtrates and solid residues obtained after decomposition of asbestos cord and the asbestos-cement flat board with phosphoric acid (%).

Component	Asbestos		Asbestos-cement flat board	
	Filtrate	Solid residue	Filtrate	Solid residue
P ₂ O ₅	21.2	0.006	19.5	0.005
MgO	6.92	0.011	1.61	0.006
CaO	0.12	0.120	12.37	0.263
Fe ₂ O ₃	0.73	0.013	0.67	0.011
Al ₂ O ₃	0.34	0.010	0.49	0.034

contain mainly silica and negligible amounts of aluminum (0.31%), iron (0.01%) and traces of magnesium.

3.3. Microscopic studies

The asbestos cord, asbestos-cement board and the decomposition products obtained in the above presented tests were examined microscopically in order to identify any changes in the asbestos fiber morphology.

Figs. 2–5 present microphotographs of the initial asbestos cord and asbestos-cement samples, as well as solid residues obtained after single stage chemical treatment of these materials.

The microphotographs of the initial materials show clear fibrous structures in the form of filament aggregates and single fibers, forming tube-like silicate structures. For the microphotograph of asbestos (Fig. 2), bunches and single chrysotile fibers can also be seen. The same refers to the asbestos-cement flat board sample (Fig. 4), however, some structures derived from the cement matrix are a prevailing phase.

Pictures of the solid residue obtained after the asbestos cord and asbestos-cement flat board decomposition (Figs. 3 and 5, respectively) have substantially different appearances; however, there are still elongated structures in these residues. This relates especially to asbestos. It is clear that there is some kind of fiber present, but they are completely different in shape from the original ones. They are much thicker and shorter, as if they underwent deep structural changes. It is very interesting to note that the chemical analyses showed minimum contents of magnesium in



Fig. 2. Microphotograph of asbestos cord sample prior to its digestion; magnification 200×.

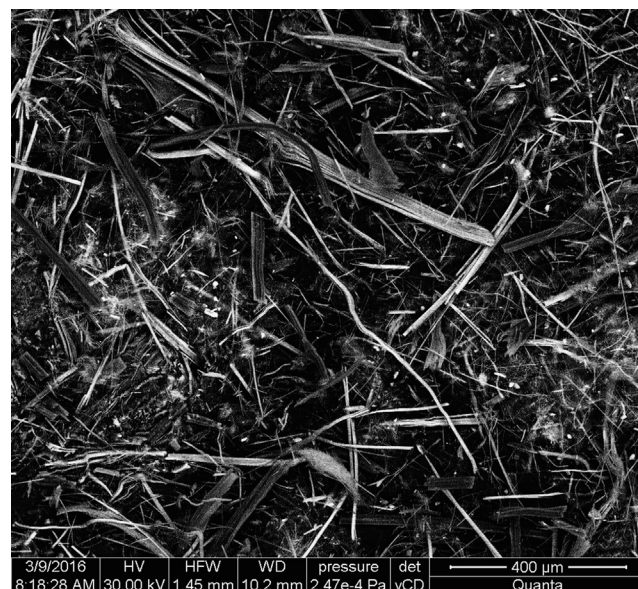


Fig. 3. Microphotograph of the solid residue obtained after single stage chemical treatment of asbestos cord (30% phosphoric acid, 90 °C and 60 min); magnification 200×.

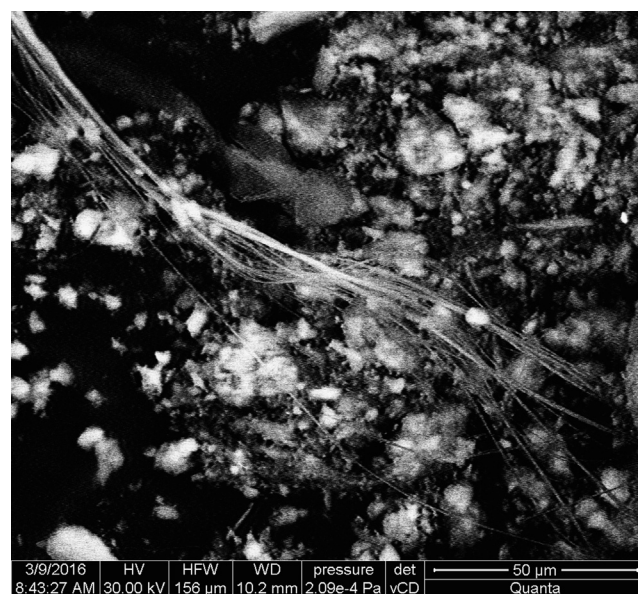


Fig. 4. Microphotograph of the asbestos-cement sample prior to its digestion; magnification 1910×.

this material, which is a typical component of asbestos. Alternatively, Mg is present in the liquid phase (Table 3). A similar deduction can be made from analysis of Figs. 4 and 5 related to

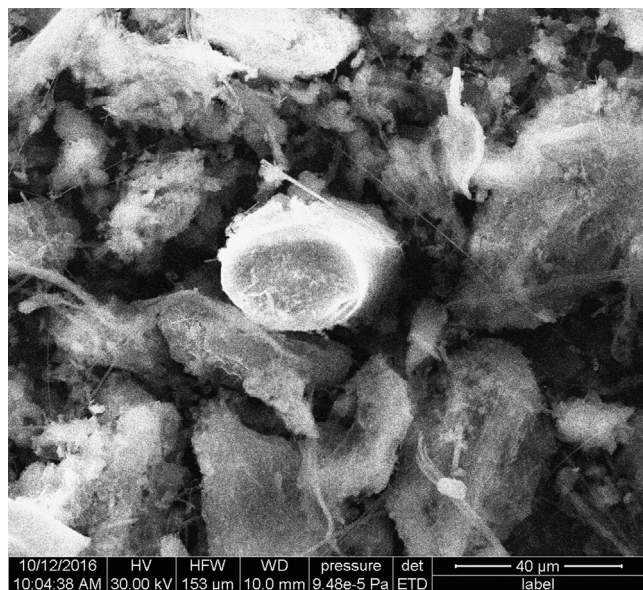


Fig. 5. Microphotograph of the solid residue obtained after single stage chemical treatment of asbestos-cement sample (30% phosphoric acid, 90 °C and 60 min); magnification 1050×.

asbestos-cement waste. This suggests that the waste samples have changed both chemically and physically.

3.4. Semi-qualitative microscopic studies

Results of the semi-qualitative microscopic analysis of the products obtained after second stage of the asbestos waste materials decomposition under various technological conditions are presented in **Tables 4 and 5**. In the tests, a 20% surplus of phosphoric acid was applied.

Comparative scale of fiber contents in the field of vision (used in **Tables 4 and 5**):

High	>11
Middle	6–10
Low	2–5
Trace	1–2
Not detected	0

The microscopic observations proved that the asbestos structure undergoes morphological changes under the applied conditions. As a result, fibrous material gradually disappears. When a short reaction time and lower temperatures are applied, some fibers can be still detected in the reaction slurry. With the increase of

the reaction time, temperature and acid concentration the fiber counts decrease. After 60 min, no fibers are noticeable in the product.

3.5. X-ray studies

X-ray studies were carried out to obtain supplementary information about the morphological changes of the examined products and to find out what kind of new phases originated in the course of the reaction with phosphoric acid. **Figs. 6–9** present XRD patterns of the examined starting materials and products obtained in the second treatment within diffraction angles between 5 and 70°. Interpretation of the pattern shown in **Fig. 6** leads to the assumption that in the asbestos cord sample, magnesium silicate $Mg_6[(OH)_8Si_4O_{10}]$ is a predominant phase. Among the mineral polymorphs of serpentine, the following were found: chrysotile (ICSD #413633), antigorite (ICSD #95343) and lizardite (ICSD #17046), all with the same chemical formula, $Mg_3Si_2O_5(OH)_4$. Polymorphous nacrite $Al_2Si_2O_5(OH)_4$ (ICSD #80083) was also identified in the sample.

In **Fig. 7**, the XRD pattern of the product derived from asbestos cord is presented. The product was obtained in the second stage after the repeated chemical treatment. One can see that new peaks appear in comparison with the initial asbestos sample pattern at different diffraction angles. Moreover, peaks specific for chrysotile disappear. Based on this observation, it was found that during the process, fibrous structures undergo destruction and new phases are formed including silica (ICSD #89277) and a small amount of aluminum silicates: gismodine - $CaAl_2Si_2O_8 \cdot 4H_2O$ (ICSD #189309) and anorthite - $CaAl_2Si_2O_8$ (ICSD #654). Other silicates are also possible.

Fig. 8 presents the XRD pattern of the initial asbestos-cement material. It includes peaks representing actinolite $Ca_2(MgFe)_5[(OH)Si_4O_{11}]_2$ (ICSD #24900) and calcite $CaCO_3$ (ICSD #150). The peaks are not as intensive as those for the initial asbestos because of significant contribution of cement components in the sample. Peaks indicating the presence of crystalline phases of ettringite $Ca_6Al_2[(OH)_4SO_4]_3 \cdot 26 H_2O$ (ICSD #16045) and caminite $Mg_7[(OH)_{10}(SO_4)_5] \cdot 24 H_2O$ (ICSD #66174) are noticeable as well. Apart from the above mentioned phases, portlandite $Ca(OH)_2$ (ICSD #73467), chrysotile (ICSD #413633) and silica (SiO_2) (ICSD #89277), as well as some silicates from the kaolinite and illite groups, were identified. The presence of certain amounts of baumite $(Mg Mn Fe Zn)_3(Si Al)_2 O_5 (OH)_4$ cannot be excluded.

In the product derived from the asbestos-cement board obtained after the second stage of acidic treatment, mainly silica and gypsum $CaSO_4 \cdot 2H_2O$ (ICSD_161622) can be found (**Fig. 9**). The presence of gypsum is not surprising considering the fact that raw industrial phosphoric acid was used for the primary material decomposition. This agent contains sulfate ions that react with calcium ions and precipitate in the form of gypsum crystals.

Table 4

Results of microscopic fiber counts in the products obtained after repeated treatment of the asbestos cord in relation to the acid concentration and reaction time at 90 °C.

Reaction time (min)	Acid concentration in terms of P_2O_5 (%)			
	10	15	20	30
	Fiber contents			
10	High	High	High	Middle
20	Middle	Middle	Middle	Low
40	Low	Low	Low	Trace
60	Trace	Trace	Not detected	Not detected
90	Not detected	Not detected	Not detected	Not detected
120	Not detected	Not detected	Not detected	Not detected

Table 5

Results of microscopic fiber counts in the products obtained after repeated treatment of the asbestos-cement flat board decomposition in relation to the acid concentration and reaction time at 90 °C.

Reaction time (min)	Acid concentration in terms of P ₂ O ₅ (%)			
	10	15	20	30
	Fiber contents			
10	High	High	Middle	Middle
20	Middle	Middle	Low	Low
40	Low	Low	Trace	Trace
60	Trace	Not detected	Not detected	Not detected
90	Not detected	Not detected	Not detected	Not detected
120	Not detected	Not detected	Not detected	Not detected

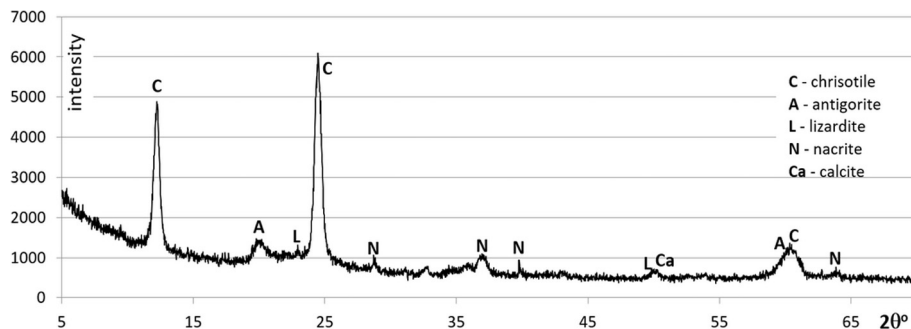


Fig. 6. XRD pattern of the asbestos cord sample used in this study.

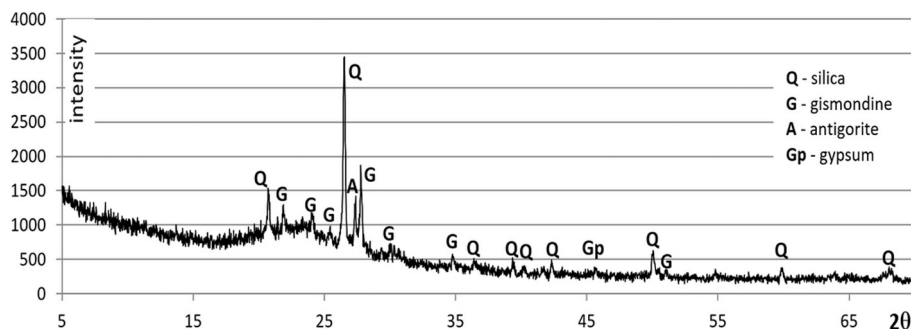


Fig. 7. XRD pattern of the product obtained after the second stage of asbestos decomposition (30% phosphoric acid, 90 °C and 60 min).

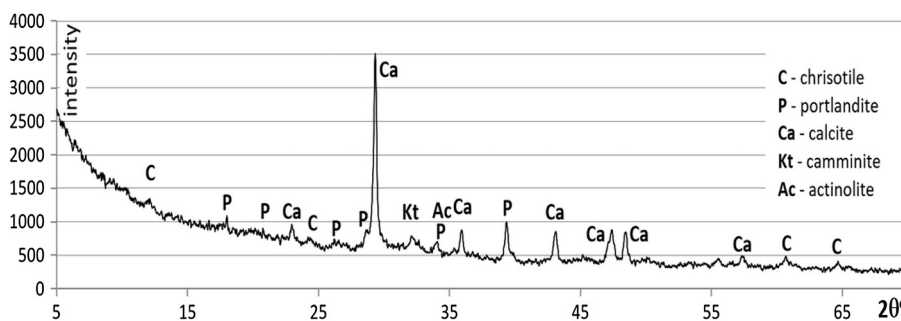


Fig. 8. XRD pattern of the asbestos-cement board sample.

4. Discussion

An analysis of the experimental data obtained in the chemical, microscopic and XRD studies, and especially a comparison of asbestos pattern with the other ones obtained from the remaining examined materials, leads to the assumption that as a result of the chemical treatment with phosphoric acid, the asbestos fibrous

structures are gradually destroyed. In the samples, the disappearance of the fibers of serpentine group minerals is observed. The built-in calcium and magnesium ions of the serpentine minerals are released to the liquid phase and constitute free ions in the solution.

After the first treatment, more than 90% of the waste weight is reduced. The solid products still contain fibrous structures;

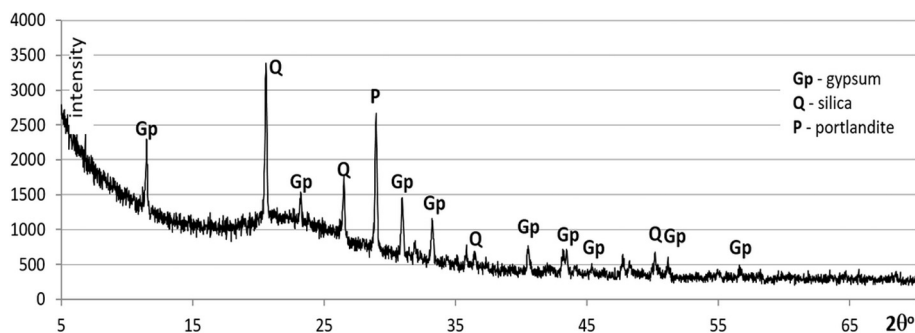


Fig. 9. XRD pattern of the product obtained after second stage of the asbestos-cement board decomposition (30% phosphoric acid, 90 °C and 60 min).

however, they undergo substantial changes. It should be noted that the technological conditions—that is, acid concentration and its stoichiometric ratio to the raw material—as well as the reaction time, applied in the first stage of treatment are not sufficient to completely destroy the asbestos structures. In spite of the dramatic waste weight reduction, consecutive repeated chemical treatment was necessary.

Examination of the final products by XRD, microscopic and chemical analysis demonstrated the formation of new phases in the process of acidic decomposition of material derived from asbestos cord and the asbestos-cement samples. The tests provided evidence for deep structural changes of the primary materials and their transformation into products that may be considered safe: the silica and a solution of calcium and magnesium phosphate. The latter might be applied, for example, as fertilizers. Heavy metals should not be problematic as their contents in asbestos is comparable to that in phosphate raw materials, Morocco natural phosphates, for instance.

The silica separated from the liquid phase can be applicable as a filling material in the manufacture of plastics, gum products, as a sorption stuff or a substitute of fossil silica used in civil engineering. Measurements of its specific surface area by the BET method showed that it amounts to about 178 m²/g. Such properties enable use of the material as an active sorbent.

The presented chemical neutralization of the asbestos from military use might also be used to treat all kinds of similar waste materials derived from civil applications.

Such an approach fits well into the European waste policy, regulated by the EU waste management law.

5. Conclusions

It has been shown by chemical, microscopic and XRD studies that the examined asbestos waste materials derived from military equipment and construction include mainly serpentine group minerals such as chrysotile, antigorite, lizardite and nakrite.

The fibrous structure of these minerals can be destroyed chemically. It was found that under certain conditions, phosphoric acid may be used for the neutralization, but two-stage treatment may be necessary. Depending on the acid concentration, complete decomposition of the asbestos fibers composed of serpentine minerals proceeds in a two-stage process at a temperature of 90 °C and acid concentration of 30% in terms of P₂O₅ and with an acid surplus in relation to the stoichiometric ratio. For safety reasons, in order to ensure total inertization of the waste asbestos materials, applying a two-stage decomposition process may be required.

Evidence of the destruction of asbestos fibers was provided by the thorough studies covering chemical decomposition tests, chemical analyses, X-ray studies and microscopic examinations of the samples. The research carried out demonstrated that the

wastes composed of magnesium and calcium silicates underwent chemical destruction under the influence of phosphoric acid. Despite these positive results, further studies may be necessary to exclude any doubts related to the safety of the products.

The reaction liquid obtained after decomposition of asbestos wastes may be used, after neutralization with lime, for further processing into fertilizer products, for example. The solid residue includes silica that can be utilized as an adsorption agent or filling material in the plastics industry.

The method proposed in this work is relatively easy and should be beneficial in terms of energy. The biggest advantage is that instead of useless waste, usable products are obtained in the form of magnesium-phosphate and active silica. The method may be applied to the processing of waste derived both directly from the demolition of military and civilian objects, and from those that come from the landfills, which should also be disposed of.

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