Chemical elimination of asbestos materials

K Necasova\textsuperscript{1} and P Buchta\textsuperscript{1}

\textsuperscript{1}Research Institute for Building Materials, Hněvkovského 65, 617 00 Brno, Czech Republic

Email: necasova@vustah.cz

Abstract. Asbestos was a frequently used material in the past, mainly in the construction industry, on account of its excellent thermal and chemical resistance. Nowadays, all uses, handling and disposal of asbestos materials are subject to strict legislation due to health hazard. This work is a research of an efficient chemical way to decompose these materials with the lowest energy costs possible so that the method could compete with patented thermal decomposition and other currently common methods. Decompositions were performed at room temperature with acids, namely hydrochloric, sulfuric, phosphoric, acetic and oxalic acid and the results were evaluated based on mass analysis. Asbestos rope and asbestos-cement roof tile were used as samples. From the experiments carried out, the best decomposing agent was hydrochloric acid for the rope sample and acid mixture (hydrochloric and acetic acid in a 1:1 ratio), for the roof tile sample.

1. Introduction

Asbestos is a common title for many natural silicate materials. It includes two large groups of minerals, amphibols and serpentines, all with fibrous structure. According to the composition, these large groups contain different types of asbestos materials. From the amphibols group, it is for example cummingtonite, amosite and crocidolite. The serpentines group is more voluminous and includes for example chrysotile, which is contained in 95% of all the asbestos waste [1]. Waste containing asbestos fibers represents a major environmental burden. This waste has a strong negative effect on living organisms, so its handling is subject to strict legislation [2]. There is a wide range of asbestos containing wastes, like coatings, facades, seals, ropes, tubes, slabs or roofing. One of the most widespread products is asbestos-cement roofing, which was widely used during the 1970s and 1980s. It is known under one of the trade names as Eternit [3]. Its former abundant use provided large amounts of this waste for the present. Therefore, it is important to find an effective way to get rid of harmful asbestos fibers in waste materials or to transform them into a safe form, eventually further applicable, for example in the building industry or in ceramics.

The most used possibility of the fiber destruction is thermal decomposition, which removes bound water and therefore transforms hazardous asbestos fibers into non-fibrous structures. The temperature changes during transformation were observed and analyzed using TG and DTA [4]. According to XRD analysis, the fibrous structure of asbestos is completely removed at around 1000°C [5]. Low-melt glass fragments are added to the mixture to lower the melting point of the asbestos-containing material and save energy [6].

Another possibility of asbestos fiber decomposition studied by other authors is microwave decomposition. According to Leonilli et al, microwave decomposition is a quick and efficient method of generating high temperature inside the material. The fiber degradation was proved by X-Ray Powder
Diffraction Analysis (XRD) and Scanning Electron Microscope (SEM). The resulting harmless material can be further used in ceramics, since it contains predominantly magnesium silicate [7]. High-energy milling can also eliminate the fibrous structure of asbestos. According to the study of Iwaszko J. et al., the original asbestos structure is decomposed within 2 hours at 650 rpm. Structure change was observed using Fourier-Transform Infrared Spectroscopy (FTIR) [8].

Finally, chemical ways of transformation were studied. It was found that different substances such as bases or organic and inorganic acids can be used for chemical decomposition, eventually their mixtures and waste solutions from chemical treatments. For example, in the work of Tabata M. et al., the waste solution after fly ash purification from heavy metals was used for decomposition. This waste solution was a mixture of sulfur and calcium hydroxide. Using this solution together with the ball mill, 99% of asbestos decomposition was achieved [9]. One of the works depicts decomposition with 30% phosphoric acid at high temperatures. The products were mainly phosphates (calcium phosphate, magnesium phosphate), further usable in production of fertilizers [10].

An innovative way is asbestos fiber decomposition by acid gases, as published in Kazumichi Y. et al. The acid gases HF and HCl emerge during thermal decomposition of freons, namely chlorodifluoromethane (CHClF₂), and cause a complete destruction of asbestos fibers. Therefore, two groups of dangerous waste substances are disintegrated [12].

2. Experimental

2.1. Materials and methods

Two types of asbestos waste materials were used for testing decomposition, a rope and a roof tile (see figures 1 and 2). The rope was formerly used frequently as sealing and insulation of boiler and fireplace doors. The roof tile sample was obtained during reconstruction of a holiday cottage.

![Figure 1. Original sample of rope.](image1)

![Figure 2. Original sample of roof tile.](image2)

Both materials were characterized by X-ray powder diffraction. The analysis was carried out on Bruker D8 Advance apparatus with Cu anode (λ Kα = 1.54184 Å) and variable divergence slits at Θ-Θ Bragg-Brentano reflective geometry. Sample of roofing was dissolved in 35% hydrochloric acid, while the rope was measured in its original state. All samples were analyzed on zero background sample holder, in an alcohol medium. The measurement records of rope and roof tile are depicted in figures 3 and 4, respectively.
Based on the rope analysis it can be said that it is mainly composed from chrysotile and talc. Chrysotile is one of the asbestos materials (Mg$_3$Si$_2$O$_5$(OH)$_4$) and talc is hydrated magnesium silicate (Mg$_3$Si$_4$O$_{10}$(OH)$_2$). Compared to that, the roof tile is composed mainly from cummingtonite, quartz and rankinite. Cummingtonite is an asbestos material containing prevalently magnesium silicate hydroxide (Mg$_7$Si$_8$O$_{22}$(OH)$_2$). Quartz is silicon dioxide, the most abundant mineral on Earth, and rankinite is calcium silicate.

The microstructure of decomposed samples was studied by petrographic polarizing microscopy using Eclipse LV100ND by Nikon.

All experiments were conducted at room temperature (approximately 22°C) to save energy. Each sample was placed into a glass container with 150 ml of decomposition agent (sulfuric acid – H$_2$SO$_4$, phosphoric acid – H$_3$PO$_4$, oxalic acid – (COOH)$_2$, hydrochloric acid - HCl, acetic acid – CH$_3$COOH and combination of the latter two). Every decomposition test lasted 24 hours and was performed with constant agitation.

3. Results and discussion

Generally, the acids caused significant surface damage and release of the fibers of the rope samples, while the roofing surface was damaged only partly and its color changed. The results of weight loss at the end of the tests are listed in table 1.
Table 1. Weight loss after acid decomposition.

| Sample       | Reagent               | Decrease [%] |
|--------------|-----------------------|--------------|
| **Rope**     | **Sulfuric acid**     | H$_2$SO$_4$  | -56.1        |
|              | **Phosphoric acid**   | H$_3$PO$_4$  | -132.7       |
|              | **Hydrochloric acid** | HCl          | 42.4         |
|              | **Oxalic acid**       | 30% solution (COOH)$_2$ | 14.2 |
|              | **Acetic acid**       | CH$_3$COOH   | -30.1        |
|              | **Mixture acid**      | CH$_3$COOH + HCl | 32.5 |
| **Roof tile**| **Sulfuric acid**     | H$_2$SO$_4$  | -4.3         |
|              | **Phosphoric acid**   | H$_3$PO$_4$  | 12.9         |
|              | **Hydrochloric acid** | HCl          | 62.4         |
|              | **Oxalic acid**       | 30% solution (COOH)$_2$ | -0.8 |
|              | **Acetic acid**       | CH$_3$COOH   | 1.4          |
|              | **Mixture acid**      | CH$_3$COOH + HCl | 67.1 |

3.1. Decomposition in sulfuric acid
The rope sample turned black and hardened after acid treatment, but the fibers remained unchanged. The material would be suitable for wet milling.

The roof tile sample changed color as well and the surface was mildly damaged. As seen from negative values in the table, weight of the samples increased after the test, which is probably due to formation of solid reaction products, for example magnesium sulfate. No observable decomposition occurred, therefore, sulfuric acid seems to be unsuitable for acid decompositions of asbestos.

3.2. Decomposition in phosphoric acid
The rope sample showed surface damage and release of a limited number of fibers. The weight increase of the rope sample listed in table 1 is caused probably by formation of unspecified solid substances.

The roof tile sample exhibit color change and mild surface damage. As opposed to the rope sample, weight loss occurred in the roof tile sample, indicating partial decomposition. As a conclusion, phosphoric acid decomposition could be applicable for asbestos roof tile. Emerging phosphates, mainly calcium phosphate, can be further used for fertilizing, as published in Pawelczyk A. et al. [10].

3.3. Decomposition in hydrochloric acid
A complete disintegration of the rope sample occurred and the fibers were released.

The roof tile sample decomposed to individual layers (see Figure 5) and part of the sample transformed into mash with fibers, which was most probably a dissolved carbonate structure. As depicted in table 1, weight loss occurred in both samples and approximately 50% decrease in weight indicates a well-chosen agent.
3.4. Decomposition in 30% solution oxalic acid

The rope samples exhibited surface damage and fiber release. The roof tile sample changed color and the surface was affected only slightly. As seen in table 1, weight loss was observed in the rope sample, while the weight of the roof tile sample increased about 0.8%. This could be due to reaction of oxalic acid with some cement components, as the cement represents around 90% of the total roof tile mass [3]. The most probable reaction is with calcium oxide which produces non-soluble calcium oxalate. Compared to the work of Valouma A. et al. [11], the results were less satisfactory, probably due to higher concentration of the acid and shorter reaction time.

3.5. Decomposition in acetic acid

The surface was disintegrated and the fibers were released in the rope sample (see figure 6). To illustrate the efficiency, the structure of the original sample is in figure 7. The roof tile exhibited color change and surface damage which exposed the fibers and the sample volume considerably increased, separating some of the structure layers as seen in figure 8. While the rope sample showed a significant increase in weight, probably caused by formation of a precipitate. The roof tile sample exhibited little loss of weight indicating decomposition. Given that the layers of the roof tile were partly separated after the test, acetic acid could represent a suitable pre-treatment before decomposition by other, more convenient agent.

![Figure 5. Roof tile sample treated by HCl.](image)

![Figure 6. Rope decomposed in CH₃COOH (image from the optical microscope).](image)

![Figure 7. Original sample of the asbestos rope (image from the optical microscope).](image)
3.6. Decomposition in acetic acid and hydrochloric acid combined

Based on the previous results, acetic acid was combined with hydrochloric acid in 1:1 ratio and the samples were exposed to this mixture. In the rope sample, short fibers were released and the whole structure hardened with no visible loss of material. However, the mass analysis showed 33% weight loss, so the hard and fragile structure of the treated sample could be suitable for wet milling and repeated decomposition.

The roof tile exhibited significant surface damage, change in color and 67% weight loss which indicates a great decomposing potential of the mixture. Presumed reaction products are calcium chloride and calcium acetate. Calcium chloride could be further used as admixture in road salt or desiccant. Calcium acetate could be used to produce flammable gel for portable cookers [13].

4. Conclusion

The aim was to find a decomposition agent suitable for asbestos treatment in laboratory conditions. Sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid and acetic acid were used and after evaluation of the efficiency, the samples were exposed to a mixture of acetic acid and hydrochloric acid. The best results were provided by oxalic acid, hydrochloric acid and the acid mixture. For the asbestos rope, the highest weight loss (42%) was achieved using hydrochloric acid. Decomposition in oxalic acid caused only 14% decrease in mass, but changes in material structure were obvious. After treatment by the acid mixture, 32% weight loss occurred.

For the roof tile samples, the most suitable was the acid mixture, which etched the individual layers from each other and decomposed 67% of the material. Using hydrochloric acid, 62% weight loss was achieved. After treatment in oxalic acid, precipitate emerged which increased the mass of the sample by 0.8%.

In further research, decomposition of asbestos in mixtures of acids will be examined, using preferably waste mixtures from chemical productions and pre-treatments, for example acid degreasing bath.

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