



Asbestos Presence in a Factory that Produced Asbestos-Containing Products

H. Fajković *

Department of Geology, Faculty of Science, University of Zagreb, Horvatovac 95, 10000 Zagreb, Croatia
Received 25 October 2009; accepted 14 April 2010

Abstract

In 2007, research was carried out to determine the type and amount of asbestos fibers in a Croatian factory with a long history of making asbestos-containing products.

Since the 1970s, asbestos fibres have been considered carcinogenic in humans i.e as a known cancer-causing agent. In the environment, asbestos fibres are inactive and naturally resist biodegradation. In time, fibres can only be ground into smaller particles by mechanical force. These small particles in the air present a health hazard. Because of their small size, shape and durability, asbestos fibres can easily be inhaled and stick to the lung tissue, causing serious respiratory problems. Among these are diseases with long latency periods of 10 to 40 years such as: asbestosis, mesothelioma and lung cancer. Asbestos is the generic, industrial name for a group of six minerals determined by common size and inherent physical properties. Crocidolite, amosite, anthophyllite, tremolite and actinolite are all asbestos minerals from the amphibole mineral group. The sixth mineral, chrysotile, is a mineral from the serpentine mineral group. Asbestos fibres are particles longer than, or equal to, five μm with a length to width ratio greater than or equal to 3:1; however, the ratio can be higher than 20 or even 1000. They are inflammable, thermally stable, resistant to biodegradation, chemically inert to most chemicals and have low electrical conductivity. Because of these attributes, asbestos was heartily embraced in industrial production.

Different methods are used to determine the type and quantity of asbestos fibres in the air. Some of the most common methods and instruments are: polarizing light microscopy (PLM), phase contrast optical microscopy (PCM), scanning electron microscopy (SEM), analysis with electron diffraction spectra (SAED) with energy dispersive X-ray analysis (EDS), powder X-ray diffraction technique (XRD), and transmission electron microscopy (TEM). Some of above-mentioned methods (PCM, PLM, XRD) are currently popular due to their low cost, but using these methods exclusively could lead to false estimates of asbestos levels. It is hard to distinguish asbestos fibres from certain other fibres like artifacts, organic or inorganic. Therefore, it is important to observe not only the habit of minerals, but also the chemical composition of them. A combination of SEM and EDS gives information about both the habit and the chemical composition of the observed fibers, and so is suitable for asbestos analysis. Different methods of analysis are displayed and compared in this paper. Analyses were made using SEM with EDS and XRD. All samples were collected in working areas of a factory which used asbestos in production. Presence of different types of asbestos was confirmed.

Keywords: Asbestos, Comparison of methods, Factory working area, Croatia, Chrysotile, Crocidolite.

1. Introduction

The coastline of Croatia is well known by the tourist industry for its natural beauty. Unfortunately, it is also home to several heavy-industry factories, some of which used asbestos in their production. One of these factories lies close to Croatia's second largest city, affecting the environment for nearly 200.000 people. Although production has been stopped at the factory, asbestos fibers remain in the vicinity as a result of nearly 80 years of producing asbestos-containing materials. In 2007, research was carried out to determine the presence of asbestos fibers and to determine the type of any asbestos found.

Since the detection and correct identification of asbestos fibers is difficult, multiple types of analysis were used to minimize error.

Asbestos is a generic name for six minerals used in industry with attributes that qualify them as asbestos. The term is commercial rather than mineralogical. Asbestos fibres are particles longer than or equal to five μm with a length to width ratio greater than or equal to 3:1; however the ratio can be higher than 20 or even 1000[1]. Asbestos minerals crystallize in a monoclinic crystal system, apart from anthophyllite, which crystallizes in an orthorhombic crystal system. Some general information and the chemical composition of asbestos are presented in Table 1.

*Corresponding author.

E-mail address (es): hanaf@geol.pmf.hr

Table 1. Comparative overview of some asbestos features

Name	Chemical Composition	Common Name	Mineral Group	Hardness	Crystal system
Crocidolite	$\text{Na}_2\text{Fe}_3(2+)\text{Fe}_2(3+)\text{Si}_8\text{O}_{22}(\text{OH})_2$	blue asbestos	amphiboles	5-5½	monoclinic
Amosite	$\text{Fe}_2(2+)(\text{Fe}(2+),\text{Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	brown asbestos	amphiboles	5-6	monoclinic
Anthophyllite	$\text{Mg}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	gray asbestos	amphiboles	5½-6	orthorhombic
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	white asbestos	serpentine	2½	monoclinic
Actinolite	$\text{Ca}_2(\text{Mg}, \text{Fe}(2+))_5\text{Si}_8\text{O}_{22}(\text{OH})_2$		amphiboles	5-6	monoclinic
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$		amphiboles	5-6	monoclinic

The first recorded application of asbestos can be traced to Finland in approximately 2500 B.C., where it was used to reinforce clay utensils and pottery [2]. Asbestos as a material was widely used in the first two thirds of the 20th century, and its increase in production ran parallel with industrial growth. The peak of asbestos consumption was in the 1973 when 800,000 tons of it was used. By 2003, the amount had been downsized to 4,650 tons per year. [3]. Asbestos fibers have many attributes that contributed to their popularity in industrial production. They are inflammable, thermally stable, flexible, resistant to biodegradation, chemically inert to most chemicals and have low electrical conductivity. Asbestos was used in countless products ranging from clothing to auto brake linings and pads up to felts for flooring and roofing. It was also sprayed on steel beams as a fire protectant. Industry did not use all six asbestos minerals equally. Chrysotile, also called *white asbestos*, was commercially used in more than 95 percent of the world's production. Chrysotile possesses some features that distinguish it from other asbestos minerals, namely softness and flexibility for weaving. Crocidolite, so-called *blue asbestos*, only accounts for 2.2 percent, but because it is such a health hazard, it is important to consider in every investigation [4]. It is 500 times more likely to cause mesothelioma than white asbestos i.e. chrysotile [5]. The other asbestos minerals were used in much lower quantities, together making up the remaining 2.5 percent. Asbestos fibres have been considered carcinogenic since the 1970s, and numerous countries have banned the use of asbestos minerals in production and the use of products containing asbestos. Because of their small size, shape and durability, asbestos fibres can easily be inhaled and stick to the lung tissue, causing serious respiratory problems. Among these are: asbestosis, mesothelioma and lung cancer- diseases with long latency periods of 10 to 40 years [6]. In the environment, asbestos fibres are inactive and naturally

resist biodegradation. In time, fibres can only be ground into smaller particles by mechanical force. Such small particles in the air present serious health issues, as they can be easily inhaled.

Unfortunately, detecting and classifying residual asbestos can be complex, time-consuming and often expensive. Some of the difficulties in asbestos analyses stem from the fact that asbestos fibres are from one of two different mineral groups: amphibole and serpentine. Furthermore, their size and shape make it hard to distinguish asbestos fibres from some other fibre-like artefacts, organic or inorganic. Therefore, it is important to observe not only the habit of the minerals, but also the chemical composition of them. Different methods need to be combined to determine the type of asbestos fibres in any sample, especially when determining fibre particles from the air [7].

Phase contrast optical microscopy (PCM), scanning electron microscopy (SEM), analysis with electron diffraction spectra (SAED) with energy dispersive X-ray analysis (EDS), powder X-ray diffraction technique (XRD) and transmission electron microscopy (TEM) are some of the most common methods in practice. Some of the above-mentioned methods (PCM, PLM, XRD) are currently popular due to their low cost, but using these methods exclusively could lead to false conclusions.

Different methods of analysis are displayed and compared in this paper. Fifteen samples from the factory yard were analyzed using a combination of analytical procedures to minimize error: SEM with EDS and XRD.

2. Methods

2.1. Samples

Different types of material were taken for analytical

proposes: some from a borehole made close to the production area, and others from the production area itself. The total depth of the borehole was 7,2 m. The first layer (0-3,9 m) was topsoil, probably brought in to cover asbestos-mud deposits. The following layer (3,9-6m) was gray in color, indicating probable asbestos contamination . From this layer, four sub-samples were sorted out and analyzed: B_b (3,9-4,2 m); B_c (4,2-4,4 m); B_d (4,4-5 m); B_e (5-6 m). The deepest layer (6-7,2m) contained recent marine sediments, possibly contaminated with asbestos. It was also divided in to the three samples: B_f (6-6,3 m); B_g (6,3-6,6 m) and B_h (6,6-7,2 m). The differences in color according to depth are shown in Figure 1. Material was also collected from different parts of the production area, as shown in Figure 2: from the channel where used material was deposited (a); from dust collected from machinery used in production processes (b and c); from waste material from production (d and e); from dust from the laboratory wall; and from accumulated particles from production on the machine (f).

2.2. Analytical Procedures

Different type of analyses can be used for asbestos detection. Some of the most common methods and instruments are: phase contrast optical microscopy (PCM), scanning electron microscopy (SEM), analysis with electron diffraction spectra (SAED) with energy dispersive X-ray analysis (EDS), powder X-ray diffraction technique (XRD), and transmission electron microscopy (TEM) [8].

In this paper, SEM and EDS were combined with XRD. Powder X-ray diffraction (XRD) is used for phase identification and the determination of crystal structure in minerals. To perform XRD, samples must be crystalline and ground into a powder. Unfortunately, there are some drawbacks to XRD: the detection limit is 1% (wt), and it is impossible to distinguish the habitus of the minerals detected, i.e. whether the mineral is fibrous or prismatic. However, it is popular

because it is relatively affordable and not too time consuming [9].

Scanning electron microscopy (SEM) has become a powerful tool in detecting asbestos particles. Recently, more and more national laws and standards have been recommending SEM-based methods for asbestos detection. Its advantage lies in very high magnification: asbestos fibers can be measured and clearly distinguished from non-asbestos particles.

Furthermore, in combination with energy dispersive X-ray spectroscopy (EDS), particles can also be chemically analyzed.

3. Results

3.1. XRD results

XRD analyses were performed on fourteen samples: seven from the factory production area, and seven from the borehole. Asbestos fibers were not the only minerals present in the collected samples.

The factory production area samples were from accumulated remains of the production process, and so they also contained all of the minerals used in recent production. In these cases, the concentration of asbestos was not very high, which is why they were treated with HCl for preconcentration. Chrysotil was detected in all the samples. In contrast, crocidolite was not found in any of these samples, indicating that crocidolite had not been used in industrial production in recent history. Analyses from the borehole were carried out on subsamples from 4 -7,2 m depth. Material above 4 m had been brought in recently to cover waste material, and so wasn't analyzed. Asbestos minerals were determined throughout the profile ranging from 4 m - 6,60 m,. In the deepest layer (6,6-7,20 m) no presence of asbestos was determined. In some layers, blue clusters were noticed, which were analyzed separately, as isolated particles, because the blue color implied crocidolite.



Fig. 1. Samples from the borehole; a) first four meters 0-4 m; b) core from 4-7 m.



Fig. 2. (a) the channel where used material was deposited; (b and c) dust collected from machinery used in production processes; (d and e) waste material from production; (f) machine used in production.

The detection limit of XRD is 1% (wt), which is why measurements of layers were retaken after a HCl treatment. Such a treatment decreases the concentration of matrix materials such as CaCO_3 . Figure 3. presents the diffraction spectra for sample B_e before (a) and after (b) the use of HCl.

The first spectrum shows all of the minerals present in the sample, while the second shows a decrease of peaks due to the dissolution of some phases with HCl. Samples B_b, B_d and B_e showed significant increases in amphibole asbestos, i.e. crocidolite, with the addition of HCl. Before treatment, the

concentration of crocidolite was under the 1% XRD detection limit, but after the use of HCl, crocidolite was detected in all three samples (Table 2). Chrysotile was determined in all layers from 4-6,6m, while crocidolite was present only from 4-6m depth. In the deepest layer (6,6-7,2), no asbestos particles were determined.

3.2. Results of SEM with EDS

With the high magnification images provided by SEM, it is possible to definitively identify suspected asbestos

particles. Furthermore, with EDS a chemical analysis can be made of just one small segment of fiber.

From the gray material procured from the borehole (depth 3,90-6 m) four samples were analyzed using SEM, and then chemically analyzed using EDS. For the analyzed depth, crocidolite and chrysotile were determined. Figure 4. presents a typical EDS spectrum of chrysotile and crocidolite from the observed samples. Figure 5. presents a selection of the SEM images.

Table. 2. Presence of asbestos minerals (crocidolite and chrysotile) in borehole.

	Depth (m)	without HCl		with HCl	
		Crocidolite	Chrysotile	Crocidolite	Chrysotile
B_b	4 - 4,2	—	+	+	+
B_b (b.f.*)	4 - 4,2	+	—	/	/
B_c	4 - 4,40	+	+	+	+
B_d	4,4 - 5	—	+	+	+
B_e	5 - 6	—	+	+	+
B_f	6 - 6,3	—	—	—	+
B_g	6,3 - 6,6	—	+	/	/
B_h	6,6 - 7,2	—	—	—	—

* separated blue fibre

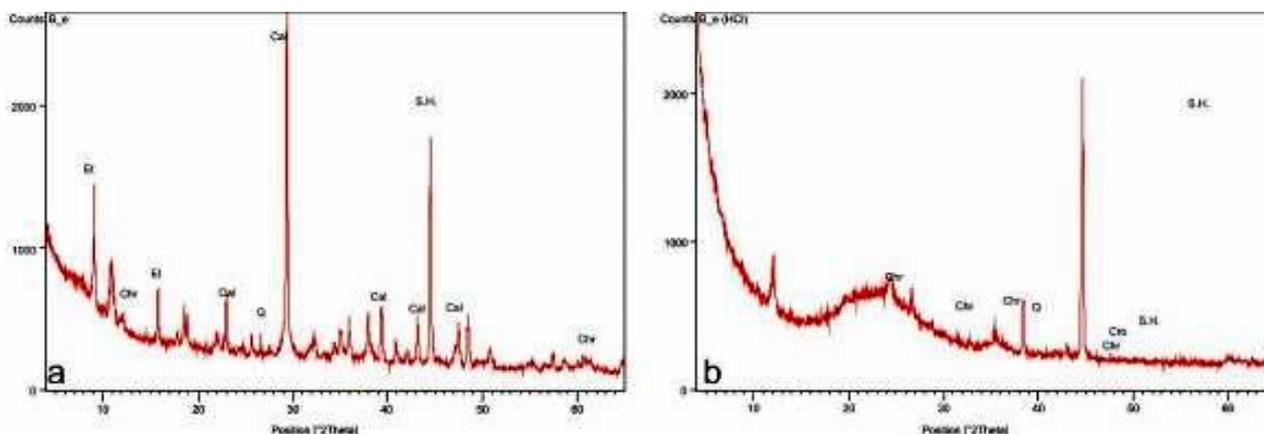


Fig 3. XRD diffraction spectra for B_e; (a) before HCl use and (b) after the use of HCl

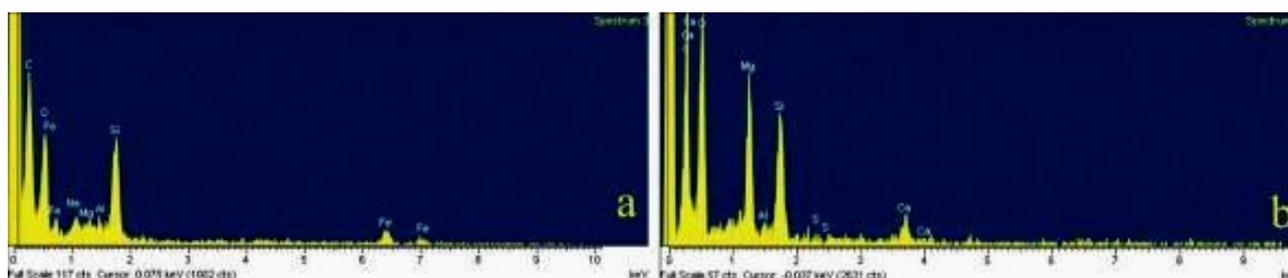


Fig. 4. EDS spectrum for chrysotile (a) and crocidolite (b).

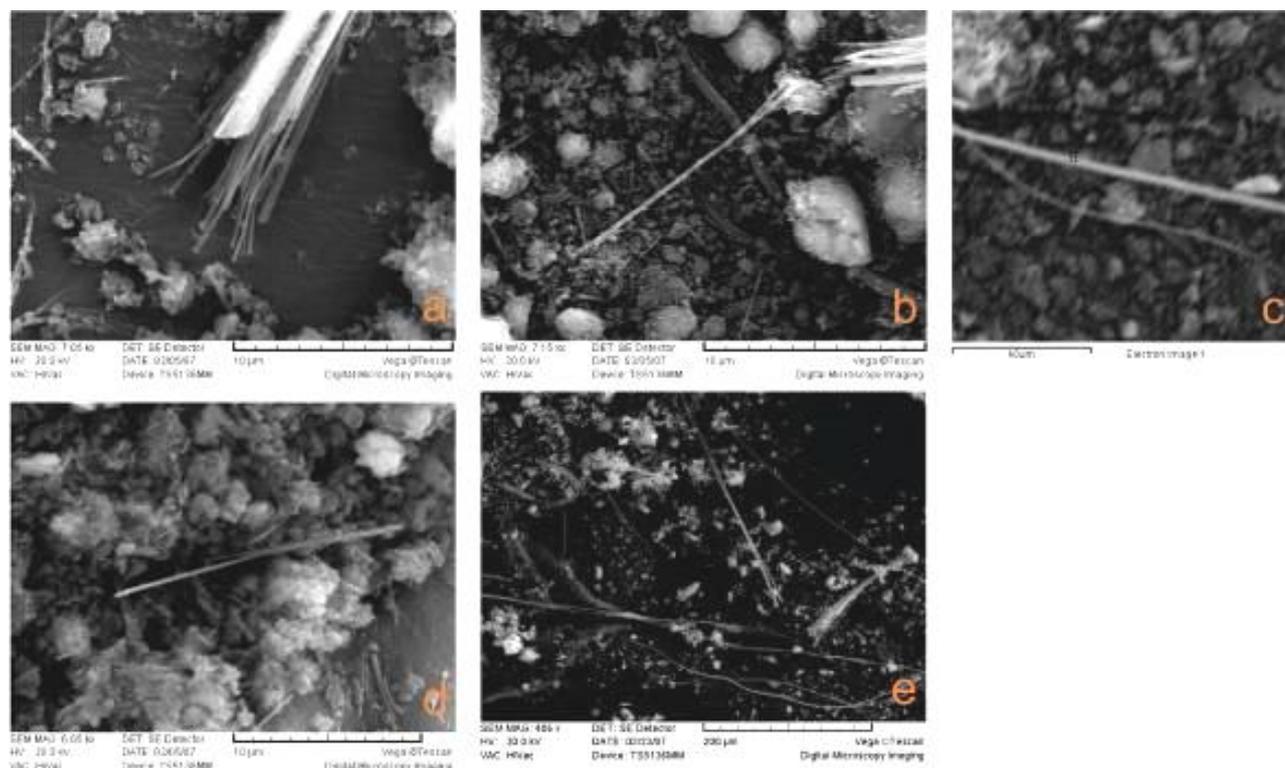


Fig. 5. (a,b and d) Crocidolite asbestos clusters from the borehole; (c) chrysotile asbestos fibre; (e) two types of asbestos fibres, crocidolite and chrysotile.

4. Conclusions

Different types of samples and materials were taken for analytical purposes. In almost all samples, asbestos fibres were determined. Samples from the borehole probably represent waste material used in production some time ago, and they contained both crocidolite and chrysotile. From that material, it can clearly be concluded that asbestos-containing material was made of serpentine as well as amphibole asbestos some time ago. The surface samples collected from the factory production area represent the material used more recently in production. In these samples, only chrysotile was found, suggesting the abandonment of crocidolite in recent production. Different analyses were carried out to minimize error in the determination of particles. The XRD diffraction spectra showed the presence of asbestos minerals, but no information on the habitus of the minerals could be concluded. With SEM, habitus observations were made and EDS analyses eliminated possible errors in the conclusion. The first bans and regulations dealing with asbestos referred to the workplace, protection of workers and the concentration of fibers in the air. Allowed exposure time is defined for workplaces, but varies among countries' regulations; it can be within 4-8 hours, with fibers concentration within 0.1-2 f/cc (fiber per cubic centimeter). Some countries have distinction between asbestos fibre types, where permitted exposure time for

amphibole asbestos is shortened from one-half to the one-tenth of that for chrysotile [10].

Because of the prevalence of asbestos in the factory area, further analyses should be performed to determine the amount of airborne particles. Additional monitoring is especially important due to the presence of crocidolite. Exposure to his form of asbestos is 500 times more likely to lead to illness than exposure to chrysotile alone.

References

- [1] LESZ, M., Asbestos in the air. Poland conference (2005).
- [2] A. Europaeus-Äyräpää, Acta Archaeol. 1, 169 (1930).
- [3] VIRTÄ, R.L., (2005), Mineral commodity profiles—Asbestos: U.S. Geological Survey Circular 1255–KK, 56 p.
http://pubs.usgs.gov/circ/2005/1255/kk/Circ_1255KK.pdf.
- [4] SAVIC, V.-I., FAJKOVIC, H., “Asbestos as Environmental and Legal Issue“, 5th Int. Conf. on Int. Env. Law (2007) 213-230.
- [5] HSE Hodgson and Darnton 2000 Ann Occup Hyg vol 44 no 8.
- [6] VIRTÄ, R.L., (2006), Worldwide asbestos supply and consumption trends from 1900 through 2003: U.S. Geological Survey Circular 1298, (2006), p. 80.
<http://pubs.usgs.gov/of/2002/of03-083/of03-083.pdf>.
- [7] DODONZ, I., Minerals: definition, Terminology, Structure, Chemistry. Erasmus Intensive Programme in Mineral Sciences, Budapest, Hungary(2007), Aug. 24-Sep.2, 2007. Asbestos 2007 Budapest.

[8] JONES, A.P. Indoor air quality and health. *Atmospheric Environment* 33, (1999), 4535-4564.

[9] VIRTÀ, R.L., (2002), *Asbestos: Geology, Mineralogy, Mining, and Uses*: U.S. Geological Survey Circular , 1255–KK, p. 28.

<http://pubs.usgs.gov/of/2002/of02-149/of02-149.pdf>

[10] National Cancer Institute. *Malignant Mesothelioma: (PD) Treatment, Health Professional Version: 2005*

http://www.cancer.gov/cancertopics/pdq/treatment/malignant_mesothelioma/HealthProfesiona