A Solution for the Full Impregnation of Asbestos: The Use of an Epoxy Polymer Resin

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ABSTRACT: Asbestos has been identified as priority substance for risk reduction and pollution prevention given its carcinogenic effects. Because of its wide occupational exposures and widespread use in commerce in the past, there is a big concern that it may present a general health hazard. Therefore, the identification of asbestos-containing materials and their neutralization has become a topic plan of social prevention and intervention in many European and American countries. If the presence of asbestos in buildings (i.e., schools) is detected, the abatement program usually accomplishes the removal of the asbestos-containing materials and displacement in controlled waste disposals (*ex situ* technique). Removal has many disadvantages: high costs, large production of toxic refuses, high risks of exposure for removal workers, and high risk of environmental pollution during and after the operations. Thus, the search for alternative *in situ* techniques has been recently promoted and full impregnation seems to be the best candidate given its reduced risks for both workers and environment, and its low costs. In this paper, a technique for the *in situ* full impregnation of asbestos by an epoxy polymeric resin is proposed, and the results of its application for the neutralization of either chrysotile or amphibole asbestos-containing materials is described. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 713–720, 2000

Key words: asbestos; epoxy resin; full impregnation; scanning electron microscopy; Rietveld refinement

INTRODUCTION

Asbestos is a commercial term embracing minerals of two different families (amphiboles and serpentines) that occur in nature as fibers. Amphiboles are double-chain silicates that may assume a fibrous habit being structurally elongated in one preferred crystal direction.

The general formula is as follows: $WX_2Y_5Si_8O_{22}(OH)_2$ with $X = Na$, $Y = (Mg,Fe)$ riebeckite; $X = Y = (Mg,Fe)$ grunerite; $X = Ca$, $Y = (Mg,Fe)$ tremolite; $X = Ca$, $Y = (Mg,Fe)$ actinolite. Serpentines are 1:1 (a tetrahedral and an octahedral sheet) sheet silicates that may roll in order to compensate for the misfit between the tetrahedral and octahedral layers assuming a characteristic fibrous habit. The formula is $Mg_3(OH)_4Si_2O_5$ (essentially chrysotile). Major industrial use of asbestos began in 1878 with mining of chrysotile in Quebec (Canada) followed by crocidolite mining in 1910 and grunerite mining in 1916 in South Africa. Given its properties (heat and chemically inert, phono-absorber, thermal insulator, and many more), it became part of the everyday life all over the world as it has been utilized for an outstandingly large number of applications. The health hazards associated with exposure to fibrous minerals were definitely rec-

ognized in the 1970s albeit the association between diffuse fibrosis of the lungs and exposure to asbestos was already known since 1930s.[1] Besides, Doll[2] observed increased mortality from lung cancer in UK asbestos workers. The 1972 asbestos standard established a Permissible Exposure Limit (PEL) for asbestos of 2.0 f/mL as an 8-h time-weighted average and the 1986 asbestos standards reduced PEL to 0.2 f/mL. Currently there is much concern about the health risks associated with exposure to asbestos since it has been associated with diseases such as asbestosis, pleural plaques, pleural effusions, pleural fibrosis, diffuse malignant mesotheliomas, and lung cancer. Concerning the relationship between hazardous effects and microstructure, the surface and physical shape of asbestos play a key role in the interaction with the interface of the organism cell.[3] The interaction of asbestos fibers with cells *in vivo* and *in vitro* has been the subject of many studies.[4–7] Epidemiological and *in vivo* studies demonstrate that crocidolite fibers have a remarkably longer lifetime in the lung tissue than chrysotile[8] and thus they are much more pathogenic.[9] Regarding the shape, it was observed that the activity among the different fiber types increases with decreasing diameter and increasing fiber length.[10] The results of the studies in Ref. 9 indicate the optimum morphology for the induction of intrapleural tumors is a diameter of 0.25 μm and a length >8 μm. Starting from the 1980s, the U.S. Environmental Protection Agency promoted the removal of asbestos in schools, homes, and commercial buildings, and later, European countries (especially Italy with the 1992/257 directive) followed such policy aimed to the neutralization of asbestos. Asbestos neutralization techniques can be classified as follows:

1. *Ex situ*
   (a) Abatement and displacement in waste disposals especially suited for toxic refuses.
   (b) Abatement and thermal inertization eventually followed by an industrial reutilization of the inert phase.[11]
2. *In situ*
   (a) Full impregnation by viscous media that penetrate and cement the fibers in place.
   (b) Isolation by chemically inert rigid panels that cover the exposed areas.
   (c) Chemical inertization by a foam sprayed on the exposed area that selectively attacks and decomposes asbestos.[12]

Even though technique 1a is still the most diffuse intervention technique as it has the advantage that asbestos is completely removed from the building after the operation, many disadvantages are entailed: high costs and long times of intervention, large production of toxic refuses, high risks of exposure for removal workers, and high risk of environmental pollution during and after the operation. Many of the disadvantages are tackled when *in situ* techniques are applied: costs are dramatically reduced because, for example, full impregnation (2a) or chemical inertization (2c) only requires a spray system for the application of the incapsulating/inertizating agent; there is a very low dispersion of asbestos in the working environment, no refuses, and very low risks for the workers; there is no risk of pollution during and after the operations.

It should be remarked that the utilization of an epoxy resins would help to definitely neutralize the surface activity of asbestos. In fact, although the monoionic polymer polyvinyl-2-pyridine N-oxide does not passivate chrysotile, some water-soluble polymers, such as carboxymethylcellulose, are effective.[13] Brown et al.[14] published a report in which they describe the modification of the surfaces of grunerite fibers with octyldimethyl-chlorosilane (C8) or octadecyl-methylchlorosilane (C18) through *in vivo* studies showing that fibers coated with C18 chains were dramatically less active at producing tumors. Besides, Pott et al.[15] reports that actinolite with 2-polyvinylpyridine-N-oxide hydrogen bonded to its surface produced fewer mesotheliomas with a longer latency period than actinolite without polymer. We are currently performing experiments to test the efficiency of the epoxy resin in terms of passivation of the surface activity for serpentine and amphibole asbestos.

This study deals with the application of an epoxy polymer resin for the full impregnation of asbestos. The results of laboratory experiments where the polymer resin has been utilized for the full impregnation of either chrysotile asbestos and amphibole asbestos containing materials are described. The samples were preventively fully characterized by X-ray powder diffraction using the Rietveld method and scanning electron microscopy (SEM). A statistically meaningful comparison of the microstructure of the samples be-

fore and after the interaction with the incapsulating agent was performed in order to ascertain the degree of impregnation, surface morphology of the fibers, and existence of free uncoated asbestos fibers after the treatment. The last part of the work is devoted to the description of the results of the application in a real case, the full impregnation of a 49 m^2 area in a test site. Samples have been collected before and after the application of the incapsulating resin to perform the SEM analyses.

EXPERIMENTAL

The material developed for the full impregnation of asbestos is a bicomponent epoxy resin that consists of two parts (epoxy polymer and hardener) in a water/alcohol mixing solution. The epoxy polymer component[16] is composed of 30% of low molecular weight epoxy monomers in a hydro alcoholic solvent. Low molecular weight amines and less than 2% amine (high molecular weight) compose the hardener part. This part is diluted in the hydro alcoholic solvent. Water and 1-methoxy-2-propanol constitute the solvent. The resin polymerization occurs approximately 4 h after the mixing to give after the solvent evaporation, an elastomer-like polymer. The solvent evaporation time depends on the porosity and thickness of the material to treat.

Two samples of asbestos containing materials employed in the past as insulators in buildings have been selected for the study of the interaction with the resin. They are classified as incoherent asbestos materials and labeled A (for the one with chrysotile asbestos) and B (for the one with amphibole asbestos). A preliminary qualitative investigation by X-ray powder diffraction revealed that A is composed mainly by amorphous material (rock or slag wool) with minor amounts of chrysotile, calcite, and brucite. Sample B is also composed of amorphous material (rock or slag wool) with grunerite, quartz, and calcite. For the quantitative analysis, the powders were added 10 wt % National Institute of Standard Technology standard corundum to carry out the Rietveld-reference intensity ratio (RIR) procedure.[17,18] The data set were refined by the Rietveld method using the Generalized Structure Analysis System program.[19] The structure factors were calculated using the formal atomic scattering factors, the background was fitted with a Chebyshev function with 16 coefficients, and the peak profiles were modeled using a pseudo-Voigt function. The lattice constants, the phase fraction, and coefficients corresponding to sample displacement and asymmetry were refined. The total number of parameters refined at the same time in the last stage of the refinements was 40 for pattern A and 50 for pattern B, respectively. Figures 1(a) and 1(b) depict the observed (crosses), calculated (continuous line), and difference curve (bottom line) of the refined patterns showing a good agreement between the calculated and observed patterns. The agreement factors are Rwp = 9 and 11% for A and B, respectively.
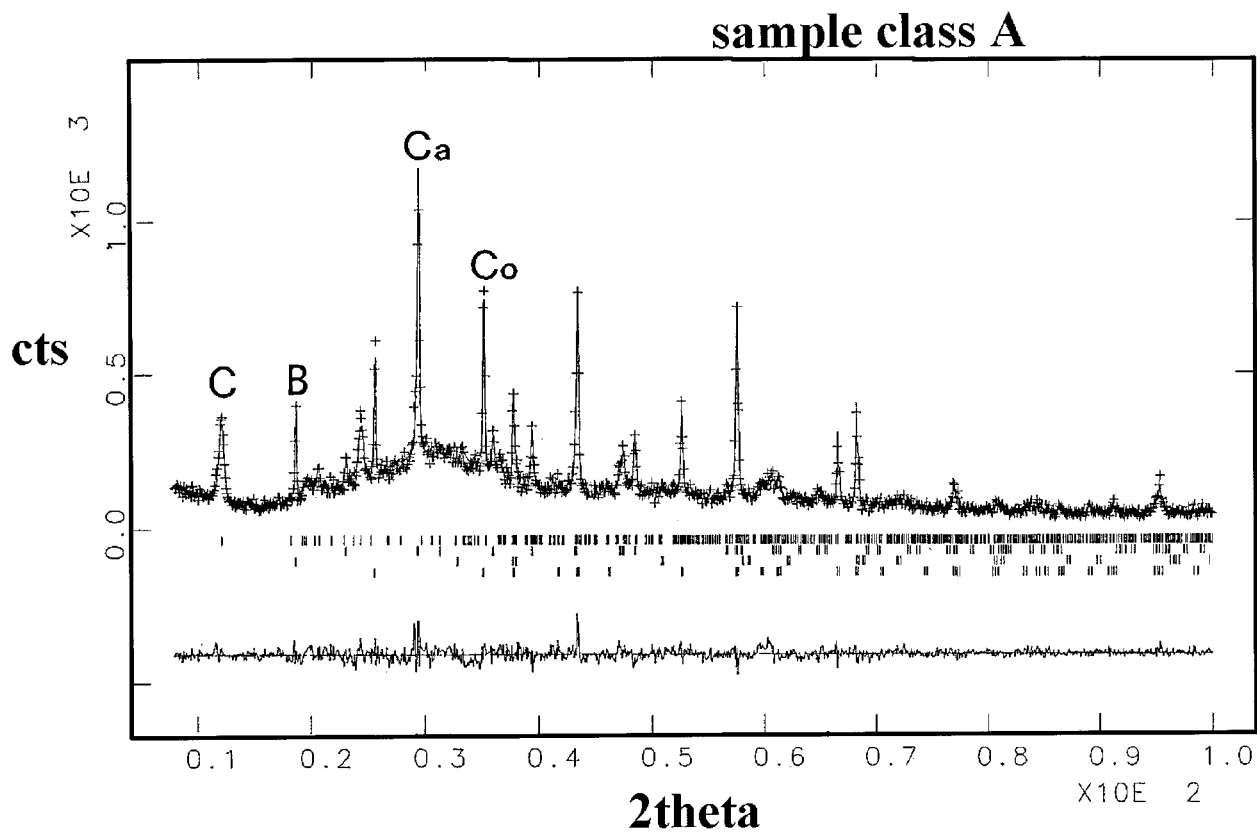
The two samples have been investigated by SEM imaging analysis before and after the interaction with the epoxy resin. Two specimens were selected for both the untreated samples A and B with size of ca. $0.7 \times 0.7 \times 0.7$ cm. Specimens were mounted on an Al holder and fixed with Ag paste. Dehydration was done under an IR lamp for 15 min and coating was performed using Au. A Philips XL 40/604 automated instrument was utilized for the observations using a vacuum of ca. 10^{-7} mm Hg. Five specimens were instead selected from each sample after the treatment and prepared in the same way for the analyses. In order to give a statistical significance to the observations, 20 frames were collected for each specimen, the size of 100×100 μm ($\times 1000$ magnifications) using a beam size of 5 μm and a beam of 25 kV. Each frame was selected using random movements of 100 μm in the x and 100 μm in the y direction, respectively. For each frame, type, number, and description of each observed fiber was reported.

The site test was carried out in a parking lot whose ceiling is completely coated with an asbestos containing material with a composition resembling sample A.
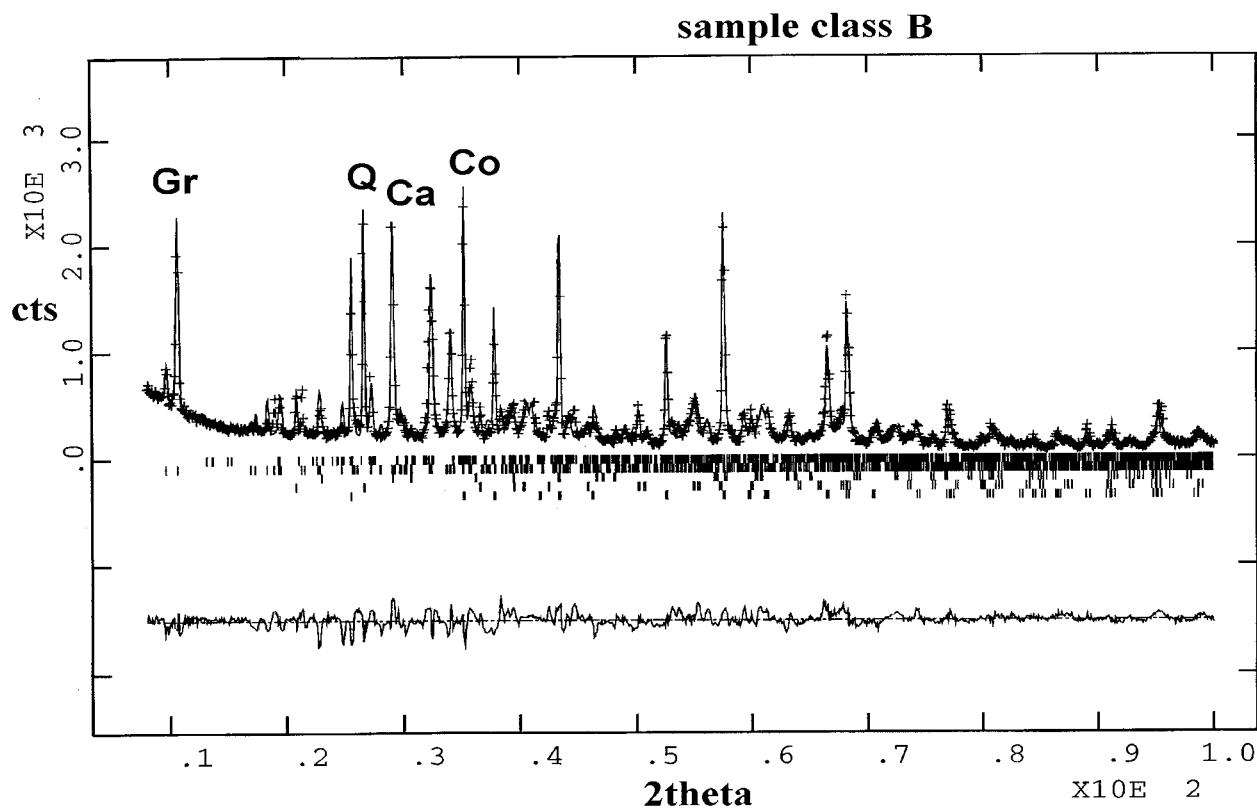
The flock spread surface is a section of 30 m^2 ceiling's paving made of concrete, delimited and separated into two equal parts by girders with a rectangular section of 600×200 mm.

The impregnation system was performed using a dilution rate adapted after flock spraying analysis. The treatment is carried out in two separate steps:
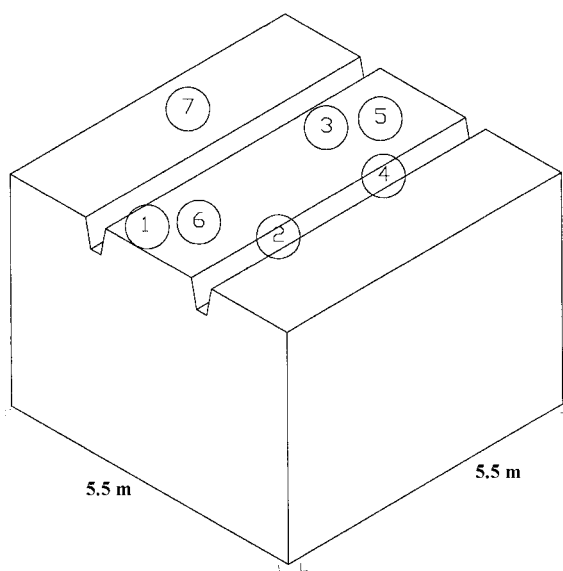
1. spraying the product at high discharge in order to ensure a watering on the whole surface and bulk;
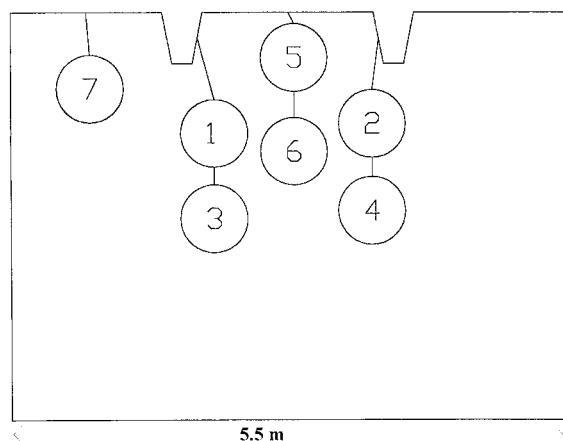2. spraying of an intumescent paint on the treated surface.

sample class A

(a)

sample class B

(b)

Table I   Composition of the Raw Materials A and B as Calculated from Quantitative Phase Analysis by the Combined Rietveld-RIR Methods

Phase Weight (%)	Sample A	Sample B
Brucite	0.6 (1)	—
Calcite	6.7 (4)	5.0 (6)
Chrysotile	6.3 (5)	—
Grunerite	—	9.5 (9)
Quartz	—	0.5 (1)
Glass wool	86.4 (3)	85.0 (3)

treatment tested by SEM analyses. Seven samples were collected from different points of the ceiling (see Fig. 2) and prepared as described above for the SEM observations.

RESULTS

The composition of the two samples calculated from the Rietveld quantitative analysis is reported in Table I. Both samples are mainly composed by a glass wool that determines the bulk properties of the material and subordinate amount of asbestos.

Figure 3(a) is a SEM image taken from sample A showing some chrysotile fibers (the single fibrils are visible). Figure 3(b) is a beautiful SEM image taken from sample B showing an intergrowth of grunerite fibers.

The analysis of 100 frames (20 for each of the 5 specimens) of either sample A or B revealed that all the asbestos and nonasbestos fibers are perfectly coated by the resin, yielding an homogeneous matrix where all the fibers, despite their nature, are cemented. The situation is perfectly portrayed in Figure 4(a), showing a frame taken from sample A after the interaction with the resin: the surface of the fibers is entirely coated by the resin and fibers are cemented in a sort of three-dimensional framework. Images taken from sample B outlines a similar situation [Fig. 4(b)].

Figure 2   The position of samples for the SEM observations collected from different points of the treated ceiling in the site test of the parking lot in Cergy. (a) Full representation of the treated area; (b) front section.

Samples from the pilot working site have been collected after 2 days from the application of the impregnating resin and the effectiveness of the

Figure 1   Observed (crosses), calculated (continuous line), and difference curve (bottom line) of the Rietveld refined patterns (a = sample A with C = chrysotile, B = brucite, Ca = calcite, Co = corundum; b = sample B with Gr = grunerite, Q = quartz, Ca = calcite, Co = corundum) showing a good agreement between the calculated and observed patterns.

Regarding the results of the SEM analyses of the 7 samples collected at the test site, none of the samples (20 frames for each specimen and 5 specimens for each sample) showed uncoated free fibers of asbestos while a variable amount of free
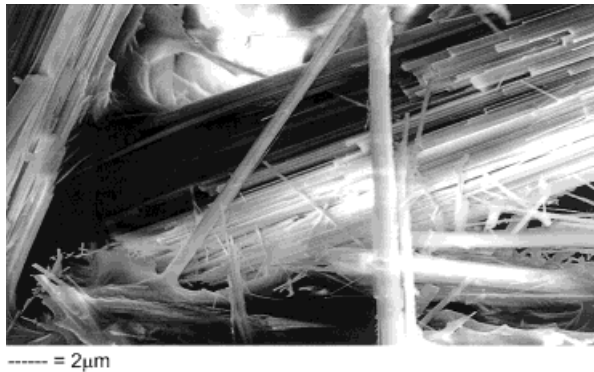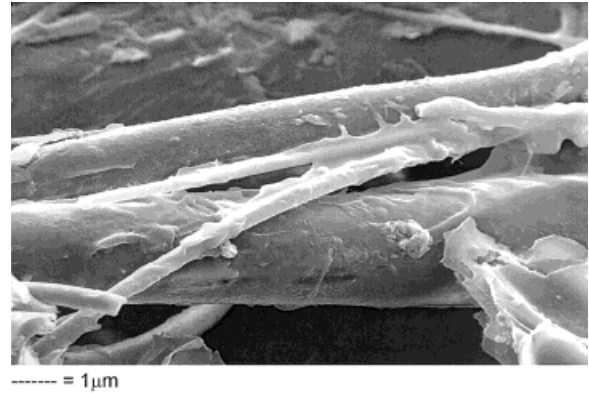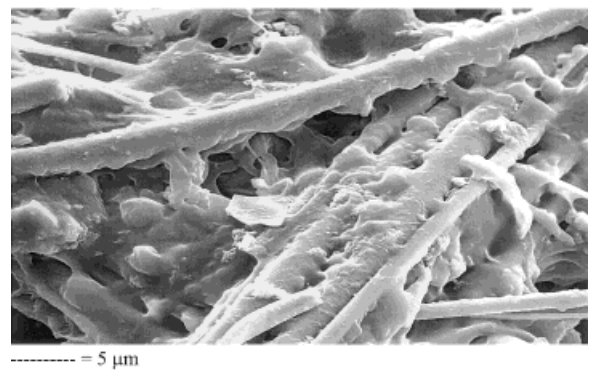

(a)
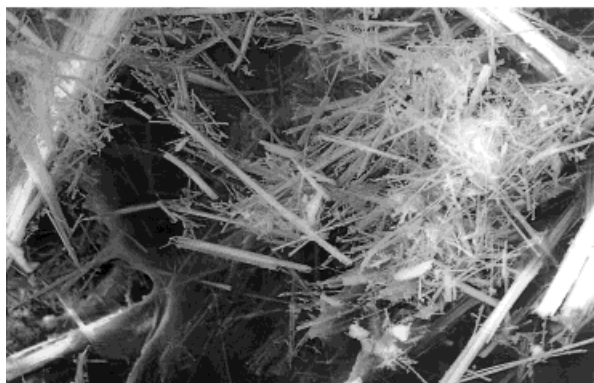
(b)

(c)

Figure 3   SEM images of the raw materials: (a) sample A, showing some chrysotile fibers (the single fibrils are visible); (b) sample B showing an intergrowth of grunerite fibers; (c) sample A, showing an intergrowth of glass fibers.

(a)

(b)

Figure 4   The materials after the treatment with the resin: (a) sample A showing the surface of the fibers entirely coated by the resin and cemented fibers forming a sort of framework; (b) sample B showing a very similar situation.

wool glass fibers was observed. Since the size of each observed fiber was glossed and the size of each frame is known ($10000 \ \mu m^2$), it is possible to calculate a percentage of glass free fibers in two dimensions. It is well known that statistical SEM observations are not effectively representative of the bulk since the volume of sampled material is dependent upon many factors. Usually corrective factors have to be applied, but in this case it is useless since glass fibers are not hazardous and the knowledge of the exact amount in the bulk would add no useful information. Table II reports the amount (wt %) of free asbestos and glass fibers per specimen. The average calculated over the 7 samples is 4.8(7) wt %. There is a clear indication that the full impregnation method is capable of coating all the asbestos fibers but incapable of achieving the same result for the glass fibers. At a first glance, we cannot rule out that

since the diameter of the glass fibers is much larger with respect to the diameter of the asbestos fibers, it is more difficult for the resin to envelop

Table II   The Calculated SEM Two-Dimensional (2D) Percentage (wt %) of Free Glass Fibers per Specimen in the 7 Samples from the Test Site in the Parking Lot in Cergy and Average[a]

	Asbestos Free Fibers (2D wt %)	Glass Free Fibers (2D wt %)
Sample 1		
Specimen 1	0	2.1
Specimen 2	0	3.5
Specimen 3	0	4.3
Specimen 4	0	5.3
Specimen 5	0	1.0
Sample 2		
Specimen 1	0	5.2
Specimen 2	0	5.2
Specimen 3	0	3.1
Specimen 4	0	2.5
Specimen 5	0	2.1
Sample 3		
Specimen 1	0	7.5
Specimen 2	0	4.6
Specimen 3	0	5.7
Specimen 4	0	7.2
Specimen 5	0	3.2
Sample 4		
Specimen 1	0	7.2
Specimen 2	0	6.0
Specimen 3	0	6.0
Specimen 4	0	4.6
Specimen 5	0	3.9
Sample 5		
Specimen 1	0	4.8
Specimen 2	0	4.2
Specimen 3	0	2.9
Specimen 4	0	7.3
Specimen 5	0	7.3
Sample 6		
Specimen 1	0	6.4
Specimen 2	0	6.1
Specimen 3	0	4.6
Specimen 4	0	5.4
Specimen 5	0	5.2
Sample 7		
Specimen 1	0	4.3
Specimen 2	0	5.2
Specimen 3	0	4.8
Specimen 4	0	3.9
Specimen 5	0	6.9
Average	0	4.8(7)

[a] The number of fibers per each specimen is the average over 20 different frames.

--- =1μm

(a)

------------ = 2 μm
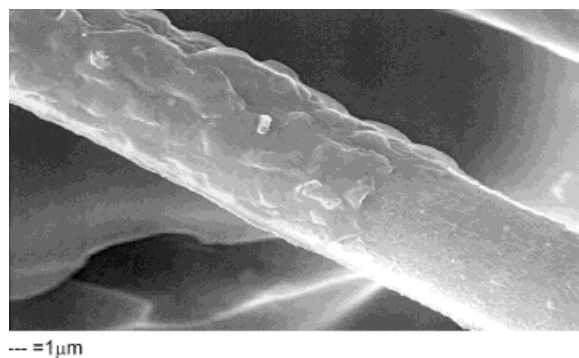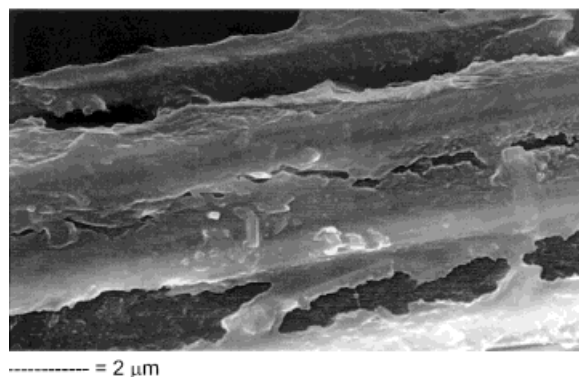
(b)

Figure 5   An example of SEM images taken from a sample collected in the test site in Cergy showing a glass fiber partially coated by the resin (a) and asbestos plus glass fibers perfectly coated by the resin (b).

homogeneously the whole fiber (i.e., the bagnability of the resin for the glass fibers is not very effective). This is clearly shown in Figure 5(a), where a glass fiber is partially coated by the resin. Figure 5(b) instead reports asbestos plus glass fibers that are perfectly coated by the resin. Notwithstanding, at a closer observation, the reason for the "selective" full impregnation of the asbestos fibers should reside in the nature itself of the surface of asbestos, which is negatively charged, and fiber has an electrical interaction with the solvent (water dispersing the resin), which tends to reside much longer on the fiber surface, allowing the resin to consolidate and coat the fiber. The same does not apply to the glass fibers (mainly silica glass,) where the surface is instead statistically neutral (albeit some local charge concentration may eventually occur) and a little interaction with the resin takes place. This difference in the resin distribution between the laboratory samples and the ones from the pilot working site

is probably due to the application condition: the resin sprayed on the ceilings experiences a non-negligible effect of gravity and fibers with low electrical interaction with the solvent–resin system tend to be less veiled.

CONCLUSIONS

This work deals with the application of a technique of full impregnation of asbestos using a specially developed epoxy resin which definitely cuts all the disadvantages of the abatement technique: the costs are low, there is no production of toxic refuses, no big risks of exposure for removal workers, moderate risk of environmental pollution during and after the operations. This research is in concert with the trend proposed for the solution of the asbestos problem by an in situ, safe and cheap techniques. It may be complementary or alternate of other new advanced techniques such as the chemical inertization by a sprayed foam that selectively attacks and decomposes asbestos [12]. It has been demonstrated that the resin perfectly works on either serpentine and amphibole asbestos which are selectively and preferentially coated in the presence of a mixture with other inorganic glass fibers. The results of a pilot working site where the full impregnation have been tested for the first time in the presence of authorities of the French Government, are promising and after the treatment no free asbestos fibers are observed and eventually released in the environment.

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