

# *In situ* ESEM study of the thermal decomposition of chrysotile asbestos in view of safe recycling of the transformation product

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## Abstract

The thermal transformation of asbestos into non-hazardous crystalline phases and their recycling is a promising solution for the “asbestos problem”. The most common asbestos-containing industrial material produced worldwide is cement-asbestos. Knowledge of the kinetics of thermal transformation of asbestos fibers in cement-asbestos is of paramount importance for the optimization of the firing process at industrial scale. Here, environmental scanning electron microscopy (ESEM) was used for the first time to follow *in situ* the thermal transformation of chrysotile fibers present in cement-asbestos. It was found that the reaction kinetics of thermal transformation of chrysotile was highly slowed down in the presence of water vapor in the experimental chamber with respect to He. This was explained by chemisorbed water on the surface of the fibers which affected the dehydroxylation reaction and consequently the recrystallization into Mg-silicates. In the attempt to investigate alternative and faster firing routes for the decomposition of asbestos, a low melting glass was mixed with cement-asbestos and studied *in situ* to assess to which extent the decomposition of asbestos is favored. It was found that the addition of a low melting glass to cement-asbestos greatly improved the decomposition reaction and decreased the transformation temperatures.

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## 1. Introduction

Due to their outstanding technological properties, asbestos minerals have been extensively used since the beginning of the last century for an endless number of industrial applications. However, since the early 1950s it is known that inhalation of asbestos fibers may cause lethal lung diseases [1,2]. Therefore, the use of asbestos is now banned and its elimination has become a priority in many countries all over the world. Generally, asbestos-containing materials (ACMs) are dumped in controlled waste plants. However, this cannot be regarded as an ultimate solution because dispersion of asbestos fibers in the air is an intrinsic risk during dumping operations and in the long term [3]. An alternative solution is thermal transformation

of ACM into non-hazardous phases which can be safely recycled in different industrial products [4–7]. In Italy, the existing laws were recently modified to include this possibility in the treatment of asbestos-containing wastes [8]. Despite the ban of asbestos in 1992 [9], a huge amount of ACM, mainly in the form of cement-asbestos on the roofs of industrial plants and civil buildings, is still present in Italy. Because of the risk of fiber dispersion in the air due to weathering-induced degradation in the outdoor environment, cement-asbestos slates shall be removed sooner or later. Since 2004, the Italian law D.M. 19/07/2004 [8] legitimates the crystal-chemical transformation of ACM through thermal, mechanical or chemical treatments and the recycle of the transformation product. The introduction of this law opened up new possibilities to ultimately solve the problem of ACM in Italy. To this aim, an industrial process was developed and patented for the direct annealing of cement-asbestos slates at a temperature of about 1200 °C for at least 16 h using a tunnel kiln [10]. The major advantage of this method is that the packages of cement-asbestos slates are treated as-received, without being opened

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and/or ground. Hence, the risk of fiber dispersion in air is minimized.

To be safely recycled, one of the requirements of the Italian law [11] is that the transformation product must be entirely asbestos-free. Recently, the temperature-induced transformation sequence of asbestos slates was studied in order to [4] (i) optimize the annealing process to obtain a recyclable material and (ii) develop a procedure for the quality control of the transformation product. It was found that the complete recrystallization process of the asbestos phases could not be ascertained only with X-ray powder diffraction (XRPD) for two reasons: (a) the phase detection limit is around 0.5–1 wt% and (b) the diffraction peaks of some high-temperature products of transformation of cement-asbestos such as ferrite overlap with those of the asbestos minerals and invalidate the application of this technique. On the other hand, investigation of a statistically representative number of specimens with electron microscopy techniques can be used to verify the complete transformation of asbestos minerals as the microstructure of the asbestos fibers before and after transformation is completely different [4].

The reaction path of cement-asbestos slates during annealing was found to be more complex than that for pure asbestos minerals [4]. This is not surprising as cement-asbestos contains Ca-rich cement phases, calcite, quartz and clay minerals in addition to asbestos minerals (mainly chrysotile and riebeckite). The thermal treatment of pure chrysotile (serpentine asbestos) in the 700–800 °C range involves dehydroxylation and subsequent recrystallization leading to the formation of Mg-rich anhydrous silicates forsterite and enstatite [12,13]. Pure riebeckite (amphibole asbestos) thermally treated at 1100 °C includes the formation of pyroxene, enstatite, hematite and cristobalite [14,15]. However, the decomposition products of these asbestos minerals combine with other phases during annealing of cement-asbestos to form clinker phases with an excess of Al, Fe and Mg, and Ca- and Mg-rich silicates such as merwinite and akermanite [4].

In previous works, the decomposition kinetics of pure asbestos minerals have been studied with *in situ* X-ray powder diffraction [15,16]. Unfortunately, this technique is not the best choice for kinetic studies of cement-asbestos because of overlapping peaks of asbestos minerals and high-temperature phases as well as low peak intensities of asbestos minerals due to their dilution in the cement matrix. An alternative technique is *in situ* SEM imaging of the sample at high temperature, as the thermal transformation of asbestos minerals can be distinguished from non-reacted material due to morphology changes [4]. In fact, sub-micron grains of newly formed crystalline phases are clearly visible at high magnification [4]. Gregori et al. used scanning electron microscopy (SEM) equipped with a heating stage to follow the thermal transformation of chrysotile, which was claimed to start at about 900 °C [17]. However, the resolution of the SEM images reported by Gregori et al. do not allow full verification of complete transformation of chrysotile to sub-micron grains of forsterite. In addition, the fiber-like transformation product was interpreted as elongated forsterite crystals [17]. This statement is erroneous as such crystal habit is prohibited by the crystal symmetry.

In the present work, *in situ* environmental scanning electron microscopy (ESEM) together with conventional high-resolution SEM imaging were used for the first time to follow the thermal transformation of chrysotile fibers in cement-asbestos. Opposed to SEM, high vacuum conditions and conductive samples are not necessary with the ESEM technique [17]. Valuable information regarding the kinetics of the transformation can be extracted, which is not possible by *in situ* XRPD. Such information is of paramount importance for the optimization of the annealing process of cement-asbestos slates.

In addition, we also investigated the possibility to accelerate the reaction kinetics of transformation of cement-asbestos by adding a low melting glass to a specimen of a cement-asbestos slate. Higher reaction kinetics would allow a cost reduce of the industrial process.

## 2. Experimental

Samples of commercial cement-asbestos slates were used for the present study. A full quantitative phase analysis of the sample using XRPD and the Rietveld method was reported in [4] and showed calcite (56.7 wt%), CHS (calcium hydrate silicates) phases and amorphous phase (21.8 wt%), serpentine asbestos clinochrysotile (13.6 wt%),  $\beta$ -larnite ( $2\text{CaO}\cdot\text{SiO}_2$ ) (6.8 wt%), quartz (0.8 wt%), hematite (0.2 wt%), and dolomite (0.1 wt%).

A FEI Quanta 200 ESEM equipped with a thermal tungsten gun, a gaseous secondary electron detector (GSED), and a 1500 °C hot stage was used for *in situ* electron imaging. A S-type thermocouple was used to monitor the temperature, and calibration was performed using the melting point of gold (1064 °C). The instrument was operating at 20 kV acceleration potential and a working distance of about 20 mm. The samples were heated with a rate of about 20 °C/min. SE images were collected at regular temperature intervals. The heating gradient and temperature interval were selected on the basis of preliminary experiments and results of previous experiments reported in [5].

During preliminary experiments aimed to optimize the instrumental conditions, it was found that the kinetics of thermal transformation of chrysotile fibers was severely affected by the type of gas atmosphere (i.e. He or water vapor) in the specimen chamber. In the presence of water vapor, the temperature of reaction was severely increased. In order to verify these preliminary observations, the following controlled experiments were performed: (1) a small fraction of cement-asbestos powder was mounted into a platinum crucible and fixed with a small drop of carbon glue to ensure heat conductivity of the sample. The crucible was mounted inside a corundum crucible holder and positioned into the resistance heater. The He pressure in the specimen chamber was maintained in the range 1.9–3.5 Torr. Images were collected at temperatures in the range 25–1150 °C; (2) a small fraction of cement-asbestos powder was mounted in a crucible as described previously. A water vapor pressure of about 2.5–3.4 Torr was maintained in the specimen chamber during the experiment. Images were collected in the temperature range 25–1300 °C.

To explore the possibility to decrease the temperature range of thermal transformation of asbestos fibers in cement-asbestos, a

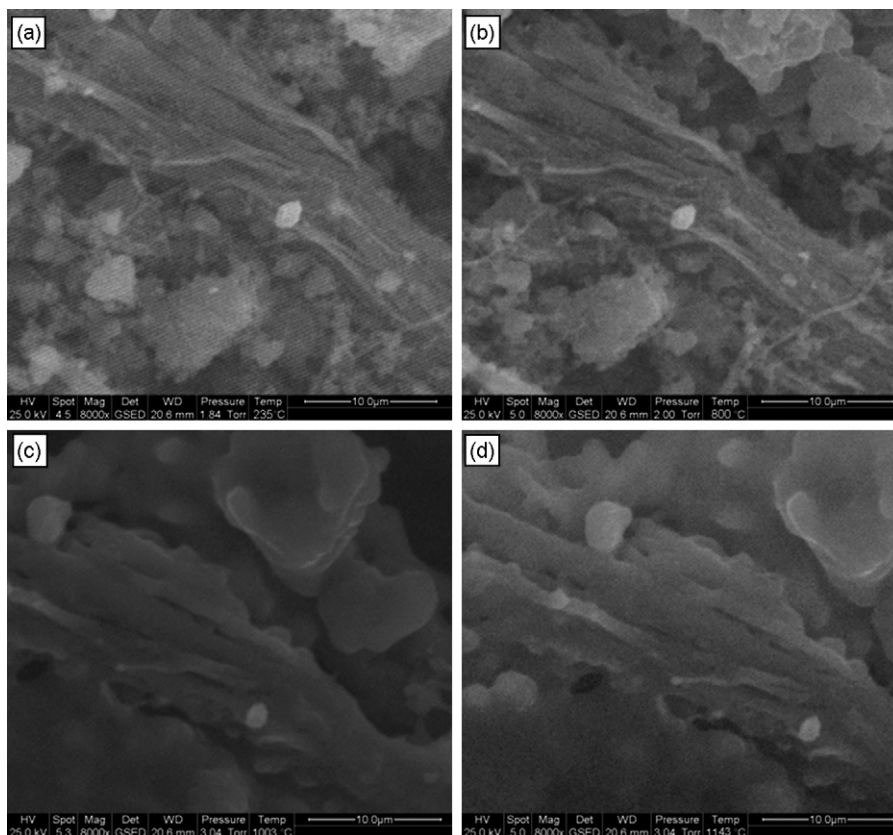


Fig. 1. SE micrographs, collected using He (1.9–3.5 Torr) as specimen chamber gas, of chrysotile fibers collected at a temperature of (a) 235 °C, (b) 800 °C, (c) 1003 °C and (d) 1143 °C.

piece of cement-asbestos was gently ground in agate mortar and mixed with a low melting glass (a ceramic frit with composition:  $B_2O_3 = 34.0\%$ ;  $Na_2O = 15.0\%$ ;  $SiO_2 = 43.0\%$ ;  $CaO = 8.0\%$ ) in the proportions cement-asbestos:glass 5:1. This experiment will from now on be referred to as experiment 3. This powder mixture was mounted in the platinum crucible in the very same way as described for the other experiments. Water vapor was used as specimen chamber gas, at a pressure of 2.5–3.6 Torr. Images were collected in the temperature range 25–850 °C.

All controlled ESEM experiments were repeated twice and gave reproducible results.

The specimens investigated with ESEM were also analyzed before and after the *in situ* experiment to evaluate the degree of reaction and achieve electron images of high resolution. High-magnification SEM micrographs were collected using a Philips XL 40/604 instrument. The specimens were mounted on aluminum stubs and gold-coated. Complementary XRPD data were also collected using a  $\theta/\theta$  diffractometer (PANalytical, Cu  $K\alpha$  radiation) equipped with a real time multiple strip (RTMS) detector. A divergence slit ( $0.25^\circ$ ), an anti-scattering slit ( $0.25^\circ$ ) and a soller slit ( $0.04$  mrad) were mounted in the incident beam pathway. A Ni filter, a soller slit ( $0.04$  mrad) and an antiscatter blade (5 mm) were mounted in the diffracted beam pathway. The counting statistics were dependent on the amount of available sample and was in the range  $15\text{--}200$  s  $\text{step}^{-1}$ . An integrated step scan of the RTMS detector of  $0.0167273^\circ$   $2\theta$  was used.

### 3. Results

Fig. 1a–d shows selected electron micrographs collected at various temperatures in the range 25–1150 °C using He as specimen chamber gas. The entire sequence recorded during this experiment as well as those recorded during the other two experiments described in the paper can be obtained upon request to

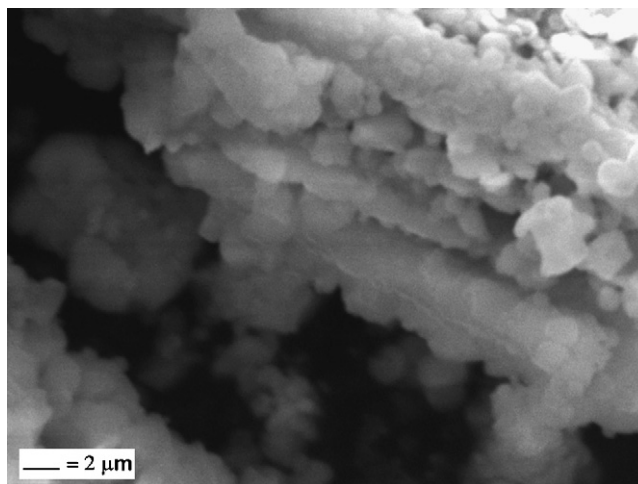


Fig. 2. High-magnification SEM image of chrysotile fibers subjected to the *in situ* ESEM experiment in which He was used as chamber gas (experiment 1).



the corresponding author as movie files with *avi* format. As can be observed, newly formed crystals on the fiber surface appear at a temperature of about 1000 °C. Crystallization continues up to 1150 °C where no further change in morphology is observed. Fig. 2 shows a high-magnification SEM image of the sample after the experiment. The typical granular morphology of the thermally transformed asbestos fibers is evident [4].

Fig. 3 shows selected SE images collected with water vapor as specimen chamber gas. In this case, complete recrystallization of chrysotile is not accomplished during the non-isothermal experiment up to 1300 °C (see Fig. 3a–d). Morphology changes due to recrystallization were however observed during prolonged heat treatment at 1000 °C, as shown in the SE images displayed in Fig. 3e and f. Obviously, the gas atmosphere in this case influ-

ences the reactivity of the fibers. After the *in situ* experiment, high-magnification micrographs of the sample were collected with a conventional SEM instrument. A representative image is shown in Fig. 4. Newly formed crystals can be observed, indicating complete transformation of the asbestos fibers [4].

Fig. 5 shows XRPD patterns collected from untreated cement-asbestos (a) and from the specimens subjected to the *in situ* ESEM experiments in He (i.e. experiment 1). The pattern collected from the specimen after the *in situ* experiment in water vapor (experiment 2) was qualitatively the same and therefore not shown. Qualitative analyses of these patterns show that the phases present in the untreated sample are clinochrysotile, calcite,  $\beta$ -larnite ( $2\text{CaO}\cdot\text{SiO}_2$ ) and minor phases such as quartz. After the *in situ* experiments the newly formed phases are

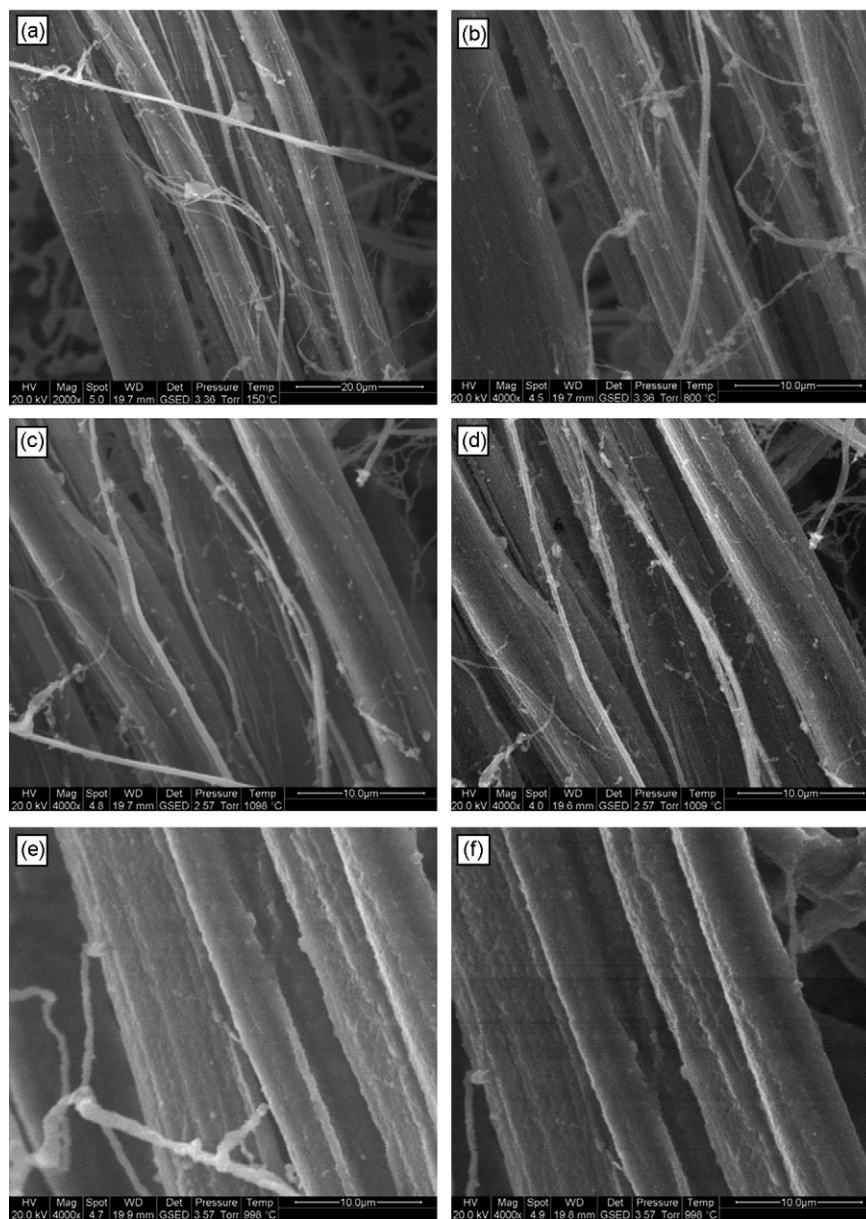


Fig. 3. SE micrographs, collected using water vapor (2.5–3.4 Torr) as specimen chamber gas (experiment 2), of chrysotile fibers collected at a temperature of (a) 200 °C, (b) 800 °C, (c) 1098 °C during the ramping up to 1300 °C and (d) 1009 °C after cooling down from 1300 to 1000 °C to reach the isothermal temperature of 1000 °C. In addition, SE micrographs collected after a 1.5 h (e) and 3 h (f) long isotherm at 1000 °C are also shown.

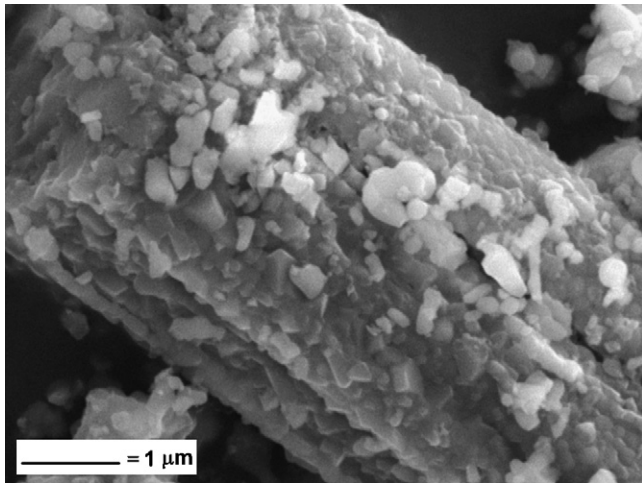


Fig. 4. High-magnification SEM image of chrysotile fibers subjected to the *in situ* ESEM experiment in which water vapor was used as chamber gas (experiment 2). The image was recorded using a conventional SEM instrument.

akermanite, merwinite, silicocarnotite and ferrite. The presence of these phases confirms that the thermal transformation has occurred during the experiments.

Fig. 6 shows SE images collected during the *in situ* experiment of the cement-asbestos mixed with a low melting glass (see Section 2 for details). Melting of the system is observed in the temperature range 600–750 °C, and the chrysotile fibers are dissolved inside the glassy phase (see Fig. 6). XRPD pat-

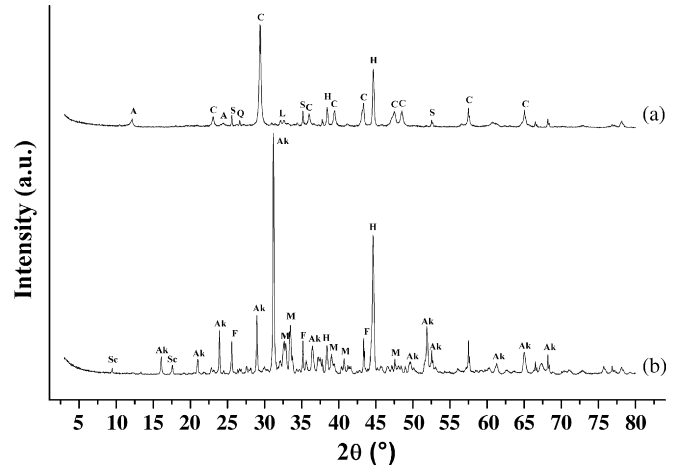


Fig. 5. XRPD patterns collected from non-treated cement-asbestos (a) and from the specimens subjected to the *in situ* ESEM experiments in He (b). Legend of pattern (a): A = chrysotile asbestos; C = calcite; H = aluminum sample holder; L =  $\beta$ -larnite ( $2\text{CaO}\cdot\text{SiO}_2$ ); S = corundum internal standard. Legend of pattern (b): Ak = akermanite; F = ferrite; H = aluminum sample holder; M = merwinite; Sc = silicocarnotite.

terns of the sample after (a) and before (b) the *in situ* ESEM experiment are shown in Fig. 7. The sample subjected to the *in situ* ESEM experiment is completely amorphous witnessing the complete dissolution of the chrysotile fibers. Thus, the asbestos fibers are not stable in contact with the B- and Si-rich forming glass and are promptly dissolved inside the glassy phase. Fig. 8

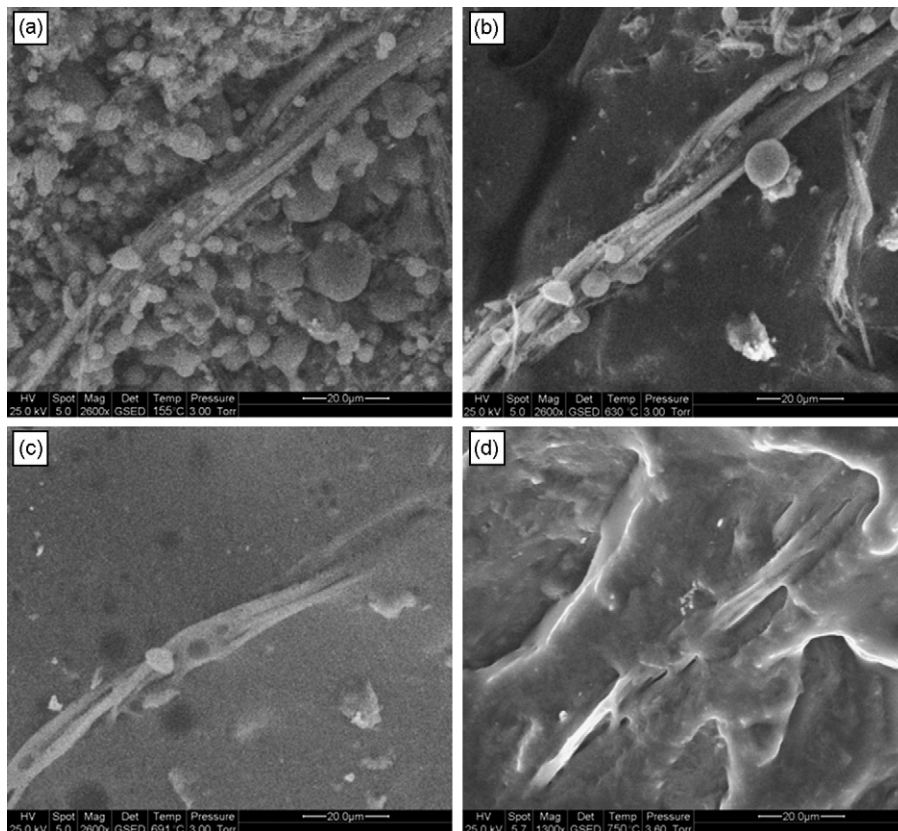


Fig. 6. SE micrographs of chrysotile fibers in the presence of low melting glass with water vapor as chamber gas (2.5–3.6 Torr), collected at a temperature of (a) 155 °C, (b) 630 °C, (c) 691 °C and (d) 750 °C (experiment 3).

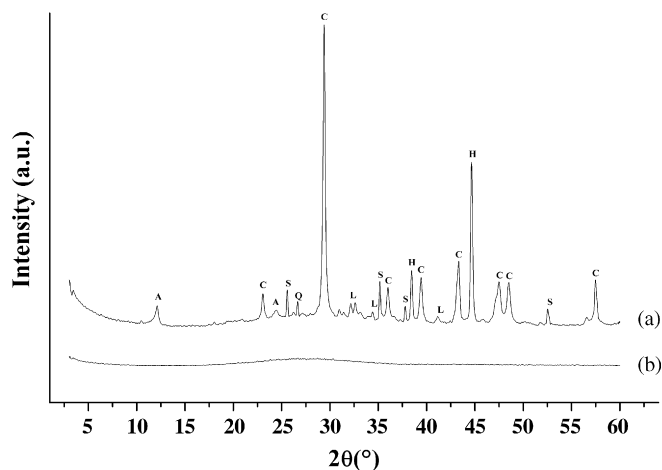
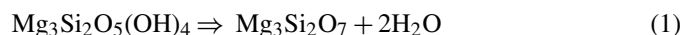


Fig. 7. XRPD patterns of cement-asbestos mixed with a low melting glass before (a) and after (b) the *in situ* ESEM experiment (experiment 3). Legend of pattern (a): A = chrysotile asbestos; C = calcite; H = aluminum sample holder; L =  $\beta$ -larnite ( $2\text{CaO}\cdot\text{SiO}_2$ ); Q = quartz; S = corundum internal standard.

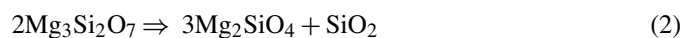
shows a high-magnification SEM image of the sample after the *in situ* experiment. As can be observed, a homogeneous phase has formed after heat treatment.

#### 4. Discussion

Pure chrysotile decomposes in the range 600–800 °C (in air) via dehydroxylation [4,11]:



The dehydroxylated product is readily converted to forsterite and enstatite:



The development of the overall reaction sequence may be followed by observing the microstructural changes of the fibers using high-magnification SE images [4]. In He atmosphere, the

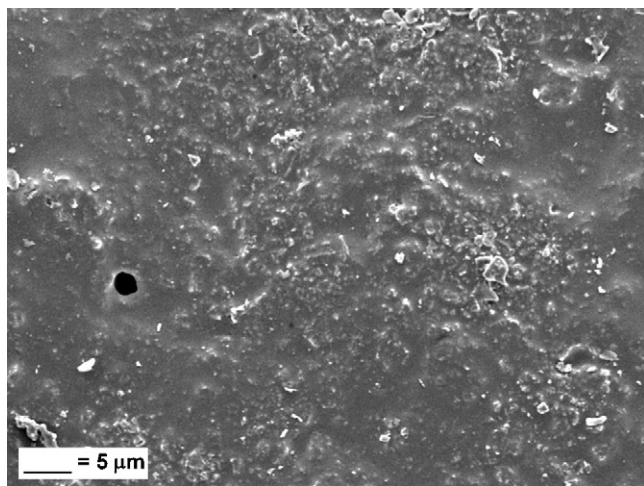


Fig. 8. High-magnification SEM image of cement-asbestos mixed with a low melting glass after *in situ* ESEM observations in the temperature range 25–850 °C (experiment 3).

temperature of reaction ( $\sim 1000$ – $1150$  °C) is in concert with the results reported by Gregori and co-workers who used *in situ* SEM to follow the thermal decomposition of pure chrysotile fibers. In contrast, results from high-temperature XRPD analyses showed that chrysotile recrystallize in the temperature range 600–800 °C [16]. The lower temperature range of reaction found by *in situ* XRPD compared to *in situ* imaging is explained both by (i) the fact that the X-ray diffraction experiments monitored the disappearance of the chrysotile diffraction peaks and not the later appearance of the diffraction peaks of the growing silicate phases; (ii) a lower detection limit in the SEM technique. In fact, resolution limitations permit visualization of the newly formed crystals only after they have reached a certain size. This is a limitation of *in situ* imaging compared to X-ray diffraction techniques for dynamic studies.

In water vapor atmosphere, the reaction kinetics were found to be remarkably slowed down with respect to He atmosphere (compare Figs. 1 and 3). In fact, recrystallization was only observed after prolonged thermal treatment at 1000 °C (Fig. 3e and f).

We believe the differences in the reaction kinetics are not due to artifacts in the experimental procedures because (i) the experiments were repeated twice and resulted to be reproducible; (ii) the sample preparation and experimental protocol were identical in all the runs; (iii) the temperature calibration was invariably performed for all the experiments by following the melting of gold. As a matter of fact, these differences in reaction kinetics of thermal transformation of chrysotile in the absence/presence of water vapor are not surprising. The kinetics of dehydroxylation reactions in other minerals such as kaolinite [18] and serpentine [19] were shown to decrease with increasing water vapor pressure at constant temperature. Brindley et al. determined the rate constant and apparent activation energy ( $E_a$ ) for the dehydroxylation of serpentine under controlled water vapor pressures in the range  $<10^{-3}$ –175 Torr [19]. It is possible to draw a parallel with this mineral because chrysotile is the fibrous variety of serpentine which in turn displays a lamellar crystal habit. They found that the rate constant  $k$  decreased from 0.0011 to 0.0008 at 1000 °C when the water vapor pressure increased from  $<10^{-3}$  to 4.6 Torr. Likewise, the apparent activation energy ( $E_a$ ) increased from 68 to 96 kcal mol $^{-1}$ . The decreased reaction rate and increased  $E_a$  with water vapor pressure were attributed to different degree of surface coverage of chemisorbed water. In fact, during the dehydroxylation reaction, water is formed as reaction product and must emigrate to the surface and desorbs (see reaction (1)). Such reactions are generally diffusion controlled. In serpentine, the  $\alpha$ -time plots under isothermal conditions were shown to fit a 3D kinetic model function which implies that the rate-limiting step is controlled by three-dimensional diffusion [19]. Hence, the entire surface of the serpentine grain is important for the overall reaction. The situation is slightly different for chrysotile, as the rate-limiting step is one-dimensional diffusion of water molecules along the fiber axis [16]. Hence, the effect of chemisorbed water should be even higher in this case, compared to serpentine.

The aim of the industrial thermal treatment processes of asbestos is to promote decomposition of asbestos and eventu-



ally the crystallization of stable and harmless reaction products. The optimization of these processes should concern the increase of yield of reaction and decrease of the reaction temperature to minimize the energy costs. In this scenario, the addition of a low melting glass, eventually in the form of a powder, to the raw asbestos-containing materials during the abatement procedures, would give the advantage to promote sintering and melting reactions involving both the cement matrix and the asbestos phases at fairly lower temperatures with respect to those needed to melt pure cement-asbestos (nearly 1300–1350 °C [5]). As a matter of fact, melting of the system and decomposition of the asbestos fibers within the reaction media are observed at very low temperature (in the range 600–750 °C; Figs. 6 and 7). The asbestos fibers are not stable in contact with the B- and Si-rich forming glass and are promptly decomposed and digested inside the glassy phase.

## 5. Conclusions

This study deals with *in situ* imaging of thermal decomposition of chrysotile fibers using ESEM. The sample under study was a specimen from a real commercial cement-asbestos. It was found that ESEM is a powerful tool for dynamic studies of overall reaction of dehydroxylation of chrysotile and the subsequent recrystallization into non-hazardous minerals. In fact, this technique provides important information regarding the reaction kinetics which may not be extracted from for example *in situ* X-ray powder diffraction due to peak overlap of chrysotile and products of transformation of the cement matrix. Such information is of great importance for optimization of industrial annealing processes for recovery of cement-asbestos slates. Furthermore, it was found that the use of water vapor as specimen chamber gas instead of He seriously affected the reaction kinetics. The temperature of reaction was increased significantly, probably due to inhibition of dehydroxylation of chrysotile. Such effects have previously been reported for dehydroxylation of other minerals. To our knowledge, this is the first time a direct evidence of the negative effect of water vapor on the dehydroxylation of chrysotile is presented.

This work also showed that the use of a low melting glass may greatly decrease the melting temperature of chrysotile. The application of such an agent on cement-asbestos slates, already in the initial stage of dismantling of cement-asbestos slates from building roofs, may increase the efficiency of industrial processes aimed for their thermal destruction.

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