

# The transformation sequence of cement–asbestos slates up to 1200 °C and safe recycling of the reaction product in stoneware tile mixtures

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Received 2 May 2007; received in revised form 6 July 2007; accepted 6 July 2007

Available online 18 July 2007

## Abstract

Cement–asbestos is the main asbestos containing material still found in most of the European countries such as Italy. Man- and weathering-induced degradation of the cement–asbestos slates makes them a source of dispersion of asbestos fibres and represents a priority cause of concern. This concern is the main prompt for the actual policy of abatement and disposal of asbestos containing materials in controlled wastes. An alternative solution to the disposal in dumping sites is the direct temperature-induced transformation of the cement–asbestos slates into non-hazardous mineral phases. This patented process avoids the stage of mechanical milling of the material before the treatment, which improves the reactivity of the materials but may be critical for the dispersion of asbestos fibres in working and life environment. For the first time, this paper reports the description of the reaction path taking place during the firing of cement–asbestos slates up to the complete transformation temperature, 1200 °C. The reaction sequence was investigated using different experimental techniques such as optical and electron microscopy, *in situ* and *ex situ* quali-quantitative X-ray powder diffraction. The understanding of the complex reaction path is of basic importance for the optimization of industrial heating processes leading to a safe recycling of the transformed product.

For the recycling of asbestos containing materials, the Italian laws require that the product of the crystal chemical transformation of asbestos containing materials must be entirely asbestos-free, and should not contain more than 0.1 wt% fraction of the carcinogenic substances such as cristobalite. Moreover, if fibrous phases other than asbestos (with length to diameter ratio >3) are found, they must have a geometrical diameter larger than 3 µm. We have demonstrated that using an interplay of different experimental techniques, it is possible to safely verify the complete transformation of asbestos minerals in this temperature-induced process.

The product of transformation of cement–asbestos (CATP) has a phase composition similar to that of a natural or a low temperature clinker with the exception of having a larger content of aluminium, iron and magnesium. This product can be safely recycled for the production of stoneware tile mixtures. The addition of 3–5 mass% of CATP does not bear significant variations to the standard parameters of white porcelain tile mixtures. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Asbestos; Thermal treatment; SEM; Rietveld method; Stoneware tile

## 1. Introduction

In Italy, law no. 248-D.M. 19/07/2004 is a road map for the management and treatment of asbestos wastes. It allows the crystal-chemical transformation of asbestos containing materials (ACM) through thermal, mechanical, or chemical treatments and the recycling of the transformation product. This law was

a prompt to ultimately solve the so called *asbestos problem* [1] in Italy because there are only a few active waste plants for the disposal of ACM on the Italian territory and such dumping sites do not assure zero risk of fibre dispersion in air and water in the short and long term. In fact, there is a widespread concern for the intrinsic risks of asbestos dispersion in air during the dumping operations and, after the disposal operation, for the physical–chemical degradation of the ACM with release of the mineral fibres and concentration in the percolating waters.

The importance of alternative ways of transforming and recycling ACM is witnessed by the number of existing research

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(laboratory and pilot) projects and patents (see for example the CORDIAM project for the production of cordierite refractories [2]; a project for the recycling in cements [3], a project for the production of glass–ceramics [4] and many others) that have been developed in Italy in the last decade but never applied to industrial scale because of the lack of regulation acts. Also within the European community, many patents and processes have been conceived (see for example, the INERTAM process [5], the Asbestex [6] process, the A.R.I. [7] process, and many others). Among these, only the INERTAM process [5] has been successfully converted into a fixed large scale industrial plant operating in Morcenx (France).

In Italy, most of the ACM is present in the form of cement–asbestos. More than 2 billion m<sup>2</sup> of cement–slates [8] mounted before the ban of asbestos in 1992 [9] are still on the roofs of Italian houses and industrial sites and, because of their degradation in the outdoor environment, will have to be removed. An alternative to disposal in waste plants regards the direct transformation of the cement–asbestos slates, avoiding the stage of mechanical milling of the material before the treatment which is a critical operation for its risks of dispersion of asbestos fibres. Unfortunately, this step is invariably incorporated in most of the other conversion processes to increase the thermal reactivity of the material and reduce the firing times. In this scenario, an industrial process was developed and patented [10] in Italy for the direct firing of cement–asbestos slates using a tunnel kiln.

A thorough analysis of the costs and a business plan of the treatment process were attempted for the Italian market. Assuming a cost of the recycled product in traditional ceramics of about €20 per tonnes, the cost of the whole process is around €100 per tonnes. This cost is highly competitive with the cost of disposal in a controlled waste dump for hazardous materials in Italy which is at the moment around €120–130 per tonnes. To be safely recycled, the Italian D.M. 12/2/97 [11] requires that the product of the crystal chemical transformation: (i) must be entirely asbestos-free; (ii) should not contain more than 0.1 mass% of carcinogenic substances such as cristobalite; (iii) may contain fibrous phases other than asbestos (with length to diameter ratio >3), if their geometrical diameter is larger than 3 μm. The content of fibrous phases with a geometrical diameter <3 μm should be less than 20% of the total fibre content. Moreover, the product should not contain fibres that, despite their diameter, exhibit a cleavage parallel to the fibre axis.

Thus, in order to securely approve the product of transformation of the cement–asbestos slates, a study devoted to understanding the thermal transformation sequence of cement–asbestos slates and a thorough characterization of the transformation product is required. This investigation is not straightforward because of the complexity of the multiphase reacting system. It should be considered that the transformation sequence of the pure asbestos minerals is totally different with respect to the transformation sequence which occurs when asbestos minerals react with the cement phases and other minerals contained in these cement–asbestos systems. In fact, in the pure asbestos minerals, the major temperature-induced transformations are dehydroxylation and recrystallization reactions [12]. The thermal treatment of pure chrysotile in the 700–800 °C range

involves dehydroxylation and subsequent recrystallization leading to the formation of Mg-rich anhydrous silicates forsterite and enstatite:  $\text{Mg}_3(\text{OH})_4\text{Si}_2\text{O}_5 \Rightarrow \text{Mg}_2\text{SiO}_4$  (forsterite) +  $\text{MgSiO}_3$  (enstatite) +  $2\text{H}_2\text{O}$ .

Similarly, the pure asbestos amphibole species tremolite undergoes dehydroxylation and subsequent recrystallization at higher temperature (900–1000 °C) to form diopside, enstatite and cristobalite:  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 \Rightarrow 2\text{CaMgSi}_2\text{O}_6$  (diopside) +  $3\text{MgSiO}_3$  (enstatite) +  $\text{SiO}_2$  (cristobalite) +  $\text{H}_2\text{O}$ .

Finally, pure riebeckite thermally treated at 1100 °C shows a more complex reaction path which includes iron oxidation [13]:  $\text{Na}_2\text{MgFe}'_2\text{Fe}''_2\text{Si}_8\text{O}_{22}(\text{OH})_2 \Rightarrow 2\text{NaFe}''\text{Si}_2\text{O}_6$  (pyroxene) +  $\text{MgSiO}_3$  (enstatite) +  $\text{Fe}_2\text{O}_3$  (hematite) +  $3\text{SiO}_2$  (cristobalite) +  $\text{H}_2\text{O}$ .

The reaction paths should be dramatically changed in the complex cement–asbestos system composed of Ca-rich cement phases, calcite, quartz, clay minerals and the asbestos minerals (mainly chrysotile and riebeckite). The understanding of the high temperature reaction sequence is of paramount importance for the optimization of the heating process to yield a safe transformed product to be recycled. To this aim, this work describes the reaction path taking place during the firing of real samples of cement–asbestos slates followed using different experimental techniques (optical microscopy, SEM, TEM, *in situ* and *ex situ* qualitative and quantitative X-ray powder diffraction). The transformation product is also fully characterized to assess whether residual asbestos fibres are found.

The last part of this work is devoted to the recycling of this safe asbestos-free product in stoneware tile mixtures and the subsequent description of the resultant materials.

## 2. Experimental procedure

### 2.1. Materials and reaction sequence of the cement–asbestos slates

Samples of commercial cement–asbestos slates were used in this study. Their standard mineralogical phase composition was verified by comparison with a number of other commercial samples and showed clinochrysotile, calcite, quartz, and minor gypsum, illite, kaolinite, and portlandite. The low content of cement phases such as portlandite or Ca-silicate hydrates is due to carbonation in air, a slow process which leads to the formation of calcite from portlandite and from the poorly hydrated crystalline phases of hydration in cement. The thermal treatments at various temperatures of commercial cement–asbestos slates (length = 122 cm, width = 57 cm, height of each single slate = 1 cm) were conducted using an industrial kiln with a maximum temperature of 1200 °C. The reconstruction of the reaction sequence was possible by the application of different experimental techniques (quali-quantitative X-ray powder diffraction, optical microscopy, electron microscopy) of samples fired at various temperatures in the range 25–1200 °C.

Mineralogical qualitative phase analysis of the samples powdered in a agate mortar was performed using a Philips PW 1730 X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation at 40 kV and 30 mA, 1/2° divergence and receiving slits, and step

scan of  $0.02^\circ 2\theta$ . Samples were collected using the side loading technique in the  $3\text{--}80^\circ 2\theta$  range.

Optical microscopy (phase contrast and light polarized) was performed in the preliminary specimen characterization using Leika microsystems.

Powdered samples were investigated with scanning electron microscopy (SEM). The specimens were mounted on Al stubs and coated with gold (10 nm thick film). Micrographs were collected using a Philips XL 40/604 instrument.

Transmission electron microscopy (TEM) experiments were performed using a Jeol JEM 2010 instrument equipped with a slow scan CCD Gatan 694 camera. Particles of the investigated material were dispersed in distilled water. Subsequently, a drop of suspension was then placed on a copper holder and carbon coated.

To cross-check the results of the *ex situ* X-ray diffraction analyses, *in situ* high temperature diffraction experiments were conducted using a Panalytical X'Pert Pro Diffractometer equipped with an Anton Paar HTK16 heating chamber and a fast RTMS detector [14,15]. Small fragments of the raw samples were placed upon the Pt strip, which serves as thermocouple, heating element, and sample holder. The calibration of the temperature was accomplished by following the thermal expansion of standard samples such as Si NIST 640c, synthetic periclase and  $\alpha$ -alumina (corundum NIST 676). X-ray diffraction patterns were collected in continuous mode, with 40 kV, 40 mA, Ni filter on the primary beam,  $1/4^\circ$  fixed divergence slits,  $0.0023^\circ$  soller slit on both the incident and secondary beam,  $1/4^\circ$  fixed anticatter slit, and fixed 5 mm RTMS slit. An integrated step scan of the RTMS detector of  $0.0167^\circ 2\theta$  was used with a counting statistics of 15 s/step. Data were collected in the temperature range  $25\text{--}1200^\circ\text{C}$ , at steps of  $100^\circ\text{C}$ .

## 2.2. Characterization of the transformation product fired at $1200^\circ\text{C}$

The product of transformation fired at  $1200^\circ\text{C}$  was characterized with mineralogical quantitative phase analysis (QPA). The analysis has been performed with the Rietveld method [16,17] using the available software GSAS [18] and its graphical interface EXPGUI [19].

Chemical analysis of the transformation product was obtained with X-ray fluorescence (XRF) using a Philips PW2480 X-ray fluorescence spectrometer.

## 2.3. Recycling of the transformation product in stoneware tile mixtures

The material was powdered and studied to see if it is suitable to be recycled in stoneware tile mixtures similarly to the protocol used in Gualtieri and Tartaglia [20]. In that paper, the cement–asbestos treated at  $1100^\circ\text{C}$  was further heated at  $1560^\circ\text{C}$  for about 1 h and quenched in water (thermal shock) to produce a glass–ceramic. The preparation of a glass–ceramic was necessary because the cement–asbestos treated at  $1100^\circ\text{C}$  contained residual CaO which prevented its direct use in the mixture slurry. In fact, it was observed that in water suspension,

Table 1

Ceramic mixtures prepared with addition of thermally transformed cement–asbestos

Raw material (mass%)	STD	1	2	3
Albite (Na-feldspar)	55	52.25	49.5	55
Quartz	15	14.25	13.5	14
Kaolinite rich clay	20	19	18	17
Plastic illite rich clay	10	9.5	9	11
CATP <sup>a</sup>	–	5	10	3
Total	100	100	100	100

<sup>a</sup> Cement–Asbestos Transformation Product.

it formed a gel which significantly increased the viscosity of the slurry. This was due to the residual CaO reacting in contact with water to form Ca-hydroxide according to the reaction  $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$ . In this study, it was possible to directly add the products of the  $1200^\circ\text{C}$  heat treatment to the ceramic mixtures because residual CaO is no longer present and rheological problems of the slurry are circumvented.

A standard mixture of porcelanised grès with 10 mass% illite rich clay, 20 mass% kaolinite rich clay, 55 mass% albite, and 15 mass% quartz sand was mixed with 5 and 10 mass% of the cement–asbestos transformation product (CATP). Moreover, another mixture with only 3 mass% of CATP substituting quartz and kaolinite was also prepared. All of the formulated mixture compositions are reported in Table 1 and were prepared by following the protocol used to simulate the production of porcelain stoneware tiles. The three mixtures were wet milled in a porcelain ball mill for 40 min with alumina balls, 50 mass% water and 0.4 mass% sodium silicate deflocculant. With this procedure, a solid residue of about 1 mass% on the 16,000 mesh/cm<sup>2</sup> (44  $\mu\text{m}$ ) sieve was obtained. The powders were homogeneously moistened up to 6 mass%, sieved and granulated. Granulated powders were uniaxially pressed to 50 MPa to form pellets of 5 mm  $\times$  5 mm. The experimental laboratory conditions (powder humidity, grain size distribution, and powder compactness) are those commonly used in the ceramic laboratories to reproduce real ceramic porcelain stoneware production parameters. The firing curve, which follows an industrial firing cycle, accomplished a maximum firing temperature of 1200, 1210, and  $1220^\circ\text{C}$  and a total firing time of 50 min. The main technological properties of the three fired mixtures were measured following the standardized laboratory methods to assess the influence of the addition of CATP. QPA were also performed on selected fired products using the Rietveld method and the addition of an internal standard following the method described in Gualtieri et al. [21] to achieve a reliable estimate of both the amorphous and crystalline fractions.

## 3. Results and discussion

### 3.1. Reaction sequence of the cement–asbestos slates

Fig. 1 reports the field of stability of the various original and newly formed crystalline phases in the cement–asbestos slate system up to the maximum firing temperature  $1200^\circ\text{C}$ , obtained

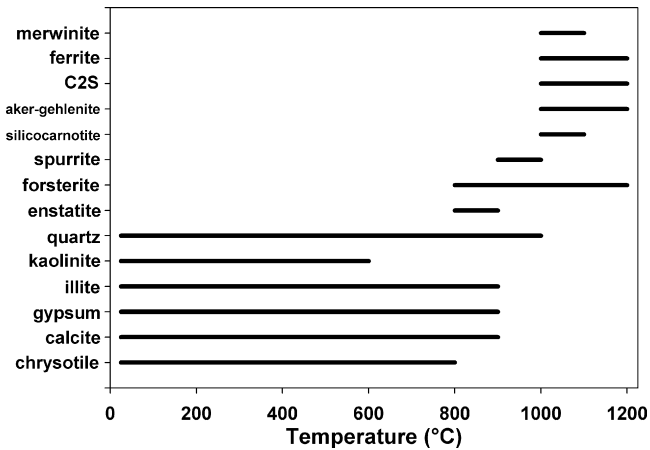


Fig. 1. The temperature stability ranges of the crystalline phases in the cement–asbestos slate system.

from the results of the *ex situ* and *in situ* diffraction experiments. The first phase to decompose is kaolinite which undergoes dehydroxylation in the range 400–600 °C according to the reaction  $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \Rightarrow \text{Al}_2\text{Si}_2\text{O}_7$  (metakaolinite) +  $2\text{H}_2\text{O}$  [22]. Al and Si are then incorporated in the pseudo-amorphous highly reactive metakaolinite phase available as a reactant for the successive high temperature crystallization reactions.

Chrysotile decomposes in the range 700–800 °C with a prompt crystallization to forsterite and enstatite. Forsterite is stable up to the maximum firing temperature whereas the small pyroxene crystals are readily decomposed to form subsequent Ca- and Mg-rich silicates such as merwinite ( $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ ) and akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ).

Calcite decomposition ( $\text{CaCO}_3 \Rightarrow \text{CaO} + \text{CO}_2$ ) [23] at about 900 °C in air is accompanied by the decomposition of minor phases such as illite and gypsum. The latter has been previously converted to anhydrite at about 350 °C. Anhydrite decomposition ( $\text{CaSO}_4 \Rightarrow \text{CaO} + \text{SO}_3$ ) releases molecular groups useful for the formation of the stable phase silicocarnotite ( $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4$ ) at high temperature which seems to persist up to about 1150 °C.

The decomposition of illite makes available Al, Mg, Si, and K for higher temperature reactions. K is likely to form a very small amount of glass phase. The large amount of CaO available after the decomposition of calcite combines with silica (quartz is then no longer stable at  $T > 1000$  °C), magnesium, and iron to form the typical clinker phases: C2S ( $2\text{CaO} \cdot \text{SiO}_2$ ) with a larnite structure; ferrite (brownmillerite,  $\text{Al}_2\text{Ca}_4\text{Fe}_2\text{O}_{10}$ ) and merwinite. Only the latter is not stable up to the maximum firing temperature (1200 °C). Hence, the product of transformation exhibits a phase composition similar to that of a natural or a low temperature clinker [24] with an excess of aluminium, iron, and magnesium.

Keeping in mind that the final goal of the process is the transformation of the asbestos minerals, the knowledge of the reaction sequence is very useful to determine the temperature reached by thermal treatment. Although reaction kinetics should not be neglected, the phases present in the system is indicative of the maximum temperature reached by the treatment. For example,

the presence of residual calcite may indicate that the highest temperature reached by the system is about 900 °C, possibly not high enough to reach full recrystallization of the asbestos minerals (especially the amphibole species crocidolite and amosite, the most hazardous asbestos species, which may be present in Italian cement–asbestos products in minor amounts ranging from 0 to 3 mass%). The remarkable presence of high temperature stable phase such as ferrite and C2S is a reliable marker that the thermal treatment has reached temperatures above 1000–1100 °C with a subsequent transformation of the asbestos minerals.

The verification of the complete recrystallization process of the asbestos phases using only X-ray powder diffraction leaves uncertainties both because the phase detection limit is around 0.5–1 mass% and because diffraction peaks of the high temperature phases may overlap with those of the asbestos phases and invalidate the application of this technique. The most prominent case regards brownmillerite (the cement phase ferrite [24]). One of its major peaks (020) occurs at about 7.2 Å and perfectly overlaps with the major peak (001) of chrysotile (invariably the only reflection present in the powder pattern when chrysotile content is less than 5 mass%). Fig. 2 shows a selected range of the powder pattern of a sample of cement–asbestos slate fired at 1200 °C with the presence of the brownmillerite peak at ca. 7.2 Å (ca. 12.2° 2θ). In this case, it is impossible to ascertain the presence of residual chrysotile.

Because powder diffraction alone is not effective, we have seen that the only experimental technique capable of safely verifying the complete transformation of asbestos minerals is electron microscopy (SEM or TEM). In fact, high magnification imaging can reveal the very nature of the microstructure of the thermally treated fibres. The fibres which underwent a full transformation exhibit a totally different microstructure with respect to the original ones (Fig. 3a) with an evident intergrowth of newly formed crystals in place of the original fibres (Fig. 3b). At low magnification the microstructure of a thermally treated fibre is not revealed and doubts may arise on the effectiveness of the thermal treatment. At higher magnification the typical microstructure of the transformed fibres becomes clear. The high magnification SEM analysis reveals differences of the cleavage of the fibres. The raw chrysotile bundle inside the cement–asbestos matrix displays a cleavage parallel to the fibre

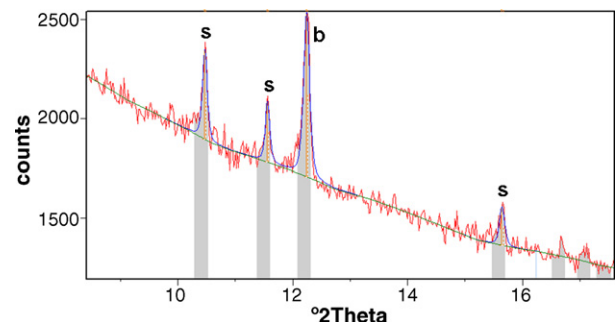


Fig. 2. Low angle region of an X-ray powder pattern of cement–asbestos fired at 1200 °C showing Bragg peaks of brownmillerite (b) and silicocarnotite (s). The major peak (020) of brownmillerite at about 7.2 Å may eventually overlap with the major peak (001) of chrysotile.



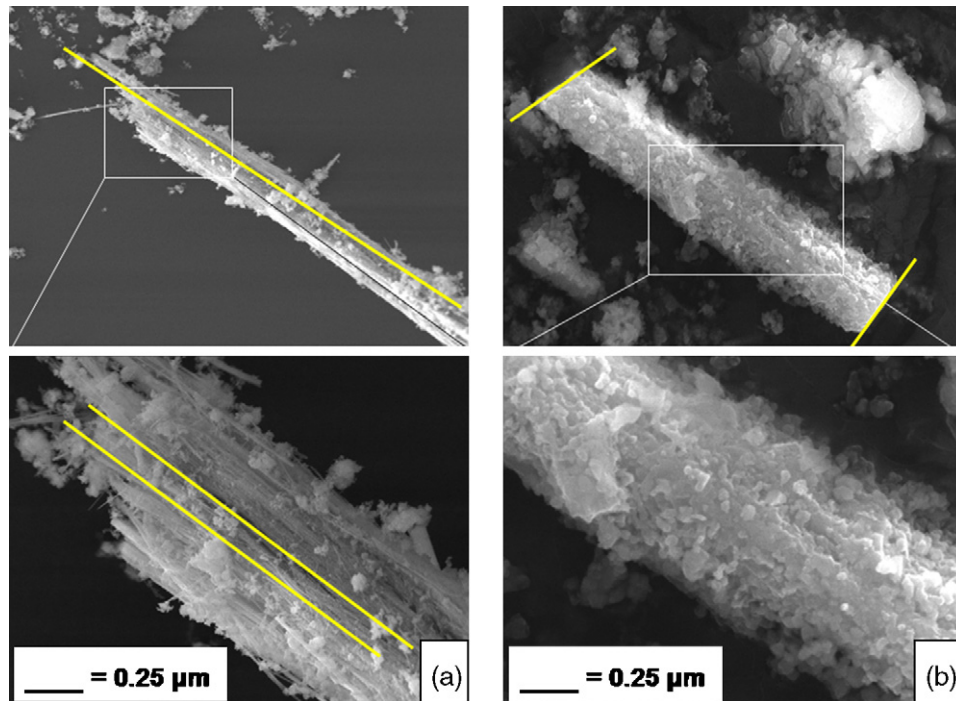


Fig. 3. The importance of high magnification in the SEM analysis of the transformation products of cement–asbestos: (a) untreated (raw) chrysotile bundle inside the cement–asbestos matrix showing single fibrils and small crystals of cement phases. The cleavage of the bundle is clearly parallel to the fibre axis; (b) the original chrysotile bundles inside the cement–asbestos matrix thermally treated at 1200 °C show that the single fibrils no longer exist and a complete pseudo-morphic recrystallization of the fibres has occurred. The cleavage of the original bundle is now perpendicular to the fibre axis.

axis (Fig. 3a) whereas the 1200 °C treated recrystallized bundles display a cleavage perpendicular to the fibre axis (Fig. 3b). Fig. 4 shows TEM images of the thermally treated chrysotile asbestos fibres which display a totally different microstructure with respect to the original chrysotile bundles. The raw bundles of chrysotile fibrils with cleavage parallel to the fibre axis are fully transformed through thermal treatment into an intergrowth of sub-spherical newly formed silicate crystals. We also discovered that TEM imaging can effectively and quickly reveal untransformed fibres. In fact, such fibres exhibit a quick *in situ* transformation with evident bloating under the electron

beam because of the release of water during dehydroxylation [25].

### 3.2. The transformation product to be recycled

The transformation product obtained at 1200 °C whose chemical and phase composition are reported in Table 2, can be safely recycled according to the Italian D.M. 12/2/97 because the SEM/TEM analysis of a statistically representative number of specimens showed that (i) it is entirely asbestos-free. The final ground product to be recycled is composed of sub-spherical

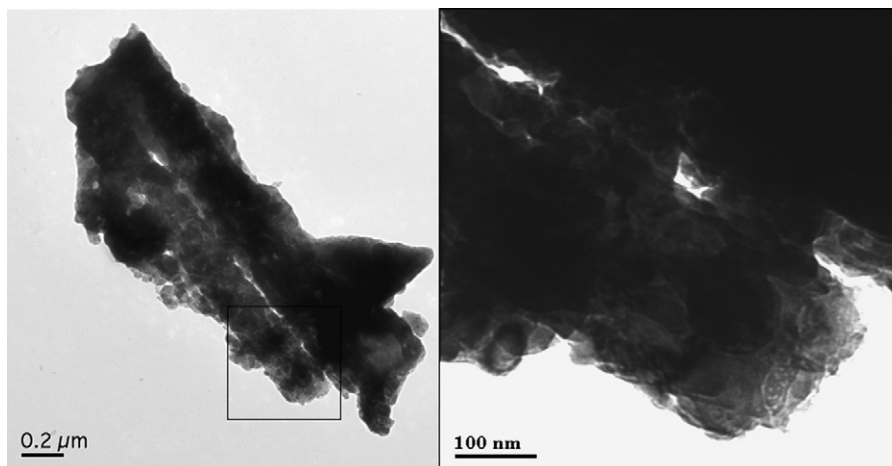


Fig. 4. A TEM image of a thermally treated chrysotile bundle, showing complete recrystallization of the fibres into newly formed silicates with a totally different microstructure originally composed of bundles of fibrils and now just an intergrowth of sub-spherical newly formed crystals.

Table 2  
Chemical and phase composition of the thermally transformed product to be recycled

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	L.O.I. <sup>a</sup>
37.1	6.25	4.24	0.27	41.5	8.44	0.58	0.38	0.61	0.45
Phase						Mass% <sup>b</sup>			
Ferrite						1.0 (1)			
Larnite						11.0 (5)			
Akermanite						46.1 (2)			
Merwinite						13.7 (3)			
Amorphous phase						28.3 (1.1)			

<sup>a</sup> Likely due to humidity water + adsorbed CO<sub>2</sub> (carbonation in air).

<sup>b</sup> Obtained with the Rietveld method. The agreement factors [18] are:  $R_{wp} = 20.4\%$ ;  $R_p = 15.9\%$ ;  $\chi^2 = 13.9$ .

particles of the newly formed crystalline phases (see the SEM image and relative EDS analysis of the grains in Fig. 5); (ii) the quantitative phase analysis reported in Table 2 shows that, within the limits of XRPD, the product does not contain residual nor newly formed carcinogenic substances such as cristobalite; (iii) the product does not contain phases with fibrous habit nor fibres that, despite their diameter, exhibit cleavage parallel to the fibre axis. The apparently residual fibres are composed of an intergrowth of crystals (pseudo-morphosis) of the newly formed silicates (Fig. 6). Hence, the eventual fracture of the transformed pseudo-morphic fibres occurs at the grain boundaries and not along the fibre axis.

It should be remarked here that Phase Contrast Optical microscopy, because of the low resolution, has a limited use in this case because of the intrinsic difficulties of ascertaining whether a fibre is transformed or not. On the other hand, polarized light optical microscopy may be used because of its capability to verify changes in the optical properties (such as pleochroism, extinction, and dispersion) of the transformed fibres with respect to the properties of the original ones.

### 3.3. Recycling of the transformation product in stoneware tile mixtures

Table 3 shows the results of the technological tests of the ceramic body mixtures (see Table 1) fired at various temperatures. In general, with respect to the standard mixtures, additions of CATP render the mixture more refractory with a shift of the

melting temperature of the system to higher values. This is due to the crystallization of anorthite in the mixtures diluted with CATP with respect to the standard mixture (see Table 4). CATP mainly composed of Ca and Si prompts the crystallization of anorthite at the expense of glass and mullite. The crystallization of the latter is clearly inhibited because aluminium and silicon are incorporated in the anorthite structure and chemically balance the oversaturation of calcium. The two competing reaction paths of crystallization which can be easily drawn from the ternary system SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–CaO [26] and are promoted at  $T > 950\text{--}1000\text{ }^\circ\text{C}$  are:

- With no calcium in the system: Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (metakaolinite from the decomposition of kaolinite) ⇒ Al<sub>2</sub>SiO<sub>5</sub> (mullite) + SiO<sub>2</sub> (amorphous silica and later cristobalite).
- With calcium in the system: Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (metakaolinite from the decomposition of kaolinite) + CaO ⇒ CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> (anorthite).

Even quartz is partly dissolved in the fired mixtures with CATP. Consequently, the mixtures with 5 and 10 mass% addition of CATP fired at 1200 and 1210 °C display a higher water absorption, a smaller linear shrinkage, and a lower density with respect to the standard mixture. At 1220 °C the properties are nearly equivalent especially for the mixture with 5 mass% CATP. The fired mixtures with only 3 mass% CATP display values of water absorption, linear shrinkage, and density similar to those of the standard mixture. The resistance to staining is unacceptable for

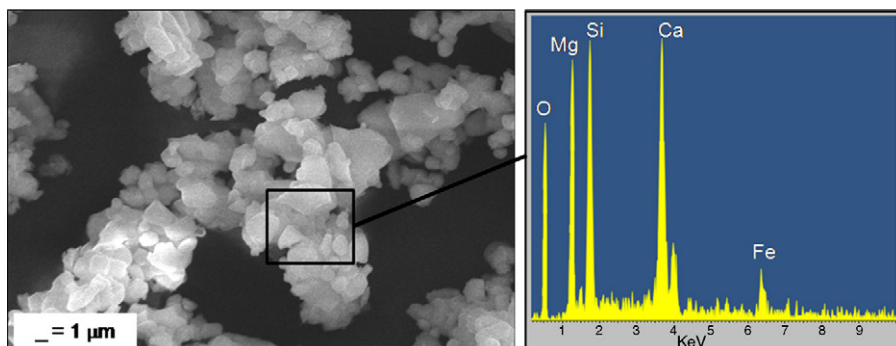


Fig. 5. SEM image and EDS point analysis of the ground ready to be recycled thermally treated cement–asbestos showing a complete recrystallization of the fibres into silicates with a sub-spherical crystal habit.

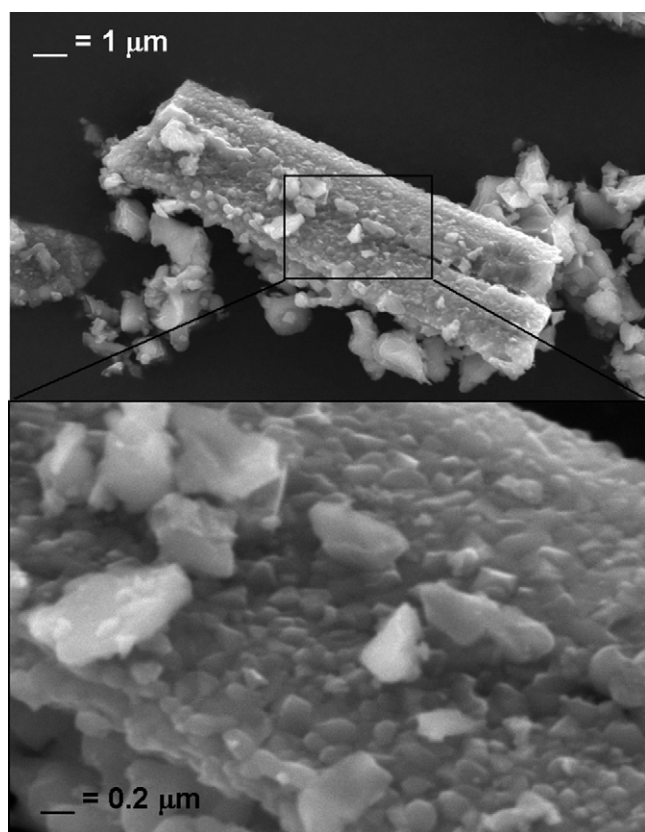


Fig. 6. A high magnification SEM image of the 1200 °C thermally treated asbestos fibres showing a complete recrystallization (pseudo-morphosis) and the loss of the original cleavage along the fibre axis.

the mixtures with 5 and 10 mass% addition of CATP fired at 1200 and 1210 °C whereas it is fairly good for all the mixtures fired at 1220 °C and for mixture 3. Despite the firing temperature, the colour parameters, and especially the  $L$  parameter which indicates the degree of whiteness of the body, are invariably worse in the mixtures with CATP with respect to the standard mixture because of the presence of iron in the CATP raw material (see Table 2). Notwithstanding, the parameters determined for mixture 3 and partly for mixture 1 fired at lower temperature are acceptable for the standard body mixtures for the production of white porcelain tiles indicating the maximum amount of CATP eventually admitted in the mixture must be around 3–5 mass%. The outcome of this study is in concert with the results reported in Leonelli et al. [27]. In that work, the authors proposed a method for the transformation of asbestos containing materials by microwave thermal treatment and found that additions up to 5 mass% of ACW does not show significant variation to the standard parameters of water absorption and linear shrinkage of porous single firing and porcelain stoneware bodies. The results are also in agreement with those described in Gualtieri and Tartaglia [20] who showed that the tiles with 5 mass% of the glass ceramic obtained from the thermally treated asbestos material show better technological properties with respect to the standard sample. The resistance to staining is clearly improved as the water absorption is lower and the apparent density is higher.

Table 3

Results of the technological tests of the fired ceramic mixtures prepared with addition of thermally transformed cement–asbestos

Technological property	STD	1	2	3
Water absorption (%) (EN ISO 10545-3)				
1200 °C	0.0	1.2	1.4	0.26
1210 °C	0.0	0.9	0.6	0.0
1220 °C	0.0	0.0	0.0	0.0
Linear shrinkage (%) (EN 98)				
1200 °C	8.6	4.6	3.2	9.0
1210 °C	8.4	6.2	5.4	8.8
1220 °C	8.2	7.0	5.2	8.6
Density (g/cm <sup>3</sup> ) (EN ISO 10545-3)				
1200 °C	2.33	2.10	2.04	2.29
1210 °C	2.34	2.19	2.13	2.30
1220 °C	2.34	2.22	2.14	2.32
Resistance to staining <sup>a</sup> (EN 122)				
1200 °C	8	3	5	8
1210 °C	9	4	6	9
1220 °C	10	9	9	10
Cielab colour parameter $L$				
1200 °C	89.7	87.6	84.0	86.6
1210 °C	88.5	85.6	79.9	84.3
1220 °C	87.0	82.1	79.3	85.4
Cielab colour parameter $a$				
1200 °C	1.6	5.8	6.0	1.9
1210 °C	1.3	5.3	5.8	1.7
1220 °C	1.2	4.1	5.1	1.7
Cielab colour parameter $b$				
1200 °C	−1.6	3.0	4.7	−1.8
1210 °C	−4.1	1.4	0.1	−2.0
1220 °C	−4.5	3.7	1.5	−2.5

<sup>a</sup> 0–10 scale with 0=totally unresistant to staining, 10=totally resistant to staining.

Table 4

Results of the quantitative phase analysis of selected fired ceramic mixtures (see text for details)

Phase mass% <sup>a</sup>	STD (1220 °C)	2 (1220 °C)	3 (1220 °C)
Quartz	17.1 (2)	8.3 (2)	12.7 (2)
Plagioclase	1.7 (2)	24.8 (3) <sup>b</sup>	9.7 (6) <sup>b</sup>
Mullite	6.3 (3)	–	5.1 (7)
Amorphous (glass)	74.9 (7)	66.9 (5)	72.5 (1.5)

<sup>a</sup> Obtained with the Rietveld method. The agreement factors [18] for the three refinements are:  $R_{wp}$  = 11.5–13.7%;  $R_p$  = 9.5–10.1%;  $\chi^2$  = 7.5–8.6.

<sup>b</sup> Anorthite structure was used for the refinement.

#### 4. Conclusions

This study deals with the description of the reaction path taking place during the firing of cement–asbestos slates up to the complete transformation temperature of 1200 °C. The reaction sequence has been investigated using optical and electron microscopy, *in situ* and *ex situ* quali-quantitative X-ray powder diffraction. Because Italian laws require that the yield of transformation of asbestos minerals due to thermal treatment should be complete, that is, no residual asbestos fibres should be present in the treated material, the analytical protocol used for the assess-

ment of the yield of transformation must take advantage of a combination of different analytical techniques, principally X-ray diffraction and electron microscopy (SEM at high magnification or TEM). It was demonstrated that X-ray powder diffraction requires further confirmation with complementary microscopic techniques.

The phases produced by heating cement–asbestos (CATP) at 1200 °C are similar to those of a natural or a low temperature clinker with an excess of aluminium, iron and magnesium elements, and absolutely no residual asbestos. We have demonstrated that the product can thus be safely and successfully recycled for the production of stoneware tile mixtures. The addition of 3–5 mass% of CATP does not yield significant variations to the standard production parameters of white porcelain tile mixtures [28].

### Acknowledgments

Thanks are due to the technical staff of the C.I.G.S. Laboratory (The University of Modena and R.E.) with a special instance to M. Tonelli, C. Rossi and M. Zapparoli for their help during the SEM and TEM experimental sessions. Thanks to A. Rossi for the use of the optical microscopes and M. Borlototti for his help with the technological tests. Two anonymous referees are greatly acknowledged for their careful revision of the manuscript. The Editor M. Fingas is also acknowledged for handling this manuscript and for his help and collaboration.

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