



Treatment and recycling of asbestos-cement containing waste

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ARTICLE INFO

Article history:

Received 27 April 2011

Received in revised form 1 August 2011

Accepted 19 August 2011

Available online 26 August 2011

Keywords:

Asbestos waste

Milling

Inertization

Recycling

Mortars

ABSTRACT

The remediation of industrial buildings covered with asbestos-cement roofs is one of the most important issues in asbestos risk management. The relevant Italian Directives call for the above waste to be treated prior to disposal on landfill. Processes able to eliminate the hazard of these wastes are very attractive because the treated products can be recycled as mineral components in building materials. In this work, asbestos-cement waste is milled by means of a high energy ring mill for up to 4 h. The very fine powders obtained at all milling times are characterized to check the mineralogical and morphological transformation of the asbestos phases. Specifically, after 120 min of milling, the disappearance of the chrysotile OH stretching modes at 3690 cm^{-1} , of the main crystalline chrysotile peaks and of the fibrous phase are detected by means of infrared spectroscopy and X-ray diffraction and scanning electron microscopy analyses, respectively. The hydraulic behavior of the milled powders in presence of lime is also tested at different times. The results of thermal analyses show that the endothermic effects associated to the neo-formed binding phases significantly increase with curing time. Furthermore, the technological efficacy of the recycling process is evaluated by preparing and testing hydraulic lime and milled powder-based mortars. The complete test set gives good results in terms of the hydration kinetics and mechanical properties of the building materials studied. In fact, values of reacted lime around 40% and values of compressive strength in the range of 2.17 and 2.29 MPa, are measured.

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1. Introduction

Asbestos-cement was extensively produced in Italy between 1904 and 1985, with the result that a huge quantity of such materials have been used all over the country and, according to the latest estimates, very large quantities of these are still on site [1,2].

Recent Italian directives (Environment Ministry Decrees 13 March 2003 and 3 August 2005) classify all asbestos-containing waste (ACW) as hazardous in line with the European Waste Catalogue code 170605* and requires its treatment prior to disposal in controlled landfills [3,4].

The Italian Environment Ministry Decree n. 248/2004 lays down guidelines for the treatment, disposal and recycling of ACW and recommends that preference be given to those stabilization and inertization processes that favour recycling in order to reduce ACW-related hazards [5–8]. In particular, high energy milling (HEM) is mentioned as being able to ensure waste amorphisation through the mineralogical and morphological transformation of asbestos phases [9].

HEM is a mechanical process that brings about the deformation, fracture and local welding of particles caused by high-energy collisions between grinding media (rings, rollers, balls hammers, etc.) and the asbestos-containing powders. The mechanical transfer of high energy to the powders may determine the destruction of the crystalline lattice as well as a major increase in specific surface area [10,11].

HEM was originally developed in the mining industry in order to obtain fine powders but it has also been used for mechanical alloying, for instance in the scale production of copper and bronze flakes [12]. Recently, HEM has been applied to the treatment of organic pollutants, such as the destruction of DDT in presence of calcium oxide [13], the dehalogenation of chlorobenzenes over calcium hydride [14,15], the detoxification of PCB-polluted soils mixed with NaH and NaBH₄ [16] and the destruction of n-C₁₆H₃₄ in model systems containing alumina and silica [17]. Finally, following studies on the amorphisation of aluminosilicate during the micronization process [18], the HEM process has been applied to the treatment of pure asbestos minerals and ACW [19].

The results of spectrophotometric and diffractometric analyses have reported a complete transformation of the chemical and crystalline structure of asbestos. The chemical composition of asbestos-free and partially amorphous powders makes them suitable for use in numerous civil engineering applications and, indeed,

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Table 1
Chemical composition of asbestos containing powders, wt.%.

Oxides	Without treatment	MP30	MP120	MP240
SiO ₂	18.76	18.64	18.95	18.60
Al ₂ O ₃	4.75	4.83	4.91	4.82
Fe ₂ O ₃	1.46	1.45	1.47	1.45
CaO	23.98	23.59	24.00	23.55
Na ₂ O	0.57	0.60	0.61	0.60
K ₂ O	1.62	1.59	1.61	1.58
MgO	2.63	2.59	2.64	2.59
MnO	0.50	0.53	0.54	0.53
SO ₃	20.56	19.67	20.00	19.63
Loss of ignition	29.11	28.72	29.21	28.67

Table 2
Composition of hydratory mixtures.

Milled powders	Mixtures		
	Milled powder/calcium hydroxide weight ratio		
	50/50	60/40	70/30
MP30	A30	B30	C30
MP120	A120	B120	C120
MP240	A240	B240	C240

Table 3
Mixture proportion of mortars, g.

Mortars	Lime	MP120	Sand	NP	H ₂ O
RM	120	–	1200	180	150
50 M	150	150	1200	–	150
60 M	120	180	1200	–	150
70 M	90	210	1200	–	150

it is well known that huge amounts of aluminosilicate amorphous powders can be recycled as a pozzolanic addition in the production of cement and mortars. Furthermore, the very high fineness of these powders means that they can be used as a fine artificial aggregate in the preparation of special mortars and concrete [20].

This work reports the results of HEM treatment of ACW and the recycling of the asbestos-free powders obtained. The pozzolanic activity of the powders is tested through the hydration of different binding mixtures containing commercial lime and 30%, 40% and 50% of milled material. Chemically bonded water, reacted lime and

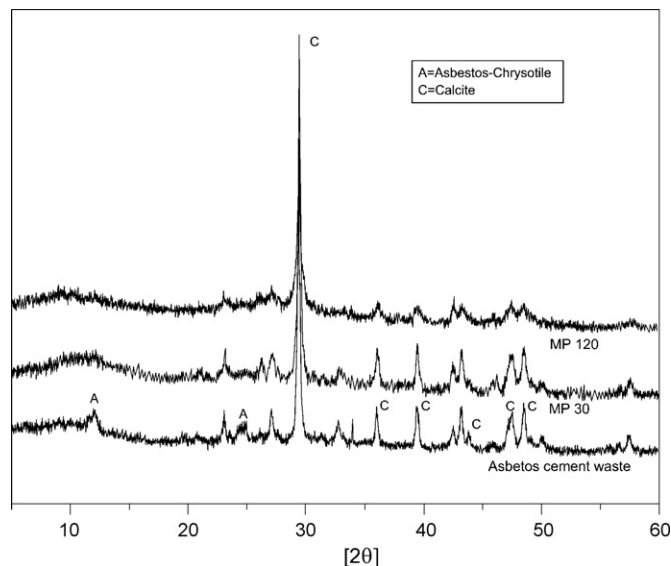


Fig. 2. XRD spectrograms of asbestos-cement waste as received and after 120 and 240 min milling.

the nature of hydration products are determined. Finally, hydraulic mortars, containing 4 h milled powders, are cast, cured and tested to evaluate their mechanical properties.

2. Experimentals

2.1. ACW handling and milling treatment

The ACW, partially wet as it had been treated prior to removal from the roof of the industrial building, was received sealed in double polyethylene bags (2 mm thick), according to the Italian Environment Ministry Decree 6 September 1994 and related acts. Each bag was opened inside a laminar flow hood to prevent any fibre dispersion into the laboratory. Some of the ACW, measuring about 10 cm in size, was dry crushed to a millimetric size in an agate mortar inside the hood. Crushed samples were carefully transferred to the ball mill enclosed in a vial.

During all the above operations, the air was monitored by filtration through cellulose filters and subsequent fibre counting by means of scanning electron microscopy (SEM) analysis, according to the Italian Environment Ministry Decree 6 September 1994. The measured fibre concentration never exceeded the units per litre threshold limit. The technicians in charge of these operations wore protective disposable full-body overalls and prescribed facial masks.

The ACW, containing about 12% in weight of asbestos chrysotile, was milled using a FRITSCH Pulverisette 9 ring-mill, with a total ring mass of 3637 g, 350 cm³ volumetric capacity and 750 rpm ring rotation speed. Weighted amounts of waste were milled for 30, 120 and 240 min using a rings/material weight ratio of 60/1. After each treatment the obtained fine powders were analyzed by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction analysis (XRD). Nitrogen-BET analysis was also employed to evaluate the specific surface area of the powders.

The chemical composition of the asbestos containing powders was determined by means of inductively coupled plasma (ICP) spectrophotometry analysis. The results relating to before milling powders (BMP) and after 30 (MP30), 120 (MP120) and 240 (MP240) min of treatment are reported in Table 1. It can be seen that the amounts of each component are very similar before and after the different milling times.

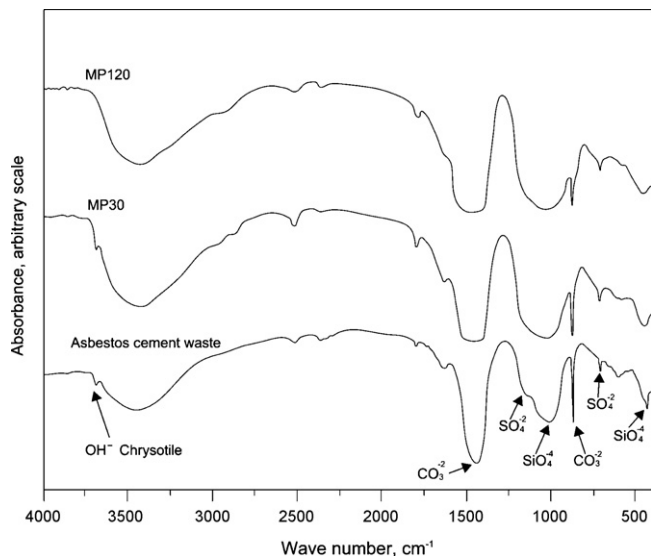


Fig. 1. FT-IR spectrograms of asbestos-cement waste as received and after 30 and 120 min milling.

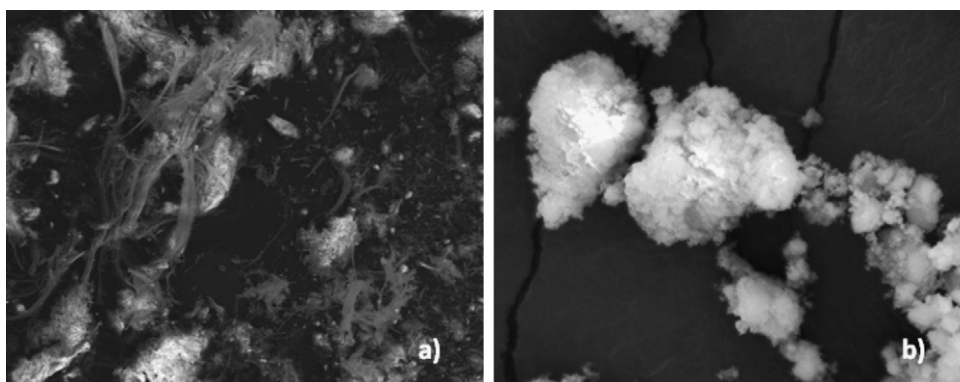


Fig. 3. SEM micrographs of ACW, before (a) and after (b) 120 min of milling treatment at 2500× magnification.

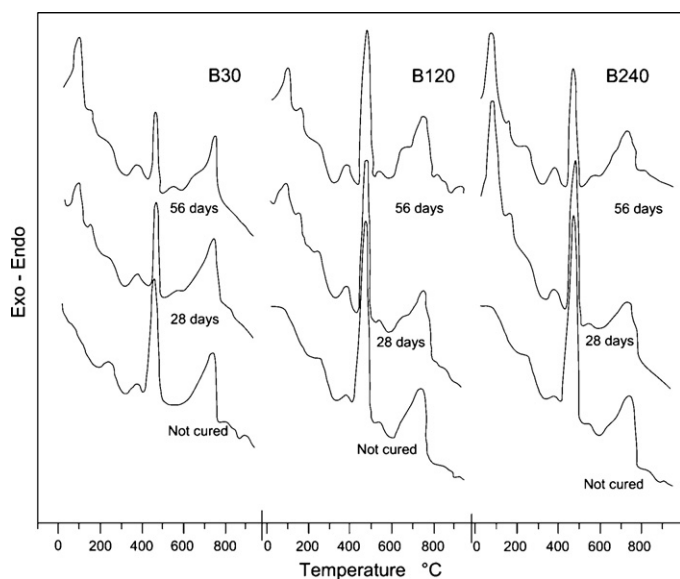


Fig. 4. DTA thermograms of the mixtures B30, B120 and B240.

The very high content of SO_3 may be due to weathering, as the roof was exposed to the attack of SO_2 emissions present in the industrial area of Naples, but the increased SO_3 content may also be attributable to prolonged acid rain attack.

2.2. Hydration behavior

The milled materials were also characterized in terms of their hydraulic behavior in presence of hydrated lime. To this end, hydra-

Table 4
Chemically bonded water and reacted lime of the systems A, B and C at different curing time.

Systems	Chemically bonded water (wt.%)				Reacted lime (wt.%)			
	Hydration time (days)				Hydration time (days)			
	7	14	28	56	7	14	28	56
A1	3.1	6.2	11.5	11.8	5.8	11.5	20.8	21.7
B1	8.0	7.2	7.0	9.7	18.5	23.8	27.1	30.2
C1	11.7	12.1	13.6	22.6	24.1	28.0	29.1	35.3
A2	8.1	7.0	4.8	3.5	14.5	16.7	27.7	29.1
B2	3.1	3.2	4.6	7.1	13.4	13.6	15.3	18.8
C2	8.1	9.3	10.7	14.8	26.4	31.3	39.3	41.3
A3	4.1	9.3	12.3	18.7	18.7	30.1	36.7	41.5
B3	9.1	11.5	16.4	24.4	18.9	31.3	38.4	42.1
C3	9.5	8.8	12.0	6.3	17.5	23.8	32.0	41.1

tory mixtures containing different amounts of milled powder and lime were prepared and tested. The compositions of all systems studied are reported in Table 2.

The hydration process was carried out with a water to solid ratio equal to 0.5 at a temperature of 25 °C and relative humidity of 100% for curing times of 7, 14, 28 and 56 days. Cylindrical specimens, 2 cm in diameter and 3 cm in height, were prepared for each experimental condition. After each curing time, specimen hydration was stopped by grinding under acetone and then the powders were dried with diethyl ether. The hydration kinetic was evaluated by means of quantitative determinations of chemically bonded water (CBW) and reacted lime. The former was measured by loss of ignition at 750 °C, while the latter by extraction and titration of residual free lime, according to the Franke method [21].

The quantitative determination of CBW content was performed as follows. A sample of mass W_0 at time 0 acquires a mass W_t after t days hydration. Of course, if X_0 and X_t are the fraction weight loss (at 750 °C) at time 0 and time t , respectively, it holds: $W_0(1 - X_0) = W_t(1 - X_t)$. Then, $W_0 = W_t(1 - X_t)/(1 - X_0)$. In conclusion, the percentage of CBW is: % CBW = $(W_t - W_0)/W_0 \times 100$. In this way, all the mix components that contribute to ignition loss are taken into account (CaCO_3 , Ca(OH)_2 , ...).

The neo-formed products' composition and morphology were evaluated by means of differential thermal analysis (DTA) and SEM analyses, respectively.

2.3. Hardened mortars

Powder milled for 120 min (MP120) was employed to prepare different kinds of mortars in which 50/50 (50M), 60/40 (60M) and 70/30 (70M) MP120 to lime ratios were used. In addition, a reference mortar (RM) containing 60% natural pozzolana (NP) and 40% lime was also prepared. The natural pozzolana was supplied by Italiana Zeoliti S.r.l. (Prignano sulla Secchia, Modena, Italy) and its chemical composition was as follows: $\text{SiO}_2 = 58.82\%$; $\text{Al}_2\text{O}_3 = 19.10\%$; $\text{Fe}_2\text{O}_3 = 4.60\%$; $\text{CaO} = 3.10\%$; $\text{MgO} = 1.11\%$; $\text{Na}_2\text{O} = 3.44\%$ and $\text{K}_2\text{O} = 9.39\%$.

According to EN 196-1 standard [22], normalized natural sand with maximum diameter less than 4 mm was employed as aggregate. The compositions of all mortars prepared are shown in Table 3.

Three prismatic specimens (4 cm × 4 cm × 16 cm) of each kind of mortar were cast, cured and tested, according to UNI EN 196-1 standard [22]. The time, temperature and humidity of curing were 90 days, 20 °C and 100% RH, respectively. Compressive strength was evaluated for all the hardened specimens by means of a Controls 50-C5600 apparatus.

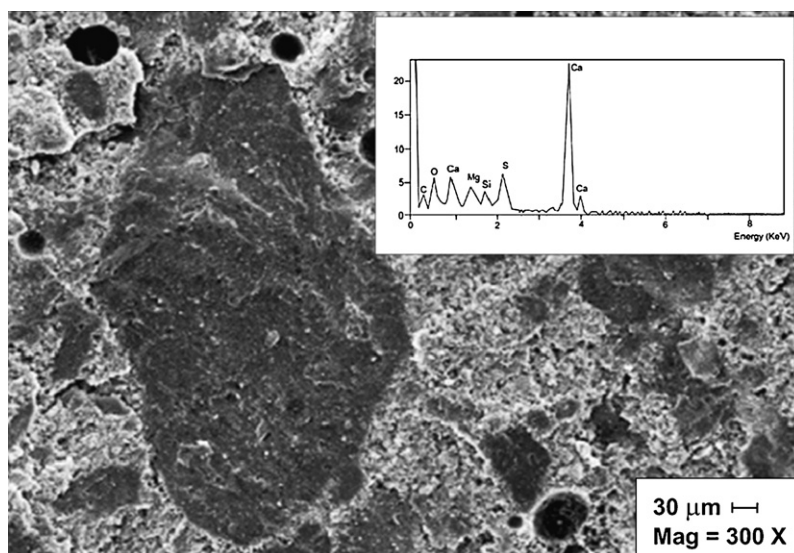


Fig. 5. SEM micrograph and EDS analysis of the B240 system after 28-day curing at 300× magnification.

3. Results and discussion

3.1. High energy milling

Fig. 1 shows the result of FT-IR investigation carried out on the asbestos-cement as received and the two powders obtained by 30 min and 120 min milling. The curves show the disappearance of the chrysotile OH stretching modes at 3690 cm^{-1} after 120 min milling. The absorption bands centered at about 1445 and 880 cm^{-1} are due to ν_3 and ν_2 modes of CO_3^{-2} , those centered at about 1000 and 450 cm^{-1} are relative to ν_3 and ν_2 modes of SiO_4^{-4} and, finally, those centered at about 1150 and 700 cm^{-1} are given to ν_3 and ν_4 modes of SO_4^{-2} . The presence of silicates, carbonates and sulphates is obviously due to the nature of ACW which also contains set cement.

As the external measured mill temperature, at equilibrium, never exceeds 80°C during the treatment, the OH bond disruption cannot in any way be attributed to a thermal action. On the

contrary, it is due to direct energy transfer between the grinding bodies and the processed materials through multiple impacts.

The observed results are in line with previous findings obtained for silicate and aluminosilicate minerals [11,12]. Indeed, it is well known that these minerals undergo amorphization during micronization or pressure rising up to a few tens of GPa. From a structural point of view, the amorphization is due to a rapid fragmentation of sheets: the direct OH bonds between the layers are destroyed or opened. The net effect of this dehydroxylation is the collapse of the crystalline long range order and a consequent amorphization of materials. The water formed during this process may well be retained as adsorbed molecules on the solid surface which is extended and made more energetic by milling. The results shown in Fig. 1 reveal that even if asbestos mineral phases are present in a complex matrix (asbestos-cement) their behavior is the same.

The results of XRD investigations are shown in Fig. 2. The reported traces refer to untreated and 120 min and 240 min high energy milled ACW, respectively. It is immediately clear that the

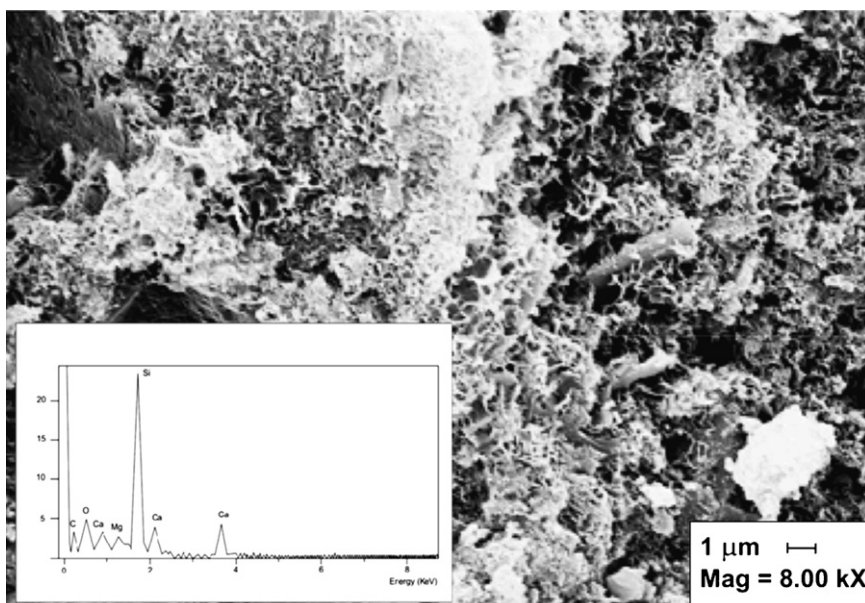


Fig. 6. SEM micrograph and EDS analysis of the B240 system after 28-day curing at 8000× magnification.

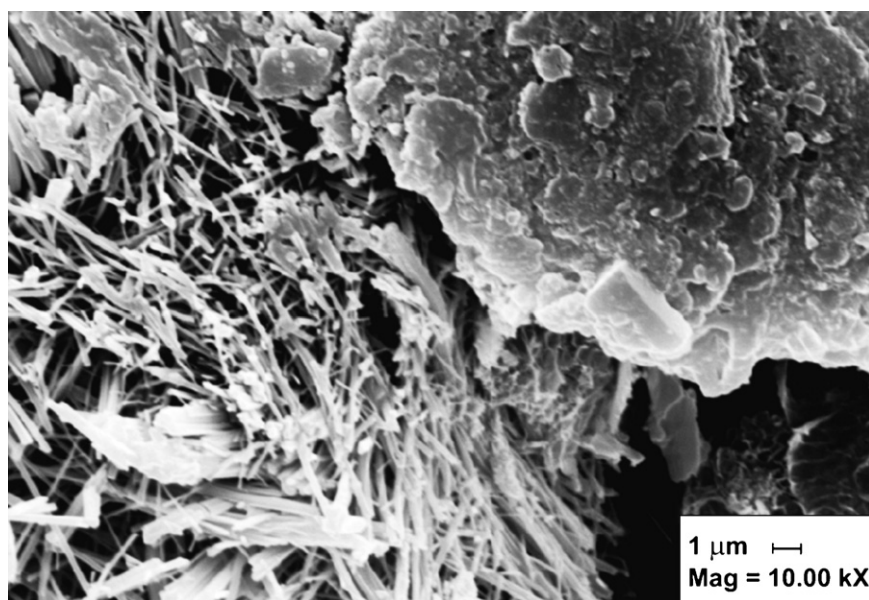


Fig. 7. SEM micrograph of the B240 system after 28-day curing at 10,000× magnification.

main crystalline chrysotile peaks fall sharply ($2\theta = 12.1^\circ$ and 24.5°) as a function of time during the micronization process. Indeed, after 120 min of milling these peaks practically disappear. Moreover, there is a clear and progressive increase in the background baseline between $5^\circ 2\theta$ and $20.2^\circ 2\theta$ which is a characteristic indication of a quantitative amorphous phases increase.

Fig. 3 shows the SEM micrographs of ACW, before (a) and after (b) 120 min of milling treatment. It is well evident that the treated ACW does not contain any fibres.

It is also worth noting that the high energy milling process acts selectively in destroying the crystalline structure of asbestos. The CaCO_3 XRD main characteristic peak ($2\theta = 29.45^\circ$), shown in Fig. 2, is almost the same after 240 min of milling. This effect is also confirmed by the loss on ignition values reported in Table 1, which remain almost the same after 30, 120 and 240 min of treatment.

Results of nitrogen-BET analysis show that the specific surface area does not increase proportionally to milling time: the measured values are: $16.18 \text{ m}^2/\text{g}$, $23.95 \text{ m}^2/\text{g}$ and $18.92 \text{ m}^2/\text{g}$, after 30, 120 and 240 min of milling, respectively. After 120 min of milling, a 48% increase is observed compared to the powder milled for 30 min. The specific surface area then falls sharply in the following 120 min of treatment (240 min in total). This suggests a competition between particle size reduction and agglomeration. The destruction of asbestos fibres due to the impact with milling bodies initially produces smaller particles so that a net increase in the specific surface area can be observed. Subsequently, these micrometric particles tend to agglomerate through electrostatic attraction and Van der Waals force, so that the specific surface area drastically decreases.

From an economic point of view, the investment cost of an industrial ball milling plant can be derived from that of similar plants used in other environmental applications. This cost is orders of magnitude less than of thermal or chemical based inertization systems [23–26].

3.2. Hydration behavior

Fig. 4 reports the thermograms relative to the B30, B120 and B240 systems (see Table 2). The traces are relative to the uncured and to the 28 and 56-day cured samples for each system.

It is possible to observe that the endothermic peaks at about $80\text{--}100^\circ\text{C}$ and $200\text{--}240^\circ\text{C}$ related to the dehydration of neo-formed phases, such as calcium silicate hydrates ($\text{CaO-SiO}_2\text{-H}_2\text{O}$, C-S-H) and calcium aluminate hydrates ($\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$, C-A-H), increase with curing time [27,28]. At the same time the endothermic peak at 450°C , dependent on dehydration of Ca(OH)_2 reactant, decreases [29,30].

The endothermic peak at about $120\text{--}140^\circ\text{C}$, due to the dehydration of the neo-formed ettringite ($6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$), is less evident because it overlaps with the calcium silicate hydrated thermal effect. The presence of ettringite is more evident in the B120 and B240 systems where a shoulder is present at about $120\text{--}140^\circ\text{C}$.

Endothermic effects present in the $600\text{--}800^\circ\text{C}$ range are due to the decarboxylation of CaCO_3 and remain almost the same even when the milling time of powders and the curing time of mixtures increase. This evidence confirms the selectivity of HEM treatment as revealed by the XRD analysis.

Other detected endothermic peaks are due to the unreacted mixture as they are already present before curing.

The results of SEM analysis carried out on the B240 system after 28-days curing are shown in Figs. 5–7. In Fig. 5, areas with very different porosity are present and EDS analysis carried out on denser areas indicates that these parts are mainly composed of calcium carbonate.

Figs. 6 and 7 report micrographs at a higher magnification in which the presence of flaky C-S-H crystals (Fig. 6) and needle-like ettringite crystals (Fig. 7) are shown. In Fig. 5 the results of EDS analysis are also reported. The spectrum confirms the typical C-S-H chemical composition of the flaky zone.

In Table 4 the weight percentages of chemically bonded water and reacted lime measured on systems A, B and C (see Table 1) are reported. The values are relative to 7, 14, 28 and 56 days curing time.

Analysis of the values of chemically bonded water makes it possible to observe that a continuous rate is not present. This is due to the continuous change in the typology of the neo-formed hydration products. The amount of chemically bonded water in the various forms of the main hydrated phases, such as C-S-H; C-A-H and ettringite, and their hydration kinetics vary considerably. The stoichiometry of calcium silicate, calcium aluminate

Table 5
Compressive strength of mortars after 90 day curing.

Systems	Strength (MPa)
RM	1.10
50 M	2.26
60 M	2.29
70 M	2.17

and calcium trisulpho aluminate hydrates changes over the curing time, determining a non-continuous variation in the amount of non-evaporable water with time.

In the case of reacted lime determination, it can be observed that the related amounts increase for all the systems when the curing time increases. Specifically, the values rapidly increase up to 14 days of curing, then almost constant values are reached after 28 days of the hydration time. These phenomena can be explained if we consider the very high specific surface area of the powders, which accelerates the hydration kinetic during the first few days of hydration.

Values of reacted lime around 40% confirm that HEM powders are able to give hydration reactions that involve considerable amounts of lime. This is very useful for the formation of new phases with a good hydraulic behavior.

3.3. Mechanical characterization

The compressive strength values measured on the cast mortars after 90 days curing are reported in Table 5.

In this table values of 2.26 MPa, 2.29 MPa and 2.17 MPa are reported for the 50 M, 60 M and 70 M systems, respectively. These values are more than twice that measured for the reference mortar prepared with natural pozzolana: in the latter case a compressive strength value of 1.10 MPa, was determined.

The good mechanical performance of the mortars containing milled powders are almost certainly due to the formation of ettringite together with C–S–H and C–A–H. This is in agreement with previous findings in which various hydratory systems able to form both ettringite and C–S–H have been studied [31–33].

Therefore, the presence of about 20% SO₃ in the composition of milled powders gives these systems an added value compared to lime pozzolana-based standard hydraulic mortars.

4. Conclusions

This study leads to the conclusion that powders obtained through the high energy milling of asbestos-cement waste are asbestos-free and can be profitably recycled in the field of building materials. Specifically, it can be drawn that:

- Two hours of high energy milling is sufficient to ensure total amorphization of waste. In fact, the typical chrysotile X-ray diffraction peaks, spectroscopy infrared bands and fibrous phase completely disappear after this mechanical treatment. This finding is of great interest considering the very high energy amount needed for the mineralogical transformation of asbestos waste by means of a much more expensive thermal treatment.
- The hydration processes of the lime-inert milled powders mixtures are very complex. The simultaneous formation of calcium silicate and aluminate hydrates and ettringite can be determined by means of differential thermal analyses and scanning electron microscopy observations.
- The mechanical characteristics of the hydraulic mortars prepared with the above mixtures are better than those lime-pozzolana based ones. These results prove the good pozzolanic activity of the employed asbestos-free powders and confirm the

possibility of being recycled as a mineral addition in the manufacture of building materials.

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