

Supplementary information

The combination of oxalic acid with power ultrasound fully degrades chrysotile asbestos fibres

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Sonochemical equipment

Figure 1 shows the reactor by which sonication can be performed with a single source or two, at different frequencies (22 kHz for the cavitating tube and 20 kHz for the classic titanium horn). Both sonotrodes stem from the optimization of models developed by some of us at the University of Torino. Their transducers consist of high-efficiency pre-stressed piezoelectric (PZT) rings (planar PZT Morgan Electronics, diameter 50 mm) compressed between two erga discs. Transducers are cooled by circulating high-dielectric mineral oil refrigerated with a chiller (800W). The cavitating tube is also cooled with refrigerated oil; power can be varied up to a maximum of 300 W (input power).



Figure 1. Immersion horn inserted in the cup-horn (cavitating tube); the inset shows the latter as seen from the top.

“Sono-chemical” treatment of chrysotile sample

The chrysotile asbestos fibres (500 mg) were suspended in 50 ml of ultrapure water (Milli-Q) or in 50 ml of a 0.5 M oxalic acid solution (fibres/solution ratio = 10 mg/ml) and placed into the US reactor. The cavitating tube frequency was set to 22.1 kHz and stabilized with an automated adjustment device (frequency hook). The fibres were sonicated for 2.5, 13 or 21 hrs at an input power of ca. 150 W.

Following the sono-chemical treatment the fibres were separated from the liquid by filtration through CA membranes (pore size = 0.20 μm). The solid residue was rinsed with pure water, weighed and subjected to surface area, morphological and crystallographic evaluation (BET, SEM, XRD and micro-Raman techniques respectively). In order to determine the amount of structural cations solubilized by the sono-chemical treatment, the solution was analysed by means of ICP-AES.

XRD characterization of the treated minerals

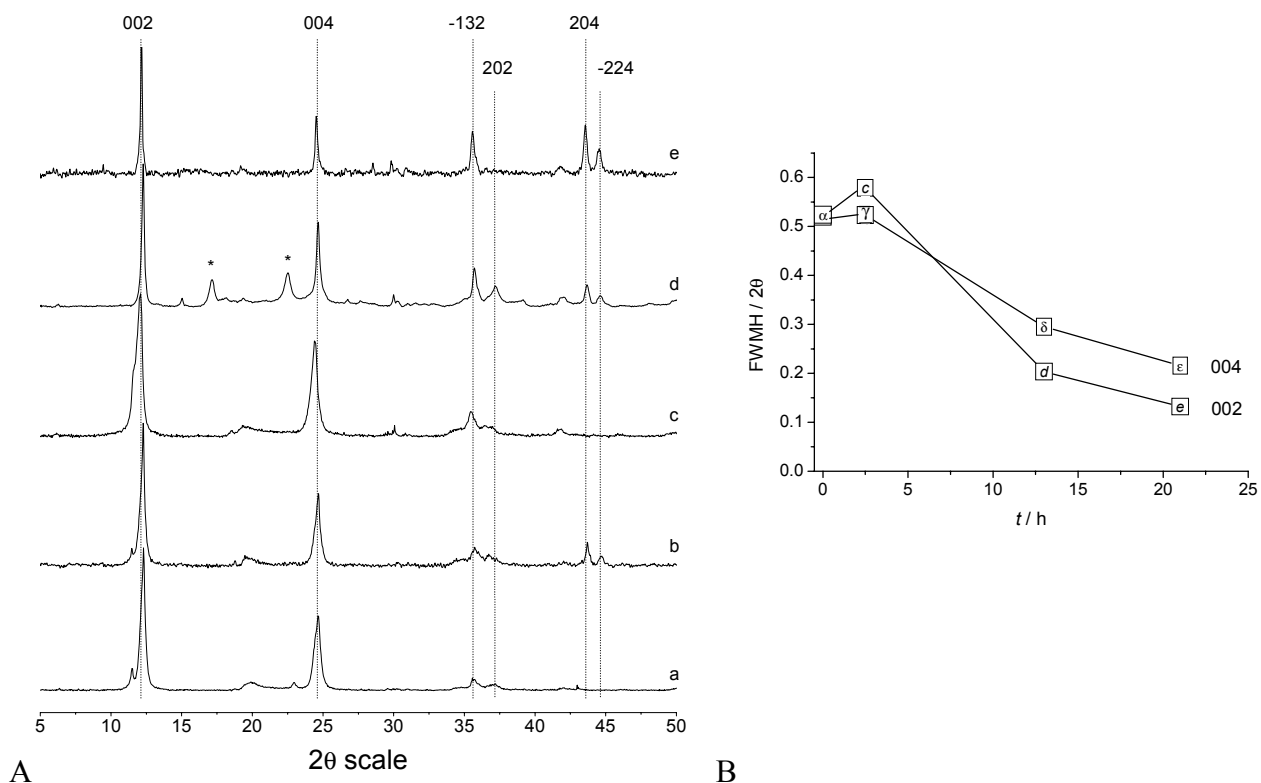


Figure 2. (A) X-ray patterns of natural (a) and treated chrysotile fibres. Asbestos was treated with US only for 12 hrs (b) or with US + 0.5 m oxalic acid for 2.5, 13 and 21 hrs (c, d and e respectively). The main X-ray reflections are marked with hkl values for crystallographic planes are reported; * indicates reflections due to the formation of Mg oxalates (consistent with findings previously reported). (B) Crystallographic peak width measured as full width at half maximum (FWMH) as function of time for 002 (Latin letters) and 004 (Greek letters) planes of chrysotile fibres untreated (a, α) and US + 0.5 M oxalic acid treated for 2.5 (c, γ), 13 (d, δ) and 21 (e, ε) hrs.

Changes in peak shape observed in XRD patterns after treatments with US + oxalic acid matched the profound modifications seen in the morphology of the surviving fibres. Untreated chrysotile fibres gave the well characterized X-ray diffractogram reported in Figure 2, pattern *a*: the intense reflections due to the parallel 002 and 004 crystallographic planes occur at $2\theta = \text{ca. } 12$ and 24 respectively. Some other less intense reflections arise at higher 2θ values. X-ray patterns from *b* to *e* were obtained from the solid residuals collected after the sono-chemical treatment. Pattern *b* was obtained after 12 hrs. of sonication in pure water. Both width and relative intensity of chrysotile main reflections were unaffected by the treatment. Patterns *c*, *d* and *e* were obtained for chrysotile fibre treated with US + oxalic acid for 2.5, 13 and 21 hrs. respectively. This sono-chemical treatment caused dramatic modification in peaks width, remarkably in reflections of 002 and 004 planes. The peak width – measured as full width at half maximum (FWMH) – of untreated fibres are what expected for natural specimen with occasional irregularities in the crystalline structure (i.e. defects, stacking faults, dislocations, heterogeneity in site size distribution, etc.). An increase in peaks width in the first stages of the sono-chemical process is consistent with a progressive fragmentation of the crystal lattice and indicates that chrysotile fibres underwent a transformation similar to what occurs in a mill during a mechanical comminution.¹ Conversely, the remarkable decrease in FWHM values observed after a prolonged sonication time) indicates that the crystal lattice of thin fibres which “survived” after sonication is less defective than that of the natural fibres. Such finding is consistent with pioneering previous work² and is likely due to the loss of interstitial material from between chrysotile fibrils and to the liberation of the basic nano-sized chrysotile fibrils, which in the original material are bound and twisted together to form more defective fibre bundles. Consequently, such fibres, which have not undergone solubilisation and/or

transformation into the amorphous silica debris will likely be those with more regular, defect-free crystallites.

- 1 E. Occella and G. Maddalon, *Med.Lav.* 1963, **54**, 628.
- 2 K. R. Spurny, W. Stoeber, H. Opiela and G. Weiss, *Am.Ind.Hyg.Assoc.J.* 1980, **41**, 198.

Micro-Raman

Micro-Raman spectra were acquired using an integrated micro/macro Raman system which includes a micro-spectrometer Horiba Jobin Yvon HR800, an Olympus BX41 microscope and a CCD air-cooled detector. A polarised solid state Nd 80 mW laser operating at 532.11 nm was used as the excitation source. Correct calibration of the instruments was verified by measuring the Stokes and anti-Stokes bands and checking the position of the Si band at $\pm 520.7 \text{ cm}^{-1}$. Each spectrum was acquired using a 50X objective, resulting in a laser beam size at the sample on the order of 10 μm . To optimize the signal to noise ratio, spectra were acquired using 10 scans of 10 seconds for each spectral region.