XRPD QUANTIFICATION OF NATURALLY OCCURRING ASBESTOS (NOA) IN SERPENTINITES: INFLUENCE OF BALL MILLING ON THE DIFFRACTOMETRIC RESPONSE

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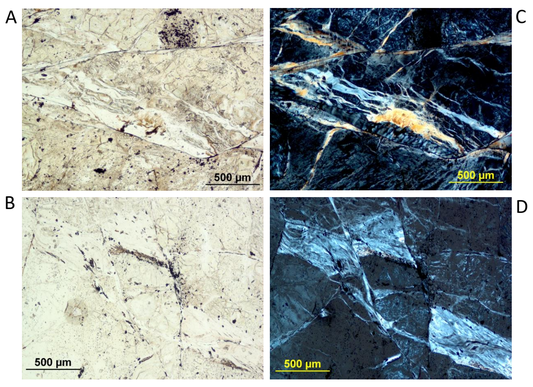
Introduction

The environmental hazard raised by naturally occurring asbestos (NOA) during construction project, mining or tunneling in asbestos-rich natural areas is a major concern for workplace safety and environment protection agencies. To estimate correctly the risk associated to NOA, new analytical tools to quantify the concentration of asbestos in its forming rock are strongly envisaged. X-Ray powder diffraction (XRPD) suitably determines the relative abundance of each mineral phase in a polycrystalline material, but the sample preparation is a critical step particularly for asbestos, because mechanical grinding may alter the crystal lattice, and the fibrous form induce sample preferential orientation, in turn affecting the diffractometric response. The aim of this work is to optimize sample ball-milling time to minimize texture effect yet collecting an intense diffractometric response.

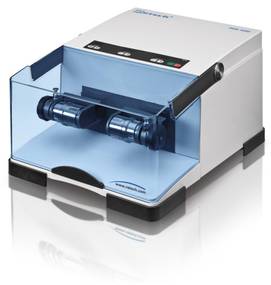
Materials and Methods

The material chosen for this project was a lizarditic serpentinite containing chrysotile previously observed using a polarized light microscope.



Optical microscopy images obtained with polarized light (A and B) and cross-polarized light (C and D).
Pictures show a generation of chrysotile veins with different interference colors (A and C) and a dislocated chrysotile vein (B and D).

The sample was ground with isopropyl alcohol (10ml), using a Retsch MM 400 tungsten carbide ball mill equipped with two 25ml jars (around 1 gram of sample each) and 25 s^{-1} oscillation frequency for 30 s, 1 min, 2 min, 3 min, 4 min, 5 min and 10 min.



- 0 s
- 30 s
- 60 s
- 120 s
- 180 s
- 240 s
- 300 s
- 600 s

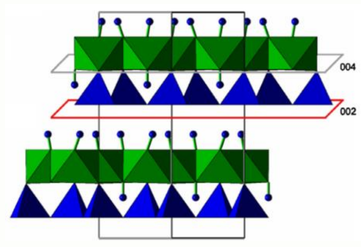
After drying at 105°C for 1 h, the powder obtained was investigated:

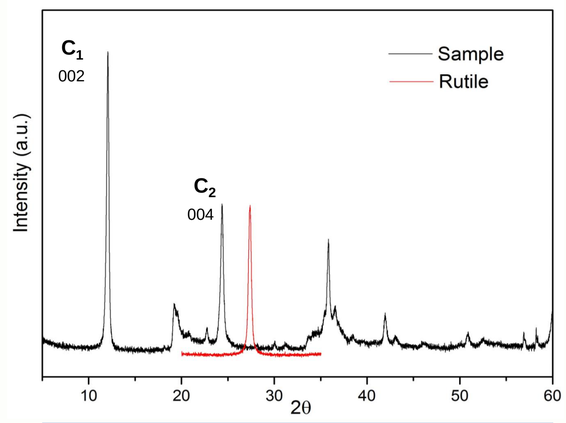
- To choose the best ball-milling time.
- To evaluate the decrease of particle dimension.
- To measure chrysotile fibers morphometry

Choice of the best ball-milling time

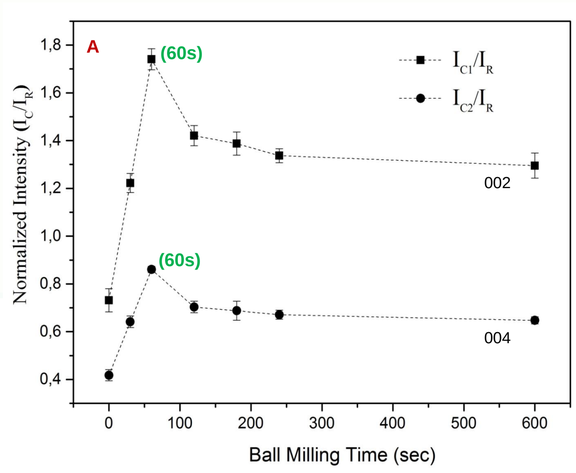
For each milling time, a mixture of sample and TiO_2, 75:25 by weight, has been prepared.

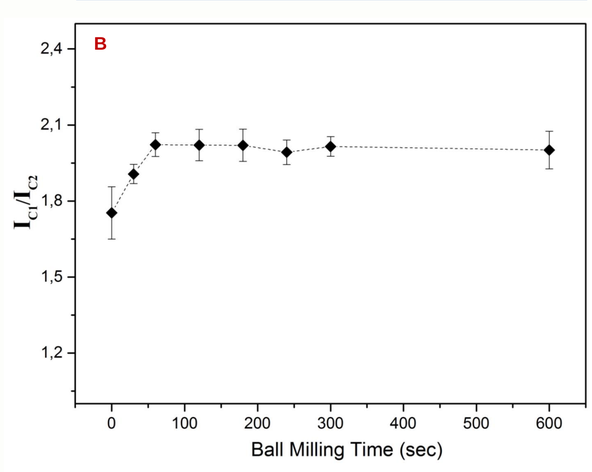
TiO_2 was chosen as a reference standard because its mayor peak at 27.4° (2θ) does not overlap with the two principal reflexes of Chrysotile (002) 12.1° (2θ) , and (004) 24.5° (2θ). The TiO_2 has not been ground with the serpentinite and its abundance is constant in each sample so intensity of the analytical peak of Rutile should remain constant. To the diffractometric analysis has been used a Bruker Advance D8. To minimize preferred orientations, the powder was loaded on the sample holder using a side loading method.

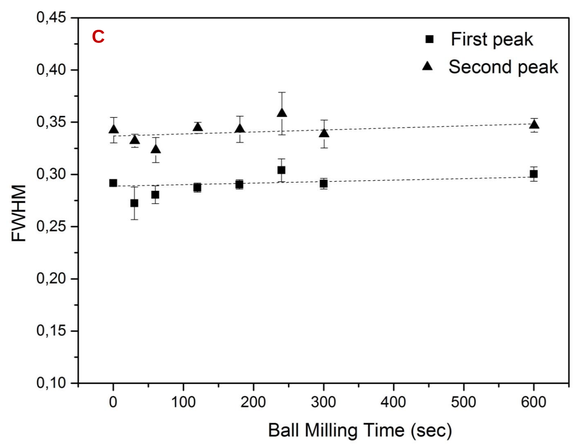




For each milling time sample, intensities of main chrysotile pecks (C_1 and C_2) has been analyzed 5 time, average of intensities and standard deviation of the mean were calculated.







It was determined:

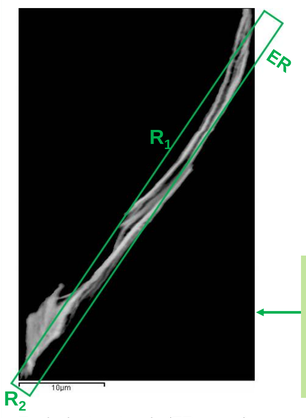
A The ratio of the intensity between the first peak of TiO_2 (I_R) and the intensity of the two peaks of chrysotile (I_{C1} e I_{C2}) for each milling period.

B The ratio between the two chrysotile main peaks (I_{C1} and I_{C2})

C The full width at half-maximum (FWHM) of the chrysotile main peaks.

Normalized intensities of 002 and 004 peaks increase up to 1 min of ball milling and then decrease with time (A). At milling time lower than 1 min relative intensities variation of C_1/C_2 are possibly due to preferred orientation of fibres. After 1 min of milling the C_1/C_2 remains constant with time (B). The value of FWHM for 002 and 004 reflexes is constant with milling time (C). Results indicate that 1 min of milling time achieve the best diffractometric response in term of intensity and texture effects.

Chrysotile fibers morphometry



Equivalent rectangle (ER, green) approximation of a typical curled chrysotile fiber.

We focused on sample milled for 60 s.

The fine powder were weighed and suspended in a surfactant solution, stirred and filtered on a polycarbonate membrane using a vacuum filtration system. The membrane was dried, mounted on an aluminum sample holder for electron microscopy and coated with a carbon layer by evaporation.

The SEM used was a Zeiss EVO MA10 with LaB_6 source and equipped with INCA Feature package software.

Particles size and shape distribution was obtained via automated SEM-EDS image analysis.
According to previous work (Cossio et al. 2018) the "equivalent rectangle" (ER) was calculated, for each particle, solving the following quadratic equation where P and A are the perimeter and area, and the two $R_{1,2}$ solutions being length and width of the ER, respectively:

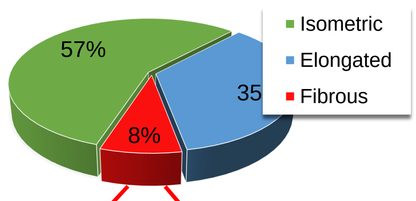
$$R_{1,2} = \frac{P \pm \sqrt{P^2 - 16A}}{4}$$

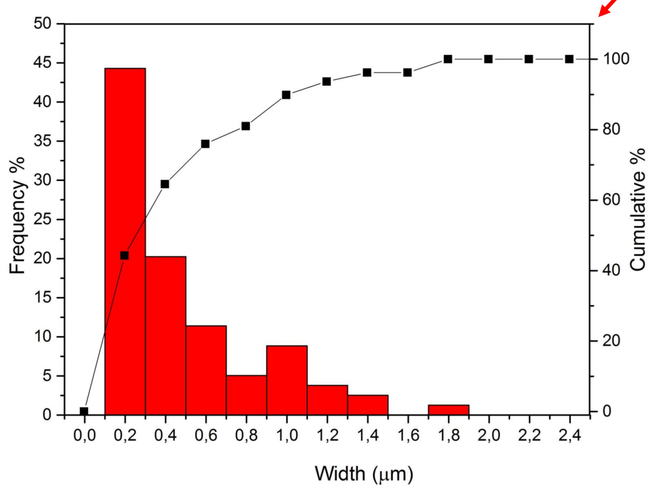
R_1 = Length

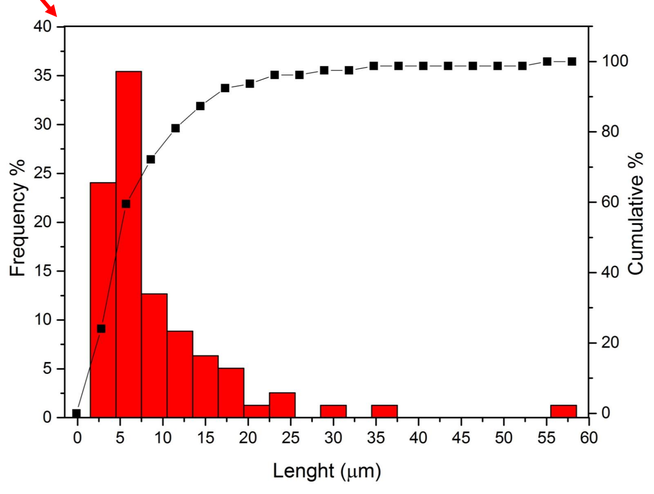
R_2 = Width

All measured particles were divided in three shape groups using the aspect ratio (length/width).

SHAPE	ASPECT RATIO
Isometric	<3
Elongated	3≤ a/r >10
Fibrous	≥10



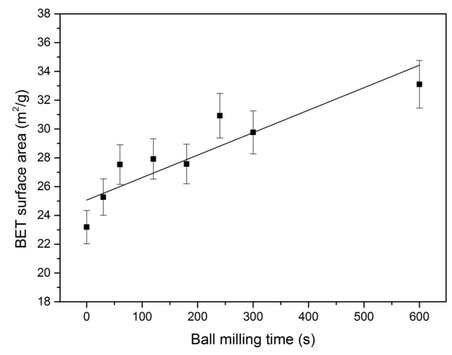




We obtained Width and Length distribution of the fibrous fraction of the sample milled for 1 minute. Around the 50% of the fibres have width lower than 0.3 µm and length lower than 6 µm.

Decrease of particle dimension

Evaluation of changing in samples surface area after ball mill was obtained by BET (Brunauer, Emmet and Teller) method. Each sample was evacuated at 150° for 12 h and then Kr_2 adsorption isotherm was measured with an ASAP 2020 instrument.



As expected surface area of sample increases with ball milling time proving the decrease of particles dimension.

CONCLUSIONS

Long grinding times induced a time-depended decrease of peak intensity due to the partial amorphization of chrysotile. Our results show that a good diffractometric response and an optimal particle size distribution can be obtained with 1 minute milling time. At this moment, more studies on particles dimension are being carried out at University of Turin and it is necessary to extend the same milling procedure on different NOA-rich serpentinites to confirm present results. This fast comminution procedure yielded XRPD suitable asbestos sample, without texture effect or loss of crystallinity. The method hence is proposed as the standard sample preparation protocol for routine quantitative analysis of asbestos in natural settings.

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