

EVOLUTION OF RESPIRABLE CRYSTALLINE SILICA IN ZIRCON SAND PROCESSING: ORIGIN, MILLING INFLUENCE AND OCCUPATIONAL IMPLICATIONS

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INTRODUCTION

Respirable crystalline silica (RCS) is widely recognized as one of the most critical occupational health hazards in industrial environments due to its well-established association with severe and irreversible respiratory diseases, including silicosis, lung cancer and chronic obstructive pulmonary disease [1, 2]. The risk associated with crystalline silica is intrinsically linked not only to its chemical composition but, more importantly, to its particle size distribution, as only particles within the respirable range (typically below 10 µm aerodynamic diameter) are capable of penetrating deep into the alveolar region of the lungs.

In industrial operations involving comminution processes, such as crushing, grinding and milling, the progressive reduction of particle size inevitably leads to the generation of fine and ultra-fine fractions, substantially increasing the proportion of particles that can become airborne and respirable [3,4]. In this context, sectors handling silica-containing materials are subject to increasingly stringent regulatory frameworks, particularly in the European Union, where respirable crystalline silica generated by industrial processes is explicitly recognized as a hazardous substance and associated with strict exposure limits and classification requirements [5].

Zircon (ZrSiO_4), a natural mineral widely used in the ceramic industry and other advanced applications due to its excellent thermal stability, chemical inertness and refractory properties is not intrinsically classified as crystalline silica [6]. However, zircon sands originating from

natural deposits may contain minor amounts of free crystalline silica, primarily in the form of quartz. Although these impurities are typically present at low concentrations, generally below 1–1.5 wt.%, their relevance from a health and regulatory perspective may increase significantly when zircon particle size is reduced through high-energy milling processes.

An additional complexity arises from the fact that mechanical activation during intensive milling may induce structural modifications in crystalline phases, particularly quartz [7, 8]. These transformations include partial amorphization and reduction of long-range crystallinity, which directly affect the analytical quantification of crystalline silica, especially when X-ray diffraction techniques are employed. As a result, the apparent content of respirable crystalline silica may depend not only on the actual material composition and particle size distribution but also on the assumptions made during analytical evaluation.

This issue becomes particularly relevant in the context of regulatory classification under the EU's CLP Regulation (Classification, Labelling, and Packaging) [9], where hazard categorization is strongly dependent on the concentration of respirable crystalline silica rather than on total dust content. Threshold values around 1% RCS are commonly used to define classification boundaries, meaning that small variations in analytical quantification may lead to significantly different regulatory outcomes. Consequently, there is a clear need for harmonized methodologies that integrate particle size effects, mineralogical characterization and structural transformations in order to ensure accurate and reproducible assessment.

Within this framework, the present study was designed to provide a comprehensive and scientifically robust evaluation of the evolution of respirable dust and respirable crystalline silica in zircon sands subjected to controlled milling processes [10]. The study specifically aims to establish the relationship between particle size reduction against increasing regulatory scrutiny of RCS in finely ground mineral products under the CLP regulation [9].

1. MATERIALS AND METHODOLOGY

The study was conducted using zircon sands supplied by different industrial partners, representing a broad range of crystalline silica contents. Initially, ten zircon samples were qualitatively analysed, from which six representative materials were selected to cover the widest possible quartz content range while avoiding the presence of additional contaminant phases.

All zircon samples were characterized following a specific lab protocol which comprehend different analytical tests. Chemical composition was conducted with a PANalytical model AXIOS wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer with a Rh anode tube and 4 kW power, fitted with flow, scintillation and sealed detectors, eight analysing crystals: LiF200, LiF220, Ge, TLAP, InSb, PE, PX1 and PX7 and provided with masks of 37, 30, 27, 10 and 6mm in diameter. These materials exhibited similar chemical compositions dominated by zircon (approximately 65 wt.% ZrO_2 and 32–34 wt.% SiO_2), with quartz contents ranging from below detection limits to approximately 1.5 wt.%.

A key aspect of the study was the definition of a reproducible and harmonized milling methodology. Experimental work demonstrated that wet milling was the only approach capable of consistently achieving the targeted particle size distributions. A sequential process combining planetary ball milling for coarse fractions ($d_{95} \approx 45 \mu\text{m}$) and horizontal microbead milling for finer fractions ($d_{95} \approx 5 \mu\text{m}$ and $3 \mu\text{m}$) was validated as the optimal strategy. The use

of dispersing additives was required to stabilize suspensions and ensure efficient ultra-fine grinding.

Identification of the crystalline phases was monitored by an X-ray diffractometer Theta-Theta D8 Advance A25 from Bruker with CuK α radiation ($\lambda = 1.54183 \text{ \AA}$), in accordance with standard UNE-EN 13925-1:2006. The generator settings were 45 kV and 30 mA. The XRD data were collected in a 2θ of $5\text{--}90^\circ$ with a step width of 0.015° and a counting time of 1.2 s/step by means of a LinxeyEYE detector. The quantification of crystalline phases was using the collected data were determined in a Rietveld refinement and validated with calibration curves prepared from certified reference materials (NIST SRM 1878b) (Fig. 1). The 6.0 version of the Rietveld analysis program DIFFRACplus TOPAS was used, assuming a pseudo-Voigt function to describe peak shapes. The refinement protocol included the background, the scale factors and the global-instrument, lattice, profile and texture parameters. The basic approach is identifying all the crystalline phases present and input basic structural data for all phases and then let the computer model the data until the best fit to the experiment pattern is obtained. Rwp (R-weighted pattern) and GoF (Goodness of Fit) parameters were calculated in order to evaluate the accuracy of the diffractogram simulation.

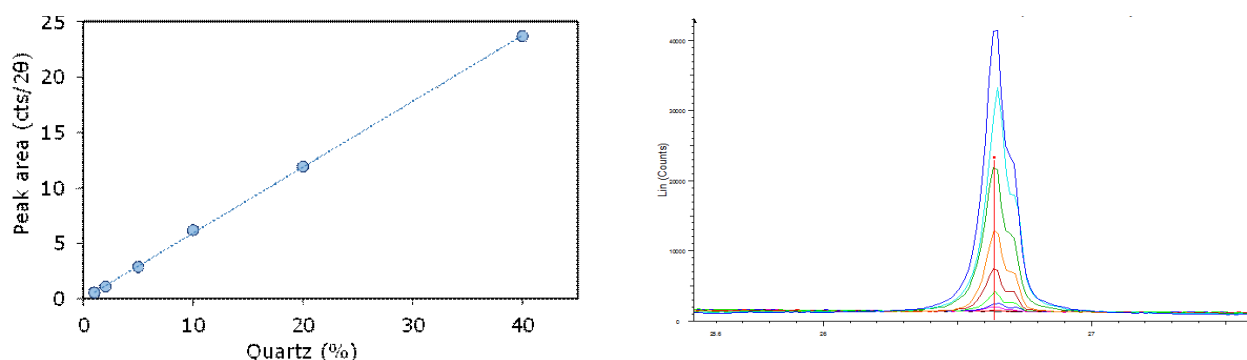


Figura 1. Calibration curve for quartz quantification based on certified reference material SRM NIST 1878b

The particle size distribution of raw zircon sands was determined using a MALVERN MASTERSIZER 3000 wet laser diffraction analyser. In this instrument, the particles pass through a laser beam and the light they scatter is collected by several detectors. The calculations were performed using the software included with the instrument, applying Mie theory to interpret the light scattering signal collected by the detectors.

To evaluate the potential health relevance of generated dust, the size-weighted fine fraction (SWFF) and the size-weighted fine fraction of crystalline silica (SWFFcs) were calculated following EN481-based methodologies, according to the standard UNE-EN 17289:2020 [11-13]. These parameters integrate particle size distribution obtained by sedimentation methodology with the probability of alveolar (lung) deposition, thereby providing a more realistic estimation of respirable exposure than simple mass-based metrics.

A critical methodological aspect of the study was the consideration of two analytical approaches for crystalline silica quantification: one assuming full preservation of quartz crystallinity and another incorporating crystallinity correction using the NIST SRM 1878b

certified reference material. This dual approach allowed the evaluation of the impact of mechanically induced amorphization on the apparent respirable crystalline silica content.

2. RESULTS AND DISCUSSION

2.1. Characterization of potentially respirable fraction and crystalline silica of raw zircon sands

The characterization of the zircon sands revealed that, in their commercial state, these materials do not contain respirable fractions. Both SWFF and SWFFcs values were systematically below 0.1%, confirming that the particle size distribution of raw zircon sands prevents the presence of particles within the respirable range.

2.2. Characterization potentially respirable fraction and crystalline silica of milled zircon sands

The experimental results clearly demonstrate that particle size reduction is the dominant factor controlling respirable dust generation. Milling to progressively finer particle sizes resulted in a significant increase in the size-weighted fine fraction (SWFF) as shown in Table 1.

These results demonstrate that particle size is the dominant parameter controlling respirable dust generation, regardless of the origin or composition of the zircon sands.

These results confirm that the transition from coarse to ultra-fine particle size distributions leads to a nearly complete shift of the particle population into the respirable range. This behaviour is consistent across all six zircon samples, indicating that respirable dust generation by milling is primarily governed by particle size rather than compositional variability.

Milling Target (d_{95})	SWFF Range (%)	Respirable powder
$\approx 45\ \mu\text{m}$	10 – 15	Limited respirable fraction
$\approx 5\ \mu\text{m}$	63 – 83	Majority of particles respirable
$\approx 3\ \mu\text{m}$	92 – 97	Nearly all particles respirable

Table 1. Evolution of respirable fraction (SWFF) with particle size

However, the evolution of respirable crystalline silica (SWFFcs) does not follow the same proportional trend. At the coarser milling stage ($d_{95} \approx 45\ \mu\text{m}$), SWFFcs values remained very low ($\leq 0.2\%$), confirming that quartz contributes negligibly to the respirable fraction at this level.

At intermediate and ultra-fine sizes, the apparent SWFFcs values increased, particularly when quartz crystallinity was assumed to be fully preserved. Representative values are summarized in Table 2.

Milling Target (d_{95})	SWFFcs	SWFFcs*	Regulatory impact
$\approx 45 \mu\text{m}$	$< 0,1 - 0,2 \%$	Despreciable	No classification required
$\approx 5 \mu\text{m}$	$< 0,1 - 1,1 \%$	Reducido a $< 1 \%$	Stays below STOT RE Threshold 1%
$\approx 3 \mu\text{m}$	$< 0,1 - 1,3 \%$	Reducido a $\leq 1 \%$	Science-based analysis /conservative classification

* Crystalline criteria applied

Table 2. Evolution of respirable crystalline silica (SWFF_{cs})

The data show that, under the assumption of fully crystalline quartz, ultra-fine milling may lead to SWFFcs values approaching or slightly exceeding 1%, which is a critical threshold for regulatory classification. However, when crystallinity corrections are applied, a systematic decrease in SWFFcs is observed across all six samples, with most values remaining at or below 1%.

This observation highlights the critical influence of mechanical activation on quartz structure. High-energy milling induces partial amorphization of the quartz, reducing the long-range crystalline order of quartz. As XRD-based quantification relies on crystalline phase detection, this structural disorder leads to lower measured crystalline silica contents. Consequently, neglecting crystallinity loss results in a conservative overestimation of respirable crystalline silica. Note that the study does not provide evidence that this reduction in crystallinity correlates with reduced or increased toxicity, indicating that the effect is primarily analytical rather than toxicological [14].

Another key observation is that the increase in respirable dust is largely independent of the initial silica content. For instance, samples with negligible quartz content exhibited high SWFF values after milling but negligible SWFFcs values, confirming that the respirable fraction is predominantly composed of zircon particles. This decoupling between SWFF and SWFFcs demonstrates that the hazard associated with respirable crystalline silica must be evaluated independently of total respirable dust.

From a regulatory perspective, these findings have direct implications. Under CLP regulation, hazard classification is driven by respirable crystalline silica content rather than total dust fraction. The results demonstrate that while ultra fine milling significantly increases respirable particle generation, the actual RCS content remains very low and highly dependent on analytical assumptions regarding crystallinity.

Therefore, accurate classification requires a harmonized methodology that incorporates mineralogical transformations induced by milling.

The present study confirms that the generation of respirable dust is primarily a physical consequence of particle size reduction, while the evolution of respirable crystalline silica is governed by both intrinsic quartz content and structural transformations induced by milling

3. CONCLUSION

The present study provides a comprehensive and reproducible framework for evaluating respirable crystalline silica in zircon sands subjected to milling processes. The results clearly demonstrate that raw zircon sands do not contain respirable crystalline silica and that the generation of respirable dust during milling is directly influenced by particle size reduction.

Despite the significant increase in respirable particles after milling to fine and ultra-fine sizes, respirable crystalline silica remains a minor component of the dust, reflecting the low intrinsic quartz content of zircon sands. Furthermore, the study highlights the decisive influence of quartz crystallinity loss (amorphization) on the quantification of respirable crystalline silica, showing that neglecting this effect leads to systematic conservative and potentially overly conservative classification.

From a technical point of view, this study demonstrates that wet milling can produce reproducible particle size distributions, and that the application of an accurate analytical system, integrating particle size analysis and mineralogical characterization is essential for accurate evaluation. It also highlights the importance of using appropriate reference materials and correction methods when dealing with ultra-fine particles.

The application of an optimized analytical methodology integrating particle size analysis, mineralogical characterization and crystallinity correction is therefore essential for accurate exposure assessment and hazard evaluation. The importance of using appropriate reference materials and correction methods when dealing with ultra-fine particles also must be highlighted.

From a regulatory and industrial perspective, the study delivers a scientifically robust basis for the non-classification of finely milled zircon sands and supports harmonized, evidence-based decision-making under CLP requirements.

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