

REACTIVITY OF CRYSTALLINE SILICA IN PROCESSING CERAMIC TILES

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ABSTRACT

Silica (SiO₂) is a major component of ceramic tiles. It can be found as part of various crystalline structures combined with other elements, either in a glassy state or in its crystalline component, quartz being the most common polymorph. The presence of crystalline silica in its respirable fraction, generated during processes such as cutting or machining, represents a potential hazard, especially in prolonged exposure to high concentrations, and may have adverse effects on human health. Its presence in different types of tiles therefore needs to be quantified.

This paper reports on the early results of the REACTMAC project, the main objective of which is to generate knowledge on the reactivity of ceramic tile raw materials and to develop procedures to improve control thereof.

The aim of the project was divided into two different lines of research. On the one hand, a study was carried out to determine the **crystalline silica content** of different types of commercially available tiles on both Spanish and foreign markets. The second line of research studied the influence of the most significant process variables that can affect **crystalline silica reactivity**, in order to determine its final concentration in the ceramic tiles analysed. The variables chosen were selection of raw materials, type of finished product, particle size of the selected raw materials, and heat treatment. Both commercially available products and synthetic samples sintered in industrial cycles were analysed during the study.

The analytical techniques used to characterise the materials in the study were X-ray diffraction (XRD), wet laser diffraction (WLD), and scanning electron microscopy (SEM).

The **results** of the study on the presence of crystalline silica in commercial tiles reflected current trends for different ceramic products: its presence in porcelain stoneware products ranges between 10 and 15% and in white-body *monoporosa* tiles between 16 and 20%. With regard to manufacturing variables, it would appear that raw material particle size has a greater influence than maximum working temperature on altering the percentage of crystalline silica in the final product. However, it is not possible to eliminate the presence of crystalline silica in ceramic tiles without changing the basic raw materials composition, even when maximum reactivity is forced using industrial parameters.

The research carried out so far has not only provided knowledge on the presence of crystalline silica in tiles but also enabled a working protocol to minimise silica in end products to be developed.

1. INTRODUCTION

Silica (SiO_2) accounts for approximately half of the earth's crust, by weight, and is the main component in ceramic tile compositions. Silica appears in various mineral forms, either in amorphous (glassy) states, which are biologically inert, or in a crystalline state. Quartz is the most widespread manifestation of crystalline silica, with variations found in polymorphs such as cristobalite and tridymite [1].

Its potential hazard to human health arises specifically from the presence of free crystalline silica in its respirable fraction. This respirable fraction of free crystalline silica is generated in formed products during processes such as cutting, polishing, forming, machining, and drilling. [2]. Failure to take adequate precautions in the presence of respirable crystalline silica may lead to irreversible adverse health effects, especially in cases of high, prolonged or repeated exposure over several years to high concentrations and may result in diseases such as pneumoconiosis and silicosis or further aggravate pre-existing respiratory conditions [3].

The Spanish ceramic sector is making arduous efforts to establish safe working environments for its employees [4] by minimising possible risks associated with the handling of raw materials and ceramic products containing free crystalline silica. To that end, manufacturers are bound to comply with the technical specifications set by law and the market, evolving towards the development of safer and more sustainable products while applying the best available technologies at all times in their production system.

The input of crystalline silica in both unfired and heat-treated ceramic products comes from its inherent presence in their composition. Fundamentally, clays provide the mineral in the form of quartz, mainly because of its great stability in the face of the weathering processes that take place on the earth's surface.

Sometimes, it can even be added in the form of silica sand or quartz to improve certain performance features during firing.

For the ceramic industry to be able to reduce free crystalline silica in formed products, a number of hurdles need to be overcome:

1. There are no specific regulations for formed products.
2. There are no certified reference materials for formed pieces (tiles) with known amounts of crystalline silica.
3. Not enough information is available on the reactivity of quartz and on whether starting particle size influences the presence of crystalline silica in the end product when subjected to industrial cycles.
4. The presence of crystalline silica in the end product is difficult to remove, which implies a need to maintain certain precautions when handling these materials in order to avoid possible contact with respirable crystalline silica.

However, improvement measures can be addressed by studying the reactivity of crystalline silica and thus choosing the most favourable conditions to minimise its presence, both in quantity and crystallinity. Such action requires R&D work to further our knowledge of the materials, to study the possible replacement of harmful components and to develop new testing methods for both products and processes.

Despite significant progress in instrumentation, the quantification of crystalline phases remains a challenge. Although many quantification methods based on the X-ray diffraction technique are considered highly accurate, interpretation of the results calls for specialist know-how by the analyst. Furthermore, sample preparation, data processing and the selection of standards play an essential role in the quantification of clay minerals [5].

Within this context, the REACTMAC project was set up to respond to the needs of the ceramic industry and other subsidiary sectors by aligning innovation challenges for people and for the circular economy with the Valencia Region's strategic lines. The intention of the project is to generate knowledge about the reactivity of raw materials and to develop hitherto non-existing procedures to improve the control and safety of working environments.

2. OBJECTIVES

The aim of this work is to determine the presence of crystalline silica in ceramic tiles and to study the variation in its concentration in different types of ceramic products after the firing process. The variables of temperature and particle size were studied under both laboratory and industrial conditions.

3. MATERIALS AND INSTRUMENTAL TECHNIQUES

3.1. SELECTED MATERIALS

COMMERCIAL CERAMIC TILES

Ceramic tiles of two types were selected: from group B1A (commercially known as porcelain stoneware tile) and from group B3 (white-body, single-fired monoporosa tile). The tiles in the study came mainly from Spain, although products from other countries such as Portugal, Brazil, Mexico and Italy, among others, were also analysed.

UNFIRED CERAMIC COMPOSITIONS

The starting point was an unfired industrial tile body, both for porcelain stoneware and white-body monoporosa tile. Table 1 shows the characterisation of the crystalline structures of each of the raw materials analysed.

Type	Crystalline phases in the composition				
	Quartz	Sodium feldspar	Kaolinite	Calcite	Others*
PORCELAIN STONEWARE TILE	28	37	22	---	13
WHITE-BODY MONOPOROSA TILE	28	20	20	13	19

*Muscovite mica, potassium feldspar, talc, dolomite, interstratified minerals

Table 1. Mineralogical composition of the two unfired products analysed in the study.

Certified reference materials

Three NIST-certified reference materials were used to quantify crystalline silica [6,7,8], with which the calibration curves presented in later sections were built:

- **NIST®SRM® 676a**: Alumina powder for quantitative analysis by X-ray diffraction
- **NIST®SRM® 1878b**: Alfa Quartz quantitative X-ray powder diffraction standard
- **NIST®SRM® 1879b**: Cristobalite quantitative X-ray powder diffraction standard

3.2. INSTRUMENTAL TECHNIQUES USED

Heat treatments were performed on the selected unfired tile bodies in a Pyrometrol laboratory electric kiln simulating industrial cycles.

The **quantification of crystalline phases** was carried out on the powder material using the X-Ray Diffraction (XRD) technique both for the fired tiles and the unfired compositions, in accordance with UNE-EN standard 13925-1:2006 [9].

Diffraction data were taken in an angle range of 5-90° 2 θ with a 0.015° 2 θ step and count time of 0.2 s per step using Cu radiation at 30 kV and 45 mA. The setup used for measurement was a Bragg-Brentano θ - θ type (Bruker D8 Advance A25), equipped with a LynxEye XE detector. Samples were measured at 15 r.p.m. rotation to improve particle statistics.

Quantitative analysis was performed with the adapted Rietveld method (Bruker TOPAS 6.0 software) and validated with calibration curves prepared from certified reference materials (NIST SRM 1878b and 1879b) and vitreous material simulating a similar composition to the products under study (Table 2). The fired samples were quantified by adding 10 wt% of the internal α -Al₂O₃ standard (NIST SRM 676a).

The samples were dried beforehand at 110°C, then ground and homogenised in a tungsten carbide ring mill ensuring that the crystallinity of the quartz and of the other crystalline phases was not altered.

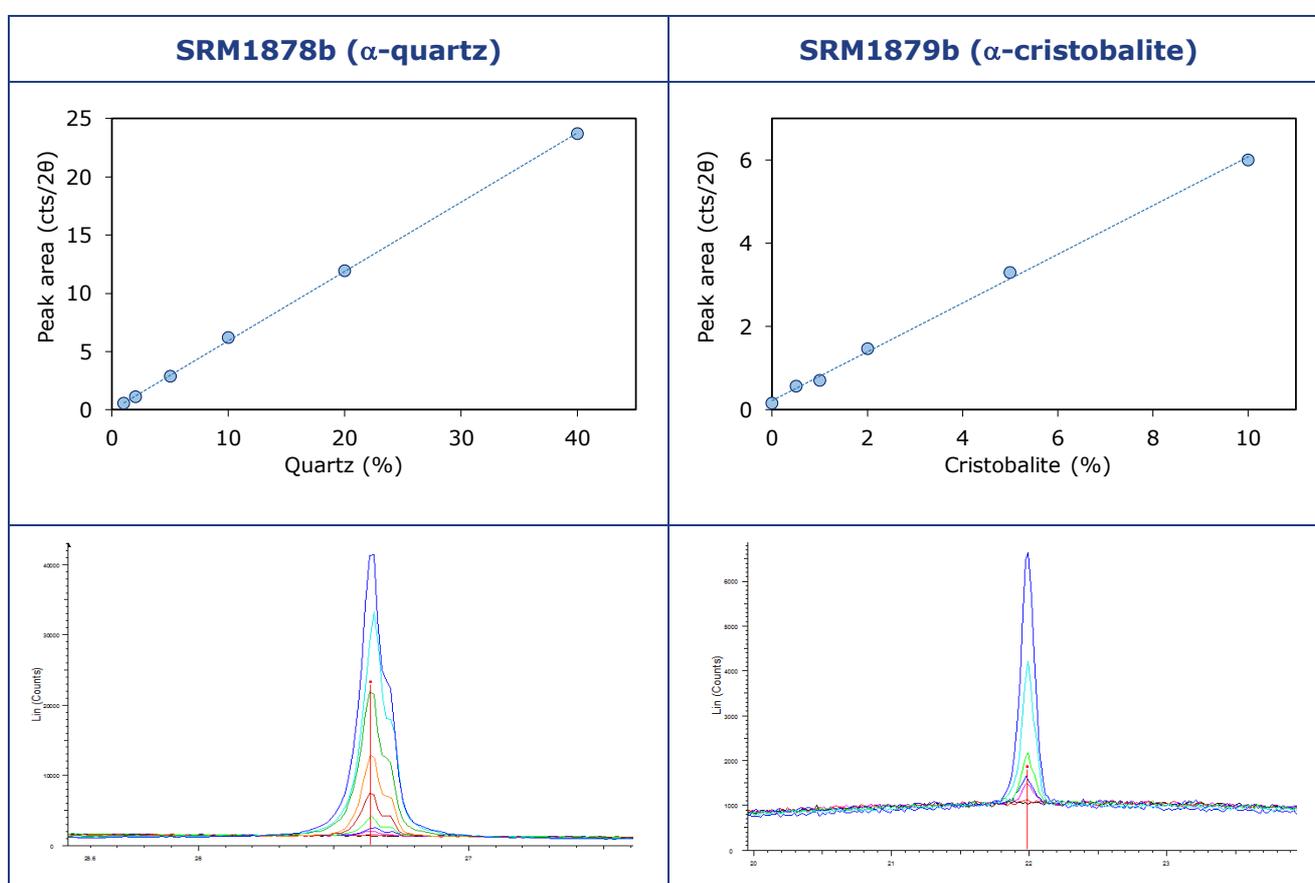


Table 2. Calibration curves showing the XRD results for the reference standards.

The **microstructure** of the pieces was studied using a QUANTA 200F field emission scanning electron microscope (FEG-SEM) made by FEI Co., USA, and a Genesis 7000 SUTW EDX unit manufactured by EDAX, USA. They were observed and photographed using the backscattered and secondary electron signal from a microscope.

The backscattered electron signal provides information on topography and composition, whereas the secondary electron signal is more superficial and allows for a clearer understanding of the sample's morphology by highlighting surface irregularities such as cracks, pores, and grain or crystal edges.

Particle size distribution was determined using a MALVERN MASTERSIZER 3000 wet laser diffraction instrument, in which the particles pass through a laser beam and the light they scatter is captured by detectors. The calculations were carried out with the software included with the unit using Mie's theory to interpret the light scattering signal collected by the detectors.

4. RESULTS

4.1. PRESENCE OF CRYSTALLINE SILICA IN DIFFERENT TYPES OF CERAMIC TILE

The following section describes a study of both Spanish and foreign commercial products in order to determine the percentage ranges of crystalline silica exhibited by goods on today's markets.

Fig. 1 shows a bar chart for both porcelain stoneware and white-body monoporosa tiles, respectively. When the samples were analysed, the vast majority of them revealed the presence of crystalline silica in the quartz polymorph. As sole exception, cristobalite was only identified in a few porcelain stoneware products from certain international markets.

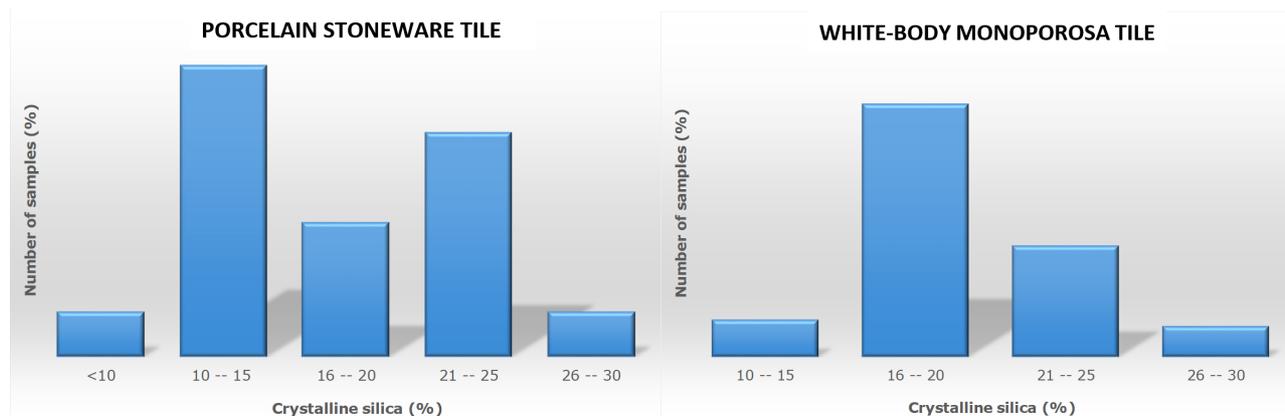


Figure 1 Distribution graphs per type of tile

After analysing the results obtained for porcelain stoneware tiles, the presence of two different populations were observed. In this instance, the populations seem to reflect two different trends in the type of product produced. The first population presents crystalline silica concentrations in a lower range (10-15%), whereas the second population moves in a higher range of crystalline silica (21-25%). The types with lower crystalline silica concentrations belong mostly to countries such as Spain and Italy.

This observation may be accounted for by a market sales trend that focuses on products of low thickness and/or large formats with a need to reduce shrinkage and dimensional changes during the firing cycle, for which quartz is responsible. On the other hand, they also strive to reduce the amount of crystalline silica in the finished goods as much as possible in order to reduce risks associated with product handling.

As for the study carried out on white-body monoporosa tiles, the trend observed is more similar across all tiles, with crystalline silica ranging from 16% to 20%.

Table 3 presents statistical data by type of sample, showing the mean, minimum and maximum values of crystalline silica concentration in the different products studied.

Type	No. of samples analysed	Crystalline silica (%)		
		Mean	Minimum	Maximum
PORCELAIN STONEWARE TILE	31	19	6	29
WHITE-BODY MONOPOROSA TILE	25	19	14	27

Table 3 Statistics by type of sample on the percentage of crystalline silica quantified by XRD

4.2. CRYSTALLINE SILICA REACTIVITY DURING THE INDUSTRIAL PROCESS

In this section, crystalline silica reactivity was studied in regard to the two processing variables that have the greatest influence on the final microstructure of the fired product: particle size of the raw materials and maximum temperature of the firing cycle.

MICROSTRUCTURE OF THE PRODUCTS ANALYSED

PORCELAIN STONEWARE TILE

Porcelain stoneware tile is a ceramic product that basically consists of a glassy matrix, mostly consisting of unmelted feldspars, mullite and quartz, and has a closed porosity of 3-7%.

Fig. 2 shows the microstructure of a standard porcelain tile in which the quartz grains embedded in the glassy matrix can be seen.

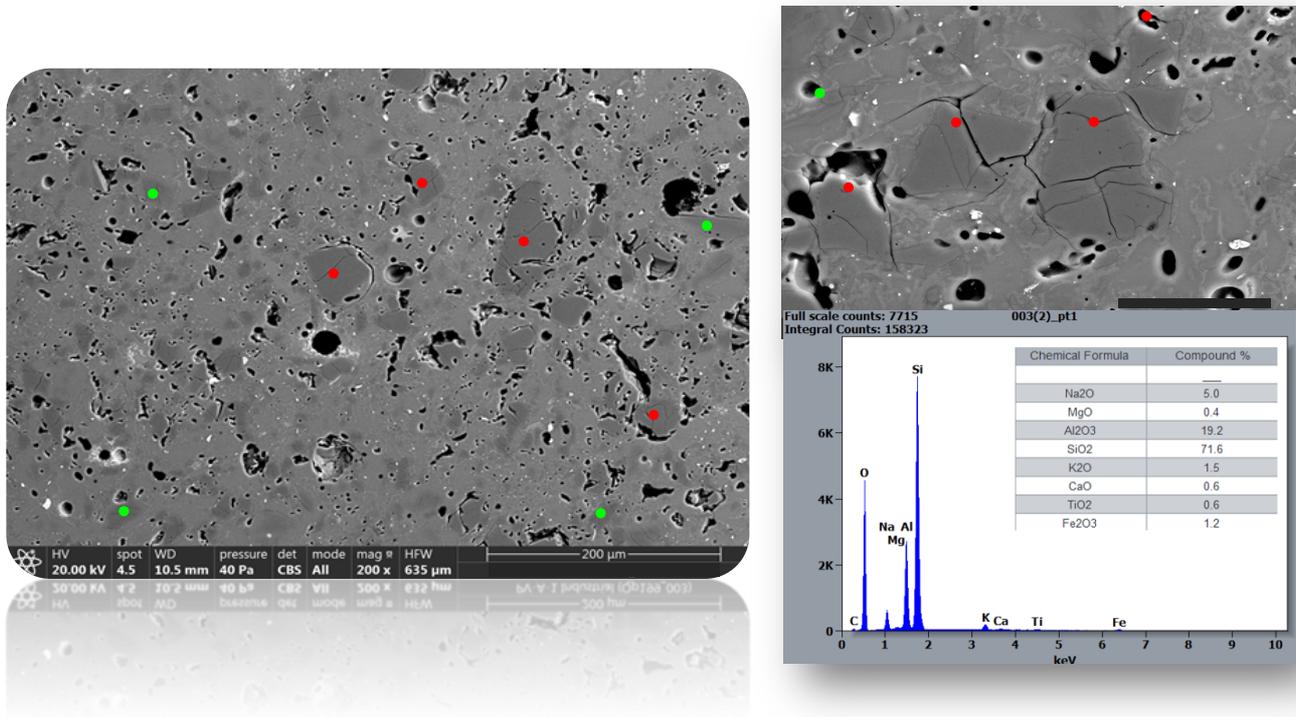


Figure 2. Microstructure and EDX analysis of a porcelain stoneware tile sample fired in a laboratory kiln. Green: Sodium feldspar; Red: Quartz.

The firing or sintering process is one of the key steps in the manufacture of porcelain stoneware tile. During the process, the components melt and react, creating a dense, glassy structure. Most of the glassy matrix comes from the melting of the feldspars, while another part comes from the clay phases that crystallise into a mullite-type structure during firing. At high temperatures, solid-state reactions take place and quartz can either transform into amorphous silica or recrystallise into new crystalline forms, depending on process conditions and the presence of different cations.

WHITE-BODY MONOPOROSA TILE

White-body monoporosa tile is a ceramic wall tile that has less glassy phase than porcelain stoneware tile but it also has quartz and mullite. The main difference with respect to porcelain stoneware tile is the presence of a characteristic crystalline phase resulting from the reactivity of calcium carbonate with feldspar during high-temperature sintering, namely anorthite. This phase gives the end product its specific properties as well as its 10-15% porosity. Most of the glassy matrix comes from the melting of the feldspars.

Fig. 3 shows the microstructure of a sample of a standard white-body monoporosa tile in which the quartz and anorthite grains can be seen embedded in the glassy matrix. The spray-dried granules are also visible due to the low sintering of the material.

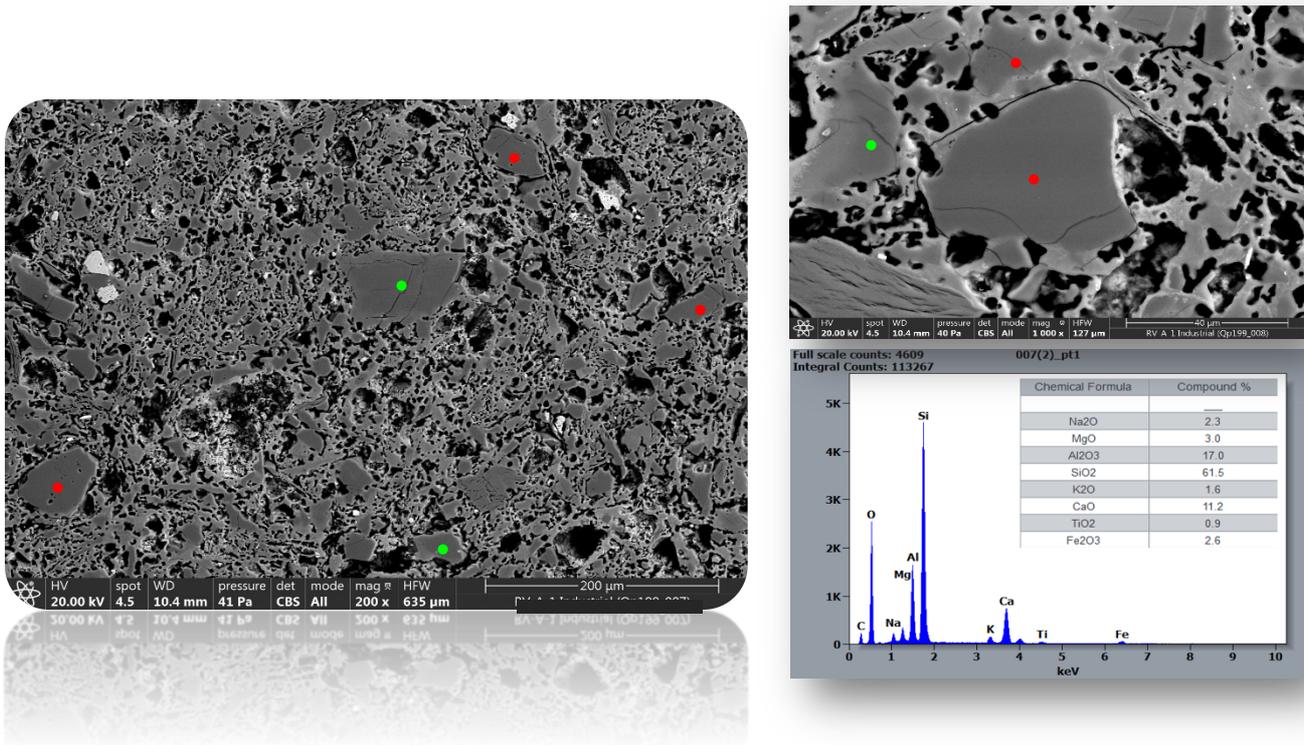


Figure 3. Microstructure and EDX analysis of a white-body monoporosa sample fired in the laboratory. Green: Sodium feldspar; Red: Quartz.

EFFECT OF QUARTZ PARTICLE SIZE

In order to study the effect of quartz reactivity as a function of quartz particle size, the particle size distribution of different commercial types of quartz was determined and compared with that of an industrial porcelain stoneware tile composition.

After observing the results obtained, it was decided to create ceramic compositions with the three selected quartzes ($d_{50}=5\ \mu\text{m}$, $d_{50}=10\ \mu\text{m}$ and $d_{50}=20\ \mu\text{m}$), as they are within the size distribution range of the industrial product. The raw materials required to make a standard porcelain stoneware tile composition were mixed and pressed, and the test pieces obtained were subjected to different firing cycles to ascertain the effects of particle size and maximum firing temperature.

Table 4 shows the results from the crystalline silica quantification as a function of the selected particle size for each composition and maximum temperature of the firing cycle.

Type	Temperature (°C)	d ₅₀ (µm)	Crystalline silica (%)
PORCELAIN STONWARE TILE	1180	5	20.8 ± 0.5
	1190	5	20.3 ± 0.4
	1180	10	24.0 ± 0.7
	1190	10	23.8 ± 0.3
	1200	10	23.1 ± 0.5
	1190	20	23.3 ± 0.7
	1200	20	23.0 ± 0.4

Table 4. Quantification of crystalline silica (quartz) as a function of maximum temperature and quartz particle size used.

The results show that the parameter with the most significant influence on the percentage of quartz in the final product is the selected particle size, as quartz content evolves from 21% to almost 24% simply by altering particle size. As far as temperature goes, it seems that regardless of quartz particle size, its influence in 10°C steps is not so significant in laboratory tests.

One phenomenon to be highlighted from the results obtained is that the production process in itself does not have such a marked effect as to be able to sufficiently reduce the amount of quartz present in the end product to values below 10% quartz when the presence of quartz in the unfired product is high. Reduction percentages varied from 14% to 28% for concentrations in the original composition of around 25%. The only way to reduce quartz below that limit is to alter the base composition of the product and start with a much lower quartz content than is currently used by the market, as shown by the study carried out in Section 4.1, which has a limited industrial feasibility.

TEMPERATURE CONTROL

In order to carry out a more in-depth study on the effect of maximum firing temperature on final quartz content in the product, different firing cycles were performed on both porcelain stoneware and white-body monoporosa tiles. The crystalline phases of each of the samples analysed were then quantified and their evolution at the maximum firing temperature was plotted. The experimental results were subsequently compared with the values obtained for tiles fired in an industrial cycle (yellow line).

With regard to the porcelain stoneware tile's behaviour (Fig. 4), a progressive decrease in sodium feldspar is noted, with full melting taking place from 1190°C onwards.

As for the mullite, phase formation is seen to increase with temperature but begins to disappear as soon as the feldspar completely melts and the glassy phase of the system increases.

Anomalous behaviour with respect to quartz can be observed, with the appearance of an inflection point. This progression is explained by the effect that temperature has on the structure of quartz. The fact that natural, and often somewhat degraded, raw materials were used to make the product composition means that the temperature applied to them causes recrystallisation in the system and, therefore, the intensity of the diffraction increases owing to an ordering of the system. The amount of quartz does not increase with temperature, but the quartz becomes more crystalline. However, from 1190°C onwards, the glassy phase does start to melt the edges of the quartz crystals and degradation of the quartz can be observed.

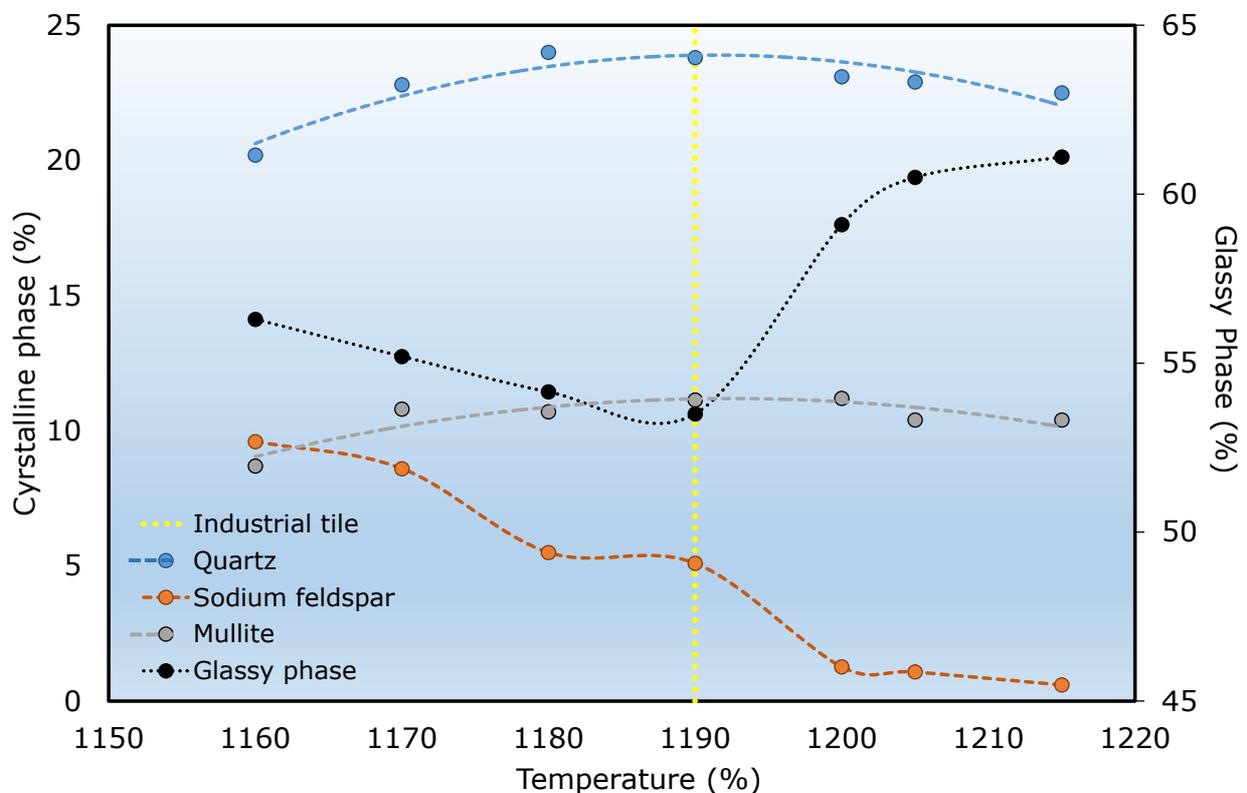


Figure 4. Evolution of the crystalline and amorphous phases of the porcelain stoneware tile as a function of maximum firing temperature.

In regard to how the crystalline phases evolve in the white-body monoporosa composition (Fig. 5), it should be noted that a progressive reduction in the percentage of quartz is seen as maximum firing temperature increases and progresses parallel to the increase in anorthite that forms with temperature. The glassy phase remains largely unchanged due to the crystallisation of anorthite. The formation of anorthite, characteristic of this type of composition, has a global effect on the microstructure, paralysing evolution of the surrounding crystalline phases in the system and preventing formation of a whole glassy phase, maintaining porosity.

In this case, the effect of quartz recrystallisation was not observed, possibly due to the strong influence of anorthite growth and calcium reactivity in this type of composition.

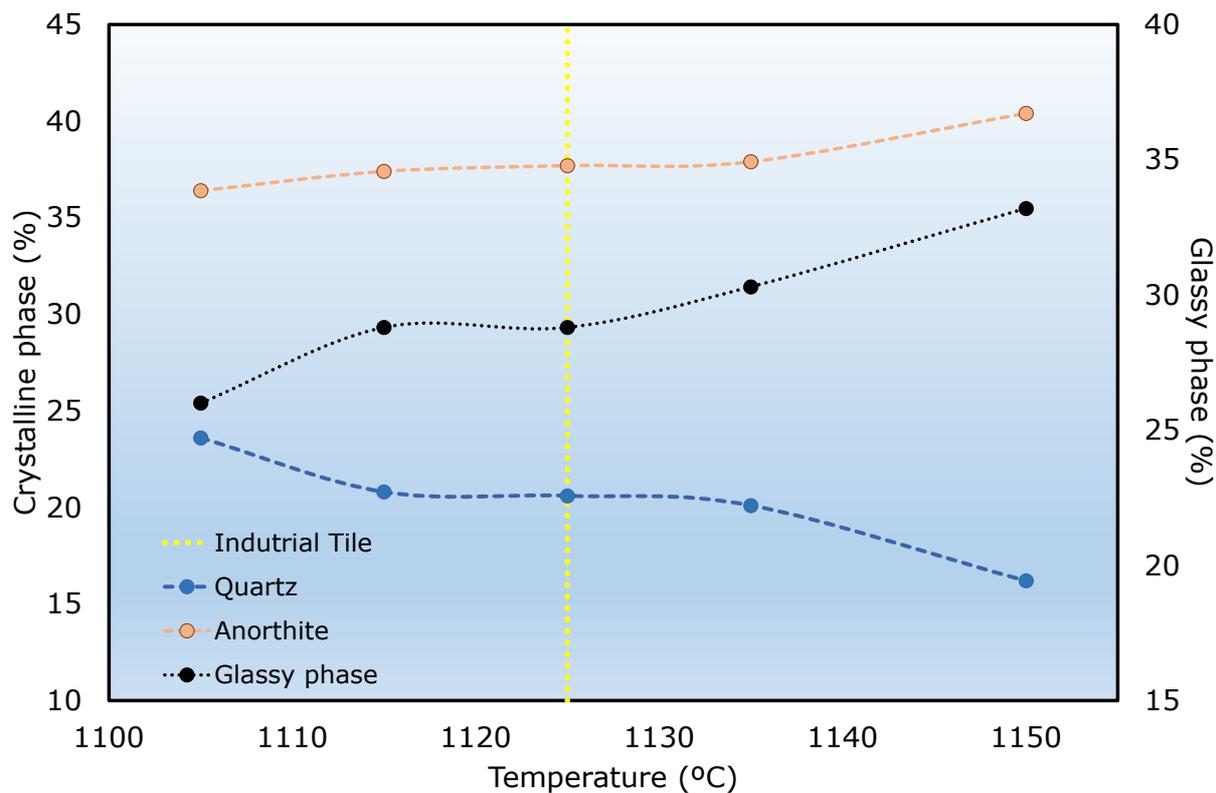


Figure 5. Evolution of the crystalline and amorphous phases of the white-body monoporosa tile as a function of maximum firing temperature

5. CONCLUSIONS

This research has involved a **study of the crystalline silica content in ceramic tiles** with different provenances from both Spain and abroad. The results obtained illustrate market trends with regard to the percentage of crystalline silica analysed, both in porcelain stoneware and in white-body monoporosa tile. According to the statistics, the white-body monoporosa tile was seen to have a silica content of mainly around 16%-20%, while in the porcelain stoneware tile, two main populations were observed: the first between 10% and 15% and the second between 21% and 25%. These values seem to correspond to different presentations of the product on the market, which are increasingly moving towards the production of large formats and low-thickness products, which in turn favours a reduction in crystalline silica content.

With regard to the influence of the **process variables**, the **particle size** of the selected raw materials was seen to be the parameter that most strongly affects any change in crystalline silica content, with variations of up to 4% being observed. As far as maximum temperature is concerned, small variations were noted but over a much smaller fluctuation range of 2%, although it is important to bear in mind that the object of study was always a standard work range.

Firing temperature influences both the total percentage of crystalline silica remaining in the matrix and its crystallinity, and indeed an increase in the results can be seen, due to recrystallisation with temperature.

Furthermore, it is impossible to minimise or completely eliminate the presence of quartz in the glassy matrix simply by altering process variables when the product's composition contains a crystalline silica concentration higher than 20%, unless the base composition is reformulated.

The research carried out so far has not only provided knowledge about the presence of crystalline silica in ceramic tiles but also a **working protocol** to minimise this component in end products.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

- [1] Carretero León, M.I., Pozo Rodríguez, M. *Mineralogía aplicada, salud y medio ambiente*. Madrid: Paraninfo, 2007. ISBN:978849732487
- [2] Exposición a la sílice cristalina respirable en materiales de construcción. INSST <https://www.insst.es/el-instituto-al-dia/exposicion-a-la-silice-cristalina-respirable-en-materiales-de-construccion-video>
- [3] Madera J., Menéndez P., Carballo M., Freijo J., Fernández E.M. Guía para el control de riesgo por exposición a sílice cristalina respirable. *Instituto Nacional de Silicosis* (2017) 183-203
- [4] ASCER. <https://portal.ascer.es/formacion-y-asesoramiento-en-prevencion-de-riesgos-laborales/#>
- [5] Zhou X. et al. XRD-based quantitative analysis of clay minerals using reference intensity ratios, mineral intensity factors, Rietveld, and full pattern summation methods: a critical review. *Solid Earth Sciences* (2018) 3, 16-29
- [6] Cline, J.P., Von Dreele, R.B., Winburn, R., Stephens, P.W., Filliben, J.J. Addressing the amorphous content issue in quantitative phase analysis: the certification of NIST standard reference material 676a. *Acta Crystallogr. Sect. A Found. Crystallogr.* (2011) 67, 357–367. DOI: 10.2138/rmg.2012.74.5
- [7] Black, D.R., Mendenhall, M.H., Windover, D., Henins, A., Filliben, J.J., Cline, J.P. Certification of standard reference material 1878b respirable α -quartz, *Powder Diffraction* (2016) 3, 1-5. DOI: 10.1017/S0885715616000336
- [8] Black, D.R., Mendenhall, M.H., Whitfield, Cline, J.P. et al. Certification of standard reference material 1879b respirable cristobalite, *Powder Diffraction* (2018) 33, 1-7. DOI: 10.1017/S0885715618000465
- [9] UNE-EN 13925-1:2006 Ensayos no destructivos. Difracción de rayos X aplicada a materiales policristalinos y amorfos Parte 1: Principios generales