Silife

LAYMAN'S REPORT

PROJECT DATA

Project number

LIFE14 ENV/ES/000238

Duration

Start - 07/09/2015
End - 27/09/2019

Total budget

1 666 059€

EC co-financing

60%

With the contribution of the financial instrument LIFE

INDEX

1 INTRODUCTION

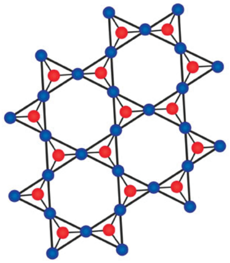
SILICA

SILICA is the common name for silicon dioxide (SiO_2), made up of silicon (Si) and oxygen (O), the two most abundant elements in the Earth's crust.

Silica may be **crystalline or amorphous**. In the crystalline forms, the atoms are organised as well-defined ordered structures (quartz, cristobalite, and tridymite), while these structures are not found in amorphous silica (colloidal silica, silica gel, and opal).

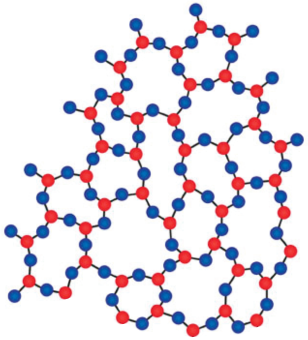
The most common form of **crystalline silica** is quartz, the second most abundant mineral in nature, after feldspars.

REPRESENTATIONS OF SILICA STRUCTURE



a) Crystalline (quartz)

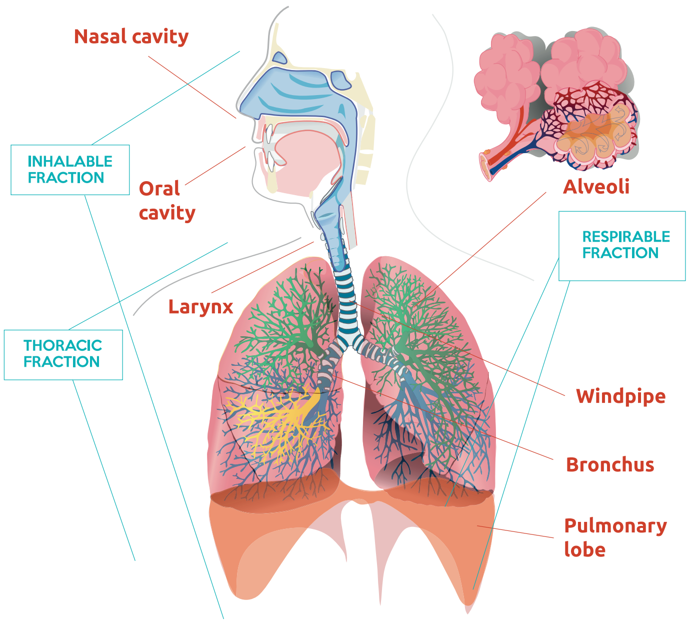
b) Amorphous



RESPIRABLE CRYSTALLINE SILICA (RCS)

What is RCS?

The smallest crystalline silica particles can penetrate into our respiratory system by inhalation. Their ability to penetrate varies with particle size, the finest particles penetrating most. **The respirable fraction (RCS)** is made up of particles that are fine enough to remain airborne for a long time and penetrate into the lung alveoli, where they lodge, this being where exchange of oxygen and carbon dioxide in the blood takes place.



RCS toxicity

The natural defence mechanisms of the human body allow most of the inhaled respirable dust to be removed. However, in cases of prolonged exposure in environments with high RCS concentrations, removal from the lungs becomes difficult; RCS build-up in the pulmonary alveoli can lead to a disease known as **silicosis**, giving rise to serious irreversible effects.

There are three types of silicosis:

- **Acute silicosis:** This can develop within weeks owing to intense exposure to high RCS concentrations.

- **Accelerated silicosis:** This is also related to exposure to high RCS concentrations and takes 5 to 15 years to develop.

- **Chronic silicosis:** This is the most common type and it advances very slowly, from 10 to 30 years after first exposure.

The International Agency for Research on Cancer (IARC) proposed in 1997 and ratified In 2012 RCS as a Group 1 **Carcinogen**: "Carcinogenic to humans". This classification means that "there is sufficient evidence in humans for the carcinogenicity of crystalline silica in the form of quartz or cristobalite".

Complexity of RCS toxicity

Unlike what occurs with most chemical substances, RCS toxicity varies highly, depending on several factors:

• Age

Scientific studies confirm that freshly generated RCS particles from high-energy wear processes (cutting, abrasion, milling, etc.) are a priori more toxic than RCS particles that have been present in the environment for some time. That is, as RCS particles "age" in the air, their surface reactivity (and hence their toxicity) decrease.

• Presence of other particles

If in the environment containing RCS particles there are also other particles that can adhere to their surface, RCS particle toxicity can also be modified. RCS particle toxicity usually decreases if the other particles exhibit no toxicity of their own.

• Origin of RCS

Various studies have demonstrated experimentally that crystalline silica toxicity decreased when crystalline silica was mixed with aluminium or aluminosilicates. Recently, in the period 2005 to 2008, a European project (SILICERAM) conducted in the ceramic sector verified that RCS stemming from the clays present in occupational environments generally displayed lower toxicity than RCS from pure or almost pure quartzes. This phenomenon was not due to the concentration, so that it may be put down to the attenuating effect of the presence of clay minerals (aluminosilicates) on the RCS particle surface.

2 Treatment of exposure to RCS in current European legislation

Status as carcinogenic agent

The European Union has recently included **"Works involving exposure to respirable crystalline silica dust generated by a work process"** as carcinogenic agent in the Directive that regulates exposure to carcinogens or mutagens at work **(Directive (EU) 2017/2398 amending Directive 2004/37/EC)**. European companies at which there are occupational environments exposed to RCS shall take the necessary measures **to minimise worker** exposure by all available technical resources, maximising protection measures during handling.

Establishment of a maximum exposure limit value (OEL) of 0.1 mg/m3.

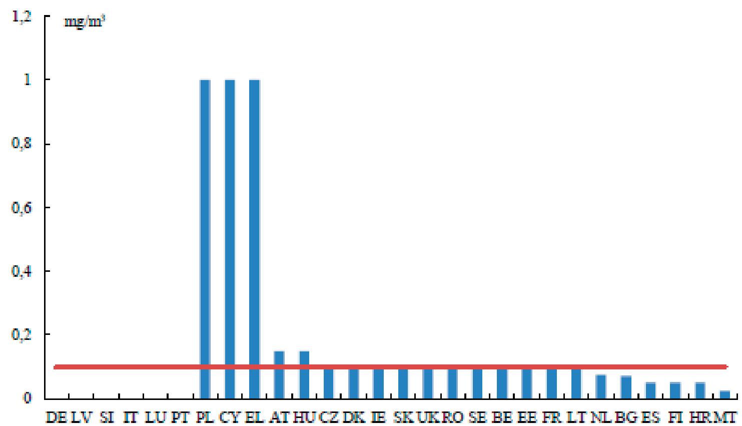
No EU Member State shall have a crystalline silica exposure limit that exceeds this value. Countries that have a higher value than that set in the EU, or that have not regulated this, shall adapt to this, while the most restrictive countries, which include Spain (0.05 mg/m³), can choose between maintaining this or adopting the new set value.

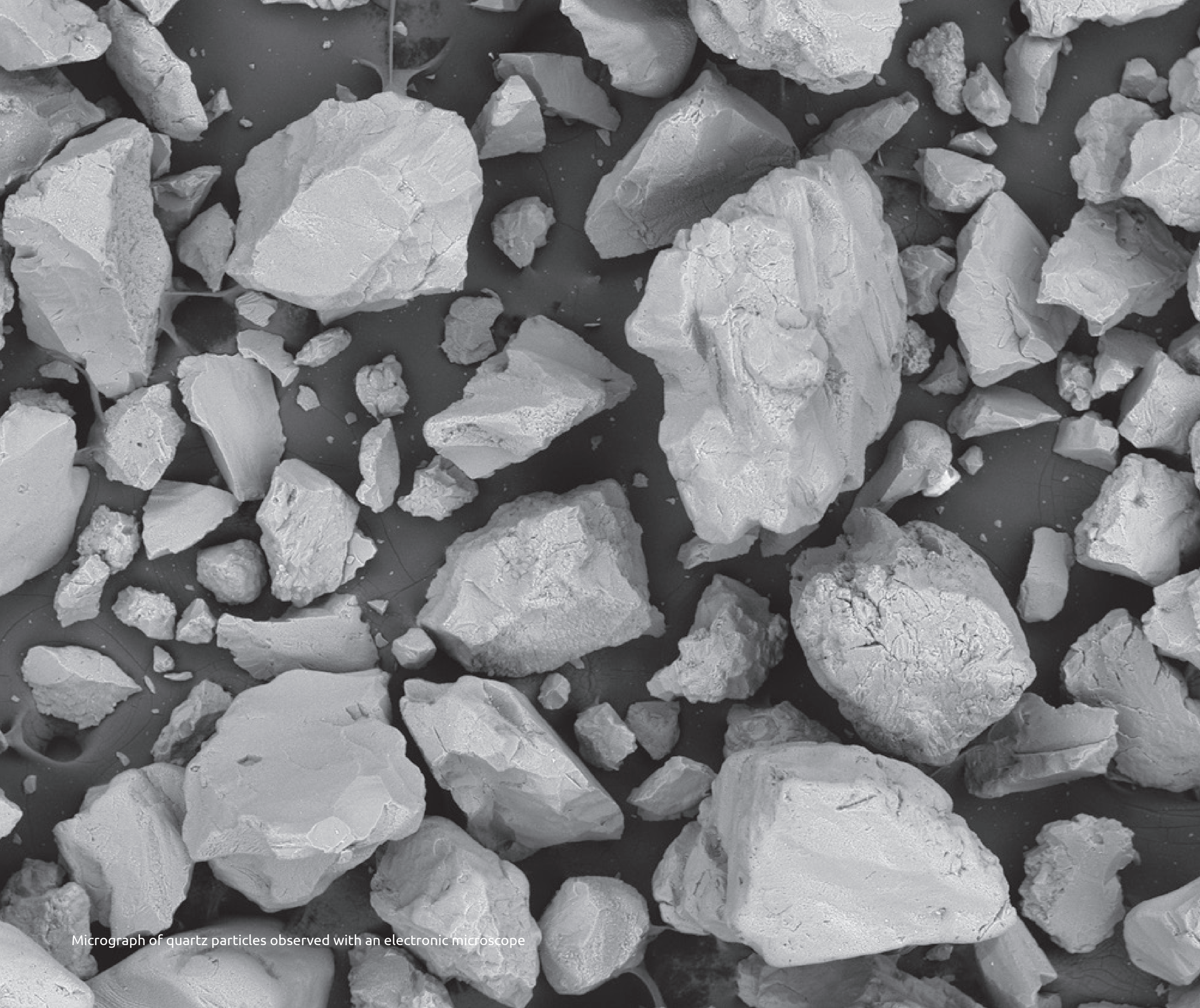
All Member States shall transpose this Directive into national law by 17 January 2020.

Occupational disease

Spain has included lung cancer by inhalation of silica dust as occupational disease in the latest update of its list of occupational diseases (Royal Decree 257/2018 of 4 May).

Occupational exposure limit values in the different EC countries





Micrograph of quartz particles observed with an electronic microscope

3

RCS exposure in industry

Industrial uses of quartz

The first industrial uses of quartz date back thousands of years. Since then, quartz has become a key raw material in global industrial development, particularly in the glass, foundry casting, and ceramic industries. In its finest form, quartz is used as a filler for paints, plastics, and rubber. As sand (coarse grain), it is used in water filtration and agriculture, among other uses.

Quartz is also used in IT materials and is irreplaceable in many high-tech applications, such as optical fibre for data transmission and precision foundry casting. It is also used in the metallurgy industry as a raw material for fabricating metallic silicon and ferrosilicon alloys. In short, quartz is used in hundreds of industrial applications found in everyday life.

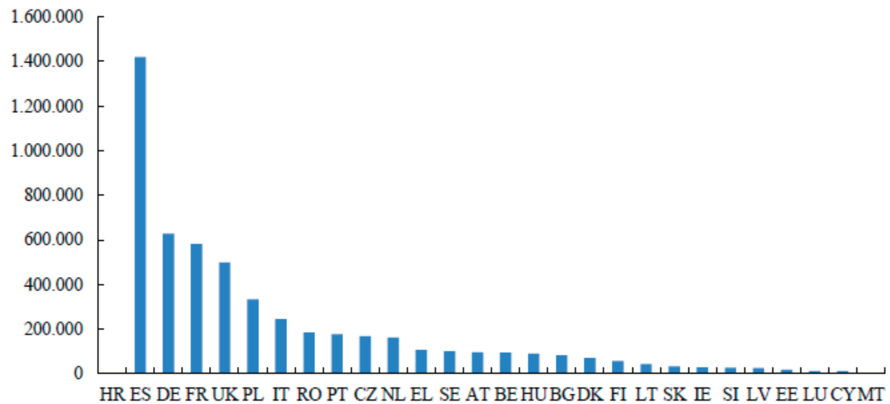
Number of workers potentially exposed to RCS in the EU

While draft Directive (EU) 2017/2398 was being drawn up, the European Commission asked the Institute of Occupational Medicine (IOM) in Edinburgh to conduct a study on the impact of RCS inclusion. It was estimated that 5 300 000 workers were potentially exposed to RCS in Europe in 2006, of whom over 70% worked in the construction sector. Of these, over 1 400 000 (more than 25%) worked in Spain.

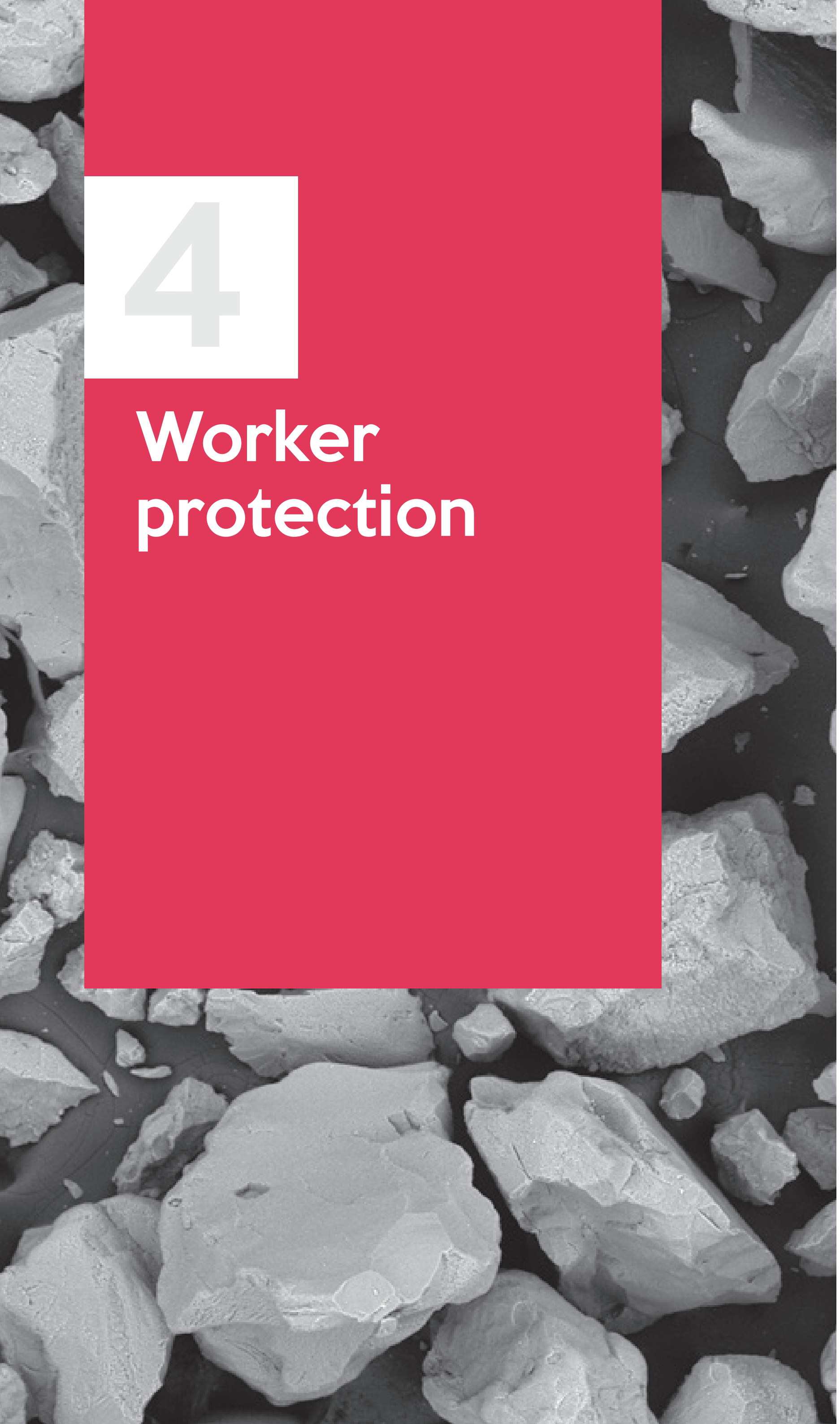
Activities most affected by RCS exposure

- **Extractive industries and public construction works**: mining, tunnel construction, rock excavation, drilling, pulling out and moving material.
- **Materials processing:** grinding, cutting, engraving, carving, polishing, etc.
- **Iron and steel industry:** furnace and ladle lining and repair.
- **Foundries:** mould making, demoulding operations.
- **Glass industry:** mixture preparation, furnace charging.
- **Refractories manufacture:** dry grinding, mixing, and separation, dry pressing, machining.
- **Ceramic industry:** raw materials milling and mixture, piece forming.
- **Metallurgy industry:** polishing by sandblasting (grit blasting).

Number of workers exposed to RCS in the different European countries

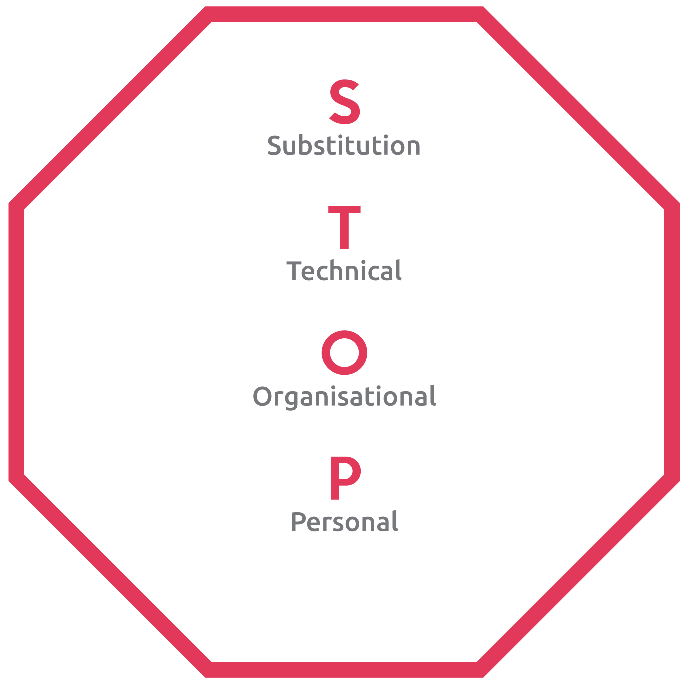


4 Worker protection



Exposure risk management

The actions for eliminating or mitigating occupational risks have been defined in an order of precedence known as the **STOP** principle.



S

Elimination and/or substitution

For quartz-containing minerals, this approach is generally relatively unfeasible. Quartz tends to be used in large quantities and though, technically, quartz could be replaced with other materials, its low price makes it difficult to find good, economically acceptable alternatives. On the other hand, in sectors like ceramics, quartz is a key ingredient owing to the unique performance features and properties it contributes to the end product. In this case, as in others, substituting quartz is technically unfeasible.

T

Control based on technical or engineering solutions

The most widely used measures for dust removal are (natural and/or forced) general ventilation and extraction systems at the points at which most dust is generated. The latter typically include the following elements:

• Extraction hoods through which the arising dust is drawn out while the source remains sealed off as far as possible.

• Filtration of the extracted air to remove airborne dust.

• Management of the dust retained by the filters: recycling, reuse, or controlled disposal.

O

Organisational measures

• Reducing the number of exposed workers by better separating the workplaces.

• Reducing exposure time and intensity by rotation at the workstations.

• Information and training.

P

Personal protective equipment (PPE)

In the case of RCS, the appropriate PPE is respiratory protection.

• The most common items are self-filtering masks made of a dust-retaining material, so that the air that crosses the mask and enters the respiratory system is practically particle-free.

• Whenever the dust concentration is very high, it is recommended to use self-contained breathing equipment, which isolates the user from the ambient air and provides the user with clean air.

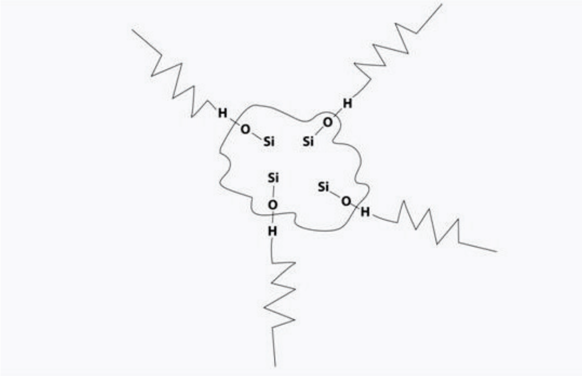
Silife

PROJECT

BACKGROUND

In the SILICOAT project, carried out in the period 2011 to 2014, a coating technology was developed that enabled addition of a reagent during the preparation of the ceramic compositions, which anchored itself to the quartz particle surface, inhibiting or reducing RCS toxicity. Applied to traditional ceramic processes, this technology proved to be technically and economically feasible for wet processes. The treated particles exhibited much less toxicity than the untreated particles.

However, RCS-containing raw materials are also used in industrial processes in which there are no wet stages. In such processes, the solution provided by the SILICOAT project is therefore not directly applicable. To address this constraint, the SILIFE project was initiated in 2015.



SILICOAT

Objective

The aim of the **SILIFE** project was to produce commercial quartz, which exhibits little or no toxicity owing to RCS, by a dry process.

THE CONSORTIUM

The project partners were as follows:

COORDINATOR

Instituto de Tecnología Cerámica
Universitat Jaume I *(Spain)*

RESEARCH CENTRES

Fraunhofer-ITEM
Institute for Toxicology and Experimental Medicine (Germany)

Centro Ceramico
Consorzio Universitario per la gestione del Centro di Ricerca e Sperimentazione per l'Industria Ceramica (Italy)

TECHNOLOGY PLATFORM

PESI
Plataforma Tecnológica Española de Seguridad Industrial (Spain)

MATERIALS SUPPLIERS

ABCR Laboratorios, S.L.
Coating materials (Spain)

Bulk Cargo Logistics, S.A.
Quartz (Spain)

QUARTZ USERS FROM DIFFERENT SECTORS:

Elastomers Union S.R.L.
Plastic materials (Italy)

Esmalglass, S.A.U.
Ceramic frits (Spain)

Fundiciones Fumbarri - Durango, S.A.
Foundry (Spain)

Mapei, S.P.A.
Adhesive materials for construction (Italy)

Innovaciones Técnicas Aplicadas a Cerámicas Avanzadas, S.A.U.
Ceramic colours (Spain)

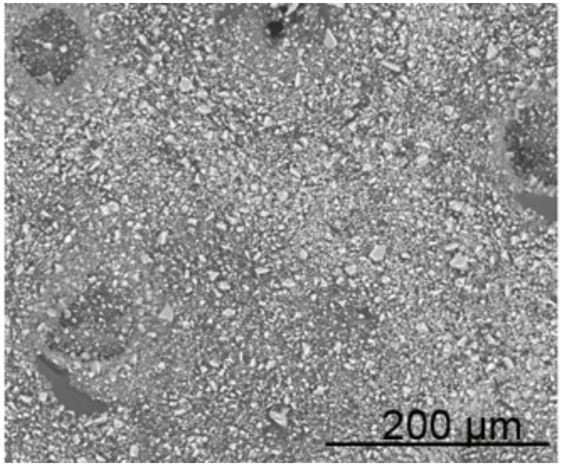
SECTORS INVOLVED AND RAW MATERIALS STUDIED

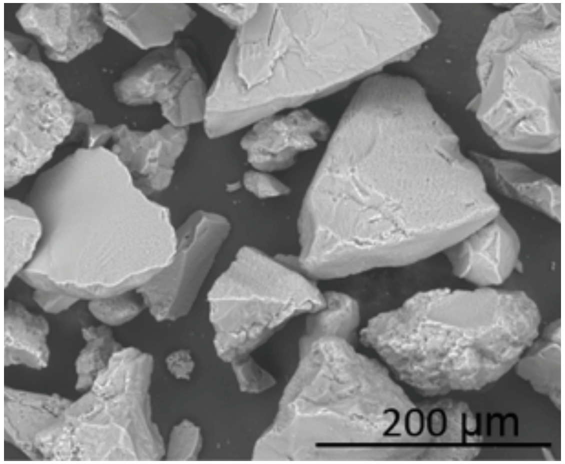
The sectors involved in the project are:

- **Foundry**
- **Ceramic frits**
- **Plastic**
- **Adhesive materials for construction**
- **Inorganic pigments**

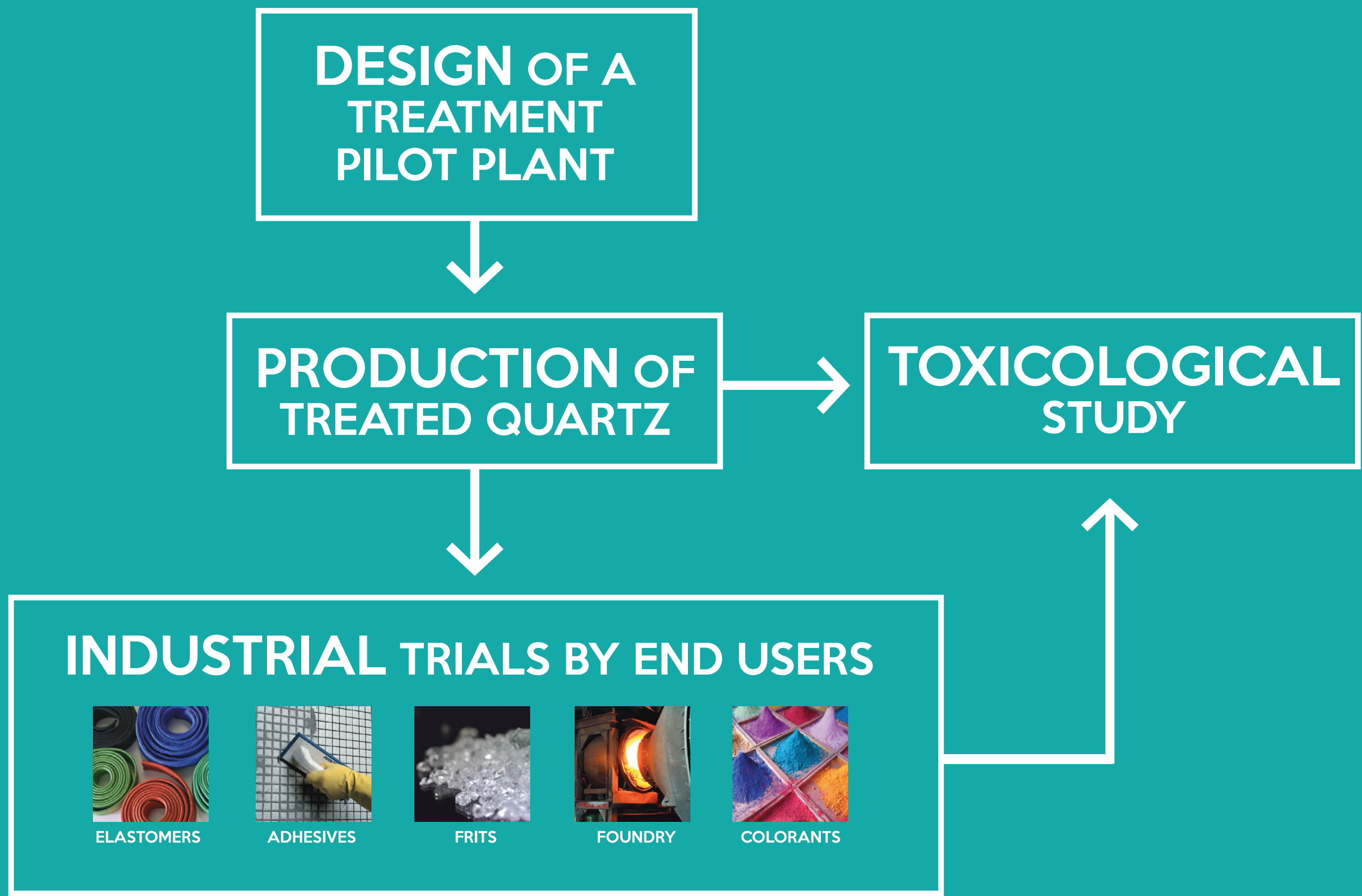
Quartzes used by the participant companies is between 3 and 300 μm.

Examples of two quartzes used





SCHEME OF THE TECHNICAL TASKS IN THE PROJECT
DESIGN OF A PILOT PLANT



METHODOLOGY USED

SILIFE has developed a dry process that is just as effective as the wet process developed in the SILICOAT project. The coating agents used (silanes) anchor themselves to the quartz particles, reducing RCS toxicity. Suitable quartzes with lower toxicity can be thus obtained for use in industrial processes.

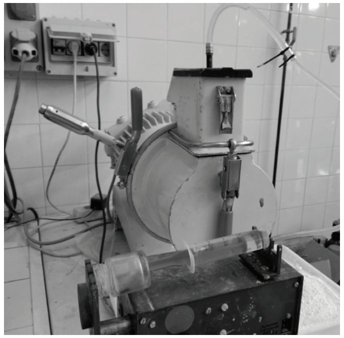
First, a laboratory mixer was used to verify the feasibility and efficiency of the method and coating stability.

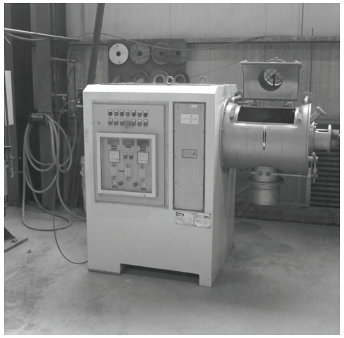
Once the laboratory-scale method had been established, this was reproduced in a specially prepared industrial mixer for this operation and the scale-up was verified to be feasible.

In this facility, a sufficient amount of each quartz provided by the user companies was prepared, using the appropriate coating agents in each case.

Finally, the treated quartz samples were sent to the corresponding companies to verify their feasibility.

Methodology used for dry coating of the quartzes

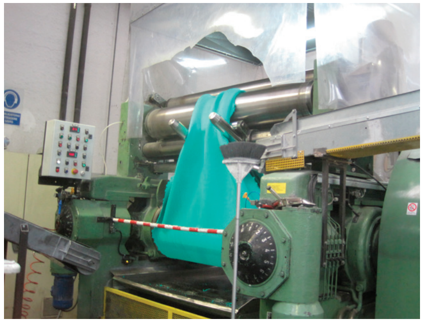




INDUSTRIAL TRIALS

Each user partner conducted industrial trials to identify possible problems. Although in certain cases some subsequent adjustments of applied coating agents or of the required coating application conditions were required, the results were generally satisfactory, from the point of view both of the execution of the production process and of end product quality.

Elastomers plant



Industrial trial in glaze plant

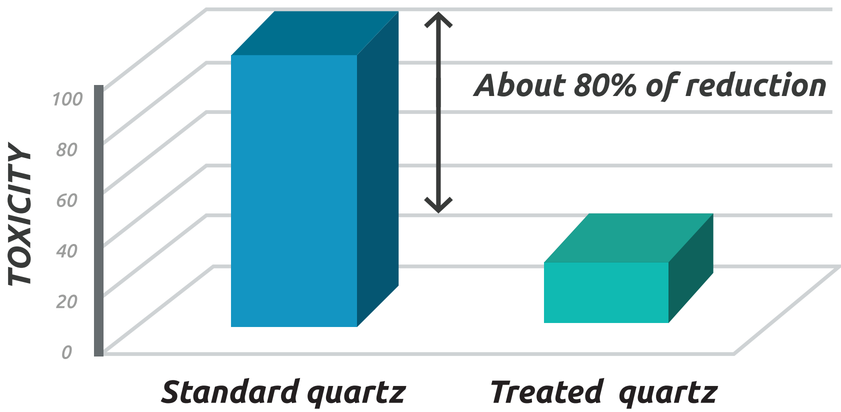
Industrial trial of adhesives

Frits plant

Foundry

TOXICOLOGICAL RESULTS

The following graph, by way of example, shows the reduction achieved with one of the treatments used.

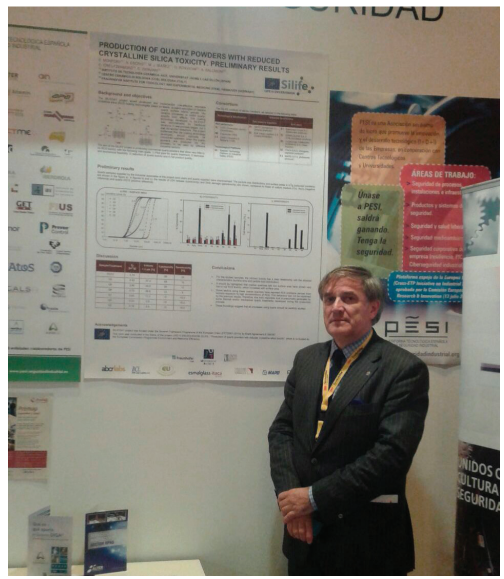


PROJECT DISSEMINATION

The advances and results reached by the work team are disseminated and discussed at congresses, technical conferences, sectorial fairs, follow-up meetings, scientific papers and through the project website *www. silife-project.eu.*

CEVISAMA – Valencia, February 2018

Event of the Campaign for the Health at Workplaces - Brussels, March 2019

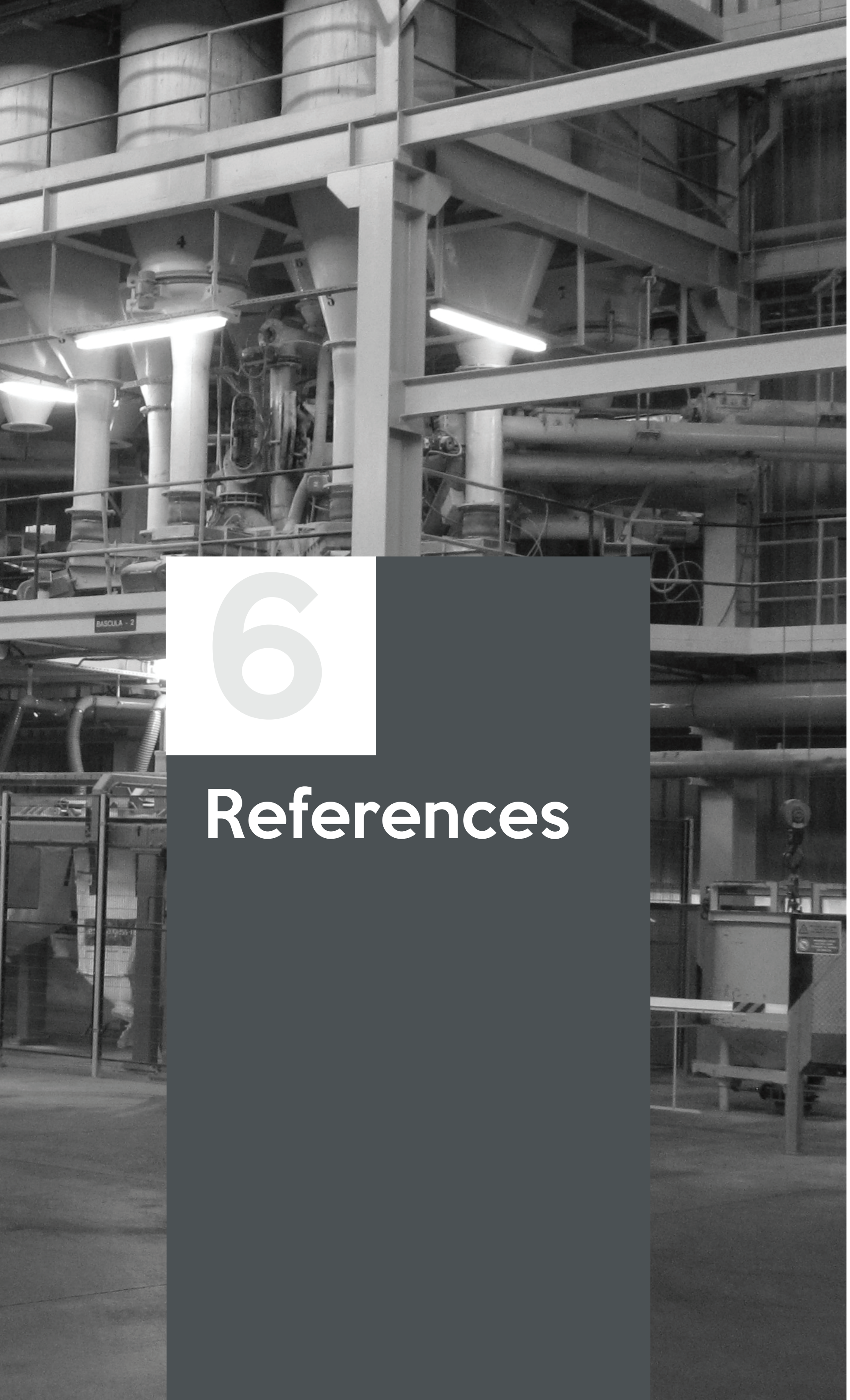


SICUR – Madrid, February 2016

WORK TEAM

FUTURE PROSPECTS

The technology developed in this project may be deemed available for use on an industrial level. The use of coated quartz in processes that differ from those studied in this project needs to be adapted in each case by means of a technical feasibility study that allows selection of the most appropriate coating agent in each case. The possibility of using raw materials with low or zero RCS toxicity can thus be extended to most of the industrial sectors affected by this issue.



6 References

Documents and websites of interest

Good Practice Guide on Workers Health Protection through the Good Handling and Use of Crystalline Silica and Products Containing it.
https://www.nepsi.eu/es

Directive (EU) 2017/2398 of the European Parliament and of the Council of 12 December 2017 amending Directive 2004/37/EC on the protection of workers from the risks related to exposure to carcinogens or mutagens at work.
https://eur-lex.europa.eu/eli/dir/2017/2398/oj

Guía técnica para la evaluación y prevención de los riesgos relacionados con la exposición a agentes cancerígenos o mutágenos durante el trabajo Royal Decree 665/1997, of 12 May BOE nº 124, of 24 May.
http://www.insht.es/InshtWeb/Contenidos/Normativa/GuiasTecnicas/Ficheros/Agentes_cancerigenos.pdf

Website of the Instituto de Tecnología Cerámica (ITC)
http://www.itc.uji.es/Paginas/default.aspx

Website of SILIFE project
http://www.silife-project.eu/

Publications related to the research line

- E. Monfort, M.J. Ibáñez, A. Escrig, et al. Respirable crystalline silica in the ceramics industries. Sampling, exposure and toxicology. cfi/Ber. DKG 85, 36–42 (2008).
- C. Ziemann, S.M. Reamon-Buettner, T. Tillmann at al., Naunyn- Schmiedeberg's. The SILICOAT project: In vitro and in vivo toxicity screening of quartz varieties from traditional ceramics industry and approaches for an effective quartz surface coating. Archives of Pharmacology 387, Suppl. 1: S104, Abstract 420 (2014).
- Ziemann C, Rahmer H, Escrig A, et al., Naunyn-Schmiedeberg' s. The SILICOAT project: approaches for an effective quartz surface coating in the traditional ceramics industry to increase workers' safety – toxicological investigations. Archives of Pharmacology, 388, Suppl. 1: S66, Abstract 263 (2015).
- C. Ziemann, O. Creutzenberg, M.J. Ibañez, et al. Selection of Additives for Reducing the Toxicity of Quartz in Ceramic Compositions. cfi/Ber. DKG 91, 63–9 (2015).
- C. Ziemann, A. Escrig, G. Bonvicini, M.J. Ibáñez, E. Monfort, Salomoni, O. Creutzenberg. Organosilane-Based Coating of Quartz Species from the Traditional Ceramics Industry: Evidence of Hazard Reduction Using In Vitro and In Vivo Tests. Annals of Work Exposures and Health, 61(4), 468-480 (2017).

Annals of Work Exposures and Health, 2017 1–13
doi: 10.1093/annweh/wxx014
Original Article
BOHS The Chartered Society for Worker Health Protection
OXFORD

Original Article

Organosilane-Based Coating of Quartz Species from the Traditional Ceramics Industry: Evidence of Hazard Reduction Using *In Vitro* and *In Vivo* Tests

Christina Ziemann[1*], Alberto Escrig[2], Giuliana Bonvicini[3], Maria Jesús Ibáñez[2], Eliseo Monfort[2], Arturo Salomoni[3] and Otto Creutzenberg[1]

[1]Fraunhofer Institute for Toxicology and Experimental Medicine ITEM, Nikolai-Fuchs-Str. 1, 30625 Hannover, Germany; [2]Instituto de Tecnología Cerámica–AICE, Universitat Jaume I, Campus Universitario Riu Sec, Avenida Vicent Sos Baynat, 12006 Castellón, Spain; [3]Centro Ceramico di Bologna (CCB), Via Martelli, 26, 40138 Bologna, Italy

*Author to whom correspondence should be addressed. Tel: +49-511-5350-203; fax: +49-511-5350-155; e-mail: christina.ziemann@item.fraunhofer.de

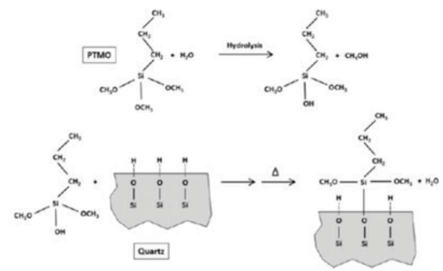


Figure 1. Hydrolysis of PTMO and coating reaction with reactive silanol groups on the quartz surface.

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