E. Monfort;
M.J. Ibanez;
A. Escrig
Universitat Jaume I. Castellón, España.

P. Jackson;
D. Cartldge
Ceram Research. Stoke-on-Trent. Staffordshire. United Kingdom.

B. Gorbonov
Naneum Limited, Canterbury, United Kingdom

O. Creutzenberg;
C. Ziemann
Institute of Toxicology and Experimental Medicine, Hannover, Germany.

Respirable Crystalline Silica in the Ceramics Industries

Sampling, Exposure and Toxicology

Abstract

This paper describes the work carried out during the development of the SILICERAM project, executed during the years 2004 to 2007, explaining both its goals and the actions carried out. It presents the equipment designed and constructed for sampling airborne particulate matter in the workplaces, and also the physicochemical determinations and toxicological tests carried out on the dust collected. Finally, it outlines the most important findings and conclusions that have been obtained in this project, as well as some measures and good practices that could be implemented in the ceramics industries to avoid or minimise the presence of dust in the atmosphere.

Background

The inhalation of crystalline silica, usually in the form of quartz, produces a reaction which results in a pathological disease known as silicosis. This is due to the accumulation of particles of crystalline silica in the pulmonary alveoli, which produces chronic scarring, leading to breathing difficulties [1]. The particles of crystalline silica must be small enough to reach the alveolar region of the lungs, not being deposited by diffusion, sedimentation or inertia in outside areas of the lower respiratory tract.

The particle size required for the alveolar deposition has been established by convention and it appears defined in the EN 481 standard [2]. The fraction of airborne particles which can reach the pulmonary alveoli (non-ciliated airways) is named, in this standard, the respirable fraction of the aerosol. For this reason, the agent able to produce silicosis is the Respirable Crystalline Silica (RCS), which is the name given to this pollutant.

Fig. 1 shows schematically the different fractions defined in the EN 481 standard, while in Fig. 2 appears the separation efficiencies to be met by the sampling systems of each one of the different fractions.

In the traditional ceramics industries, quartz containing mineral substances are used as raw materials, such as clays, sands and kaolin. Furthermore, in many cases, separated quartz is also used. Consequently, in the workplace environments of such industries there can exist quantities of RCS, where the exposure can be prevented by strategically placed extraction systems, minimizing its dispersion into the environment. Thanks to the implementation of these systems and the design of processes with less release of aerosols, diagnosis of silicosis associated with the manufacture of ceramic products have been reduced gradually, currently resulting in very little incidence of this disease in these sectors.

Despite the achievements in the eradication of silicosis in the ceramic manufacturing sector, the goals must be revised, since in 1997 the *International Agency for Research on Cancer (IARC)* classified the RCS as "carcinogenic to humans (category 1)" [3]. In addition, promoted by this pronouncement, the *Scientific Committee on Occupational Exposure Limits to Chemical Agents from the European Commission (SCOEL)* recommended that the levels of exposure to RCS inhaled in the form of quartz or crystobalite, remain below 0,05 mg/m^3 [4], a value that is more restrictive that the current exposure limit that is in force in most EU coun-

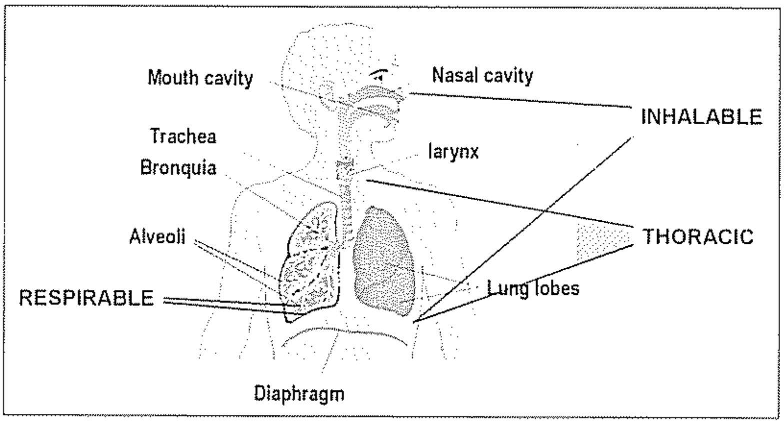


Fig. 1
Schematic representation of the respiratory tract, indicating the different areas of particle deposition

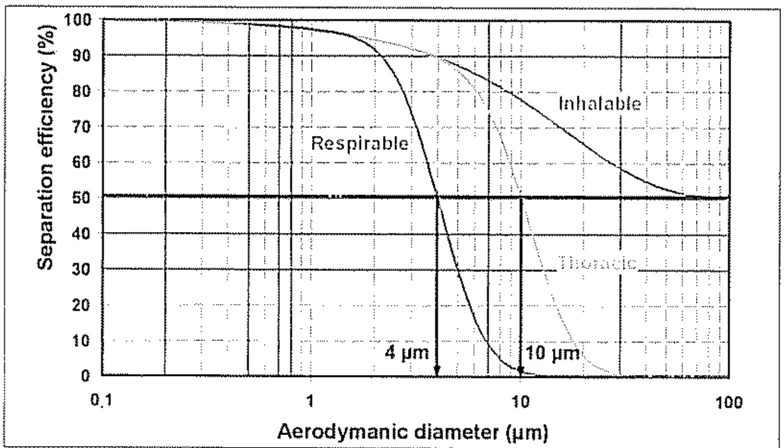


Fig. 2
The inhalable, thoracic and respirable conventions as percentages of total airborne particles, from EN 481

tries (from 0,1 to 0,3 mg/m³ for quartz) [5].

The SILICERAM Project

There is some controversy about the IARC's position on the classification of the RCS as a carcinogen for humans. On the one hand, epidemiological studies seem to indicate that, indeed, the fact of suffering from silicosis increases the likelihood of contracting lung cancer, but does not seem to have a direct and conclusive cause-effect relationship between the exposure to this agent and the risk of contracting cancer, without the previous presence of silicosis [3,6]. On the other hand, the laboratory studies aimed at clarifying this issue are often carried out with reference materials, such as quartz DQ12, whose particles have a clean surface, with a higher pathological effect than the industrial samples [7].

The European collective project SILICERAM "Studies legislation aimed at assisting and encouraging continual improvement strategies in the field of respirable crystalline silica" intended to clarify some of these issues in the field of ceramics industries. In this regard, one of the main objectives of the project was to obtain information about the toxicity of aerosols containing RCS present in the companies belonging to different sectors of traditional ceramics.

The present article gives a brief overview of the work methodology followed in the SILICERAM project and presents a summary of the more significant findings and conclusions. The consortium formed and the project objectives are described in detail in a previously published article [8].

SILICERAM was structured in 6 work packages (WP), the outline of which can be seen in Fig. 3.

As a preliminary stage, which is necessary for the development of the subsequent investigation, it was needed to identify a "positive control" (WP1). That is to say, a sample of silica (reference material) with proved toxicity for contrasting the industrial samples. In parallel, it has been necessary to build some equipment for sampling (WP2), which is explained in paragraphs 2.1.2 and 2.1.3. The WP3 began to complete the WP1 and WP2, and includes the capture of samples for both physicochemical (2.1.2) and toxicological (2.2.2) testing. With regard to WP5, it was carried out in an independent way, and consisted in the evaluation of the exposure to RCS by workers, as well as training activities for them. Finally, WP6 includes the labours about the reporting of the results.

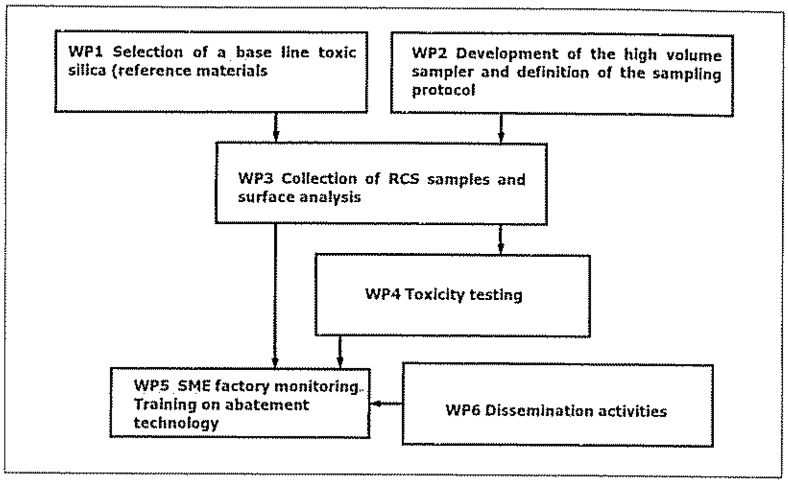


Fig. 3
Work packages and interrelation between them

Experimental

Sampling in Industrial Environments

Personal sampling

To quantify the presence of RCS in the different workplaces of the companies, conventional personal samplers have been used. These samplers are portable devices for measuring the RCS concentration to which a worker is exposed while he carries out his activities. They are equipped with a portable pump, which is secured to the waist of the worker, and that is responsible for the air flow through the system. The respirable size fraction is selected by a cyclone which is placed at the height of the worker's clavicle. The dust with respirable size is deposited in a filter located between the cyclone and the pump. The amount of crystalline silica in the filters was determined by X-ray diffraction. Fig. 4 shows the pump and the cyclone which constitute one of these samplers.

Samples for chemical and toxicological characterization

To characterize samples chemically and toxicologically a novel instrument allowing the capture of the sufficient quantity of material meeting the particle size requirements established by the respirable convention was required. To this end, two high-volume (static) samplers (HVS), which work at 1000 l/min, were designed and built, allowing the collection of large amounts of particulate matter (Fig. 5). Instruments were equipped with a pre-separator with a cut off diameter of 4 m according to EN 481. The pre-separator utilised a concept of self-stabilisation of air trajectories and acts as a cyclone with cut off insensitive to the pressure drop in the working regime. Samples were collected onto 150 mm porous silver filters.

With the HVS, five samples were collected from four subsectors of the ceramics industry: bricks, tiles, table-

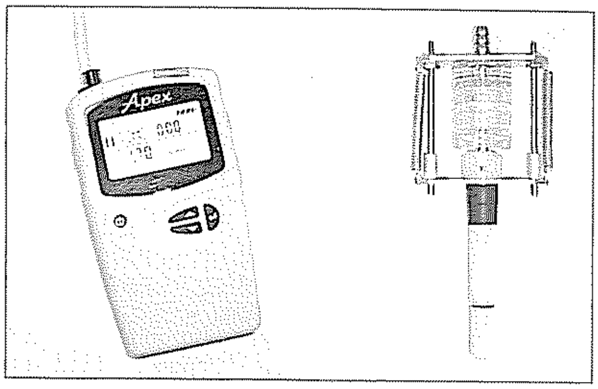


Fig. 4
Suction pump staff (left) and cyclone (right)

Industrial sector	Process step	RCS (%)
Tiles	Pressing	8,1
Bricks	Pressing	7,8
Tableware	Spray drying	5,8
Tableware	Slip casting	3,1
Refractories	Pressing	3,7

Tab. 1
Samples tested contained in SCR and the same

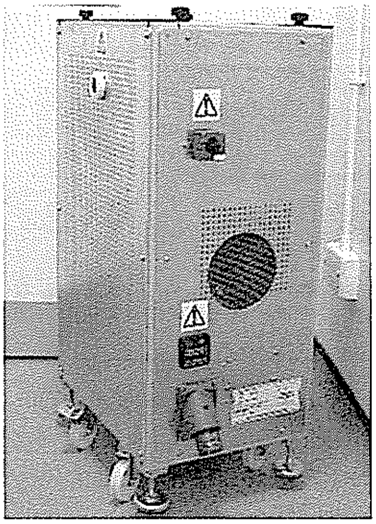


Fig. 5 High volume sampler (HVS)

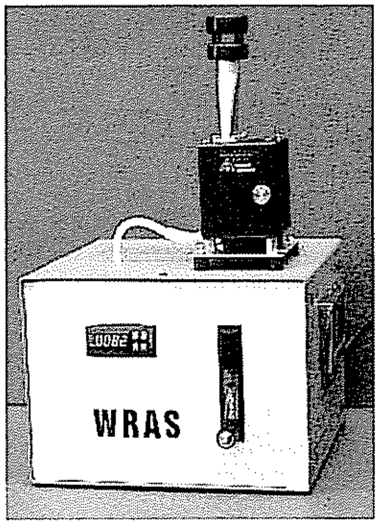


Fig. 6 WRAS cascade impactor

ware (granulate and cast) and refractories The sampling points were the sections of the factories where the exposure to RCS was higher, identified on the basis of the results obtained with personal samplers.

Determination of particle size distributions

Samples were also obtained with a unique cascade impactor fitted with an iso-kinetic inlet to determine the aerodynamic size distribution of the airborne particles in the studied industrial environments. The mechanism of separation of the particles according to their aerodynamic size in such engine is based on the inertial impaction The particles are forced to change of direction at each stage on which the equipment is divided: those particles which have too much inertia to follow the flow line are retained on the surface of the particle collector. Since larger particles have a higher inertia, they are deposited in the early stages, while the thinner particles are captured in the last ones

The sampling system used is called a WRAS (Wide Range Aerosol Sampler) Fig 6, Originally it was designed by *WRAS Technology Limited* (now *Naneum Limited*, www.naneum.com). This equipment had been developed in an earlier EC funded project by Middlesex University, but the original apparatus was redesigned to meet the needs of the SILICERAM project The WRAS is a static sampler for determining the particle size distributions of airborne matter in the range of aerodynamic sizes between 0,25 μm and 20 μm, in seven stages with geometrically spaced cut off diameters. Moreover, it is possible to determine the amount of quartz present at every stage by X-ray powder diffraction, and consequently obtain the size distribution of airborne quartz.

Characterization of the Samples

Physicochemical characterization

The physicochemical characterization of the samples consisted of:

- The identification of crystalline phases present in the samples and quantification of RCS by X-ray diffraction (XRD)
- The observation of the samples by scanning electron microscopy (SEM).
- The energy dispersive microanalysis (EDXA) of the particles observed by electron microscopy. This analysis was made at several acceleration potentials of the electrons in order to obtain a better knowledge about the composition of its surface.

Toxicological characterization

One of the difficulties that are often found in characterizing the toxicity of a particulate pollutant is that a general, particle-induced toxicity effect cannot be clearly separated from a toxic effect mediated by a component of interest, e.g in this project from that of quartz. However, in the case of quartz-related biological effects this problem could be resolved partially within this project by comparing the biological responses of the dust samples in the presence and absence of aluminium lactate Aluminium lactate inhibits the toxic action of crystalline silica, by covering its reactive surface [7] Thus, it was possible to distinguish the RCS contribution to the overall toxicity of the dust samples tested. However, this tool succeeded only partially, because the quartz content in the collected factory dusts was < 10 mass-%. For that reason, other dust components or particle-like effects seemed to contribute overproportionally to the total dust activity observed.

In order to establish a toxic scale, the collected industrial samples were compared with DQ12 quartz (positive control) which, as quoted above, has a greater adverse activity than other quartz varieties usually found in workplaces. Therefore, DQ12 is used as a standard positive quartz in the EU [7]. In addition, a particulate negative control was established for the in vitro assays, i.e fumed alumina A contrived sample prepared from feldspar, china clay and DQ12 quartz (CS 30 %), was also included in the toxicological tests, in order to assess the impact of quartz accompanying minerals on quartz toxicity.

The toxicological characterization of the dust samples was performed using a battery of tests on cell cultures (in vitro tests) and an animal study (in vivo) In the in vitro assays, the RCS-containing dust samples were dosed on an equal particle mass basis, whereas in the in vivo test, the quantity of sample administered to the animals was calculated taking into account the content of quartz of each sample, in order to use equivalent quartz doses.

In vitro testing

In the in vitro tests primary alveolar macrophages and an alveolar macrophage cell line were used to assess dust-induced biological reactions. Alveolar macrophages are a first site of contact for particles in the lung and are responsible for the biological process known as phagocytosis, which is the mechanism for removal of particles in the pulmonary alveoli They surround and trap any strange matter and drag it, due to their motility, to the ciliated tracheal escalator or through the lymphatic vessels Therefore, if some particles have the ability to harm these cells, then the drainage process is limited and particles accumulate in the alveoli

The battery of in vitro tests carried out was focused on biological events known to occur after particle deposition in the alveoli of the lung, i.e cell damage (cytotoxicity), inflammation, and DNA-alterations (genotoxicity).

In vivo testing

Based on the results obtained from the in vitro tests, two factory dust samples were selected for the subsequent 28-day in vivo pilot study. Tableware granulate and tableware cast, the two factory samples with the highest and lowest effects as detected in the screening assays, were administered by intratracheal instillation to a group of rats. The positive and negative controls were quartz DQ12 and titanium dioxide (Bayertitan T), respectively. Both, the acute effects (after 3 days) and the subchronic effects (at 28 days) were evaluated using inflammatory endpoints (bronchoalveolar lavage and histopathology).

This pilot study aimed at providing legislators with first in vivo data while devising modifications of existing threshold limit values for quartz-containing ceramic dusts.

Results and Discussion

Physicochemical Characterization of Respirable Aerosols

A total of five samples of respirable dust in four sectors of traditional ceramic products manufacturing were obtained with the HVS. Tab. 1 describes the sampling points selected in each sector and the RCS content of the samples, determined by XRD. The process compositions can be prepared solely from clays containing quartz (such as bricks or some ceramic tiles) or adding quartz as an individual raw material (porcelain). Nevertheless, the quantities of RCS identified in the respirable samples ranging in a quite narrow interval, from 3,1 % to 8,1 %.

Morphology of the samples was observed using a scanning electron microscope and several particles were selected in each of them for EDAX. Tab 2 contains average concentrations of SiO_2 and Al_2O_3 obtained in the microanalysis of the selected particles. These values indicate the amount of aluminosilicates present in the samples, as it will be seen below; they play an important role in the quartz toxicity.

The surface coating of the particles of quartz by other minerals, or by molecules adsorbed on its surface, can inhibit the toxic action [10,11]. To assess this effect the methodology described in [12] was followed, which consists in conducting microanalysis of the quartz particles at different acceleration potentials of the electrons in the electron microscope. By reducing the potential, it also diminishes the penetration of the electron beam, which results in a more superficial analysis. Thus, if the particles of quartz are coated, for example with clay, it should be expected that the reduction of the potential of the electron gun will increase the aluminium content in the analyzed area, as are shown in Fig 7.

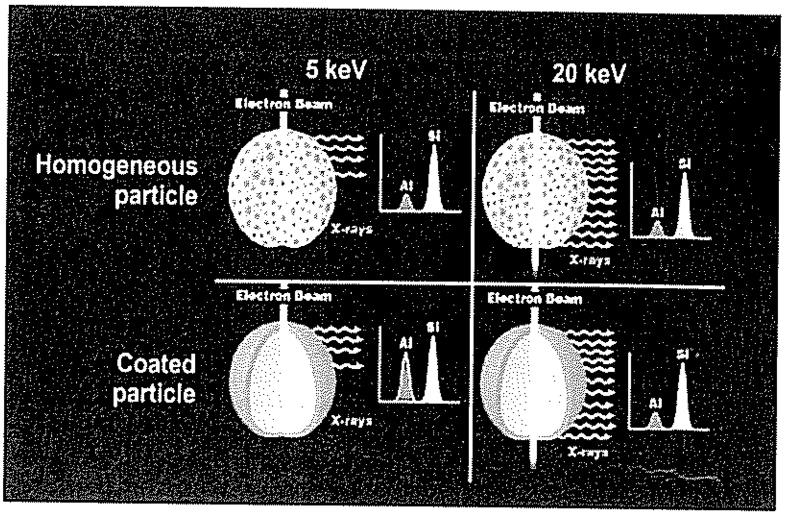


Fig. 7
Effect of the acceleration potential of the electrons on the intensity of the resulting peaks. The particle with relatively homogeneous aluminium content (above) provides similar microanalysis, while the coated particle (below) shows an enrichment in aluminium when the potential is reduced.

By applying this method of analysis on the samples tested, enrichment in aluminium in the surface analysis of the particles has been appreciated in some cases, which may be indicative of the presence of these coatings.

Toxicological Characterization of Respirable Aerosols

Important outcomes of the project came from the toxicology studies.

Concerning the in vitro part, it was possible to establish an in vitro screening battery which was able to differentiate the toxic potential of quartz-containing ceramic dust samples and to evaluate its quartz-dependent proportion by aluminium lactate treatment. It could be demonstrated that there were striking differences in the cytotoxic, pro-inflammatory, and genotoxic potential of the different dust. However, due to the low quartz content of the samples, it was impossible to directly compare the different quartz varieties. A quite interesting finding arose from the contrived sample. Although the contrived sample exhibited a higher quartz content than the factory samples, it seemed to be less or equally active in the in vitro tests, pointing to a quartz covering effect of the other dust components (feldspar and china clay) or impact of the mixing procedure.

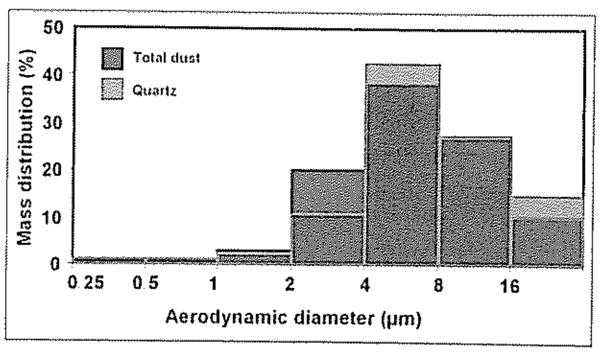
The interesting observation concerning the contrived sample could be confirmed in the in vivo study, which also demonstrated that the lung toxicity of various quartz-containing dusts can indeed be differentiated. Irrespective of its quartz-content, the contrived sample was nearly inactive in the in vivo study, whereas the two factory samples mediated graduated adverse effects, which were however less pronounced and not progressive as compared to the positive control DQ12.

In conclusion, the results of the toxicology studies demonstrate that the regulatory discussion on quartz-containing dusts needs individual approaches to the type (physicochemical properties, intrinsic toxicity) of particle sample under concern (see also separate papers on toxicological studies within the SILICERAM project; Particle & Fibre Toxicology: under preparation).

Personal Sampling of RCS

For the exploitation of available data from personal sampling of RCS, the workplaces studied were grouped into common operations within dif-

Fig. 8
Mass size distributions of total airborne dust and quartz for a sample taken at the pressing section of a ceramic tile manufacturing company (note that total dust and quartz distribution are stated in percentage not in absolute values)



Sample	SiO_2 (%)	Al_2O_3 (%)
Tiles	57,6	22,2
Bricks	65,7	20,8
Tableware (spray drying)	69,6	27,0
Tableware (slip casting)	64,0	20,4
Refractories	34,6	15,1

Tab. 2
SiO_2 and Al_2O_3 content in the samples

ferent ceramic sectors. In particular, the raw materials preparation includes both the body conditioning for shaping (milling, granulation, etc.), and the processing of the glaze. Similarly, the shaping workplaces are grouped according to the techniques used, distinguishing whether the composition was ceramic slurry (wet shaping) or in dusty form (dry shaping). Likewise, there are some operations that only occur in some factories, such as glazing and firing.

The results obtained from personal sampling are summarized in Tab. 3. It has been found that the values obtained show a rather skewed distribution with a characteristic tail toward elevated RCS concentrations. For this reason, it was opted for the median (percentile-50) as a robust estimator of the distribution, which has been supplemented by the upper quartile (percentile-75) which may indicate the existence of sporadic high values.

A review of Tab. 3 shows that the most critical operations, from the standpoint of exposure to RCS, are those where ceramic compositions with quartz are processed in dusty form: raw materials preparation and dry shaping. These are the sections where the proposed limit of 0,05 mg/m³ would have a greater impact, since more than half of the samples would exceed it. Occasional excesses in some workplaces, such as with maintenance workers, are also noted which may be due to exposures in other sections, malfunctions of equipments or punctual auxiliary operations.

Distributions Aerodynamic Sizes and Dosimetric Calculations

The aerodynamic size distributions (ASD) of the aerosols in the workplaces with a greater presence of RCS were obtained with the WRAS. One could also obtain the quartz ASD from the XRD analysis of the dust collected at each of the stages which constituted the WRAS. For example, Fig. 9 demonstrates the ASD of total dust and quartz for a sample obtained in a ceramic tile factory.

Fig. 9 is quite representative of the ASD obtained, as it was noted that, given the DTA globally, the quartz seems a coarse component of the aerosol. However, in the stages corresponding to the finer sizes (0,25 ÷ 2 μm) high contents of quartz were found. It should be noted that the uncertainty associated with the latter stages is higher, because the mass caught on them is much less than in the upper stages.

The purpose of the determination of the ASD was to calculate doses of RCS received by the workers. To this end, there are mathematical models used to establish the amount of aerosol that is deposited in each region of the respiratory tract [13]. The total deposition curves obtained from these models have the shape illustrated in Fig. 10. For large aerodynamic sizes the deposition mechanisms are the sedimentation and the inertial impact, while for small sizes Brownian diffusion predominates. For intermediate sizes, all types of mechanisms are less important, which means a decrease in the deposition.

Let's denote $E(D_{ae})$ the deposition efficiency of particles in the alveolar region of the lungs. Then the mass of deposited particles is given by:

$$c\,f\,(D_{ae})\cdot V\cdot E(D_{ae})$$

where c is the concentration of particles, $f\,(D_{ae})$ is the probability density of existence of particles with aerodynamic size D_{ae} (DTA) and V is the air volume inhaled during the exposition. Fig. 11 shows schematically the meaning of the of pulmonary deposition efficiency.

Based on the concentrations and the ASD obtained with the WRAS doses of RCS were calculated and compared with those obtained with the respirable convention. Doses calculated from the models have been a 53 70 % of those obtained with the convention.

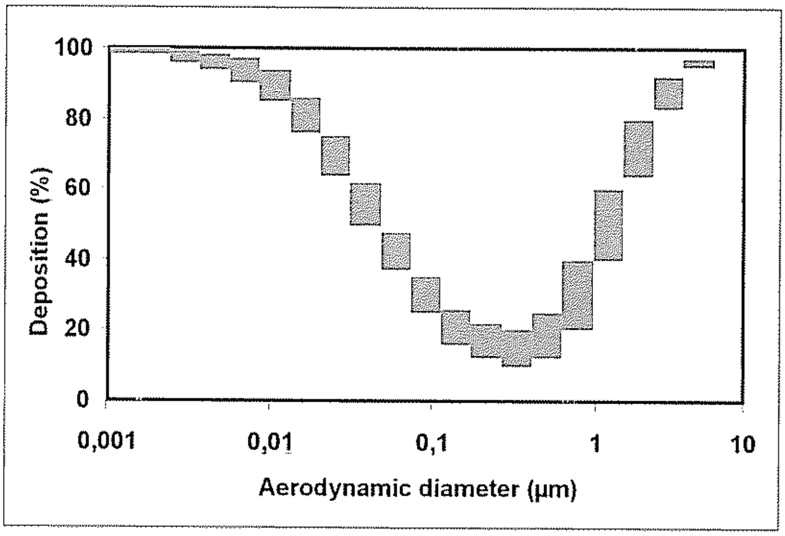


Fig. 9
Lung deposition as a function of aerodynamic size. The ranges of variation are due to uncertainties in age, breathing rate, etc

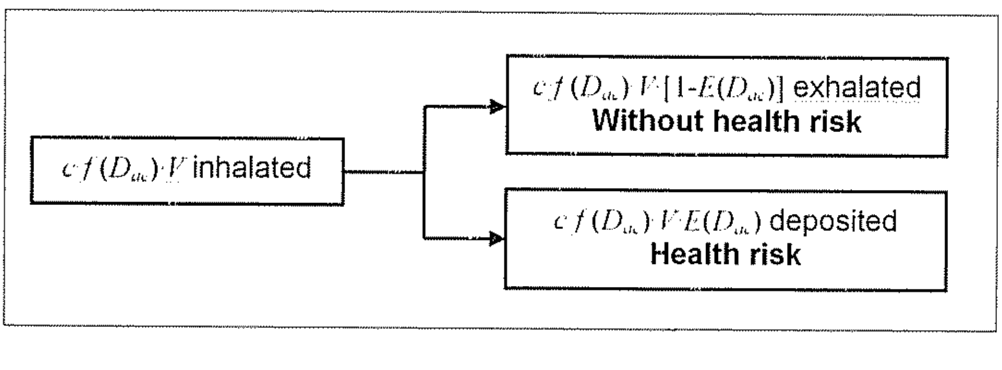


Fig. 10
Fractions after inhalation of particles

Conclusions

The work has made the following findings and conclusions:

- A high volume sampler (HVS) has been developed that enables collecting enough sample of respirable dust in industrial environments to carry out its physicochemical and toxicological characterisation.

- It has been found that the quartz content of the respirable dust captured with the HVS is significantly lower than the composition used in the industrial sections where the samples were taken.
- A battery of in vitro assays has been selected that allow the classification of toxic effects involved in the development of diseases associated with crystalline silica (inflammation, cytotoxicity and genotoxicity)
- The usefulness of aluminium lactate in cell culture experiments to distinguish the toxic effect of crystalline silica from the effect of other dust components was confirmed. Thus, it is possible to determine the part of toxicity of dust samples linked to respirable crystalline silica in industrial samples.
- All samples have submitted lower industrial biological activity in in vitro tests than the positive control, consisting of quartz DQ12. Similarly, the contrived sample of DQ12 quartz, together with clay and feldspar, has been less active than the positive control, containing exclusively DQ12. Therefore, a certain inhibitory effect of clay minerals on the toxicity of quartz can be supposed.
- The in vivo tests have proved consistent with those obtained by in vitro tests, both for the acute effects and for the chronic ones. It thus confirms the smallest biological activity of the samples obtained in industrial environments with respect to DQ12 quartz.
- The workplaces with higher exposure to RCS were, as expected, those associated with the handling of raw materials with quartz dust in the composition
- A wide range sampling system WRAS has been used for the determination of the mass aerodynamic size distributions of aerosols present in the workplace environments of the ceramics industries. From these distributions, doses in the alveolar region are calculated using state of the art mathematical models. These have proved to be significantly lower than those calculated by the definition of the respirable fraction of EN 481
- The actual health risk determined from the size resolved sampling (WRAS) is lower than the health risk obtained with current methodology based upon total respirable fraction sampling using the personal sampler. Therefore, the current methodology seems to overestimate the actual health risk

Process step	number of samples	RCS concentration	
		Median (mg/m³)	Upper quartile (mg/m³)
Raw materials preparation	53	0,060	0,110
Wet shaping	43	0,037	0,058
Dry shaping	16	0,119	0,145
Glazing	70	0,026	0,052
Firing	30	0,008	0,036
Sorting, packaging	31	0,011	0,027
Maintenance	11	0,004	0,073

Tab. 3
Results of the assessment of exposure to RCS in the ceramics industries

Recommendations for the Ceramics Industry

While it is true that currently the incidence of silicosis is virtually non-existent at traditional-ceramic companies, it is desirable to keep the working atmosphere clean, avoiding as much as possible the presence of dust in the working environment.

In that sense, it is necessary, especially in the areas of business in which raw materials are handled, have effective means of extracting powder, are kept in good condition. Among the measures that could be implemented to avoid the presence of dust in the atmosphere, some of them could be highlighted as follows:

- Installing located extractions in the dusty operations.
- Separation, whenever possible, of the sections which produce dust, thus avoiding contaminating other cleaner sections
- Installation of ventilation and localized systems.
- Installation of water sprays to clean the atmosphere of work
- Installation of air purification eliminated abroad: fabric filters.
- Avoid cleaning facilities with pressurized air, replacing it by vacuuming or cleaning with water.
- Control circuits of raw material, waste, and any dusty material.
- Implementation of cleaning and preventive maintenance.

In addition to these measures, precautions in extreme cases are necessary where pure quartz is handled as a raw material. Particularly important is to have efficient local extractions in specific points in the handling of this material, so that the spray does not spread. Moreover, if workers carry out operations at the point of unloading or cleaning those quartz dusts, must have, if the risk assessment of the operation so determines, masks and adequate protection, and some form of locker or closet where they are able to store them and keep them clean when they are not used. Also, they should be kept duly informed about the impact on their health associated with respirable crystalline silica dust and must be trained on the prevention of exposure to dust, finding that controls function and how to use them, when and how to use the masks provided and what should be done if something goes wrong [14].

In many cases, before having to make investments to install new measures for dust removal and disposal, the situation would be much improved incorporating some of the above measures, related to the organization of work, especially with regard to periodic cleaning measures of plants and preventive maintenance of facilities.

It is worth noting that although the periodic revisions of dust concentration and RCS reveal that they are, in general, below the limits currently allowed. Nevertheless, companies should be very concerned about the observance of good practice in the handling of dusty materials and crystalline silica in particular, to maintain the concentration as low as possible, because the EU, may in the future, opt for legislation that sets lower limit levels. In this sense, the authors strongly recommend following the advices given in the Good Practice Guide [14]. Whilst companies will be encouraged to review their position with respect to the possible new limits, in order to take the necessary steps before its entry into force, the Siliceram project has created a strong case to say that crystalline silica encountered in the ceramics industry has a particle size distribution, chemistry (and so toxicity) that suggests current limits are an effective protection against worker ill-health.

Acknowledgments

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