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Airborne free silica particles: a hazard to workers health

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Resumen

Las actividades relacionadas con la extracción, transformación y manejo de materiales que contienen partículas de sílice libre son tan antiguas como la historia de la humanidad. Las condiciones geológicas de Brasil han atraído un significativo número de compañías mineras y posteriores industrias manufactureras que emplean materias primas que presentan cuarzo en su paragénesis. Entre los riesgos que afectan a los trabajadores involucrados en estas actividades, la exposición a polvo permite la posibilidad de enfermedades del sistema respiratorio. La mas critica entre ellas es la silicosis una enfermedad del pulmón crónica e incurable, causadas por la inhalación de polvos que contienen cristales de sílice libre. La evolución de la silicosis es progresiva e irreversible, conduciendo a la invalidez, tuberculosis, cáncer pulmonar y finalmente la muerte. Este artículo presenta la metodología empleada en Brasil para monitorear ambientes de polvos que contienen cristales de sílice libre. Se presentan y se discuten datos cuantitativos recogidos en ambientes industriales, nominalmente una mina subterránea de oro y una operación de soplado de arena, en las que se requiere de máscaras especiales para los trabajadores de estas faenas.

Palabras claves: sílice libre, polvos ambientales, silicosis.

Abstract

Activities related to the extraction, transformation, and handling materials containing free silica particles are as old as the mankind history. The geological conditions of Brazil attracted since the colonial period a significant number of mining companies and later transformation industries operating with raw materials presenting quartz in their paragenesis. Among the risks affecting the workers involved in those activities, the exposure to dusts enhances the possibility of breathing system diseases. The most critical among them is silicosis, a chronic and incurable lung disease, caused by inhaling dusts containing crystalline free silica. Silicosis evolution is progressive and irreversible, leading to invalidity, tuberculosis, lung cancer, and finally to death.This paper presents the methodology utilized in Brazil for monitoring environmental dusts containing crystalline free silica. Quantitative data collected in industrial environments, namely an underground gold mine and a sand blasting operation, are presented and discussed. Special masks are required for underground gold mine workers and sand blasting will be banned in 2010.

Keywords: free silica, environmental dusts, silicosis

1. Introduction

Silicosis is the oldest, most common, most serious and most important among the pneumoconioses, being understood as the accumulation, in the lung, of dusts containing free or non combined silica. As in most of the nations, silicosis is recognized by the Brazilian legislation as a professional or labor disease, the consequences being classified as labor accidents. Free silica particles contained in dusts reach the lungs alveoli whenever their average size is between 0.5 μm and 10 μm.

Since 1995, the Brazilian government, concerned with activities presenting potential for generating air pollution, developed programmes for preventing environmental risks and protecting the respiratory system. The importance of these programs arises from the fact that workers, who perform activities under unhealthy environments, inhaling dusts containing free silica, are prone to acquire silicosis, a chronic disease, with irreversible evolution, lacking of specific healing.

The correct evaluation of the concentration and average size of free silica particles present in a sample of environmental dust requires careful procedures in order that the analytical results represent with accuracy the environment under investigation (Cançado, 1996). The most significant procedures are:

1. the knowledge of the raw materials utilised in the process, the unit operations, the final products, and the adopted control techniques;
2. the correct preparation of the collecting system (cassette, filter, filter holder, and pump) as well as the adequate performing of the in situ operations;
3. the adequate choice and procedure of the analytical method utilized in the quantitative determination of the weight of free silica in the sample, as well as the determination of the average size of the airborne particles.

Among several activities in the mining and metallurgical business that produce airborne free silica particles, sand blasting and underground mining are particularly hazardous

This paper presents the analytical methodology for quantifying the concentration and average size of free silica particles present in a sample of environmental dust.

The procedure is illustrated by results of field monitoring, performed at Brazilian companies presenting potential for the emission of free silica in the work environment, namely an underground gold mine and a sand blasting industry.

2. Silicosis

Several symptoms of respiratory diseases are associated with inhaling, retaining, and tissue reactions of mineral dusts (Fishman, 1985). These dusts produce different effects on the lungs. According to the International Labor Organization, pneumoconioses are defined as "lung diseases caused by the accumulation of dust in the lungs and tissues reaction to the presence of these dusts".

Pneumoconioses probably exist since men started to excavate the earth's crust. Among all pneumoconioses, silicosis has caused the largest number of victims, affecting workers from different branches of activity. Silicosis is caused by inhaling crystalline free silica in any of its main species: quartz, cristobalite, tridymite. This lung disease has no cure, presents progressive evolution, is irreversible, may lead to incapability for work, invalidity, and increase in susceptibility to tuberculosis, and, frequently, causes the death of the affected patient. It manifests as a nodular lung fibrosis and, in general, it may take many years or even decades to present symptoms. The disease progress even after the exposure is interrupted.

Materials containing small amounts of crystalline free silica may also be dangerous if used in a way that produces high concentrations of dust. Extremely high exposures are associated with shorter latency time and faster progression of the disease.

Despite being one of the oldest occupational illnesses, with earlier reports coming from the XIXth century, silicosis still kills thousands of workers every year in the whole world. Thousands of new cases are diagnosed in many parts of the world, predominantly in

developing countries, where industrial activities involve the exposure to silica.
The development of the disease depends on several risk factors, such as: length of exposure, particles dimensions, concentration and mineralogical composition of breathable dust, integrity of the mucous cilliary transport system and of the immunologic responses, concomitance with other respiratory diseases, bronchial hyper-reactivity, individual organic response.

Particles smaller than 10 μm are more prone to penetrate the alveoli, from where the macrophages try to remove them. Nevertheless, these crystalline free silica particles break and kill the macrophages. The lung tissues react producing fiber nodules and scars around the retained silica particles. The formation of a large number of scars after long exposure renders the alveolar surface less elastic, decreasing the breathing capacity, causing the death of the worker.
Some illnesses often occur in association with silicosis. A frequent death cause of persons suffering from silicosis is lung tuberculosis or silico-tuberculosis. Other causes of death are respiratory insufficiency (due to massive fibrosis), lung emphyzema, and heart failure.

The chronic obstruction of the aerial ducts may also be associated with exposure to silica.

It is difficult to clearly determinate the minimum exposure level at which no adverse effect to the worker health is observed. This difficulty is due, mainly, to confusing factors caused by illnesses associated with silicosis, besides the smoking habit, common among workers.

3. Brazilian legislation

The Brazilian legislation (Standard NR-15, annex 4) defined tolerance limits for mineral dusts, establishing limits for occupational exposure to three types of mineral dusts: asbestos, crystalline free silica, and manganese and their compounds (Labor Ministry, 1992).

The Brazilian tolerance limits were based on recommendations of the ACGIH (American Conference of Governmental Industrial Hygenists) issued in 1974, being corrected for the 48 hours per week work journey in effect in 1978. Most of these limits have not yet been reviewed, without taking into consideration that many substances present in the Brazilian list received the indication of carcinogenic potential, including silica.
The current occupational exposure limit, recommended by ACGIH, for crystalline free silica as quartz, in the breathable fraction is 0.05 mg/m^3, while the Brazilian limit is still calculated by the equation:

$$TL = 8/(\%SiO_2 + 2) \qquad (1)$$

Upgrading analytical methodologies and developing new detection techniques, resulting in enhanced sensitivity and specificity, may be integrated with procedures for early diagnosis, prevention of illnesses and correction of deviations from acceptable levels for working environments.
Sand blasting activities will be banned in 2010.

3.1 National action: national program for elimination of silicosis

Actions for setting up the National Program for Elimination of Silicosis (PNES, in Portuguese initials) started in December 2000, receiving incentive from the Brazilian branch of the International Labor Organization (ILO). The PNES proposes the development of a group of multidisciplinary actions aiming at reaching the objectives of the international program jointly proposed by the International Labor Organization and the World Health Organization (WHO). The targets of this group of actions are a sharp decrease in the incidence rate of silicosis by 2010 and its complete elimination as an occupational health problem until 2030.
Incentives are being given to the cooperation among governmental agencies, employers and workers organizations, and labor safety and health experts. The objective of this cooperative action is building a solid infrastructure for preventing and controlling the exposure to dusts containing silica.

Aiming to strengthen the political will and the commitment, the PNES is in charge of promoting upgrading and education programs for workers and information dissemination actions. Special attention must be given to harmonize the diagnosis criteria.

The program aims also to promote partnerships among industrialized and developing countries involving the exchange of technical information and of accumulated experience in actions concerning the primary prevention of silicosis.

The principles of action of the ILO/WHO joint program are:

1. formulating regional, national and global plans of actions;
2. making available funds for prevention;
3. epidemic surveillance;
4. monitoring and evaluating results;
5. supplying funds for enforcing the local laws concerning national programs.

4. Monitoring of environmental dusts bearing free silica

4.1 Gravimetric analysis

The gravimetric analysis of dust samples collected in industrial environments aims at determining the weight of dust collected on membrane filters, which are weighed before and after sampling. The method is not specific for any component of the sample, for it determines the weight (mass) of all solids retained on the filter.

The gravimetric analysis must register small changes in the weight of the filter, so the determination must be performed under carefully controlled environment, especially to avoid the effect of humidity.

Before being weighed, the filters are stabilized under controlled humidity and temperature conditions for at least three hours. Two laboratory proof filters from the same batch are also weighed. Eventual changes in the weight of the filters utilized for dust collection occurring between weighing the virgin filter and the sample containing filter are observed by means of the changes in weight of the laboratory proof filters.

The weight of the sample is corrected with the use of a factor that compensates the changes in weight of the same filter determined in different dates. Equations for the weight of the sample and for the correction factor are presented next.

$$Ws = Wlf - W vf + F \quad (2)$$

$$F = [(c-a)+(d-b)]/2 \quad (3)$$

where: Ws = weight of sample; Wlf = weight of loaded filter; Wvf = weight of virgin filter; F = correction factor; a = initial weight of proof filter # 1; b = initial weight of proof filter # 2; c = final weight of proof filter # 1; d = final weight of proof filter # 2

4.2 Silica analysis by X-Ray diffraction

Cullity (1978) and Klug and Alexander (1977) describe the principles of X-Ray diffraction. The analysis of crystalline free silica in the dust samples collected on the filters follows the steps:

1. determination of the weight of the dust sample collected on the PVC membrane filter via gravimetric analysis;
2. calcination of the filter at 800 °C and dispersion of the calcined residue in distilled water aided by ultrasonic bath;
3. addition of a fluorspar (CaF_2) internal standard;
4. deposition of the calcined residue onto a PVC-acrylonitrile copolymer filter;
5. identification of crystalline free silica species (quartz, cristobalite, tridymite) and other phases that may cause matrix interference, by means of qualitative X-Ray diffraction;
6. quantitative determination of the content of each crystalline free silica phase by comparing with an adequate calibration curve.

Some minerals present X-Ray diffraction peaks coincident with the primary peaks of the crystalline silica phases, interfering with the identification and quantification of the latter. In the presence of interfering species, quantification must be performed based on secondary peaks, with loss of sensitivity and precision.

The qualitative X-Ray diffraction analysis is performed by a short and slow scan of the sample in the regions of the most intense peaks of silica phases. The fluorspar internal standard is also identified in this scan. The primary and secondary peaks of silica phases and fluorspar are presented in Table 1.

Table 1: Primary and secondary X-Ray diffraction peaks of crystalline free silica phases and fluorspar

Mineral	primary 2θ	primary d	secondary 2θ	secondary d
Quartz	26.66	3.34	20.85	4.26
cristobalite	21.93	4.05	36.11	2.49
tridymite	21.62	4.11	20.50	4.33
fluorspar	47.10	1.93	28.30	3.15

The quantitative analysis is performed after the confirmation of the presence of silica and the definition of the peak to be utilized. The quantification of each phase is performed by comparison with an adequate calibration curve.

For samples containing only pure quartz, cristobalite and tridymite, the method requires 0.01 to 0.50 mg. This working range of the method depends on the presence of interfering species.

The detection limits for primary and secondary peaks, respectively, are: quartz (0.01 mg; 0.10 mg); cristobalite (0.02 mg; 0.15 mg); tridymite (0.02 mg; 0.05 mg).

For reliable determinations the weight of the sample should be at least 15 times the detection limit.

The sample preparation method for the X-Ray diffraction analysis yields a thin layer that attenuates significantly the variations of the absorption coefficients, this fact being observed when the calibration curves are plotted.

The linearity of the calibration curves, produced by the standard samples utilized in quantitative X-Ray diffraction analyses, is strongly improved when they are split in two, one for low grades and the other for high grades, as demonstrated by the calculation of the maximum percent error of the method.

The maximum percent error, calculated by the calibration of the ratio of intensities of quartz and fluorspar peaks, as a function of the mass of silica in the samples, reaches 5% for high grades and 10% for low grade curves.

4.3 Results evaluation

Sampling volume:

$$Qa = (Qi - Qf)/2 \quad (4)$$

$$Vs = Qa \times ts \quad (5)$$

where: Qa = average sampling flowrate (L/min); Qi = initial sampling flowrate (L/min); Qf = final sampling flowrate (L/min); Vs = sampling volume (L); ts = sampling time (min).

Considering that the tolerance limits are usually expressed in mg/m^3, the sampling volume should be divided by 1000, to be expressed in m^3.

Dust concentration:

$$C = w/Vs \quad (6)$$

where: C = dust concentration (mg/m^3); w = weight of the collected sample (mg)

Tolerance limit:

$$TLtd = 24/(\%SiO_2 + 3) \quad (7)$$

$$TLbd = 8/(\%SiO_2 + 2) \quad (8)$$

where: TLtd = tolerance limit total dust (mg/m^3); TLbd = tolerance limit breathable dust (mg/m^3).

Risk evaluation (Cs):

Cs ≥ TL: risk situation; Cs < TL: no risk situation.

4.3 Size distribution quantification

The samples collected in the field, according to the current technical standards of environmental evaluation and labor safety, are prepared according to the following methodology:

1. the filter is placed in a porcelain crucible covered with a lid and taken to muffle at room temperature (or temperature below 300ºC if it had been previously utilized);

2. the temperature is adjusted to 800ºC, the filter being burned during the heating period. After reaching this temperature, a period of two hours is recommended for totally calcining the filter;
3. the calcined residue is transferred to a 50 mL erlenmeyer flask by means of the addition of a few mL of water, the crucible being scrapped with a glass rod;
4. the flask is hand shaken and placed in an ultrasonic bath for 30 minutes for dispersing the agglomerating agent;
5. the material is collected by means of a dropper, placed onto a cylindrical piece of polished metal or acrylic and left in a dryer for 24 hours;
6. the samples are coated with a carbon conducting film via a vacuum evaporator (metallizer);
7. the sample shaft of the scanning electron microscope is connected to the support by means of a conductive carbon paint and is then taken to be analysed in the scanning electron microprobe.

Images processing is a technique that consists of obtaining computer aided information on a sample. The computer converts the image into numerical shape, a process known as image digitalization that divides the image in several tiny regions known as pixels (Picture Elements), which occupy a position inside a matrix. Each pixel is identified by a line and column numerical reference corresponding to its position in the matrix.

Image - Pro Plus for Windows (1995), a software that performs advanced images processing and characterization, was utilized. The main features of the software are:
1. plotting and counting objects automatically;
2. measuring properties such as: projection area, perimeter, diameters (maximum, minimum, average) and radius;
3. classifying and presenting objects by range of values of the measured property, using colors contrast to enhance visualization;
iv. presenting the results numerically as tables and/or graphs.

The procedure utilized in the determination of the mass average diameter of the SiO_2 particles in environmental dusts is described next:
1. the image of the sample is produced and photographed by means of a scanning electron microscope, then the image is saved in disc or scanned in a format compatible with the software;
2. a correspondence between the unit of the picture scale (μm) and the standard scale (pixel) is established via calibration;
3. a preliminary idea concerning the particles is then performed after selection and automatic counting;
4. the image is scanned and corrections are made in the selection for analysis. Objects may be grouped (two or more objects are measured as one), separated (grouped objects may be individualized) or hidden;
5. after the definition of the particles to be analyzed, the software measures the average diameter of each particle (average of the length of the plotted lines passing by the centroid at 5° intervals) and then calculates the average diameter (arithmetic average) of each size range, for each picture;
6. the average diameter and the number of particles in each range permit the calculation of the mass average diameter.

5. Case studies

A typical example of field evaluation, showing that among 15 samples collected in an underground gold mine 12 presented concentrations above the tolerance limit, is illustrated in Table 2.

These results stress that the use of special masks to protect the workers is required in this type of environment.

Table 3 illustrates results of an evaluation performed at a sand blasting facility. All 10 samples presented concentrations above the tolerance limit.

6. Conclusions

The method that was developed for quantifying the concentration and the size distribution of airborne free silica particles in industrial environments is simple and reliable. It represents a powerful tool to reduce the risk of silicosis among workers of underground mines and sand blasting operations.

Underground gold mine workers must wear adequate protective masks to prevent the risk of silicosis.

Table 2: Evaluation of crystalline free silica in environmental dusts collected in an underground gold mine

Sample	Average flowrate (L/min)	Sampling time (min)	Sampled volume (m^3)	Mass sample (mg)	Mass silica (mg)	SiO_2 %	Concentration (mg/m^3)	Tolerance limit (mg/m^3)
1	1.75	220	0.385	0.38	0.02	5.3	0.99	1.10
2	1.57	263	0.413	0.21	0.02	9.5	0.51	1.92
3	1.67	139	0.232	1.00	0.06	6.0	**4.31**	**1.00**
4	1.63	154	0.251	6.00	0.48	8.0	**23.90**	**2.18**
5	1.42	127	0.180	1.00	0.10	10.0	**5.56**	**1.85**
6	1.69	253	0.428	1.21	0.12	9.9	**2.83**	**0.67**
7	1.69	360	0.608	1.74	0.17	9.5	**2.86**	**0.70**
8	1.67	215	0.358	1.54	0.11	7.1	**4.30**	**2.38**
9	1.63	360	0.587	1.21	0.12	9.9	**2.06**	**0.68**
10	1.67	180	0.301	1.81	0.16	8.8	**6.01**	**2.03**
11	1.65	360	0.594	1.60	0.08	5.0	2.69	3.00
12	1.71	132	0.226	2.10	0.12	5.7	**9.29**	**1.05**
13	1.61	360	0.580	6.00	0.48	8.0	**10.34**	**2.18**
14	1.50	186	0.279	4.10	0.34	8.3	**14.70**	**2.76**
15	1.50	221	0.332	2.07	0.04	1.9	**6.43**	4.90

Table 3: Evaluation of crystalline free silica in environmental dusts collected in a sand blasting operation

Sample	Average flowrate (L/min)	Sampling time (min)	Sampled volume (m^3)	Mass sample (mg)	Mass silica (mg)	SiO_2 %	Concentration (mg/m^3)	Tolerance limit (mg/m^3)
1	1.51	248	0.374	1.10	0.59	53.6	**2.94**	**0.42**
2	1.70	106	0.180	1.42	0.68	47.9	**7.89**	**0.16**
3	1.71	182	0.311	2.16	1.27	58.8	**6.95**	**0.13**
4	1.69	204	0.345	2.72	1.34	49.3	**7.8**	**0.16**
5	1.70	220	0.374	2.45	1.41	57.6	**6.55**	**0.13**
6	1.68	215	0.361	2.09	1.02	48.8	**5.79**	**0.16**
7	1.69	240	0.406	1.12	0.09	8.0	**2.76**	**0.80**
8	1.70	295	0.502	1.04	0.07	6.7	**2.07**	**0.92**
9	1.71	310	0.530	1.08	0.06	5.6	**2.03**	**2.05**
10	1.70	430	0.731	1.22	0.07	5.7	**1.69**	**1.04**

7. References

Cançado, R.Z.L., 1996. Characterisation of silica in environmental dust. Ph.D. thesis. Belo Horizonte: UFMG. (in Portuguese)

Cullity, B.D., 1978, Elements of X-Ray Diffraction. Addison Wesley, Reading, MA.

Fishman, A.P., 1985, Pulmonary Diseases and Disorders. McGraw-Hill, New York, p. 754-769.

Image – Pro Plus for Windows, 1995, Operating Manual.

Klug, H.P., Alexander, L.E., 1977, X-Ray Diffraction Procedures. John Wiley, New York.

Labour Ministry, 1992, Labour Legislation. Labour Safety and Medicine. Atlas, São Paulo. (in Portuguese)