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Mixed dust exposure in the ceramics industry

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Abstract

Workers in ceramics factories may be exposed to a number of potential toxicants beside quartz, including iron. Both quartz and Fe-bearing phases can undergo chemico-physical changes in the cycle of production which can change their toxicity. In this paper, the nature and properties of quartz and Fe-bearing minerals in clay brick and pottery productions, their modifications in the progress of production and the possible mutual interactions between them have been evaluated by means of integrated individual particle characterisation-bulk chemical analyses of both the raw materials and the airborne dust particles. The results show a combination of critical points such as the relative abundance and solubility of Fe-bearing clay minerals (mainly chlorite) as a source of iron, provided the similar morphology and exposure doses of quartz in the studied ceramics contexts.

Keywords: Quartz; chlorite; SEM; XRD; ICP-AES; quartz-Fe synergistic effects.

1. Introduction

Health risk assessment in ceramics industry traditionally rests upon crystalline silica toxicity and exposure levels (*e.g.*, NIOSH 2002). Notwithstanding, workers in ceramics factories may be exposed to a number of potential toxicants, including iron (Fubini & Fenoglio, 2007). Iron, which is a major element in the pastes of clay brick and pottery productions, is known to be involved in cell damage through free radical and ROS production (Stohs & Bagchi, 1995). More recently, it has been shown to modulate quartz

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toxicity through enhancing or inhibitory effects depending on surface concentrations upon quartz grains (Ghiazza et al, 2011). Therefore, both individual and synergistic effects by quartz and iron bearing particles are worth of interest for health risk assessment.

The science of risk assessment basically rests on toxicity and exposure information. Toxicity depends on the physico-chemical characteristics of particles (e.g., shape, size, composition, concentration in air), while the exposure conditions are related to particle morphostructure and surface characteristics (e.g., crystal structure, micromorphology, specific surface). The structural properties, in particular, may affect the particle biosolubility with direct influence on the biopersistence and bioaccessibility of toxic elements and/or chemical species in the body fluids.

In this paper, the nature and properties of quartz and Fe-bearing minerals in clay brick and pottery productions, and the possible mutual interactions between them, have been evaluated for health risk assessment by means of integrated individual particle characterisation-bulk chemical analyses of both raw materials and airborne dust particles.

2. Sampling and methods

Aerosol dust samples have been collected from different working stations in different clay brick (13 samples) and pottery (20 samples) factories in Umbria (Central Italy). Following standard reference methods (Metodo UNI 9751, 1991), the sampling has been performed on polycarbonate filters using an open-faced pumping apparatus operated at a constant flow rate of 2 l/min. In addition, six samples of clay raw materials (4 from clay brick, 2 from pottery production) from the same factories have been taken for comparison.

Individual particle characterization has been performed on each sample by means of scanning electron microscopy (SEM) coupled with 2D image analysis (Image Tool 3.0; ftp://ddsdx.uthscsa.edu), 3D surface reconstruction from stereoscopic pair images (Alicona GmbH; MeX 5.0) and EDS microanalysis. Results of 2D image analysis provide a set of morphological parameters for each particle grain. Among them, the Feret diameter

$$FD=\sqrt{\frac{4A}{\pi}},$$

where A is the area of the grain, and the shape factor

$$SF=\frac{P^2}{4\pi A},$$

where P is the perimeter of the grain are mentioned in this paper. FD, in particular, is the equivalent diameter of the grains and, thus, gives a measurement of the mean grain size, while SF gives a measurement of the border complexity of grains. 3D surface reconstruction gives a measurement of the surface roughness of grains. Measurement of the geometrical projection of particles within the plane of the image (Pa), obtained using image analysis and 3D surface reconstruction methods, give the same values. Therefore, the ratio Ta/Pa between the true area (Ta) and the projected area (Pa) provides an estimation of surface morphological complexity of each grain. EDS microanalysis has been performed at 15 kV beam current and 60 s count time.

The bulk mineralogical analysis of the pastes before and after firing has been obtained by means of X-ray powder diffraction (XRD) using an automated Panalytical X'Pert Pro modular diffractometer equipped with a X'Celerator detector. Operating conditions were: monochromatised Cu$K\alpha$ radiation, 40 kV, 40 mA, 2θ-range from 4 to 100°, step size of 2θ = 0.017°, counting time of 240 s per step. The Rietveld/RIR method (Gualtieri, 2000, Gatta et al., 2010) was applied for the quantitative phase analysis with the GSAS computer package (Larson and Von Dreele, 1994). The starting structure models used for the Rietveld fit were obtained from the MSA Crystal Structure Database (http://www.minsocam.org/MSA/Crystal_Database.html).

The concentration and solubility degree of Fe at pH 4.6 (i.e., the pH of lysosomal fluids) in the raw materials and the airborne dust have been determined by chemical extraction, followed by quantitative analysis of the metal in both the soluble and insoluble fractions by ICP-AES. Chemical extraction has been performed by sonication in ultrapure water for 1 h followed by centrifugation, whereas total concentration of elements has been determined after acid digestion (1 ml H_2O_2 + 5ml HNO_3) in a microwave oven using an ICP-AES (Ultima 2000, Jobyn Yvon) spectrometer operating at 900 W equipped with ultrasonic nebulizer (U-5000AT, CETAC Technologies). The precision of analysis is better than 4%.

3. Results and discussion

3.1 Quartz properties and toxicity

Quartz morphology revealed similar grain size and surface morphology of raw materials in both sectors, although a higher variability was observed in the clay brick production (Fig. 1). A remarkable, though predictable, decrease of the grain size was evidenced in the gross transition between the raw materials to the airborne dust. On the other hand, the shape factor was almost unchanged. No significant differences were observed among the samples as for the grain boundary and the surface morphological complexity, but values for the airborne dust grains were much more dispersed.

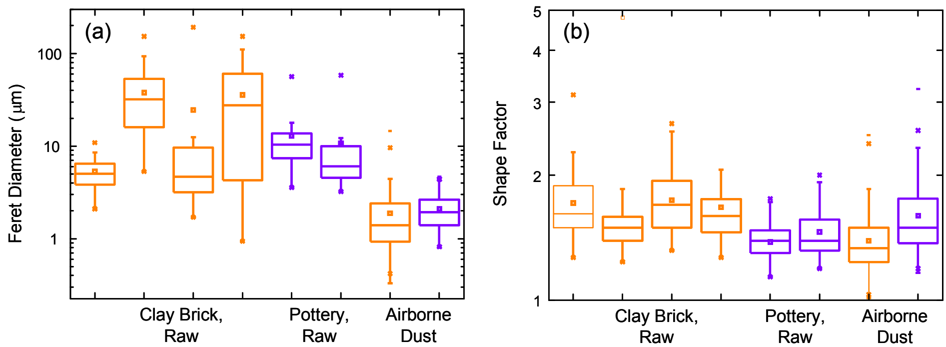

Fig. 1. Box and whisker diagrams of Feret diameter (a) and shape factor (b) of quartz grains from raw materials and airborne dust samples in clay brick (orange) and pottery (violet) productions.

Aerosol mass concentration of quartz is significantly higher, and above the threshold limit value (0.025 mg m^{-3}) in the clay brick than in the pottery production (Fig. 2). This is likely due to the largely dry conditions operated in the clay brick production with respect to the wet conditions applied in a large part of the pottery production. For water insoluble particles, such as quartz, measurement of surface area provides a better estimation of the dose than that obtained by the usual gravimetric expression (Lison et al., 1997). Assuming spherical quartz grains of radius FD/2 and a constant density ρ, the exposure doses, C_{exp}, in our samples were estimated using the following expression:

$$C_{exp} = \frac{\rho \cdot V}{A} = \frac{\rho \cdot FD}{6}$$

where V is the mean volume and A is the mean area of grains. The values obtained (93 µg cm^{-2} and 84 µg cm^{-2} for clay brick and pottery, respectively) greatly exceed the minimum dose (40 µg cm^{-2}) found to be able to induce significant cytotoxic and inflammogenic effects on cell cultures (Ghiazza et al., 2011), although the particle mass concentrations in the factories being lower than the threshold limit value in the case of pottery. This experimental finding suggests the necessity of employing surface area instead of gravimetric measurements to evaluate quartz occupational exposure.

3.2 Fe-bearing particles: mineralogy, firing technology and Fe solubility

Fe-bearing particles in the ceramics factories consist of sheet minerals and Fe-oxide. The sheet minerals are, by definition, minerals formed by multilayers of tetrahedra-octahedra-tetrahedra. Fe-oxide is mainly in the form of hematite. Studies on Fe solubility at low pH (Journet et al., 2008) revealed better solubility of the clay minerals than the Fe-oxide, and better occurrence among them in the Fe(II) substituted aluminosilicates. Therefore, the main source of Fe in our case is the clay mineral chlorite followed by illite.

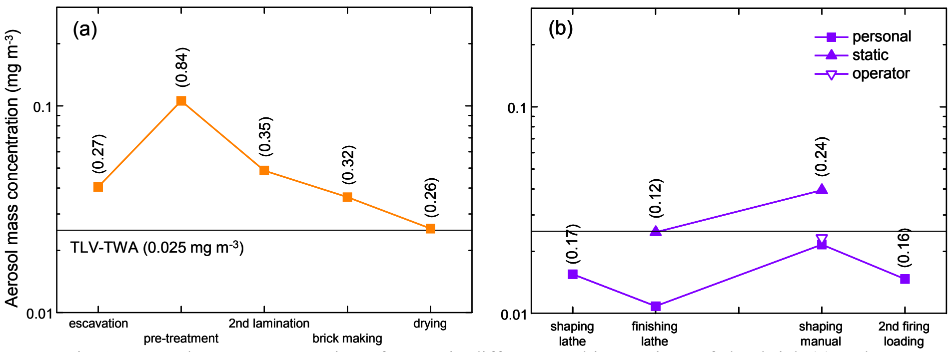

Fig. 2. Aerosol mass concentration of quartz in different working stations of clay brick (a) and pottery (b) productions. Data obtained from X-ray diffraction (INAIL, personal communication), after recalculation from the total respirable dust mass concentration (mean values, by gravimetry; data in parenthesis). In the plots the threshold limit value for the quartz aerosol mass concentration (TLV-TWA) is reported for comparison.

The mineralogical composition of the analyzed pastes is similar, with a not so pronounced variability in the clay brick for the presence of both high-Ca illitic-chloritic and low-Ca illitic clays. After firing, silicates (diopsidic clinopyroxene and gehlenite) and Fe-oxide (hematite) developed in different amounts; no amorphous phase was evidenced (Fig. 3).

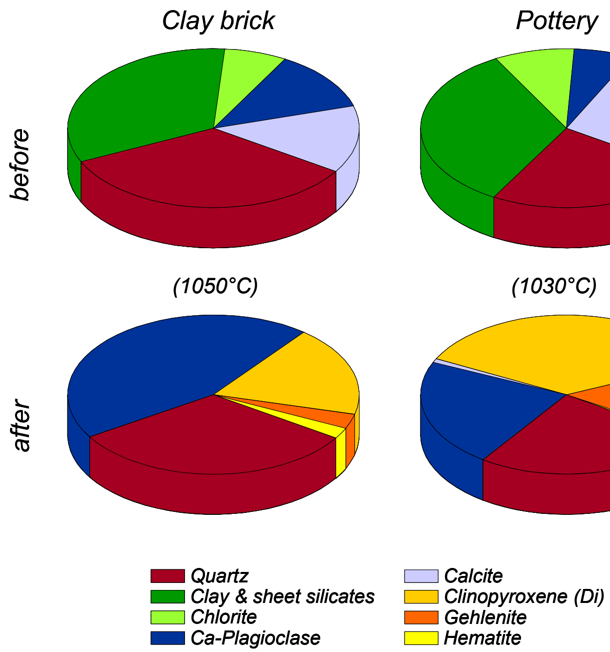

Fig. 3. Quantitative phase analyses of the crystalline species in clay brick and pottery raw materials before and after firing. The firing peak temperatures are reported in parenthesis.

Pastes in the pottery production show significantly higher total Fe contents in the powder, while the total and soluble Fe amounts of the airborne dusts are, on average, quite similar (Fig. 4). However, when the values are normalized to the sampled air volume, results for clay brick remarkably exceed those for pottery. This means that, despite the generally similar compositions of clay raw materials, the airborne dust may be more enriched in Fe in the clay brick than in the pottery production.

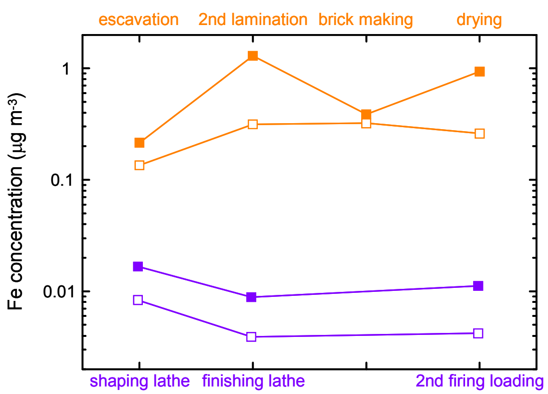

Fig. 4. Total (solid symbols) vs soluble (open symbols) Fe amounts of clay brick (orange) and pottery (violet) productions.

3.3 Possible synergistic effects

When considering the possible occurrence of synergistic effects between quartz (Qz) and Fe, the mean values of the Fe/Qz ratio have been estimated based on the values of iron and quartz concentrations in the samples. The results (Fig. 5) show increasing values for the clay brick, and decreasing values for the pottery. However, only the values obtained for pottery are in the range of possible adverse health effect (Ghiazza et al., 2011), while the values for clay brick seem too high to attain adverse health effects. Rather, a protective action may be postulated in this case. In the light of all these points, significant reduction of the health risk in the ceramics industry may be attained only after a deep examination of the properties and the exposure conditions of the whole materials even in the same working environment. Also, generalization of the results should be kept with caution and the situation be analysed case by case.

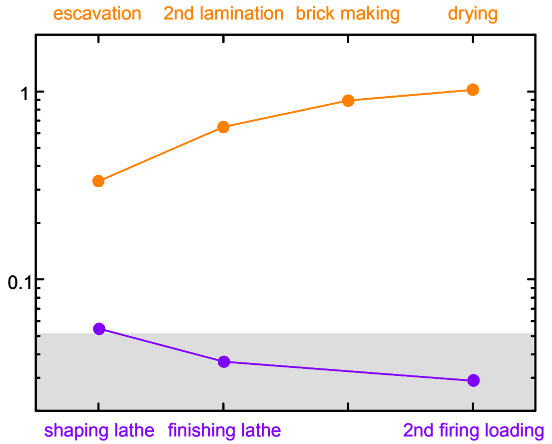

Fig. 5. Values of the Fe/quartz mass ratio of clay brick (orange) and pottery (violet) productions.

4. Concluding remarks

In this study some aspects of health risk assessment in the ceramics production have been discussed focussing on the properties of the constituent particle types. Despite the low number of samples analysed, the results show a combination of critical points such as the composition of raw materials, the mineralogical-chemical evolution of the firing products and the solubility of Fe-bearing phases (mainly chlorite from the clay raw materials) in modulating quartz toxicity, provided the similar morphology and exposure doses of quartz in different contexts of production. Therefore, the possible occurrence of mixed dust fibrogenetic processes rather than simple silicosis should be evaluated when considering the incidence of pulmonary occupational disease among the ceramics workers (Mossman & Churg, 1998). From a general point of view, this fact points to the necessity of a deeper characterization of the structural properties of different particle types in the same working environment. Also, *in vitro* and *in silico* tests on chemical mixtures and real airborne dust from industrial contexts should be promoted to provide a contribution to the epidemiology of lung diseases in a context which, still, involves a large working population in the world.

Apart from strictly industrial hygiene applications, studies on the properties of quartz and clay minerals in the ceramics production may be a step of a more general study on the properties of similar aerosols occurring in natural environments. Dusts from ceramics factories show similarities with Saharan dust advections as for the size, shape and composition of quartz and clay minerals in the dust (Bhagia, 2007). Epidemiological studies on the health impact of Saharan dust outbreaks have shown some association between coarse particles and increased mortality/morbidity during the events, although the results for the PM_{10} fraction are quite contradictory. Such a discrepancy may arise, among other reasons, from the variety of source areas for dust advections, which can result in a variable composition of the coarse (crustal) fraction of dust (Karanasiou et al., 2012). The relationships between the structure/texture and the toxicity of Saharan dust need, thus, to be further explored. In this respect, studies on the ceramics context can be very useful in evaluating the possibility of adverse health effects of similar polycrystalline aggregates on the populations involved by Saharan dust outbreaks, especially in the African regions.

5. Acknowledgements

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