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Physico-chemical properties of quartz from industrial manufacturing and its cytotoxic effects on alveolar macrophages: The case of green sand mould casting for iron production

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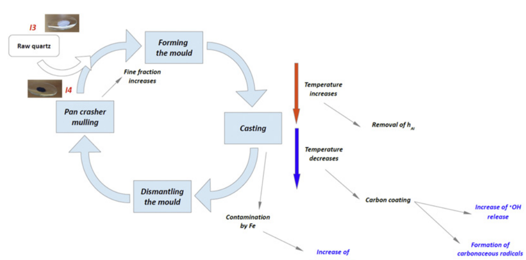
HIGHLIGHTS

- Industrial processing of SiO_2 contributes to the variability of its hazard.
- Modifications affecting a SiO_2-rich sand in cast iron production were investigated.
- Numerous changes in sample morphology and surface reactivity were traced.
- No cellular responses were observed with the processed powder.
- Temperature change and contamination by C represent critical steps in the process.

GRAPHICAL ABSTRACT



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This paper is dedicated to the memory of Prof. Dario Ghigo, who recently passed away. We all remember our friend as a gifted teacher and a brilliant researcher and we hope he will continue to help us from the place where he is now.

ABSTRACT

Industrial processing of materials containing quartz induces physico-chemical modifications that contribute to the variability of quartz hazard in different plants. Here, modifications affecting a quartz-rich sand during cast iron production, have been investigated. Composition, morphology, presence of radicals associated to quartz and reactivity in free radical generation were studied on a raw sand and on a dust recovered after mould dismantling. Additionally, cytotoxicity of the processed dust and ROS and NO generation were evaluated on MH-S macrophages. Particle morphology and size were marginally affected by casting processing, which caused only a slight increase of the amount of respirable fraction. The raw sand was able to catalyze $^{\bullet}OH$ and $CO_2^{\bullet-}$ generation in cell-free test, even if in a lesser extent than the reference quartz (Min-U-Sil), and shows h_{Al} radicals, conventionally found in any quartz-bearing raw materials. Enrichment in iron and extensive coverage with amorphous carbon were observed during processing.

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They likely contributed, respectively, to increasing the ability of processed dust to release CO_2- and to suppressing •OH generation respect to the raw sand. Carbon coverage and repeated thermal treatments during industrial processing also caused annealing of radiogenic h_{Al} defects. Finally, no cellular responses were observed with the respirable fraction of the processed powder.

1. Introduction

Professional exposure to quartz and cristobalite may cause relevant health effects, such as silicosis and lung cancer [1]. Lung diseases, however, do not occur in all occupational settings since biological effects depend on physico-chemical properties of quartz, which may differ from one dust to another and may be modified during industrial processing [2–4]. Grinding, heating, mixing are the most common processes that can be experienced by silica-bearing materials and several efforts have been addressed in the past to better understand their effects on the quartz toxicity. Nevertheless, to date, few data on properties and biological activity of the workplace silica dusts are available [5–9].

Foundries operating the sand casting of the cast iron are listed among the industrial sectors with the longest tracks of exposure to silica, and larger occurrence of silica-related diseases [10–14]. Moreover, this industrial sector has a high carcinogenic risk: beyond silica, workers being also exposed to formaldehyde, metallic smokes, asbestos, and organic products related to the combustion process. Accordingly, the IARC [15] rated the production of cast iron and steel as having a proven carcinogenicity for humans. This rate was successively verified through epidemiological studies [16–20].

The purpose of this study is to characterize a quartz-rich sand used in the "green sand" iron casting and investigate the main physico-chemical modifications, which occur during processing and may affect its toxicity [2].

The quartz rich sand, before enter in the industrial process and after mould demolition, was analysed to assess the changes in the speciation of inorganic radicals associated with quartz and in the potential to generate free radicals in cell-free environment. Free radicals generated by reactive sites at the silica surface (particle-derived free radicals) together with oxidant species produced by phagocytes (cell-derived ROS) are thought to play a significant role, namely during a late stage of toxicity of silica [21,22]. Inorganic radical speciation was carried out by Electron Paramagnetic Resonance (EPR) and Electron Spin Echo Envelope Modulation (ESEEM) spectroscopies. Free radical release was monitored by spin trapping technique associated to EPR spectroscopy. Changes in size and particle morphology, mineralogical composition, and amount of bioavailable iron were also evaluated.

The respirable fraction of the sand recovered after mould demolition was also tested for its ability in activating alveolar macrophages. Cytotoxicity and the potential to stimulate the production of Reactive Oxygen Species (ROS) and nitric oxide (NO) from cells were evaluated on a murine alveolar macrophage (MH-S) cell line and compared with cellular damage induced by Min-U-Sil, a fibrogenic quartz widely employed in experimental studies on silicosis and lung cancer.

2. Materials and methods

2.1. Sample description

The two considered samples belong to the processing line of the sand mould casting. In this process, cast iron coming from blast-furnace is introduced as raw material, melt and poured in moulds. These, in turn, are assembled by suitably modelling quartz (or quartz rich) sands. There are two ways to accomplish the mould assemblage by loose sands of mineral: pressing them (the so-called "*green sand*" procedure) or mixing them with resins, and then pressing and forming them. In both cases, after casting, sands are recovered by the demolition of the mould and by homogenisation in a pan crasher. Then, they are fed back into the industrial cycle, to prepare a new mould. If mixed with resins, sands undergo a thermo-mechanical treatment, the "regeneration", to remove most of the residual resin, before being re-used.

The two sands, hereafter labelled as I3 and I4, were sampled at a foundry operating just with the "green sand" processing line, so they were not mixed with resins. I3 consists of raw quartz rich sands, sampled before they enter in the industrial process. Sands are white at the sight (Fig. S1). I4 consists of powder materials sampled in the industrial process point where sands, recovered after the mould demolition, were stocked. The only relevant difference is the colour, turned to black (Fig. S1). Both samples were considered in previous studies by our group [9,23].

2.2. Mineralogical investigation

The samples were characterised as concerns the particle morphology and the phase composition through a set of techniques well established in the solid state investigations. Micromorphological information was provided by the Scanning Electron Microscopy (SEM), whereas phase composition was obtained through the combined use of X-ray Powder Diffraction (XRPD), Fourier Transform Infrared spectroscopy in the Attenuated Total Reflectance mode (FTIR/ATR), and micro-Raman spectroscopy. Specific surface information was provided by the BET technique. Further experimental details are summarised in the Supplementary materials (Section B).

2.3. Speciation of inorganic radicals

The investigation of inorganic radicals was mainly performed through X-band EPR spectroscopy. In order to get a certain attribution of the radical species, three set of measurements were done: a preliminary survey through conventional continuous-wave (cw) EPR at room temperature, followed by a characterisation at 35 K, and by a set of measurements through pulsed EPR spectroscopy (field swept Echo-EPR and time-domain ESE experiments). The samples were analysed without any manipulation. Further details