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Exposure assessment to engineered nanoparticles handled in industrial workplaces: The case of alloying nano-TiO_2 in new steel formulations

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ABSTRACT

This experimental study addresses the occupational exposure assessment to nano-TiO_2 (AEROXIDE ® TiO_2 P 25, EVONIK GmbH) along the processing steps of ingot steelmaking at three sites, whose characteristics range from conditioned room to multi-source industrial environments (MSIS). In Site A, which is a MSIS of multiproduct flexible production, the alloying tablets are manufactured through compression of bulk nano-powder at room temperature. Tablets are then assembled in Site B, which is a lab room equipped with local exhaust ventilation (LEV). The alloying of steel takes place in Site C, which is a full-scale casting hall where substantial amounts of material per batch (3000 kg steel/batch) are processed in open-face molds and severe working conditions prevail.

A comprehensive experimental strategy based on simultaneous measurements using direct reading instruments (DRI) and time integrated filter-based sampling has been set up. The main goal of this unusual campaign at an industrial site was to determine the suitability of the various options within the decision frame of the current methodological approaches, mainly chemical- and site-dependent.

In Site A the DRI were of limited applicability for the quantification of exposure, because of a high-variability of the background and a characteristic low but unstable counting in the coarse size range where agglomerates of nano-TiO_2 are present. In Site B, under controlled environmental conditions no interferences were relevant. Therefore, real-time devices showed no change in the total particle concentration suggesting that tasks performed did not result in any detectable release of the nano-powder. Readings in the size range > 0.3 μm showed low-signals, in the order of the device accuracy, that could not be linked to any potential release. However, the mass concentration of TiO_2, as obtained by the off-line analysis of personal breathing zone (PBZ) samples, spans from 0.021 to 0.296 mg/m^3 in both Sites, which seems to be due to big agglomerates observed by scanning electron microcopy (SEM). In Site C (steel foundry) the on-line instruments could not be used due to access restrictions and severe working conditions. Therefore, only personal sampling approach was used, including the comparative study with and without nanomaterial, which indicates no additional or TiO_2 specific workers exposure.

This work highlights how, in this particular case, occupational exposure to engineered nanoparticles (ENP) is better assessed through off-line analysis of personal filter samples.

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The DRI, however, are of unquestionable applicability as real-time monitors to quantify engineering controls efficiency and, thus, for risk management activities and decision making. The need for a scientific consensus in performing such an exposure assessment in industrial contexts is stressed.

1. Introduction

The incorporation of ENPs to a growing number of industrial products is driven by promising new applications, although the possible health effects derived from the exposure to these new materials are still under discussion (Grassian, O'Shaughnessy, Adamcakova-Dodd, Pettibone, & Thorne, 2007; Maynard et al., 2006; Shi, Magaye, Castranova, & Zhao, 2013). Titanium dioxide nanoparticles (nano-TiO_2) are one of the most widely used nanoscale materials to date; it is incorporated into a great variety of already commercially available products such as paints, paper, plastics, coating material, cosmetics, etc. (Robichaud, Uyar, Darby, Zucker, & Wiesner, 2009). Alloying steels with nanoTiO_2 improves its mechanical, thermal and chemical properties and therefore open up new applications and enable a new range of performance expectations. In the case of automotive parts, the higher strength allows for a reduction in weight and consequently a further reduction in CO_2 emissions. Other properties of these new steel formulations are of interest, such as the case of Oxide Dispersion Strengthened (ODS) alloys (Mathon et al., 2015) for applications at severe conditions of radiation and high-temperature due to their intrinsic resistance to radiation damage and high creep strength. However, the industrial development of these high-performance steels can be seriously hindered without a risk management system adapted to the use of ENPs and based on the precautionary principle.

One of the key steps for a proper risk management system is the exposure assessment. Exposure has been defined as the "contact between an agent and a target", while exposure assessment is "the process of estimating or measuring the magnitude, frequency and duration of exposure to an agent, along with the number and characteristics of the population exposed" (Zartarian, Bahadori, & McKone, 2005). Workers producing and handling these ENPs are a priority as they are potentially more exposed. Current recommendations emphasize the control and reduction of the potential exposure of operators as much as possible. However, methods and techniques to provide accurate results for quantitative exposure assessment to nanoparticles are still under development (Dahmann, 2016). Clark et al. (2012) identified the international harmonization of measurement strategy as one of the research priorities in a short timeframe.

Here are presented the results of a comprehensive experimental study aimed to quantify the occupational exposure to nano-TiO_2 along the three processing steps for the production of nano-alloyed steel: manufacturing and assembly of the alloying tablets and mixing with molten steel. Each step is conducted in a specific working area. Measurements have been conducted at three sites, two of them industrial multi-source environments (MSIS) (López de Ipiña, Vaquero, Gutierrez-Cañas, & Pui, 2015). Full-scale production of this nano-alloyed steel requires previous information about the potential contribution of the nanoTiO_2 to the occupational exposure, this study is limited to the production of a batch of 3 t steel and has been conducted in the frame of an industrial research project. The goal of this study was to measure the occupational exposure to nano-TiO_2 using different metrics, and to compare the results with available reference limits for conclusions about occupational risk. Furthermore, these metrics have been discussed in terms of their appropriateness to the quantitative assessment of the efficiency of the engineering controls. This work provides data on occupational exposure to nano-TiO_2 actually quite scarce in industrial environments other than those producing the bulk powder. Also, we discuss measurement strategies for these distinct working environments, focusing on the suitability of direct reading instruments (DRI) versus personal sampling for off-line analysis. Specifically, the distinction of the dynamic background (BG) and its potential interference when using DRI (Ono-Ogasawara, Serita, & Takaya, 2009) not selective for nanoTiO_2 is of utmost importance for both a quantitative exposure assessment and engineering control of workplace atmosphere.

2. Methods

2.1. Processes and workplaces description

Exposure measurements were conducted at three sites where several activities were performed to produce steel alloyed with nano-TiO_2. The material used was nano-particulate titanium dioxide AEROXIDE ® TiO_2 P 25 supplied by EVONIK GmbH. The nano-TiO_2 was added to the steel in the form of tablets made of compacted nano-powder. A total of 30 kg of powder was used to produce 98 tablets then assembled to conform four strings to be incorporated to an open-face steel ingot mold. The nominal capacity of the mold is of 3000 kg, thus for alloying grade with nano-TiO_2 about 1% wt. The information related to each site and process is shown in Table 1.