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# Process-generated nanoparticles from ceramic tile sintering: Emissions, exposure and environmental release

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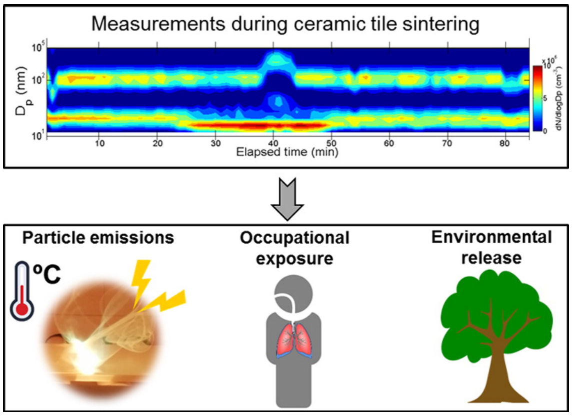
## HIGHLIGHTS

- Particle emissions and impact on worker exposure and the environment were assessed
- Nucleation processes were detected during thermal treatment
- Nanoparticles were emitted into workplace on a statistically significant level
- Workers exposure concentrations would exceed the recommended exposure limits
- A potential risk of nanoparticle release to the outdoor air was identified

## GRAPHICAL ABSTRACT



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## ABSTRACT

The ceramic industry is an industrial sector in need of significant process changes, which may benefit from innovative technologies such as laser sintering of ceramic tiles. Such innovations result in a considerable research gap within exposure assessment studies for process-generated ultrafine and nanoparticles. This study addresses this issue aiming to characterise particle formation, release mechanisms and their impact on personal exposure during a tile sintering activity in an industrial-scale pilot plant, as a follow-up of a previous study in a laboratory-scale plant. In addition, possible particle transformations in the exhaust system, the potential for particle release to the outdoor environment, and the effectiveness of the filtration system were also assessed. For this purpose, a tiered measurement strategy was conducted.

The main findings evidence that nanoparticle emission patterns were strongly linked to temperature and tile chemical composition, and mainly independent of the laser treatment. Also, new particle formation (from gaseous precursors) events were detected, with nanoparticles <30 nm in diameter being formed during the thermal treatment. In addition, ultrafine and nano-sized airborne particles were generated and emitted into workplace air during sintering process on a statistically significant level. These results evidence the risk of occupational exposure to ultrafine and nanoparticles during tile sintering activity since workers would be exposed to

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concentrations above the nano reference value (NRV; $4 \times 10^4$ cm$^{-3}$), with 8-hour time weighted average concentrations in the range of $1.4 \times 10^5$ cm$^{-3}$ and $5.3 \times 10^5$ cm$^{-3}$.

A potential risk for nanoparticle and ultrafine particle release to the environment was also identified, despite the fact that the efficiency of the filtration system was successfully tested and evidenced a >87% efficiency in particle number concentrations removal.

## 1. Introduction

According to the Ceramic Industry Roadmap to 2050 (Cerame-Unie, 2012) by the European ceramic industry association, the European ceramic industry employs over 200 000 people in the EU-27, around 80% of them in small and medium-sized enterprises (SMEs). Ceramic manufacturing from the EU-27 Member States accounts for 23% of global production of ceramics. Ceramic manufacturing is, thus, considered a robust industrial activity at the global scale. It is also a growing industrial sector, which has benefited from advances made available through nanotechnology and through innovative industrial processes. However, processes applied in ceramic industries where heating or combustion are involved or where electrical and high energy equipments are used, such as the case of firing of the ceramics in kilns (Voliotis et al., 2014), laser tile sintering (Fonseca et al., 2015), or fracturing and abrasion activities (Fonseca et al., 2015), have evidenced that large ultrafine particle concentrations may be released to the workplace environment (up to $10^5$ cm$^{-3}$) and that these particles may have potentially harmful mean diameters (<100 nm, ultrafine and <50 nm nanoparticles). The materials and the technology used may thus be significant sources of process-generated ultrafine and nanoparticles which may impact worker exposure.

The inhalation pathway is considered the predominant route of workplace exposure and uptake (Schmoll et al., 2009; Hansen, 2009). As particles reach smaller diameters they can travel deeper into the lungs (Oberdorster, 2001; Hoet et al., 2004; Heal et al., 2012; Weichenthal, 2012). The health outcomes of exposure to ceramic dusts are chronic obstructive pulmonary disease, reduced lung and respiratory symptoms such as risks of wheezing and breathlessness, dry cough and chronic bronchitis (Trethowan et al., 1995; Jaakkola et al., 2011; Kargar et al., 2013). Therefore, there is a need to characterise ultrafine and nanoparticle release mechanisms in these workplace settings similarly to what is done in industries dealing with engineered nanoparticles, in order to decrease workers exposure (Hameri et al., 2009; Van Broekhuizen, 2012; SER, 2012). However, exposure assessment studies for process-generated ultrafine and nanoparticles, especially as a result of innovations in the manufacturing processes, have received little attention in the scientific literature. Laser sintering of ceramic tiles is an innovative technique with a large potential for global-scale implementation in real-world ceramic industrial facilities. Laser sintering of tiles has numerous advantages such as speed, temperature and enhanced durability and surface properties of structural materials (de Francisco et al., 2011; Lahoz et al., 2011).

In this framework, this study addresses this knowledge gap by characterising particle release mechanisms and their impact on personal exposure during a tile sintering process using a high power $CO_2$ laser. As a follow-up to a previous study (Fonseca et al., 2015), the present work aims to identify and characterise nanoparticle formation and release mechanisms, as well as their impact on exposure, during the next step of the industrial up-scaling process in a 7 m-long industrial furnace (as opposed to a 3 m-long laboratory scale one) and in a facility emulating industrial-scale manufacture (as opposed to laboratory conditions). In addition, these industrial pilot-plant conditions allowed for the study of possible particle transformations in the exhaust system, the potential for particle release to the outdoor environment, and the effectiveness of mitigation strategies (such as the filtration system) already in place in the pilot plant.

## 2. Materials and methods

### 2.1. Measurement strategy

Aerosol measurements were conducted over six consecutive days in January 2015 in an industrial pilot plant scale furnace (length = 7 m) during a laser-based tile sintering process at the Instituto de Ciencia de Materiales de Aragón (ICMA) located in Zaragoza, Spain. It makes use of a 2000 W Rofin DC 025 SLAB $CO_2$ laser, equipped with the galvanic scan mirrors head emitting at a wavelength $\lambda = 10.6$ μm and an optical beam steering system (Estepa and de la Fuente, 2006; de Francisco et al., 2011). While the furnace applies heat to the tiles in the conventional sense, the laser is applied to the surface in order to reach higher temperatures which provide enhanced surface properties (Larrea et al., 2002; Mora et al., 2003; Lennikov et al., 2004, 2007, 2010; Estepa and de la Fuente, 2006; Gutiérrez Mora et al., 2009; de Francisco et al., 2011; Fonseca et al., 2015).

The main differences between the laboratory-scale furnace and industrial-scale furnaces should be highlighted here regarding the used fuel, gas flow and furnace length:

i. *Fuel*: industrial furnaces are powered by gas, as opposed to electricity in the case of the laboratory-scale furnaces.
ii. *Gas flow*: because of the different fuel used, the gas flow inside the industrial-scale furnaces is much higher than in laboratory-scale furnaces, and therefore, particle release to workplace air is expected to be lower.
iii. *Length*: industrial-scale facilities are frequently larger in length size and thus, lower particle concentrations at the breathing zone are expected, mainly due to the largest distances between the emission source and the breathing zone.

Based on these differences it seems acceptable to conclude that it is not possible to directly extrapolate the results regarding particle emissions obtained in the laboratory-scale furnace to the industrial-scale ones. In this work, the emissions from the furnace running were not included as they are considered negligible. The industrial furnaces usually are operated with gas, but in case of the present work an electrical furnace was used and therefore no emissions from the fuel are generated. Hence, the particle emissions are generated by the ceramic tile processing.

For the experimental procedure 6 of the most frequently used types of tiles in the ceramic industry were selected: red clay raw (#1), red clay raw with frit (#2), red clay raw with frit and decoration (#3), raw porcelain (#4), raw porcelain with frit (#5) and raw porcelain with frit and decoration (#6). The tile samples were 20 × 30 cm in size. Three replicas for each material were analysed. The tiles were introduced in the furnace at a constant velocity (8 m h$^{-1}$) in an orthogonal direction to the laser focus, and were gradually externally heated from ambient temperature up to 1000 °C and 950 °C for porcelain and red clay tiles, respectively. Upon reaching the peak temperatures, the laser beam was introduced and directed through an optical beam steering system, which transformed the circular cross-section beam into a line measuring 1 mm in thickness.

The methodology employed in this study followed the tiered measurement strategy described by various authors (Methner et al., 2010; VCI et al., 2011; Ramachandran et al., 2011; Asbach et al., 2012; Brouwer

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