EMISSIONS OF NANOPARTICLES GENERATED IN THE CERAMIC PROCESS

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1. SUMMARY

In recent years there has been increasing interest in the study of occupational exposure to nanoparticles in work environments.Nanoparticles can be emitted both during the manufacture and application of nanomaterials and generated in certain high-energy (mainly thermal or mechanical) industrial processes.The nanoparticles generated in processes may be primary or secondary in nature and, in contrast to manufactured nanoparticles, are characterised by their chemical composition and non-specific and highly variable morphology.Occupational exposure to nanoparticles associated with processes can occur in many industries, and improving knowledge about occupational exposure to them is therefore considered of utmost importance.

Regarding nanoparticles and the adoption of measures to protect and monitor workstation environments from a legislative point of view, reference values currently exist but there are no defined environmental limits in place.

In the case of the ceramic industry, the presence of different high-energy processes implies a significant potential for the generation of nanoparticles.The present work focuses on the study of nanoparticle emissions and exposure scenarios in ceramic industries dedicated to the manufacture of ceramic tiles and pigments.

The study has been carried out in ceramic plants under real operating conditions.The established experimental methodology requires the measurement of nanoparticles at the source and in exposure zones, as well as the interior and exterior background of the plant, to evaluate the possible contribution of external sources, such

as, for example, the presence of other sources generating particles on the floor or the presence of roads.

First, a sweep was performed to determine nanoparticle concentrations throughout the manufacturing process and, subsequently, the operations that recorded the highest concentrations were selected for carrying out a study in greater detail.The results obtained show the presence of specific scenarios with significant concentrations of nanoparticles.

In order to reduce the exposure of workers to nanoparticles, specific corrective measures have been proposed and evaluated for the main sources identified in the ceramic industry.The measures evaluated have permitted efficiencies higher than 50%.

The identification of conflicting points and the characterisation of nanoparticle emissions have made it possible to propose effective preventive measures to improve indoor air quality in businesses, as well as to evaluate the technical feasibility to comply with the proposed reference values.

2. INTRODUCTION

The ever-expanding field of the study of exposure to nanoparticles (Dp <100nm) in work environments has shown that in addition to the manufacture and handling of manufactured nanometric materials (MNMs), there are other sources that can contribute to overall exposure.Among these sources, certain high-energy industrial processes, both thermal and mechanical, are identified, and the particles associated with them are referred to as Process-Generated Nanoparticles (PGNPs) (van Broekhuizen, 2012).Other emission sources related to the workplace, can include nanoparticles released from conventional materials that contain a significant fraction of nano-sized particles, which can be released when handling said material in their dry state.These particles are known as nanoparticle fractions in conventional components (FCNPs) (van Broekhuizen, 2017).Additionally, exposure to nanoparticles in work environments can be affected by the contribution of exterior background elements, such as road traffic for example.

Therefore, the evaluation of occupational exposure to nanoparticles is a broader challenge, not only subject to the study of MNMs.When a risk assessment is carried out in the workplace, the identification and characterisation of PGNPs and FCNPs should be included (SER 2012).However, the characterisation of this heterogeneous mixture of nanoparticles in the air is complex and can complicate the risk assessment (van Broekhuizen, 2017).

Occupational exposure to Process-Generated Nanoparticles (PGNPs) associated with processes can occur in many industries, and improving knowledge about occupational exposure to them is therefore considered of utmost importance.PGNPs can be primary or secondary in nature and, in contrast to MNMs, are characterised by their chemical composition and non-specific and highly variable morphology.The damages derived from exposure depend on several factors, among which particle size is significant as depending on their size they can penetrate the specific surface and composition via different routes (respiratory or dermal).These particles are usually highly unstable and when released into the air can agglomerate or join other compounds.

From a legislative point of view, toxicological and epidemiological data do not allow us to establish occupational exposure limits currently for the control of nanoparticles in work environments.However, reference values have been proposed according to the type of manipulated nanomaterials.In the case of exceeding these reference values, it is recommended to adopt preventive and corrective measures to reduce the exposure values.Table 1 shows the proposed reference values, defined as an environmental limit value for 8 hours of exposure.

Type of Nanoparticles	Reference Values
Rigids, biopersistents, for which effects similar to asbestos are not excluded: carbon nanotubes or metal oxide fibres	0.01 fibres/cm^3
Non-biodegradable granular nanomaterials in the range of 1 to 100 nm and density >6 kg/L: Ag, Au, CeO_2, CoO, CuO, Fe, Fe_xO_y, La, Pb, Sb_2O_5, SnO_2	20,000 particles/cm^3
Non-biodegradable granular nanomaterials in the range of 1 to 100 nm and density <6 kg/L: Al_2O_3, SiO_2, TiN, TiO_2, ZnO, nanoclays, carbon, C60, dendrimers, polystyrene, nanotubes, nanofibers and nanowires for which effects similar to asbestos are excluded	40,000 particles/cm^3

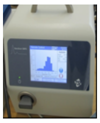
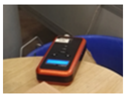
Table 1. *Reference Values for Nanoparticles (van Broekhuizen et al., 2012).*

In the case of the ceramic industry, the presence of different energy-intensive processes implies a significant potential for the generation of nanoparticles.The present work focuses on the study of emissions and scenarios of exposure to nanoparticles in ceramic plants dedicated to the manufacture of ceramic tiles and pigments, with the aim of identifying the main emission sources and evaluating the effectiveness of proposed corrective measures to minimise its impact.

In this sense, previous studies on nanoparticle emissions in the ceramic process indicate that during the manufacture of traditional ceramics significant concentrations of nanoparticles were recorded in the firing stage (140,000 - 250,000 particles/cm^3) (Voliotis et al 2014). Also, the sintering and ablation of ceramic products by laser have also been identified as significant processes, registering concentrations of nanoparticles higher than 900,000 particles/cm^3 (Fonseca et al., 2015).This situation can lead to chronic exposure of workers if these type of emissions are not adequately controlled and appropriate mitigation measures are established.

3. METHODOLOGY

The sampling methodology adopted in the framework of the present study follows the approach described by Ostraat et al.(2015).This methodology consists of determining the concentration and particle size simultaneously both in the emission centre itself and in reference points to determine an interior background, far enough from the emission source so that it is not affected by it, and an external background to evaluate the possible contribution of external sources, such as road traffic.In the different experimental campaigns carried out, the concentrations of particles in the micro and nanometric ranges have been determined.The characteristics of the sampling equipment used, as well as the general location of the same, are detailed in Table 2.

Equipment		Range Size (nm)	Data Recorded	Sampling Points
NanoScan		10-420	Nanopartile concentration (#/cm^3) and DTP [(a)]	Emission source
DiscMini		10-700	Concentration nanoparticles (#/cm^3) and d_{50} [(b)]	Emission source Interior reference Exterior reference
Grimm		> 300	Concentration (µg/m^3): inhalable, thoracic and breathable fractions	Emission source Interior reference Exterior reference

a) PSD: particle size distribution, b) d_{50}: average size.

***Table 2.** Methodology and Sample Equipment*

In the different emission sources examined, it has been evaluated whether there is a significant increase in the concentrations associated with the activity studied.To this end, the net concentrations at the point of emission have been calculated applying an approach similar to that described by Asbach et al.(2012), Kaminski et al.(2015) and Fonseca (2015).The recorded concentrations are considered significant when the average concentration of particles in the studied source is higher than the background concentration at the interior reference point plus three times the standard deviation of the concentration in the interior background.This calculation methodology permits us to identify the impact of sources other than the one studied.

The use of different sampling equipment of similar parameters at the source of emission was aimed at maximising the recording of data.However, all the equipment used to determine the concentration of nanoparticles do not have the same size range.For this reason, the concentration and average diameter obtained with the DiscMini equipment are presented in the results section, since it is the only instrument for which simultaneous data are available at the source of emission and at the interior and exterior reference points.The NanoScan equipment data have been used to study the size distributions at the source of emission.

First, a map of nanoparticle concentrations has been made throughout the ceramic process in order to identify points of environmental interest, in which more exhaustive point sampling has been carried out.

4. RESULTS AND DISCUSSION

The study has been carried out in ceramic plants under real operating conditions, applying the experimental methodology described in section 2.First, a sweep was performed to determine nanoparticle concentrations throughout the manufacturing process of ceramic tiles and pigment and, subsequently, the operations that recorded the highest concentrations were selected for carrying out a study in greater detail. Table 3 shows the concentration range ofnanoparticles in number (#/cm^3) andof the same size recorded in each emission source studied.

Process Stage	Emission Source	Concentration Range (#/cm^3)	Range Size (nm)
Raw materials preparation	Storage of raw materials	9 897 – 15 556	21-86
	Handling of raw materials	6 758 – 22 647	19-184
	Atomisation	6 964 - 33 899	24-136
Forming	Pressing	16 899 - 88 631	26-47
Vitreous enamel	Enamel mill power	24 180 - 305 573	38-42
	Drying of special pieces	13 253 - 1 288 001	12-53
Decorations	Inkjet	4 285 - 81 791	24-300
	Physical vapour deposition	14 061 - 41 019	31-46
	Laser ablation	11 832 - 16 103	42-46
Firing	Firing	73 132 - 957 454	22-45
Mechanical treatments	Dry grinding	52 387 - 125 168	34-46
Sorting and dispatch	Passage of diesel forklifts	76 180 - 321 964	46-47
	Shrink wrapping	18 901 - 4 445 726	<52

Table 3. *Emission Sources Studied in the Different Stages of the Process.*

The map of concentrations obtained has allowed us to identify emission sources associated with the manufacturing process of ceramic tiles and pigments, which have higher nanoparticle levels.Among these are the high-energy process stages, such as the firing and drying of ceramic tiles in the decoration line of special ceramic pieces.On the other hand, it has been observed a priori that significant concentrations are not reached in the laser ablation and physical vapour deposition processes, although both involve vapourisation of the material.However, it is worth mentioning that the exposure risk depends both on the levels that are the subject of this study, and on the danger level of the substance to which the worker is exposed.Finally, in the sorting stage, two significant sources have been identified: the use of diesel forklifts and the shrink wrapping procedure.However, it must be taken into account that shrink wrapping is a short procedure and that it occurs infrequently.

Based on the results obtained in the map of concentrations prepared, considering the periodicity, the duration of the activity and the exposure potential of the workers, the following process stages that require a more exhaustive study have been selected: firing stage, drying in the decoration line stage and the sorting stage.In addition to the sources that have high concentrations, it has also been considered interesting to include the detailed study of the inkjet decoration process, due to the size of the particles the inks used contain.In these sources the concentrations of particles in the micro and nanometric ranges, the average size and the granulometric distribution have been determined, applying the experimental methodology described above, with the aim of evaluating the significance of the sources studied.

Figures 1 to 5 present the concentrations in the micro range of the inhalable, thoracic and respirable fractions (expressed in$\mu g/m^3$) and of the nanoparticles (expressed in $\#/cm^3$) registered in the different sources selected during at least one hour of exposure.In the specific case of the firing stage, concentrations were recorded in two kilns in which different types of tiles, coating (kiln A) and pavement (kiln B) were being manufactured. Both of these kilns were also in vastly differing states of upkeep.In the kilns, measurements have been taken in the area of maximum temperature, where the pressure of the kiln is higher than the outside (atmospheric pressure).

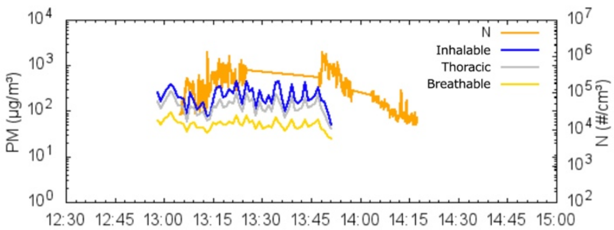


Figure 1. *Concentration of Particles in the Drying Stage in the Decoration Line.*

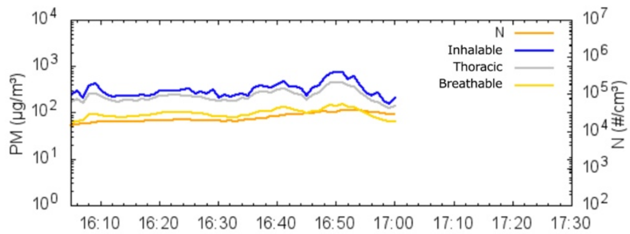


Figure 2. *Concentration of Particles in the Inkjet Decoration Stage.*

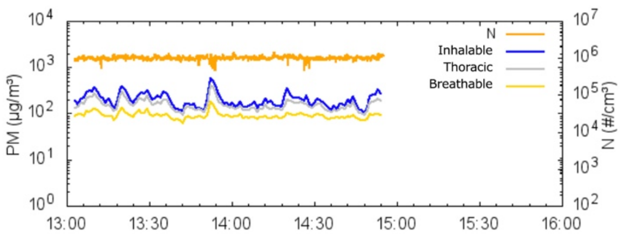


Figure 3. *Concentration of Particles in the Firing Stage.Kiln A.*

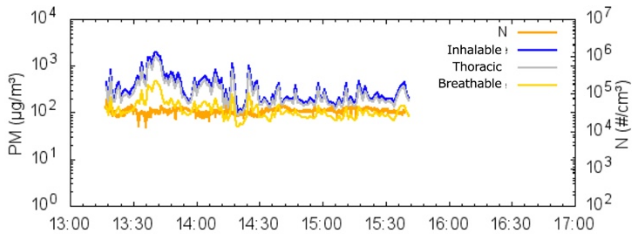


Figure 4. *Concentration of Particles in the Firing Stage.Kiln B.*

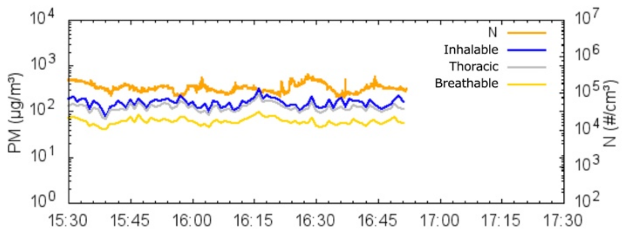


Figure 5. *Concentration of Particles in the Sorting Stage.*

Next, we comment on the main observations extracted from Figures 1 to 5:

- Drying of pieces from the decoration line: average values of close to 300,000 $\#/cm^3$ nanoparticles have been recorded in this source.In Figure 1 it can be seen how these concentrations of nanoparticles decrease when the dryers stop working (approximately 2:00 pm). In the micro range, peaks of inhalable particulate material greater than 400 $\mu g/m^3$ have been reached. The results obtained show that dryers with natural gas burners, whose combustion gases are not perfectly isolated from the plant, are a potential source of nanoparticles.
- Inkjet decoration stage: the average concentrations of nanoparticles are close to 40,000 $\#/cm^3$ and, therefore, in spite of the size of the particles contained in the inks used, the results obtained show that the application system is watertight.
- Firing stage: in kiln B the average concentration obtained (≈35,000 $\#/cm^3$) is less than kiln A (≈1,000,000 $\#/cm^3$). This situation may be due to the age and condition of the kiln studied since kiln A is older and requires maintenance. As regards the inhalable fraction, values close to 2000 $\mu g/m^3$ have been recorded in kiln B compared to 500 $\mu g/m^3$ obtained in kiln A, these levels being influenced by the interior background.
- Sorting stage: The sorting zone is considered an important source of nanoparticles, probably due to the constant passage of forklifts in this area, reaching nanoparticle levels of the order of 150,000 $\#/cm^3$.

In Figure 6, the distribution of particle sizes in the nano range obtained for the different sources studied is shown to be approximately 30-50 nm. The particles emitted in the drying stage of the decoration and sorting lines have a finer granulometry, probably due to the fact that the main emission source in them is associated with combustion processes. A similar trend is observed in the firing stage, although kiln A has a slight enrichment in particles with a size greater than 100 nm. The inkjet decoration stage in which a thicker granulometric distribution has been recorded.

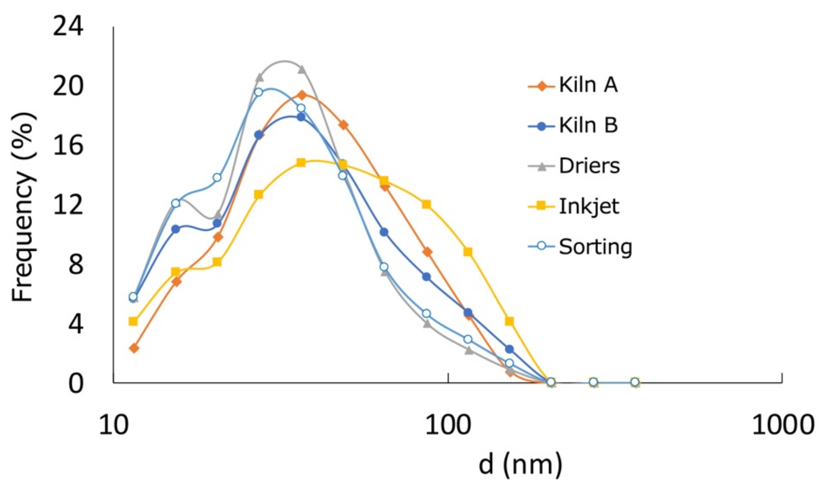


Figure 6. *Average Distribution of Particle Sizes Recorded in the Different Sources Studied*

From the concentrations of particles shown in Figures 1 to 5 and from the levels recorded in the interior and exterior backgrounds selected for each of the sources studied, the significance of them in terms of particle emission has been evaluated, with the methodology described in section 2 being applied. Table 4 shows the significant sources identified in the different scenarios being studied.

Emission source	Inhalable, thoracic and respirable fractions	Nanoparticles
	Significant source	Significant source
Decoration by inkjet	Yes	No
Drying of the decoration line	Yes	Yes
Kiln A	Yes	Yes
Kiln B	Yes	No
Sorting area	Yes	Yes

***Table 4**. Identification of Emission Sources of Significant Particles*

The data treatment applied has allowed us to identify the sources that make a more significant contribution to the levels of inhalable, thoracic, respirable fractions and nanoparticles in the work environments studied.

The different sources are significant in the inhalable, thoracic and respirable fractions. However, in these areas the occuptional exposure limit values of 10 and 3mg/m^3, for the inhalable and respirable fractions respectively, are met.

In the nanometric range, the drying of special pieces, the maximum temperature zone of the kilns, when the state of repair of the same is not optimal, and the sorting zone have been identified as significant.The registered concentrations exceed the proposed reference value, 40,000 #/cm^3, for this type of nanoparticles in these areas.

In order to reduce the exposure of workers to high concentrations of nanoparticles, in the sources considered significant, specific preventive and corrective measures have been proposed. Specifically, the effectiveness of the implementation of measures in the firing and sorting stages has been evaluated. In the drying stage of the decoration line, the standard operating conditions have not allowed the simple implementation of corrective measures.

Figure 7 shows the observed decrease in nanoparticle concentrations, obtained when carrying out maintenance operations in kiln A, in which an average nanoparticle concentration of 1,000,000 #/cm^3 was previously obtained. This maintenance has consisted of an improvement in the insulation of the kiln and has meant an efficiency close to 50% has been reached.

On the other hand, the levels of nanoparticles emitted in the firing stage were compared in the zone of maximum temperature, for a relatively new kiln (<2 years, referred to as kiln C) with those emitted by kiln A (>10 years), observing that the perfect condition of the new kiln reduces the concentrations by 80%.

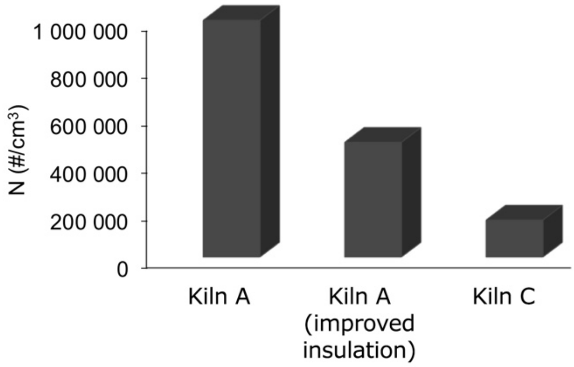


Figure 7. *Concentrations of Nanoparticles Emitted by Different kilns.Kiln A:>10 years, kiln C:<2 years.*

Figure 8 shows the concentrations of nanoparticles registered inside a pilot plant when diesel forklifts were circulating. Subsequently, samples were taken at the same points inside the plant, replacing all diesel trucks with electric ones. The results obtained show that the concentration of nanoparticles in the studied work environment was reduced by

approximately 50%.

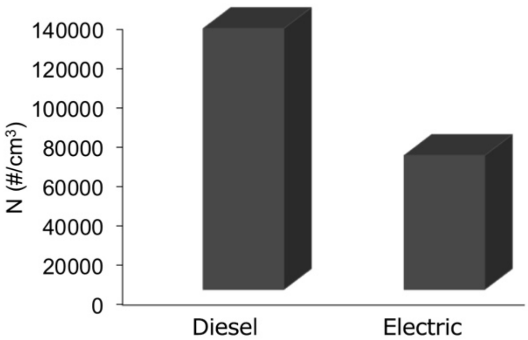


Figure 8. *Concentration of Nanoparticles Emitted by Different Types of Forklifts: Diesel and Electric.*

The identification of conflicting points and the characterisation of nanoparticle emissions have made it possible to propose effective preventive measures to improve indoor air quality in companies, as well as to evaluate the technical feasibility to comply with the proposed reference values.

5. CONCLUSIONS

The determination of the concentration of particles, in the nano and micro ranges, throughout the ceramic process has made it possible to evaluate the contribution of the different stages of the process on the levels of indoor air quality obtained, and to identify the main sources of emission. The main conclusions reached are highlighted below:

- The following significant sources of nanoparticles in the ceramic process have been identified:
  - The drying of the decoration lines of special pieces, as a result of which the combustion gases were not perfectly isolated from the plant.
  - The zone of maximum temperature of the kilns, when the condition of the kiln is sub optimal.
  - The sorting zone, mainly due to the continuous passage of diesel trucks.
  - The shrink wrapping operation, which has a short duration and occurs infrequently.
- Therefore, attention must be paid to highly energetic processes, especially thermal processes, since they have turned out to be potential emitters of nanoparticles.
- Once the risk has been identified, the effectiveness of the implementation of preventive and/or corrective measures has been evaluated in order to significantly reduce the levels of exposure to nanoparticles during ceramic processing. The proposed measures have enabled the following improvement efficiencies to be achieved:
  - The maintenance and renovation of the kiln studied has meant a reduction of 50 and 80%, respectively.
  - The substitution of diesel forklifts for electric ones has meant a reduction of 50% in the concentration of nanoparticles in the plant studied.
- Finally, it is interesting to note that the present study focuses on the evaluation of the concentration of particulate material. However, the risk of exposure to particulates depends both on the levels of exposure and the hazardous nature of the substance to which the worker is exposed. Therefore, this type of studies should be complemented with toxicological and epidemiological studies, in order to have enough information to fully understand the dangerous nature of the particles and to establish appropriate exposure limits.

6. ACKNOWLEDGEMENTS

This study has been carried out within the CERASAFE project, with reference PCIN-2015-173-C02-01, which has been funded through MINECO within the SIINN ERA-NET framework for a "Safe Implementation of Innovative Nanoscience and Nanotechnology".

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