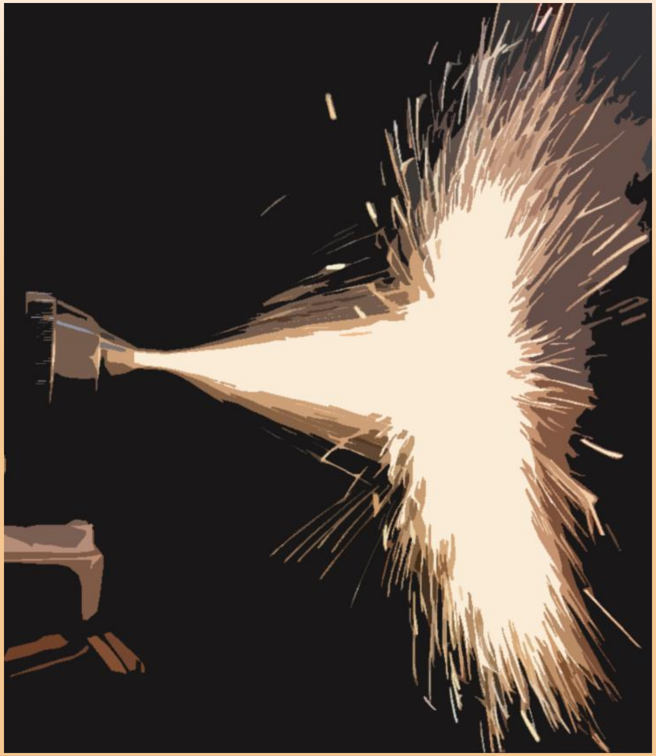
EXPOSURE TO CERAMIC AND PROCESS-GENERATED NANOPARTICLES DURING ATMOSPERIC PLASMA SPRAYING



IDAEA-CSIC, BARCELONA, SPAIN

APOSTOLOS SALMATONIDIS, A.S. FONSECA, M. VIANA, X. QUEROL, A. LÓPEZ, P. CARPIO, E. MONFORT

Framework: CERASAFE

CERASAFE is a European project which addresses the issue of **"Safe production and use of nanomaterials in the ceramic industry.** It proposes an integrated approach to environmental health and safety (EHS) in the specific industrial sector :

- Characterize **NP release scenarios** in this sector and assess **exposure** by addressing the release mechanisms, toxicity, NP characterization, as well as mitigation measures
- Develop an online tool to discriminate engineered nanoceramic particles from background aerosols
- Establish a set of Good Manufacturing and Use Practices for nanoceramic materials, including risk assessment and recommendations

Project Partners

AICE jtc Universitat Jaume I
Instituto Nacional de Saúde Doutor Ricardo Jorge
UNIDEMI
FCT Faculdade de Ciências e Tecnologia Universidade Nova de Lisboa
IDAEA Institut de Diagnosi Ambiental i Estudis de l'Aigua
Técnico Lisboa CERENA Centre for Natural Resources and the Environment
ulco Université Littoral Côte d'Opale
icma Instituto de Ciencia de Materiales de Aragón
Universitatea Babeș-Bolyai
CSIC Consejo Superior de Investigaciones Científicas

Motivation

Nanoparticles (NP)

Engineered nanomaterials (ENM)

'Commercial' nanomaterials, according to EU-specification [2011/696/EU],
(1-100nm, content >50%)

Non Engineered Nanoparticles (NENP)

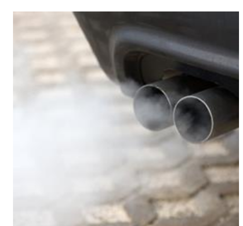
NPs unintentionally generated during processes, machining and applications of materials and surfaces

Requirement of field measurements to support health risk assessments

Background (BG)

"Natural sources" nanoparticles
(e.g., forest fires)

Anthropogenic sources
(e.g., diesel)

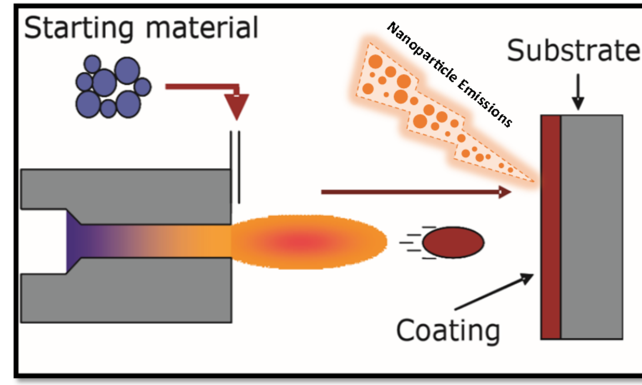


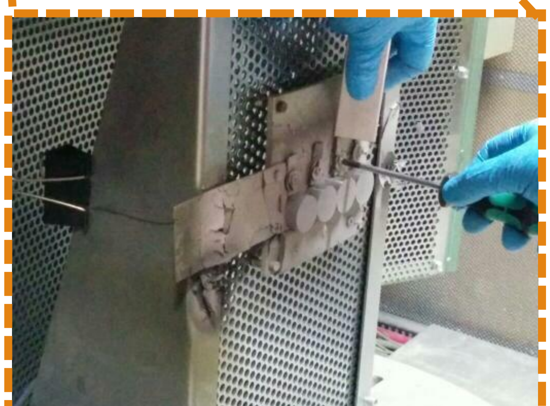
Worker exposure to harmful airborne nanoparticles in ceramic industry workplaces has been reported (*Monfort et al., 2008; Voliotis et al., 2014; van Broekhuizen et al 2012*)

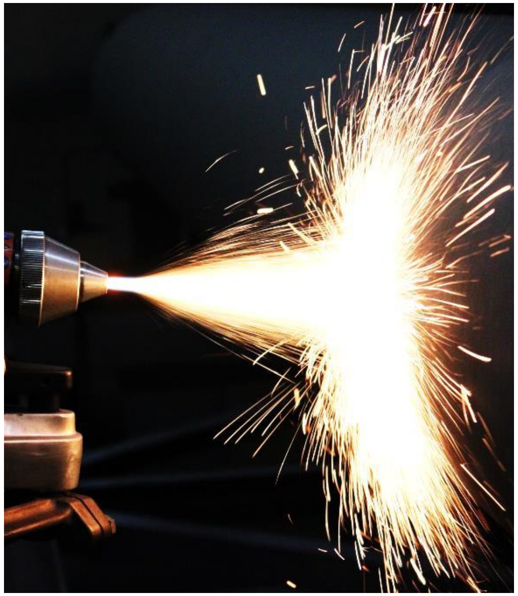
- Identification and quantification of nanoparticle emissions
- Assessment of potential worker's exposure to nanoparticles

Atmospheric Plasma Spraying

- Atmospheric pressure (ambient conditions)
- The feedstock material is spayed on the substrate
- Application of high-performance coatings (e.g. wear and corrosion resistant, thermal barriers)
- High energy process
- High potential for NP formation and release







Measurement Methodology

N

M

D_p

LDSA

Plasma chamber

DiscMini
(10 - 700 nm)

NanoScan
SMPS
(10 to 420 nm)

TEM
samples

Outdoor

Breathing zone

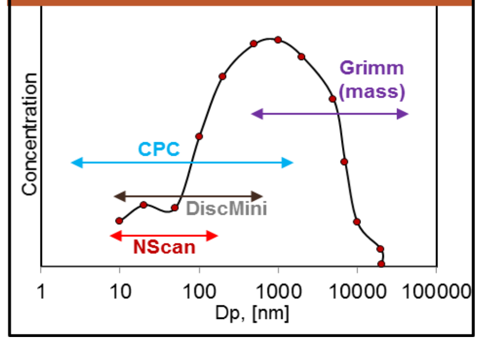
CPC TSI 3775
(4-1500 nm)

DiscMini
(10 - 700 nm)

Grimm 1.108
(300 to 20 000
nm)

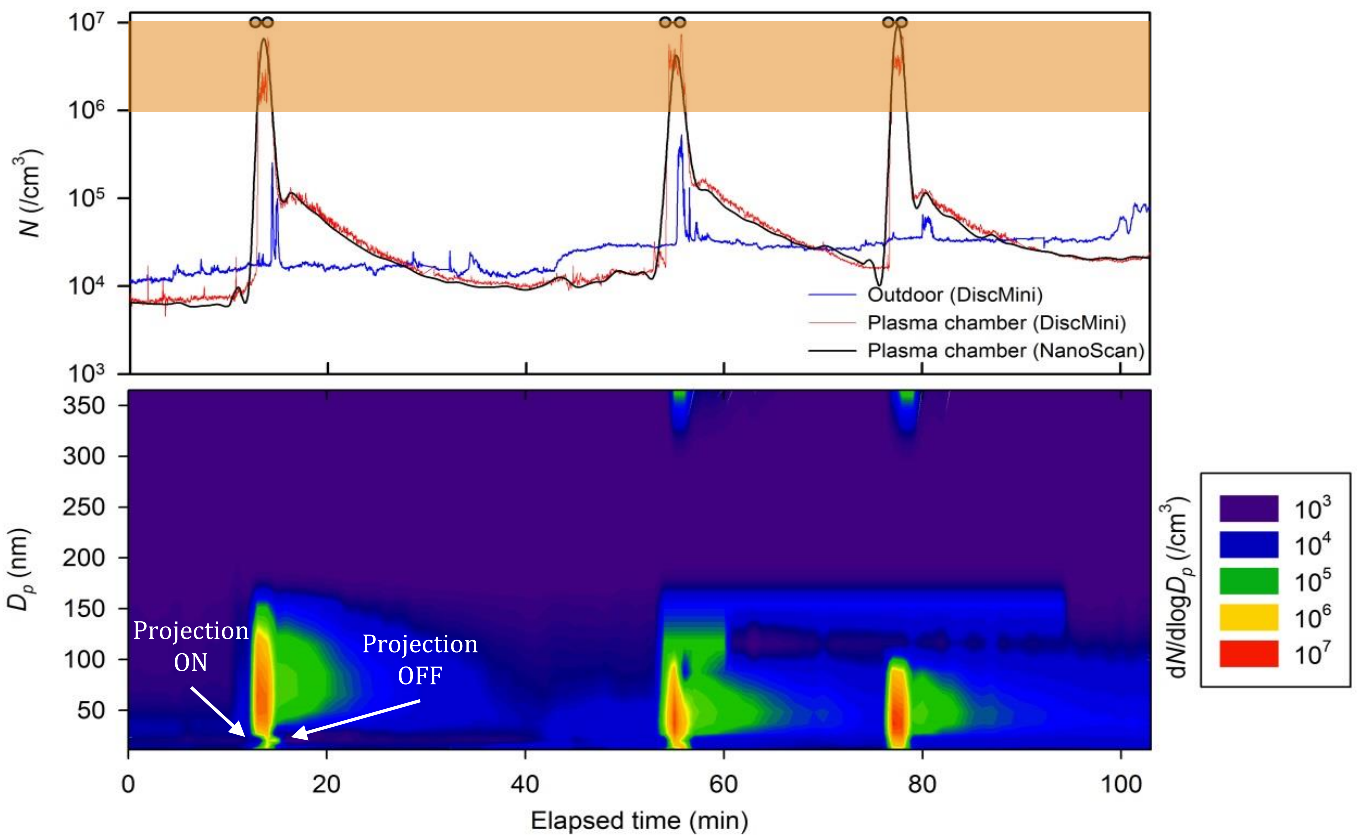
TEM
samples

Particle number and mass concentrations



Results: N and D_p

Feedstock: micro-suspension (ceramic glass powder <63 µm + 1% of fluidized nano-7 nm)

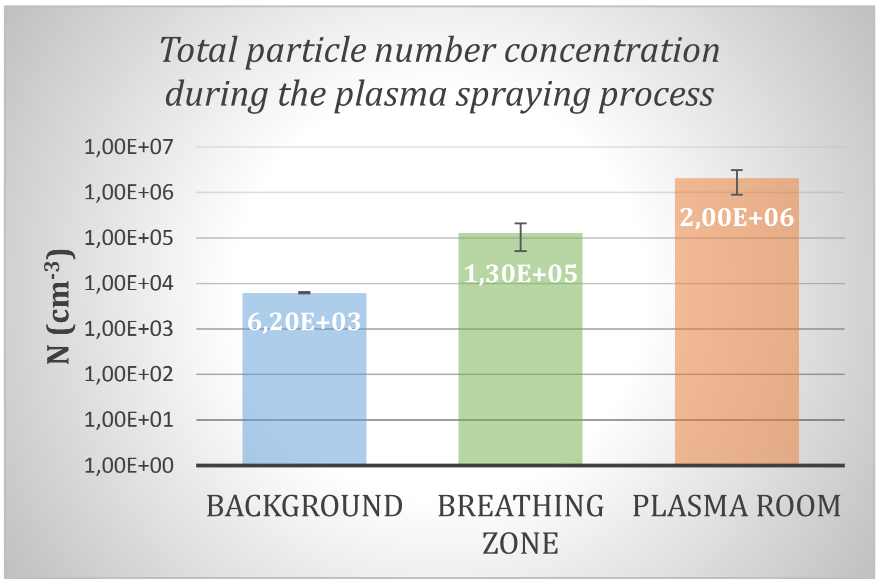


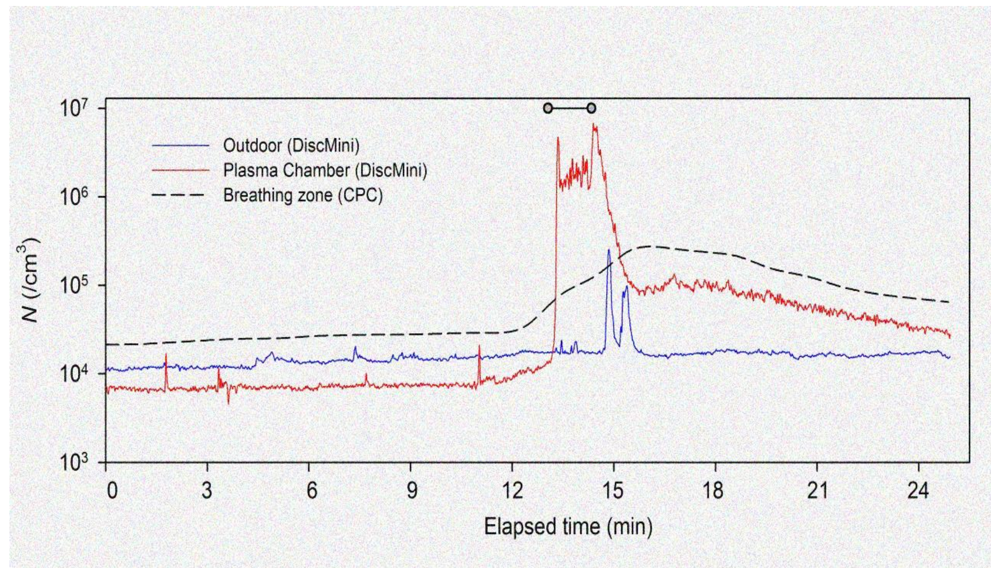
- Feedstock material: Na-Si-Ca-P (Na_2O; SiO_2; CaO; P_2O_5)
- Reproducibility over the repetitions
- 48 nm NPs are generated at the start of each projection
- NPs are generated even with micro-scaled feedstock (NENP)

Viana M., Fonseca A.S., Lopez-Lilao A., Monfort E., 2016 submitted

Results: Number concentration

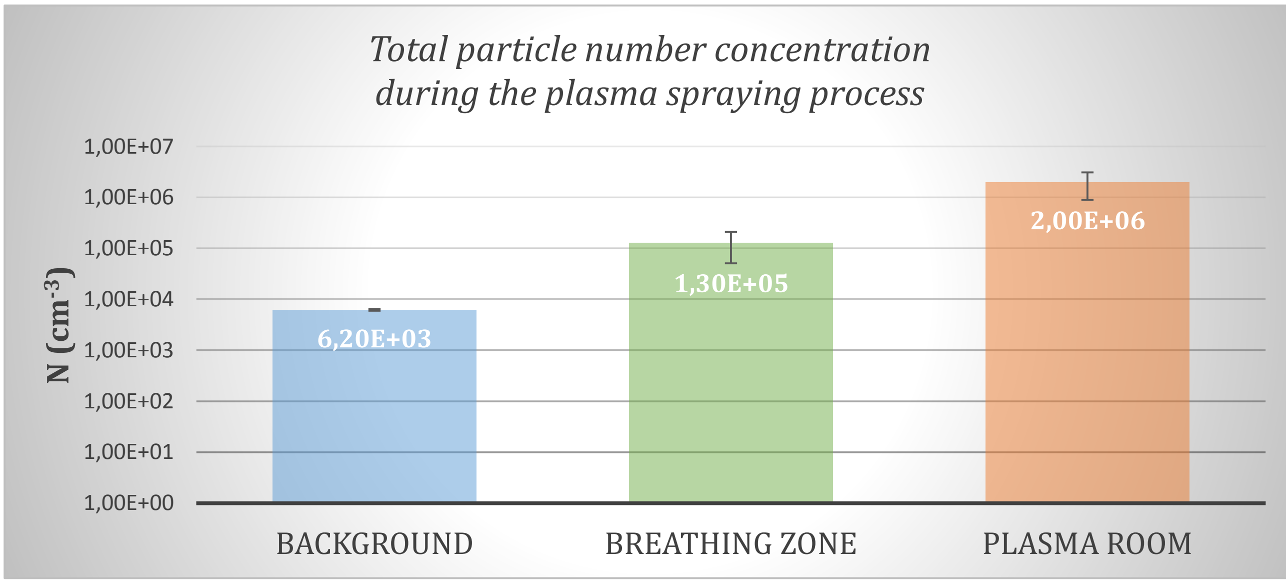
Feedstock: micro-suspension (ceramic glass powder <63 µm + 1% of fluidized nano-7 nm)





- Number concentration (N) values from the plasma chamber are **322** times higher than the background values
- Number concentration (N) values from the breathing zone are **21** times higher than the background values

Results: Number concentration



Statistical significance of **breathing zone** emissions

1. Released particle concentration = (Total particle number N_{total} in workplace air during spraying) - (Total particle number background)

2.

$$\frac{Release\ particle\ concentration}{3 \cdot \sigma_{g\ theoretical\ Background\ Work\ area}}$$

Ratio <1: not statistically significant

Ratio >1: statistically significant

RATIO=19

Asbach et al. (nanoGEM, 2012)

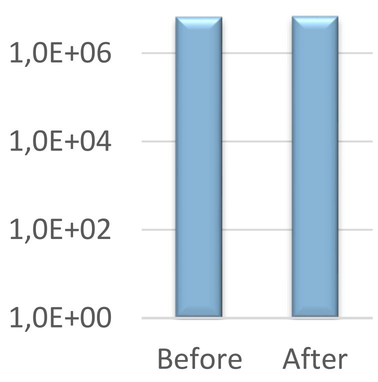
Mitigation strategies

Leak detected

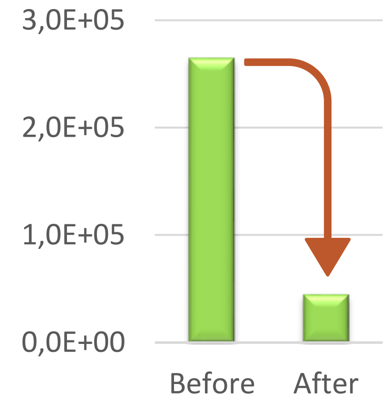
Sealing

New measurements

Plasma chamber



Breathing Zone



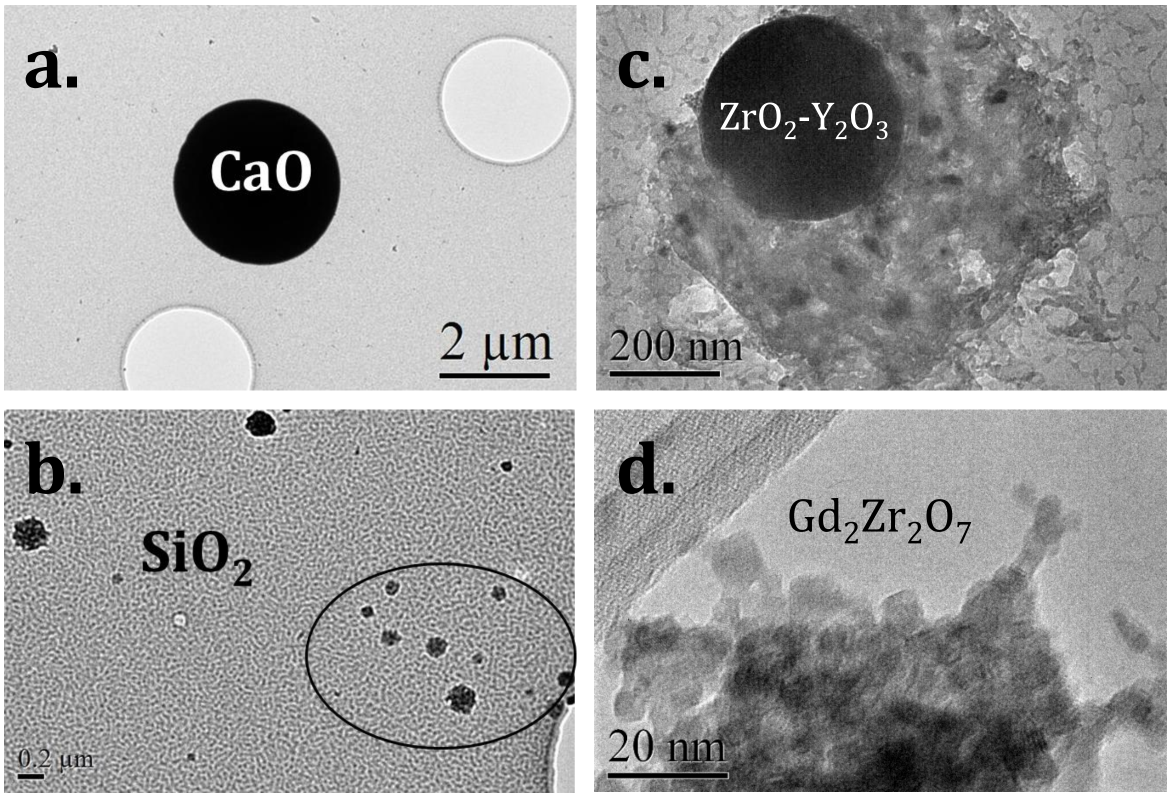
	Initial state	Final state
Breathing zone	▪ Ventilation by natural convection (ACH<2)	▪ Force ventilation (ACH~14) ▪ A precise protocol for opening and closing the plasma room door (delay)
Plasma chamber	▪ Air entrance in the plasma chamber by a single point from the breathing zone	▪ Air entrance in the plasma chamber from outside ▪ Improved air entrance distribution using a multipoint system surrounding the plasma chamber ▪ Enhanced sealing of the extraction system (ACH~11)

***ACH**: Air Change per Hour (h^{-1})*

- Reduction of **80%** in terms of **N** in the breathing zone, after mitigation measures
- However, number concentration values still above the NRV (N > 40 000 cm^{-3})

TEM analysis (EDS add-on)

TEM samples were collected from the Plasma chamber

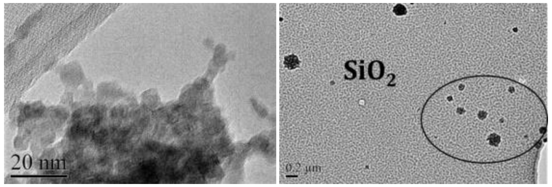


Grain size (feedstock)	Composition (feedstock)	TEM
Micro	Na_2O; SiO_2; CaO; P_2O_5 (1% nano)	**a. , b.**
Micro	Na_2O; SiO_2; CaO; P_2O_5 (1% nano)	**a. , b.**
Nano	ZrO_2-Y_2O_3	**c.**
Nano	$Gd_2Zr_2O_7$	**d.**

- Spherical shaped particles are unintentionally generated, resulting from fusion processes due to high energy condition (*Lahoz et al.,2011; Fonseca et al.,2015*)
- Cubic NPs are probably the original engineered NPs in the feedstock (d.)
- Process-generated NPs from the micro-scaled feedstock also detected

Conclusions

- High NP emissions in terms of particle number were recorded, which for the specific process (atmospheric plasma spraying) have not been reported before
- Major NP emissions were emitted from two sources:
  - due to the high energy processes
  - directly from the feedstock during the projection



- The mitigation measures that have been applied were efficient (80% reduction), but not-yet-sufficient
- NP emissions have been recorded in all of the experiments, regardless the respective feedstock material used (micro or nano)
- **The emissions are mainly related to the process rather than to the particle size distribution of the starting material**

Acknowledgements

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- **CERASAFE** framework and its respective founding agencies, organizations and institutions

www.cerasafe.eu

CERASAFE

SAFE PRODUCTION AND USE OF NANOMATERIALS IN THE CERAMIC INDUSTRY

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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

European Commission

SIINN

FP7 ERA-NET on Nanosafety
Safe Implementation of Innovative Nanoscience and Nanotechnology

Thank you for your attention!

APOSTOLOS SALMATONIDIS

SPANISH NATIONAL RESEARCH COUNCIL (**CSIC**)

INSTITUTE OF ENVIRONMENTAL ASSESSMENT AND WATER RESEARCH (**IDAEA**)

Nano Reference Values (NRV)

- NRVs serve as provisional precautionary Occupational Exposure Limits for nanomaterials
- Workers will be exposed to concentrations >> NRV; thus, mitigation measures must be implemented

Description	NRV (8-hr TWA)
Rigid, biopersistent, insoluble, fiber form nanomaterials for which effects similar to those of asbestos are not excluded ▪ SWCNT or MWCNT or metal oxide fibres	0.01 fibers/cm^3
Non-biodegradable granular nanomaterials in the range of 1–100 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 1–100 nm and density < 6 kg/L ▪ Al_2O_3, SiO_2, TiN, TiO_2, ZnO, nanoclay ▪ Carbon Black, C_{60}, dendrimers, polystyrene ▪ Nanotubes, nanofibers and nanowires for which asbestos-like effects are excluded	40 000 particles/cm^3
Biodegradable/soluble granular nanomaterials in the range of 1–100nm ▪ e.g. NaCl-, fats, flower, siloxane particles	Applicable OEL

Source: van Broekhuizen et al 2012, AnnOccHyg 56:515-524