

SAFE PRODUCTION AND USE OF NANOMATERIALS IN THE CERAMIC INDUSTRY:

OVERVIEW OF RESULTS FROM THE CERASAFE PROJECT



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NanoSAFE'18, Grenoble, 06/11/2018

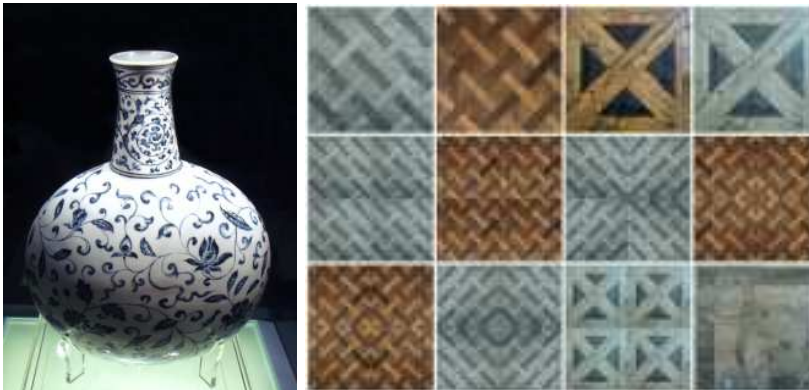


The ceramic industry

A ceramic is an inorganic, non-metallic, solid material comprising metal, non-metal or metalloid atoms primarily held in ionic and covalent bonds.

Conventional ceramics

Traditional ceramic raw materials include clay minerals such as kaolinite,



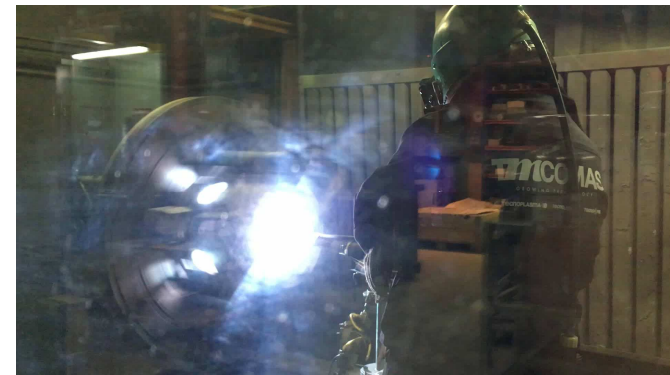
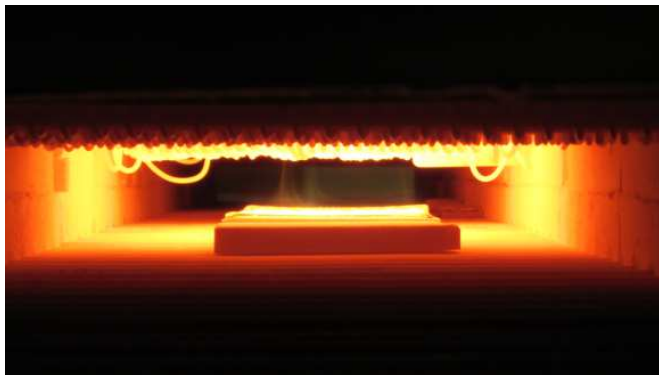
Advanced ceramics

Alumina, zirconia, silicon nitride, silicon carbide, steatite, cordierite etc.



Porsche Carrera carbon-ceramic (silicon carbide) disc brake

Innovative processes



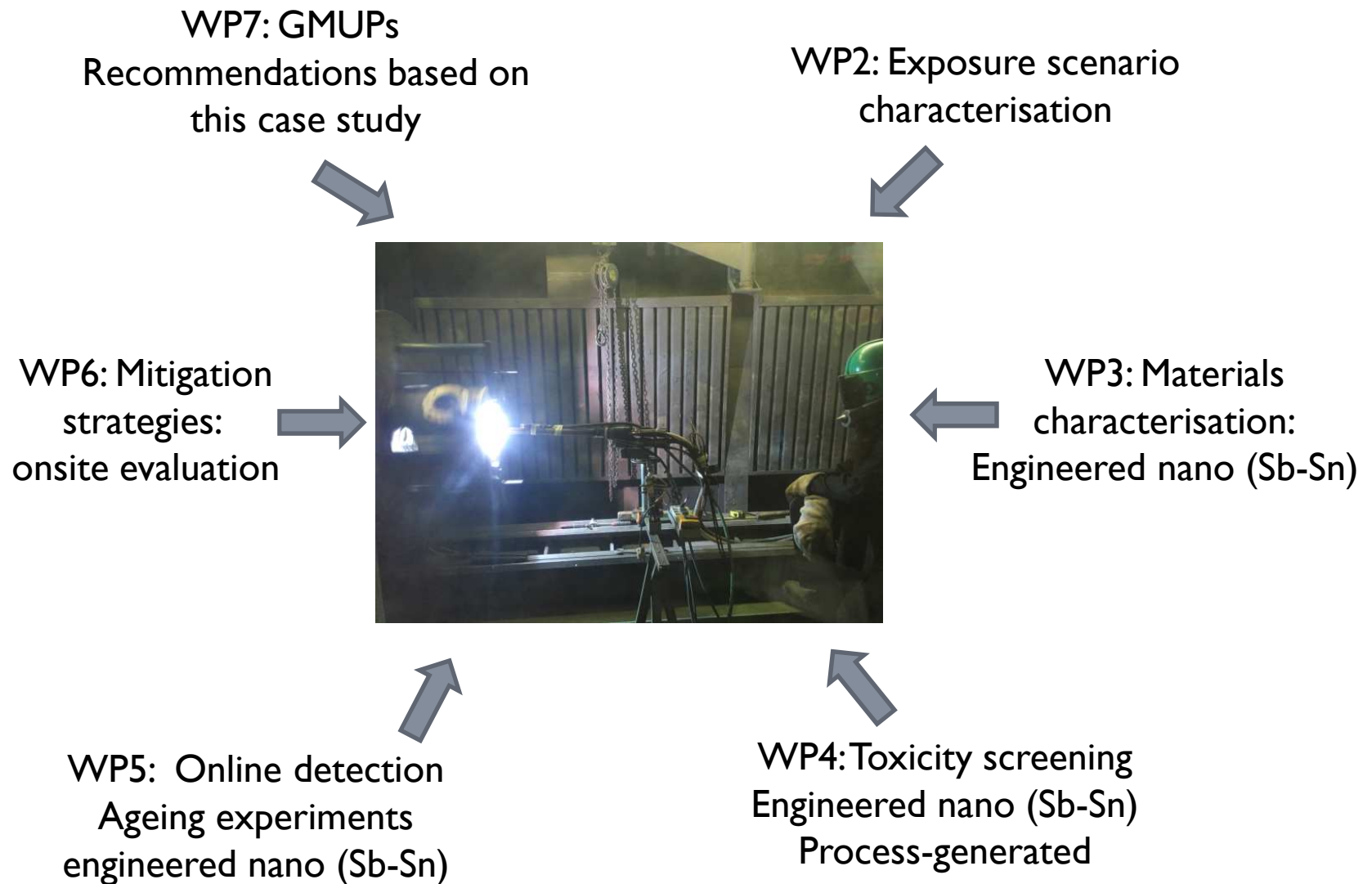


Objectives

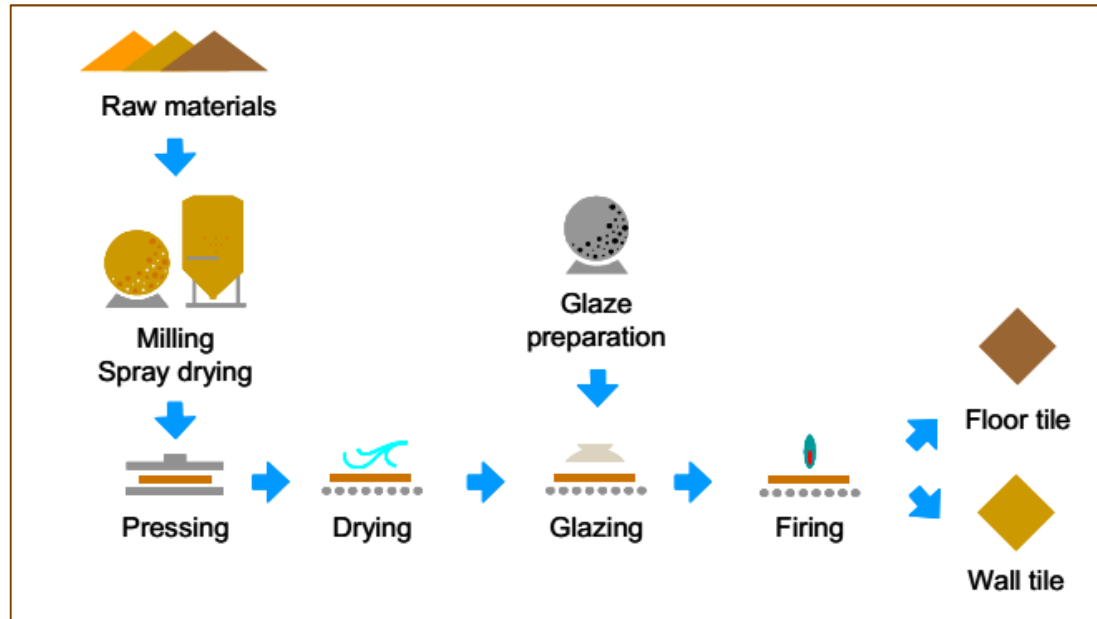
CERASAFE proposes an integrated approach to environmental health and safety (EHS) in the ceramic industry

1. Exposure characterisation (emission/release mechanisms, toxicity)
2. Develop an online tool to discriminate emissions from background particles
3. Apply exposure and risk assessment models
4. Produce guidelines on good manufacturing and use practices
5. Contribute to international databases

Project structure and approach



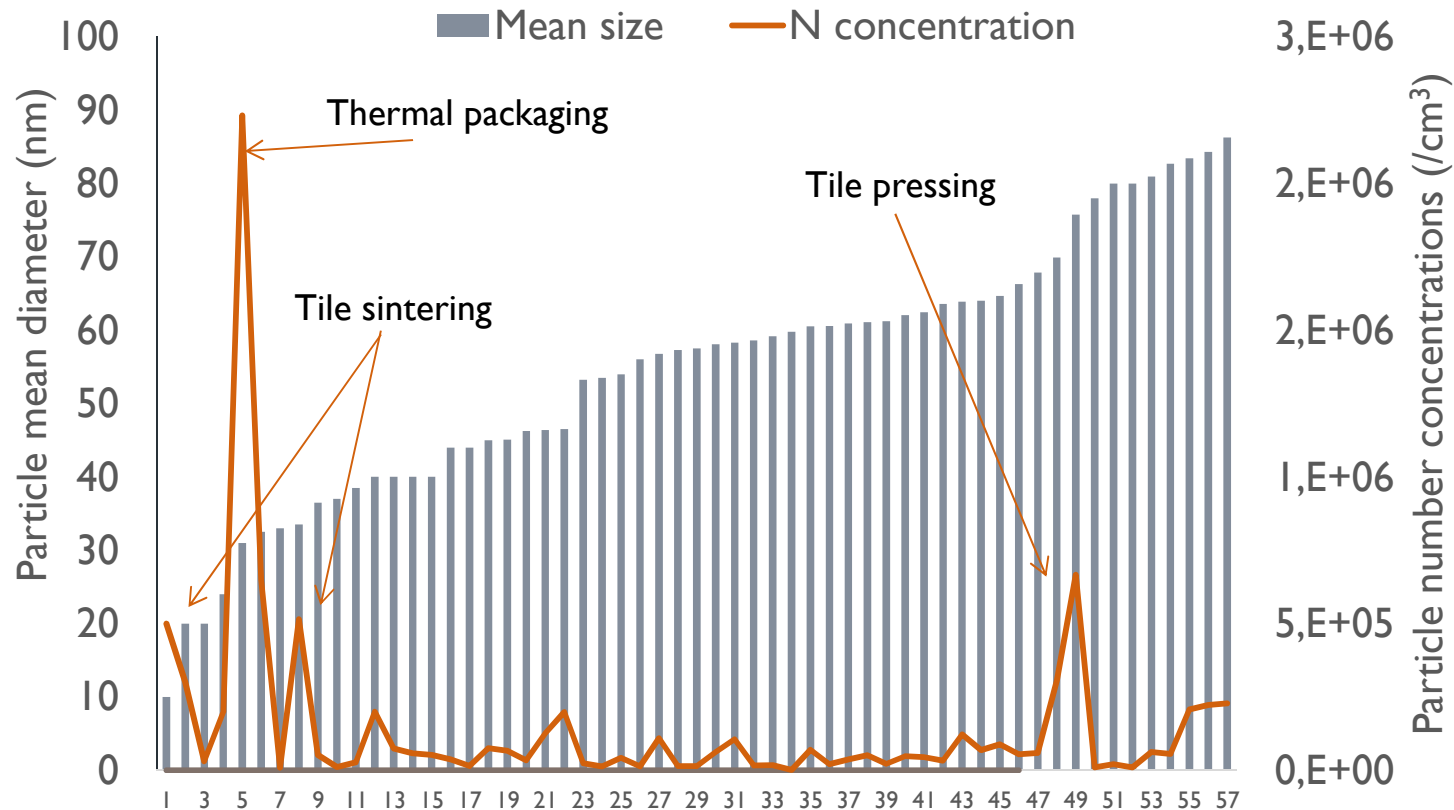
Results: Exposure characterisation



- Raw material handling (micro and nanoscale)
- Mixing and molding
- Tile sintering
- ➔ • Tile and metal laser ablation
- ➔ • Plasma spraying (pilot plant and industrial scale)
- ➔ • Packing and bagging
- ➔ • Thermal packaging
- ➔ • Inkjet printing
- PVD
- Tile pressing
- Glazing
- Tile cutting
- Sieving
- ...



Results: Exposure characterisation



- Exposures monitored in the worker area
- Major emissions: tile sintering, thermal packaging, pressing, diesel forklifts
- Max $N > 2 \times 10^6 / \text{cm}^3$ – thermal packaging
- Min $D_p < 10 \text{ nm}$ – tile sintering at industrial scale (new particle formation)

Further details in upcoming presentations

Results: NP characterisation

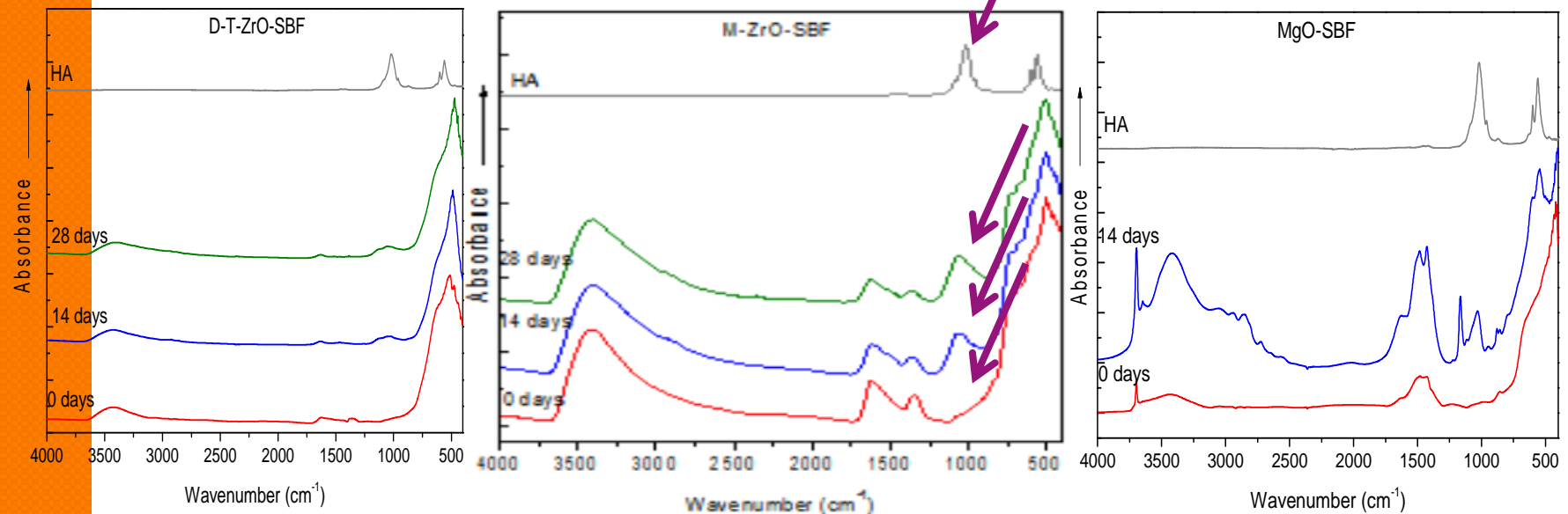
2 teams: working on solid NPs and on NP suspensions

Morphological and structural characterisation of engineered NPs: T-AlO; G-AlO; CeO; CuO; MgO; SrO; SnO; ZnO | 4; Zn₂O₅; D-T-ZrO; M-ZrO; D-C-ZrO; T-ZrO; A03 | 8 Stano solution; SbSn-Ox (ATO); SnO₂ stano stat.

Sterilised and not-sterilised

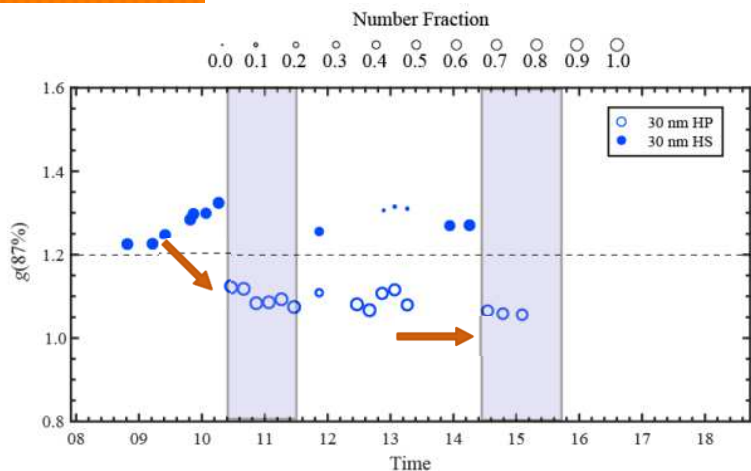
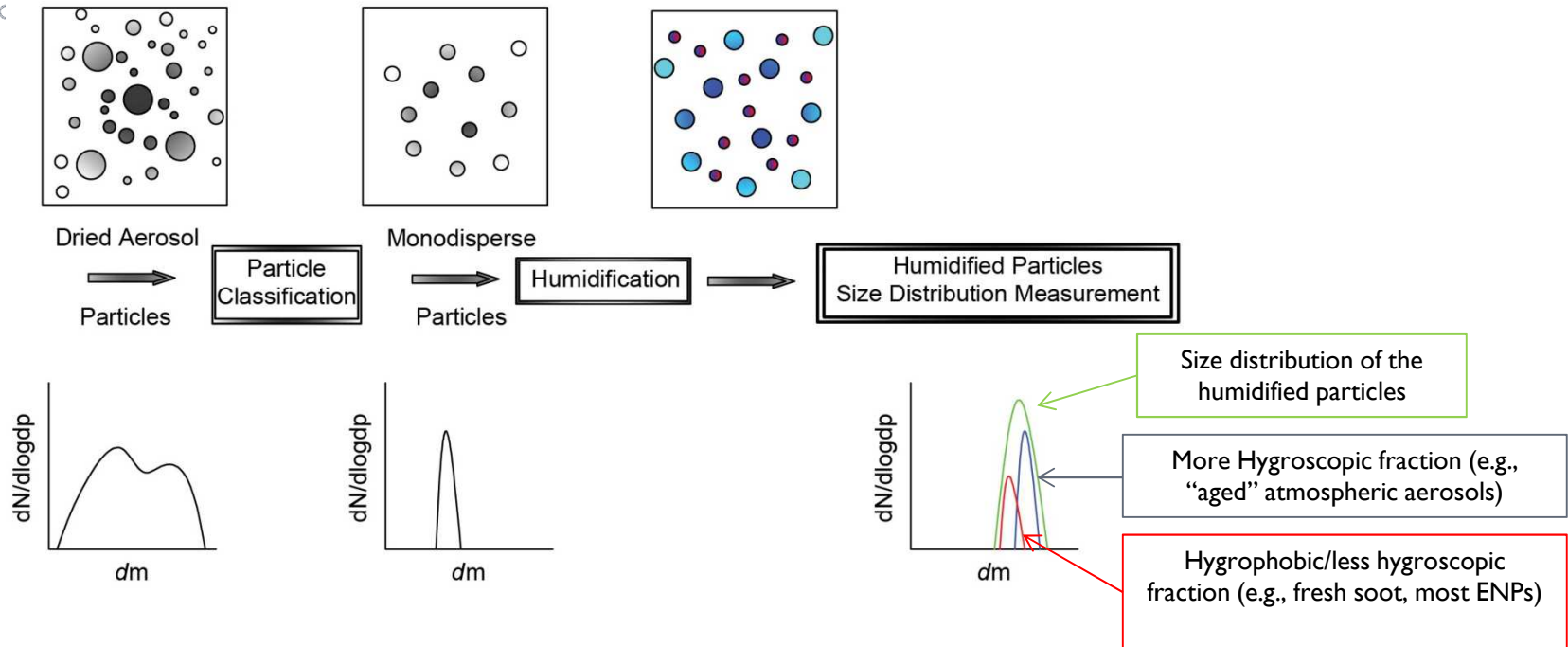
High energy XRD, HRTEM, ... Particles not always what the manufacturers say!

In vitro bioactivity (immersion in simulated body fluid, SBF/SBFA)



Results: Online tool

Salmatouidis, et al. 2019, submitted Env Sci Nano



- During plasma activity periods, a mix of PGNPs and background particles was detected.
- PGNPs are hydrophobic and can be distinguished from background aerosols (i.e., more hygroscopic).
- Sampled PGNPs exhibited shrinking upon humidification due to restructuring to more spherical-like structures.

Results: Exposure modelling

Packing of an industrial fertiliser



[$\mu\text{g}/\text{m}^3$] (ratio <small>modelled/measured</small>)	SB1	SB2	BB1	BB2	Ratio mean \pm (s.d)	
					Small bags	Big bags
One box with outdoor	325 (1.16)	404 (1.27)	759 (1.14)	546 (1.03)	1.22 (0.07)	1.09 (0.08)
Two box with outdoor (FF)	311 (1.11)	316 (0.99)	745 (1.12)	538 (1.02)	1.05 (0.08)	1.07 (0.07)
One box	310 (1.11)	270 (0.85)	501 (0.75)	488 (0.92)	0.98 (0.19)	0.84 (0.12)
Two box (FF)	296 (1.06)	223 (0.70)	487 (0.73)	480 (0.90)	0.88 (0.25)	0.82 (0.12)
Measured respirable fraction in Worker Area	279	318	668	528	-	

Presentation Ribalta et al., Wednesday afternoon

Results: Toxicity screening

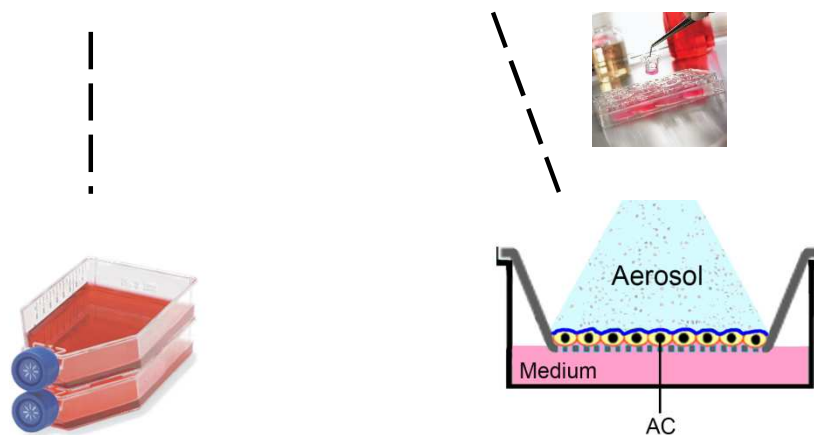
In Vitro Cytotoxicity and Mechanistic Studies

Selected NPs: Engineered (ZrO_2 , CeO_2 , SnO_2 , $\text{Sb}_2\text{O}_3 \cdot \text{SnO}_2$) and airborne nanoparticles (PGNPs):

Cell Models: Human alveolar epithelial A549 cells (polarized and non-polarized cultures) and human 3D upper airway epithelium – MucilAir™ cells;

Exposure conditions:

At Submerged and Air-Liquid Interface (ALI)



VITROCELL® Automated Exposure Station



Results: Toxicity screening

To rank the selected NPs according to their *in vitro* cytotoxicity

To identify the mechanism of action of the NPs

- ✓ Changes in cell metabolic activity;
- ✓ Alterations of plasma membrane integrity;
- ✓ Primary and oxidative DNA damage;
- ✓ Immunotoxicity

To compare the concordance between submerged vs ALI exposures and A549 vs 3D cultures findings.

To link with results from SBF immersion

Abstracts NanoSAFE'18:

- Bessa et al. (2018) TOXICITY ASSESSMENT OF ENGINEERED AND AIRBORNE NANOPARTICLES IN HUMAN ALVEOLAR EPITHELIAL A549 CELLS
- Fraga et al. (2018) TOXICITY OF CERAMIC NANOPARTICLES IN HUMAN ALVEOLAR EPITHELIAL A549 CELLS AT AIR-LIQUID INTERFACE



Results: Exposure mitigation

Literature review on the effectiveness of technical measures and personal protective equipment

- ❑ More attention should be paid to nanoparticles that involve unknown risks, such as process-generated nanoparticles (PGNPs)
- ❑ There is a significant number of studies on PPE effectiveness
- ❑ However, less information was found about the effectiveness of technical measures – and mostly lab-scale
- ❑ Sometimes the results cannot be easily generalised beyond the specific cases
- ❑ More experimental studies needed

**Effectiveness of specific mitigation strategies
implemented in scenarios: upcoming presentation**



Risk assessment and database

- Risk assessment models: Stoffenmanager-nano, Nanosafer, Nanotool, ART:
 - CSIC and U. Lisbon datasets
 - Collaboration with H2020 Calibrate for model testing
- Database: NECID (exposure database) – big adventure!
- Database for toxicity data?
- Task force on exposure assessment for the NanoSafety Cluster

Guidelines for industry

- Ongoing work



General conclusions

- Relevance of thermal/mechanical processes in the ceramic industry – emission and exposure to NPs: thermal >> mechanical
- Lower relative relevance of manufactured nanomaterials, for the scenarios assessed
- Toxicity results – coming soon
- Useful tools for exposure assessment: dustiness and 1-2 box models
- HTDMA – valuable information but logistically challenging tool (yet)
- High value of contributions to international databases – what about toxicity?

Research team

- Spanish Research Council CSIC (M.Viana)
- Universidade Lisboa (J. Gomes)
- Nova ID (R. Miranda)
- ITC-UJI (E. Monfort)
- Babes-Bolyai University (S. Simon)
- INSA (J. Teixeira)
- University of Littoral Côte d'Opale (E. Bychkov)



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CERASAFE
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Thank you for your attention!

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