EXPOSURE TO CERAMIC AND PROCESS-GENERATED NANOPARTICLES DURING ATMOSPHERIC 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.
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

**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

- **Background (BG)**
  - “Natural sources” nanoparticles (e.g., forest fires)
  - Anthropogenic sources (e.g., diesel)

**Requirement of field measurements to support health risk assessments**
Atmospheric Plasma Spraying

- Atmospheric pressure (ambient conditions)
- The feedstock material is sprayed 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

**Plasma chamber**
- DiscMini (10 - 700 nm)
- NanoScan SMPS (10 to 420 nm)
- TEM samples

**Breathing zone**
- CPC TSI 3775 (4-1500 nm)
- DiscMini (10 - 700 nm)
- Grimm 1.108 (300 to 20 000 nm)
- TEM samples

**Outdoor**
Results: N and $D_p$

**Feedstock:** micro-suspension (ceramic glass powder $<63 \, \mu m + 1\%$ 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

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

2. Release particle concentration = \frac{3 \cdot \sigma_{g \text{ theoretical Background Work area}}}{\text{Work area}}

Asbach et al. (nanoGEM, 2012)

RATIO = 19

Statistical significance of breathing zone emissions
Mitigation strategies

Leak detected | Sealing | New measurements | Plasma chamber | Breathing Zone

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
</tr>
</thead>
</table>
| 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) |

\[ \text{ACH: Air Change per Hour (h}^{-1}\text{)} \]

- 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

- 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

<table>
<thead>
<tr>
<th>Grain size (feedstock)</th>
<th>Composition (feedstock)</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro</td>
<td>Na₂O; SiO₂; CaO; P₂O₅  (1% nano)</td>
<td>a, b</td>
</tr>
<tr>
<td>Micro</td>
<td>Na₂O; SiO₂; CaO; P₂O₅  (1% nano)</td>
<td>a, b</td>
</tr>
<tr>
<td>Nano</td>
<td>ZrO₂-Y₂O₃</td>
<td>c</td>
</tr>
<tr>
<td>Nano</td>
<td>Gd₂Zr₂O₇</td>
<td>d</td>
</tr>
</tbody>
</table>

Na₂O: Sodium oxide; SiO₂: Silicon dioxide; CaO: Calcium oxide; P₂O₅: Phosphoric pentoxide; ZrO₂-Y₂O₃: Zirconium oxide-yttrium oxide; Gd₂Zr₂O₇: Gadolinium-zirconium oxide.
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

- Institute of Ceramic Technology, Castellon (Spain)
- A.S. Fonseca, M. Viana, X. Querol, A. López, P. Carpio, E. Monfort
- CERASAFE framework and its respective founding agencies, organizations and institutions

This project is funded by the Spanish Ministry of Competitiveness and Economy, supported by SIINN ERA-NET and the European Commission
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

<table>
<thead>
<tr>
<th>Description</th>
<th>NRV (8-hr TWA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid, biopersistent, insoluble, fiber form nanomaterials for which effects similar to those of asbestos are not excluded</td>
<td></td>
</tr>
<tr>
<td>- SWCNT or MWCNT or metal oxide fibres</td>
<td>0.01 fibers/cm³</td>
</tr>
<tr>
<td>Non-biodegradable granular nanomaterials in the range of 1–100 nm and density &gt; 6 kg/L</td>
<td>20 000 particles/cm³</td>
</tr>
<tr>
<td>- Ag, Au, CeO₂, CoO, CuO, Fe, FeₓOᵧ, La, Pb, Sb₂O₅, SnO₂</td>
<td></td>
</tr>
<tr>
<td>Non-biodegradable granular nanomaterials in the range of 1–100 nm and density &lt; 6 kg/L</td>
<td>40 000 particles/cm³</td>
</tr>
<tr>
<td>- Al₂O₃, SiO₂, TiN, TiO₂, ZnO, nanoclay</td>
<td></td>
</tr>
<tr>
<td>- Carbon Black, C₆₀, dendrimers, polystyrene</td>
<td></td>
</tr>
<tr>
<td>- Nanotubes, nanofibers and nanowires for which asbestos-like effects are excluded</td>
<td></td>
</tr>
<tr>
<td>Biodegradable/soluble granular nanomaterials in the range of 1–100nm</td>
<td>Applicable OEL</td>
</tr>
<tr>
<td>- e.g. NaCl-, fats, flower, siloxane particles</td>
<td></td>
</tr>
</tbody>
</table>