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Ultrafine particle generation from plasma processing of graphite

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Background and scope

- The concern for human exposure to nano- and ultrafine particles at workplaces has been rising during recent past years; however, data for the assessment of workers' exposure are still scarce as well as information on the atmospheric emission from manufacturing plants.
- Present work reports on fine and ultrafine particle concentrations levels measured at a pilot plant for the production of graphite-based nanomaterials engineered for different applications.
- Measurements were taken at the indoor open-space, at the closed chamber where production occurs, and in the stream of air extracted form the chamber and released to the atmosphere, both before and during production process operation.
- Results are expected to provide information on the impact concentration levels at indoor environments, on the potential exposure to ultrafine particles of workers during process operation, with the ensuing need for specific personal protective equipment, and on the relevance of atmospheric emissions.

Methodology

Production process

- Ultrafine nanoplatelets of graphene (Fig. 1), ranging from 1 to 10 μm of lateral dimensions and 1 to 5 nm of thickness, are obtained by means of plasma thermal expansion of graphite (at a temperature of about 7000 °C), followed by both a liquid and a dry state exfoliation.
- The expanded graphite (Fig. 2) is collected in plastic bags by cyclonic separation, immediately after the expansion process. The bags are manually sealed and delivered to the following exfoliation process.
- Gases from the expansion process (argon, air and SO_X deriving from the graphite intercalation) are filtered and released to the atmosphere.

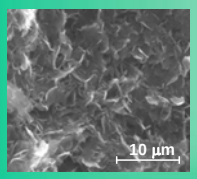
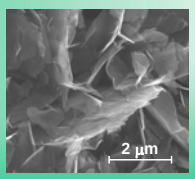


Fig. 1 – Graphene nanoplatelets



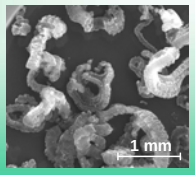


Fig. 2 – Expanded graphite

Monitoring instruments and points

Particle number concentration (PNC, cm^{-3}) were monitored by means of:
- TSI P-TRAK 8525: portable condensation particle counter for total particle number in the 20 nm-1 μm range ($PNC_{0.02\text{-}1\ \mu m}$)
- TSI UFP 3031: ultrafine particle monitor for size-resolved particle number in 6 bins between 20 nm and 1 μm
- Con.Tec P-Dustmonit: optical particle counter for size-resolved particle number in 8 bins between 300 nm and 10 μm

Before and during production process operation measurements were taken at:
- closed chamber (≈ 20 m^3) where production occurs *(Inbox)*
- indoor open-space *(Outbox)* at about 3-4 m from the chamber
- air stream extracted form the chamber and released to the atmosphere after filtration *(Stack)*
- outside ambient air *(Ambient)*

Measurements considered different process phases:
- expansion process only
- concurrent expansion and exfoliation stages
- plastic bag change and surface cleaning during production process

Results

Concentration levels (PNC)

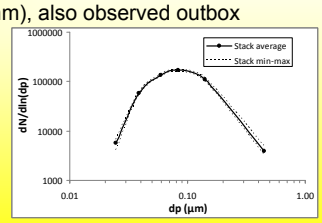
- $PNC_{0.02\text{-}1\mu m}$ levels in the workplace around $1.6 \cdot 10^4$ cm^{-3} as a daily average, with no relevant differences with the outside ambient air
- $PNC_{0.3\text{-}10\mu m}$ levels higher (+60%) indoors than outside
- Increasing PNC trend observed during the day both inbox and outbox, resulting from the superposition of process emissions and workers presence
- No significant inbox-outbox difference in PNC levels during normal operation
- Process operations (change of expanded graphite bag, surfaces cleaning) responsible for inbox PNC peaks as high as $5.0 \cdot 10^4$ cm^{-3} (up to $3.0 \cdot 10^5$ cm^{-3} if ventilation system switched off), also affecting larger particles

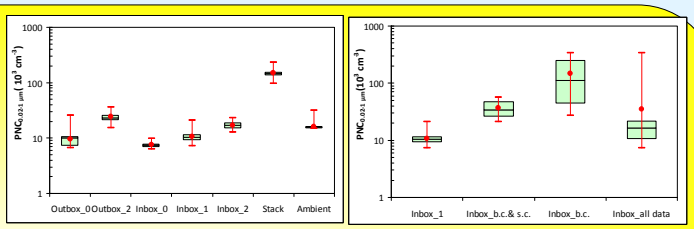
Size distributions (PSD)

- All PSDs measured indoors dominated by UFPs, with a rather flat distribution below 100 nm; larger presence of nanoparticles in outside
- Process emission resulting in increased abundance outbox of nanoparticles (20-30 nm size-bin), responsible for the daily trend in PNC levels.
- Process operations strongly affecting inbox PSD, with sudden huge enrichment in the smallest size-bins (20-50 nm), also observed outbox

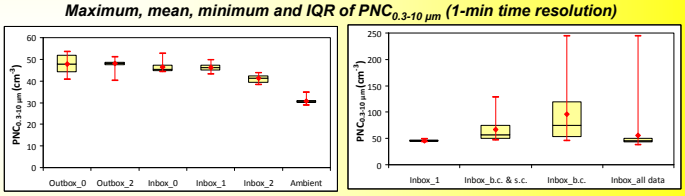
Stack emission

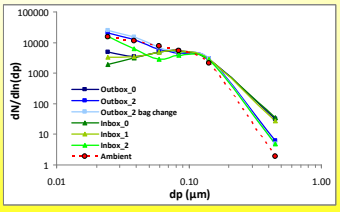
- Stack PNC levels around $1.5 \cdot 10^5$ cm^{-3}
- Bell-shaped PSD around 100 nm likely as a consequence of particles aggregation in the venting duct out from the chamber

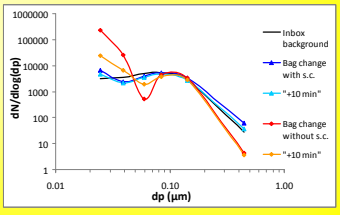




Maximum, mean, minimum and IQR of $PNC_{0.02\text{-}1\ \mu m}$ (1-sec time resolution)
0 = no operation; 1 = production process only; 2 = production process & exfoliation
b.c. = bag change; b.c & s.c. = bag change & surface cleaning
Maximum, mean, minimum and IQR of $PNC_{0.3\text{-}10\ \mu m}$ (1-min time resolution)







Mean particle size distributions

Conclusions

- Experimental results show that the normal process operation has a very limited impact on the concentration levels at indoor environments
- Conversely, maintenance and process operations can result in high concentration peaks, determined by a sudden increase of the finest particles, followed by an exponential decline pattern lasting 10-15 minutes.
- During these events workers may suffer of high exposure to UFPs: proper personal protective equipment should be adopted and process automation should be implemented at the full-scale production plant.
- Atmospheric emissions do not appear to be of any concern and relevance.

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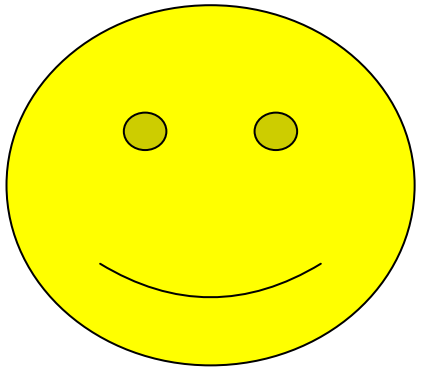

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