FROM RESEARCH TO INDUSTRY

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nanoSAFE'16

Occupational exposure during the production, simulated use and end-of-life stages of nanoenabled products for energy harvesting and energy storage

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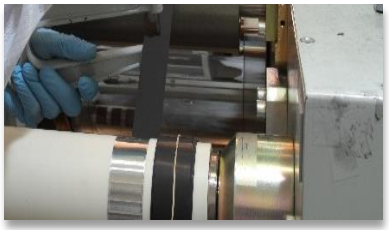
Univ. Grenoble Alpes, CEA Tech LITEN - DTNM, **PNS**, F-38000 Grenoble, France

PNS PLATE-FORME NANO SÉCURITÉ

THE LEADING PUBLIC FRENCH INSTITUTE FOR ENERGIES & MATERIALS

SOLAR / BUILDING

ELECTROMOBILITY



NANOMATERIALS / LARGE SURFACE ELECTRONICS

THERMAL / BIOMASS / H2

ENERGY / TRANSPORTATION

- *Production of nano-enabled electrodes for Li-ion batteries*

RECYCLING

- *End-of-life of nano-enabled electrodes for Li-ion batteries*

ENERGY HARVERSTING

- *Production of thermoelectric generators*
- *Simulated use of TE generators*

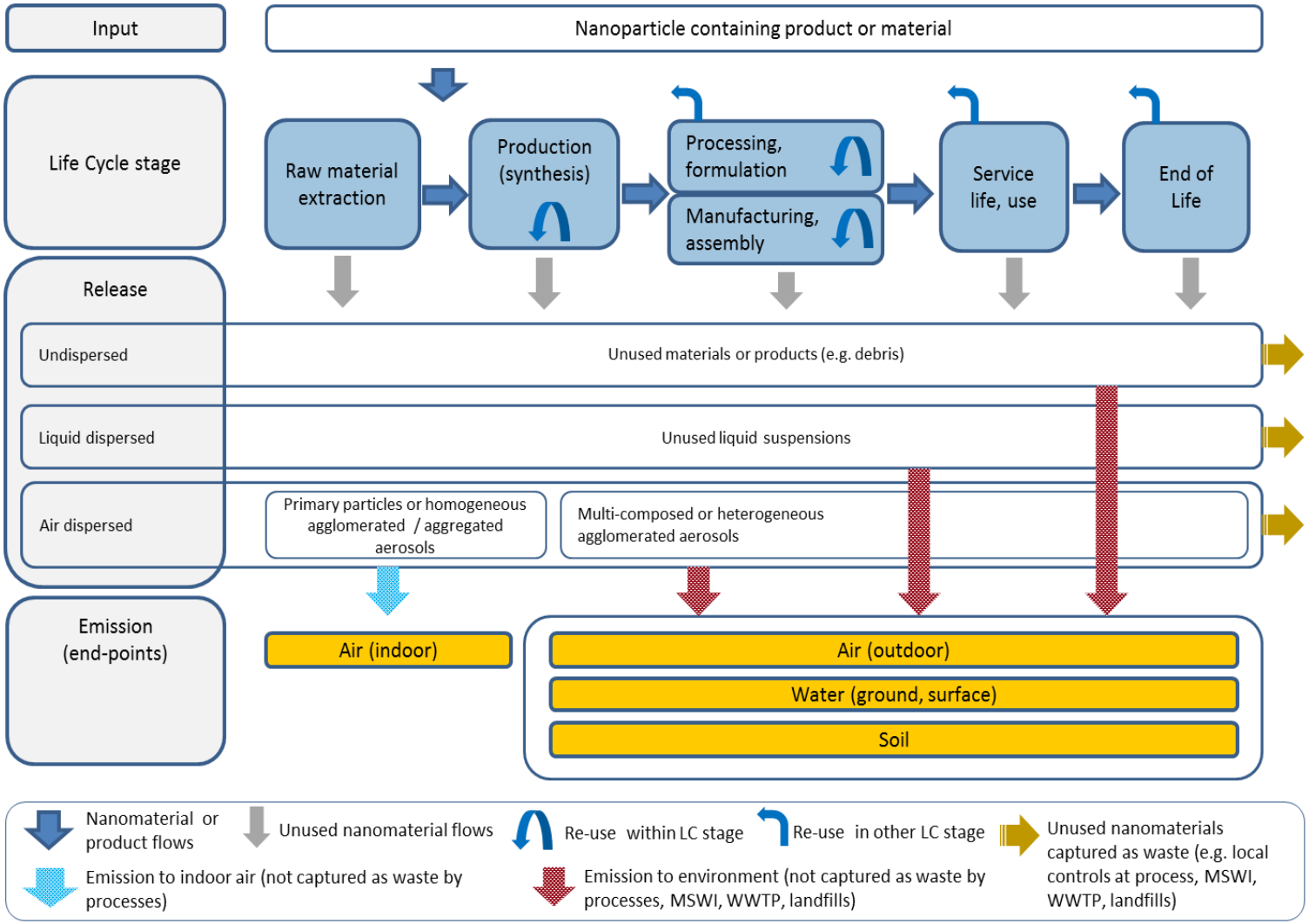
VALUE CHAIN CASE STUDIES

- *VC2 – Energy sector – Nanomaterials for Lithium-Ion batteries*
- *VC3 – Energy / transportation sectors – Silicon based nanomaterials for thermoelectric generators*

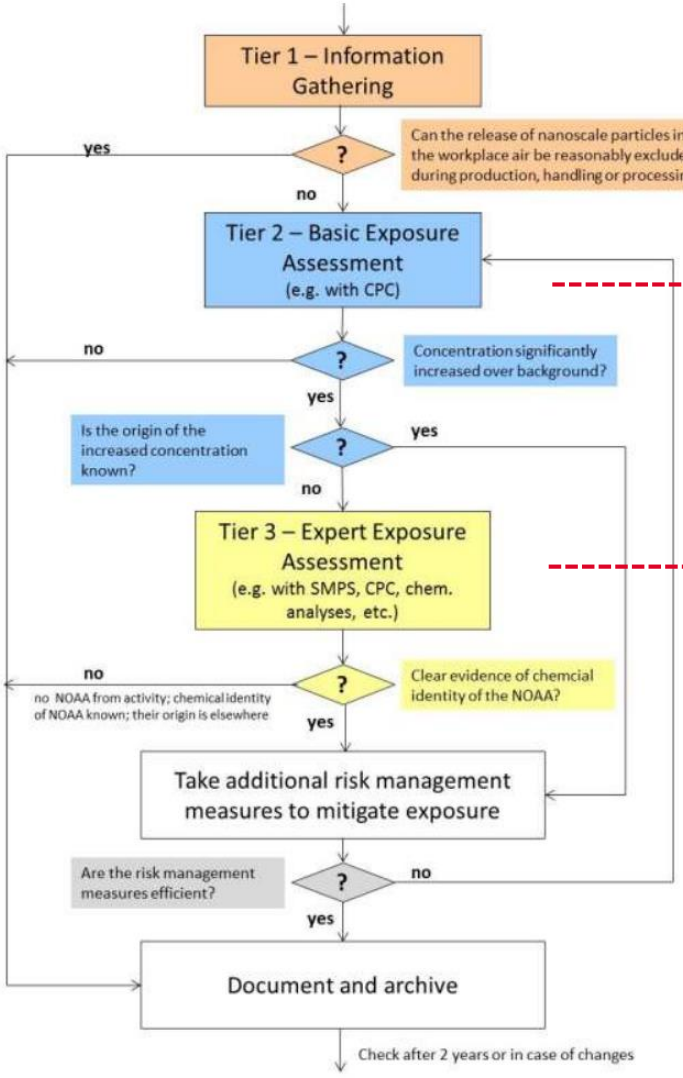
SAFETY VALUE CHAIN CASE STUDY

- *Use of carbon-based nanomaterials in electronic goods (with special emphasis on batteries and end-of-life)*

FRAMEWORK WITH NANOMATERIAL RELEASES AND EMISSIONS ALONG DIFFERENT LIFE CYCLE STAGES



MEASUREMENT STRATEGY: OECD HARMONIZED TIERED APPROACH



OECD report, ENV/JM/MONO(2015)19

NanoBadge sampler[1]

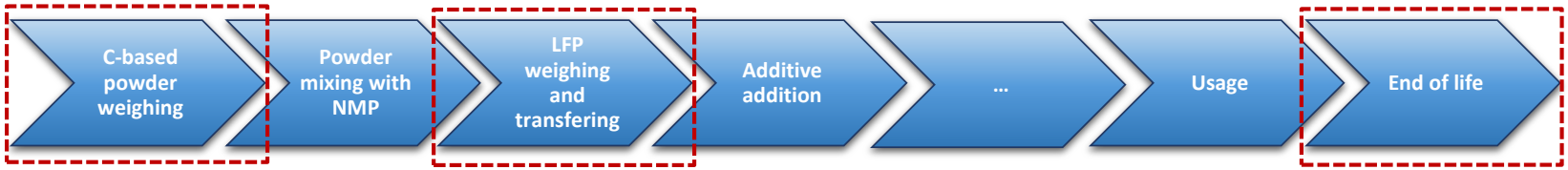
Handheld CPC TSI 3007

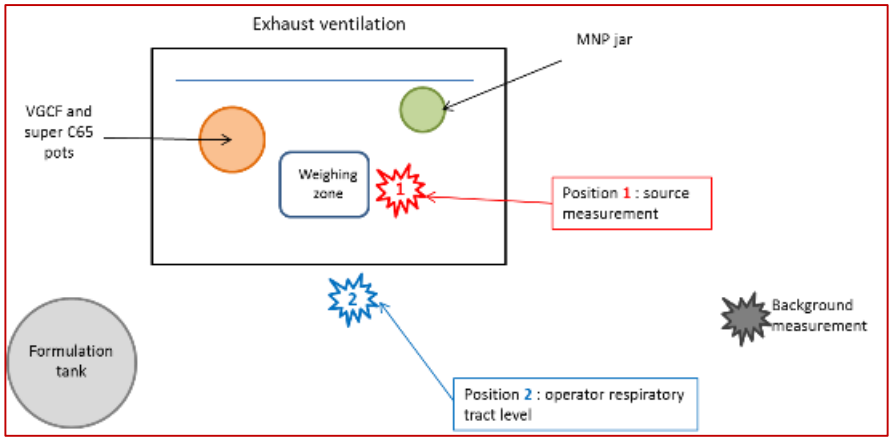
DiSCmini[2]

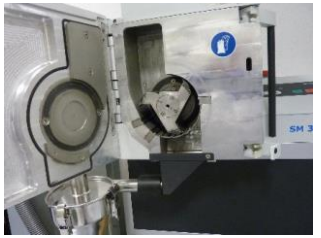
CEA's equipped mobile cart (CPCs, NSAM, FMPS, ELPI …)

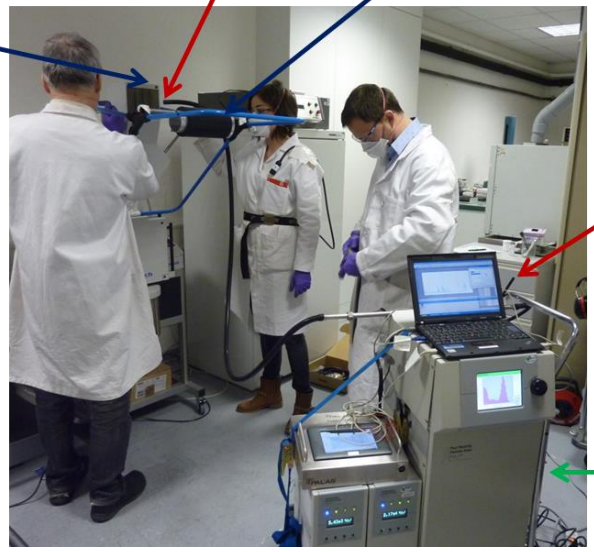
[1] Faure et al., *J. Aerosol Sci.* (submitted)
[2] Todea et al., *J. Aerosol Sci.* **89**: 96-109, 2015; Todea et al., *Sci. Total Environ.* (close to submission)

VCCS ON CARBON-BASED NANOMATERIALS FOR LITHIUM-ION BATTERIES (PILOT SCALE)

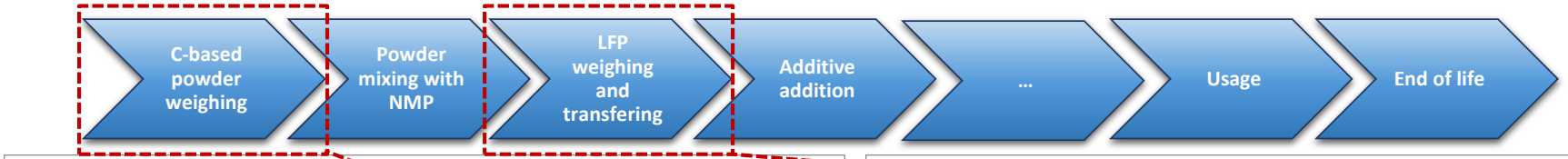


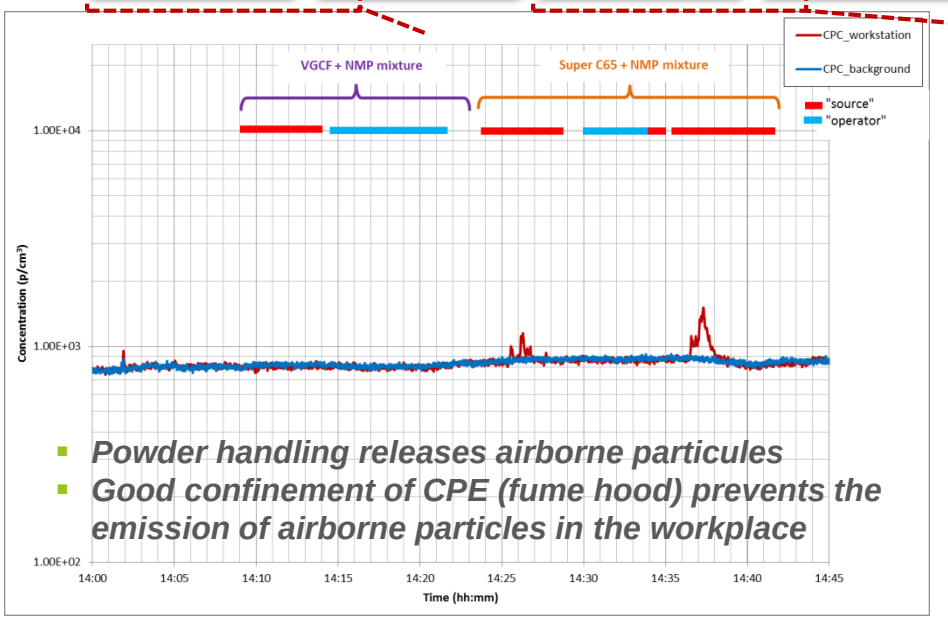




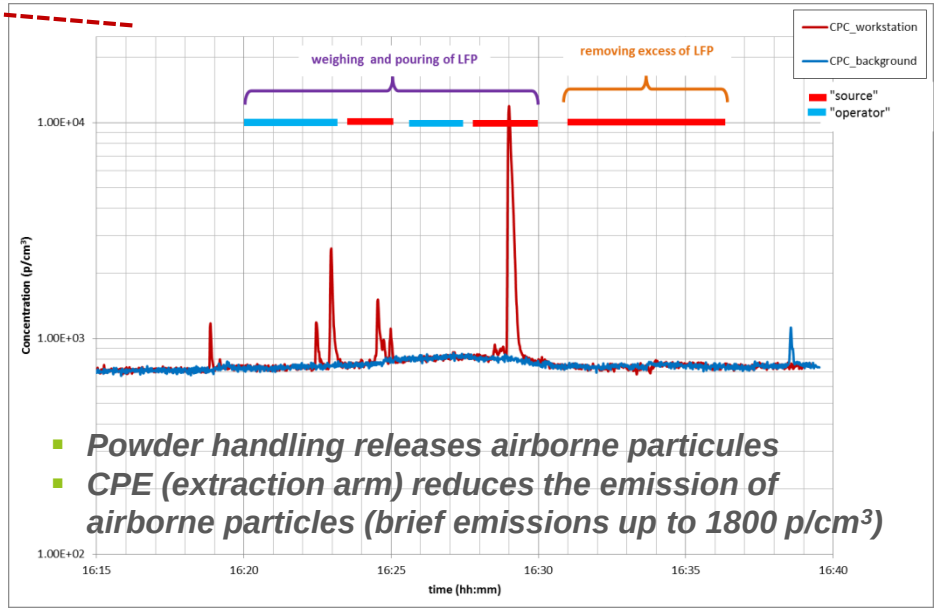


VCCS ON CARBON-BASED NANOMATERIALS FOR LITHIUM-ION BATTERIES (PILOT SCALE)



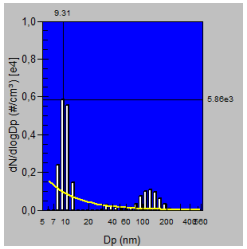


- *Powder handling releases airborne particules*
- *Good confinement of CPE (fume hood) prevents the emission of airborne particles in the workplace*



- *Powder handling releases airborne particules*
- *CPE (extraction arm) reduces the emission of airborne particles (brief emissions up to 1800 p/cm³)*

FMPS



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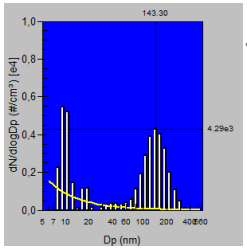
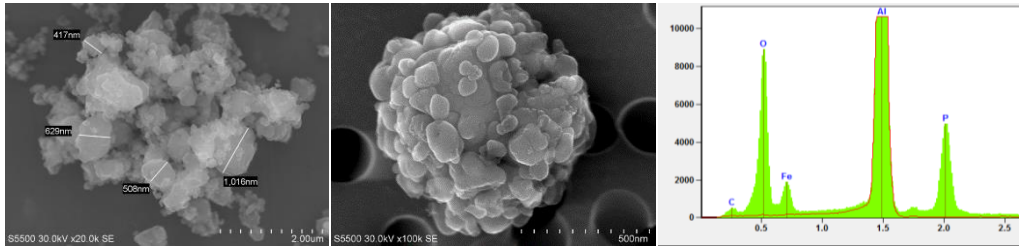


Emission measure

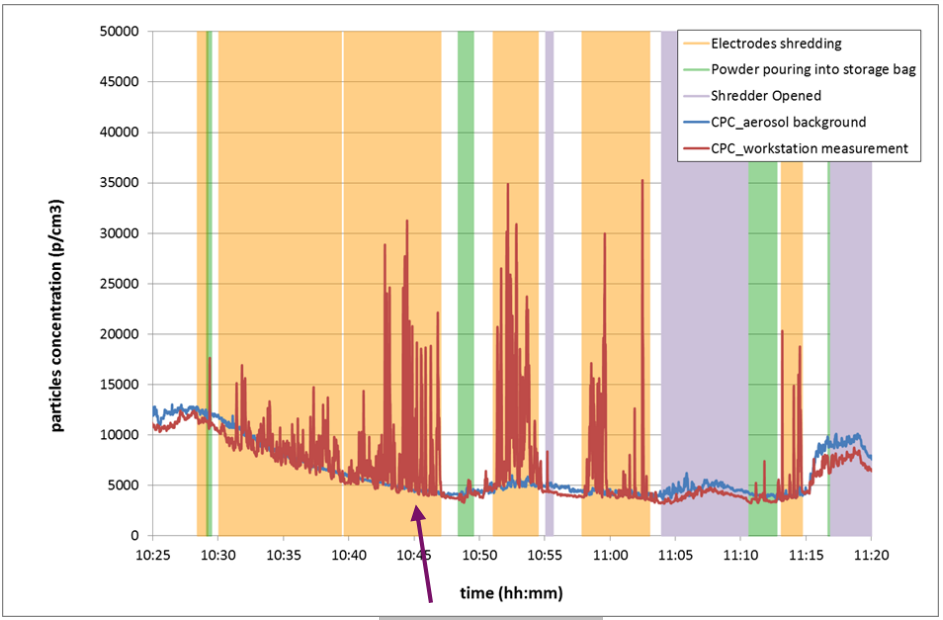
SEM-EDS

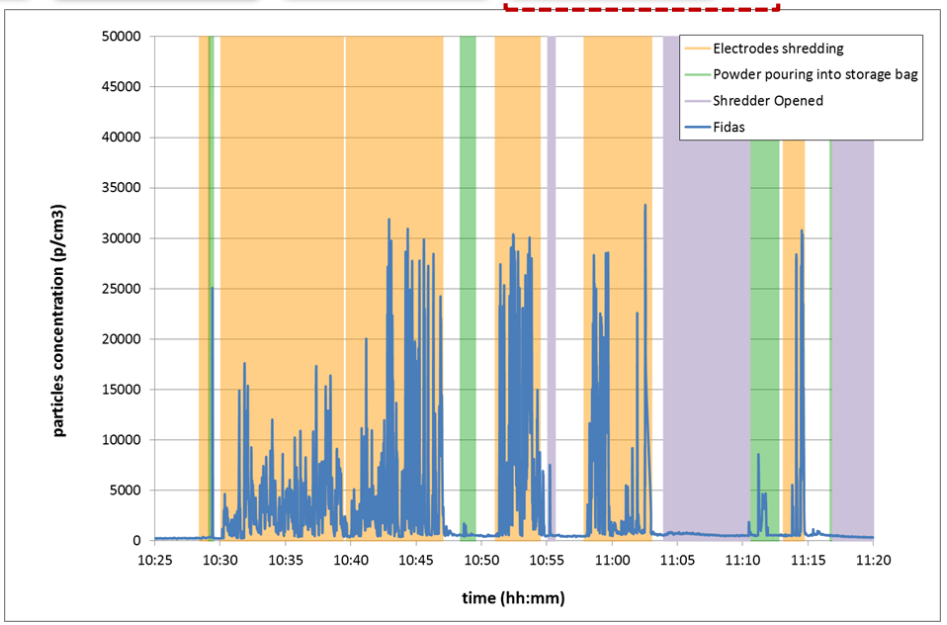


VCCS ON CARBON-BASED NANOMATERIALS FOR LITHIUM-ION BATTERIES (PILOT SCALE)

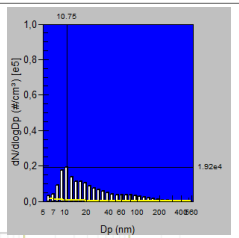
C-based powder weighing → Powder mixing with NMP → LFP weighing and transfering → Additive addition → ... → Usage → End of life

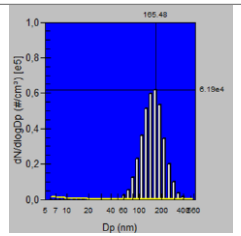
LFP & VGCF deposited on Al foil



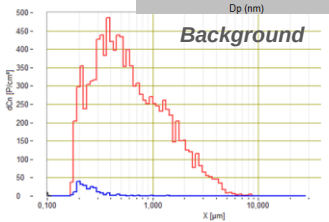


FMPS





FIDAS



Background

Emission measure

Worst case scenario: shredding of 4 kg of electrodes (Li-ion batteries)

- *Significant emission of airborne NOAA during shredding (submicronic particles containing C, Fe, P)*
- *Moderate release during powder transfer operations*
- *CPE should be adapted to this non frequent worst case scenario=> confinement*

VCCS ON CARBON-BASED NANOMATERIALS FOR LITHIUM-ION BATTERIES (PILOT SCALE)

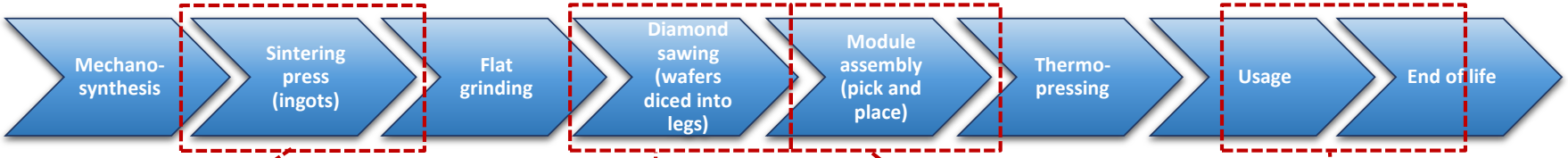
During the early stages on this VC:

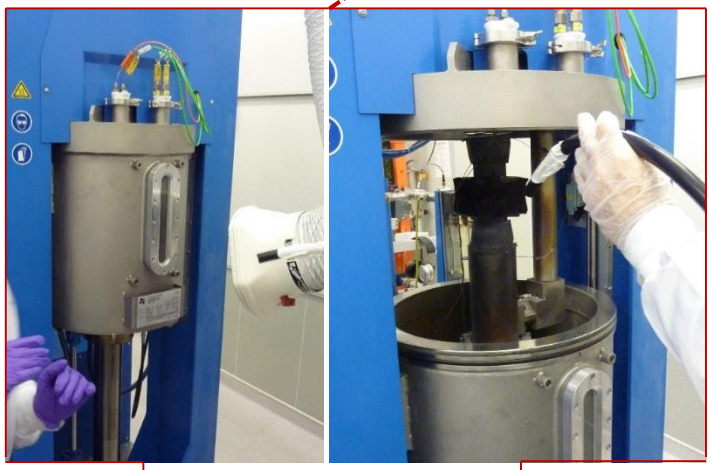
- **Powder handling** releases airborne NOAA
- Good **confinement** prevents (or reduces) the emission of airborne NOAA
- Worn **PPE** seems appropriate and are recommanded (gloves and disposable forearms, non-woven fabric worksuit and disposable headware, FPP3 masks, safety glasses)

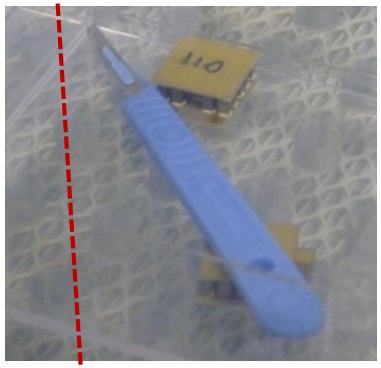
During the end-of-life stage on this VC:

- **Shredding** as a high-energy mechanical process emits large amounts of submicronic particles
- **Powder transfer** releases moderate quantities of airborne NOAA
- **Confinement** should be promoted to control the emission during the process (CPE)
- Worn **PPE** seems appropriate and are recommanded (gloves, non-woven fabric worksuit, FPP3 masks, safety glasses). However due to the high amount of generated dust, FPP3 masks were replaced twice.

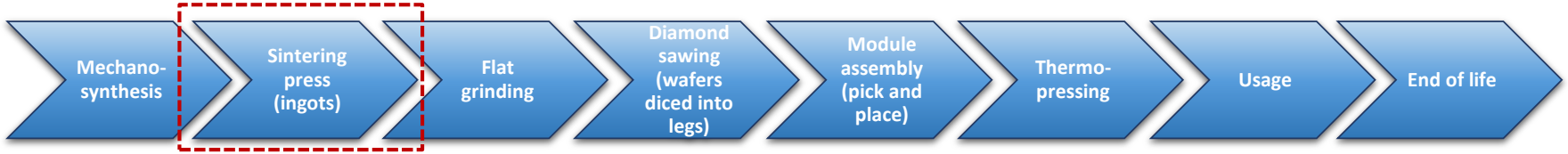
VCCS ON NANO-ENABLED THERMOELECTRIC GENERATORS

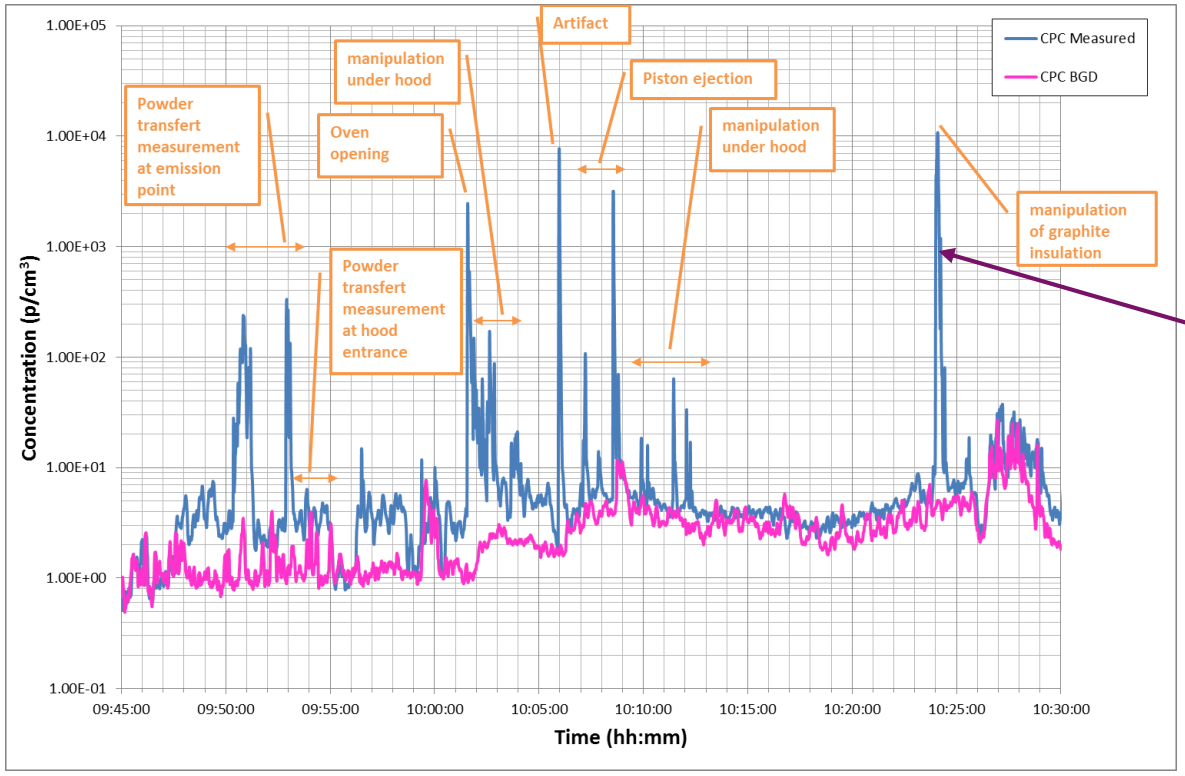






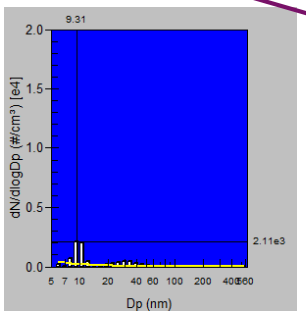
VCCS ON NANO-ENABLED THERMOELECTRIC GENERATORS





Phase (source)	CPC (p/cm³)	Dustmonitor (p/cm³)
Powder transfert	332	460
SPS equipment opening	2360	50
Manipulation under hood	160	80
Piston ejection	3160	60
Manipulation under hood	60	23
Voluntary manipulation of graphite insulation	10600	2900

FMPS



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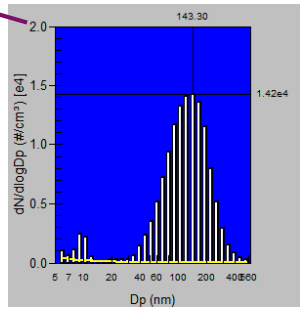
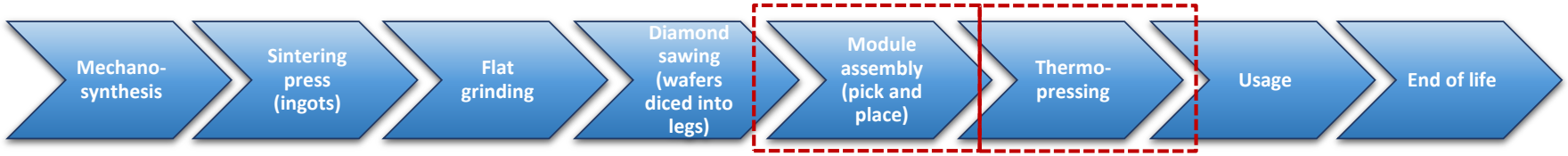
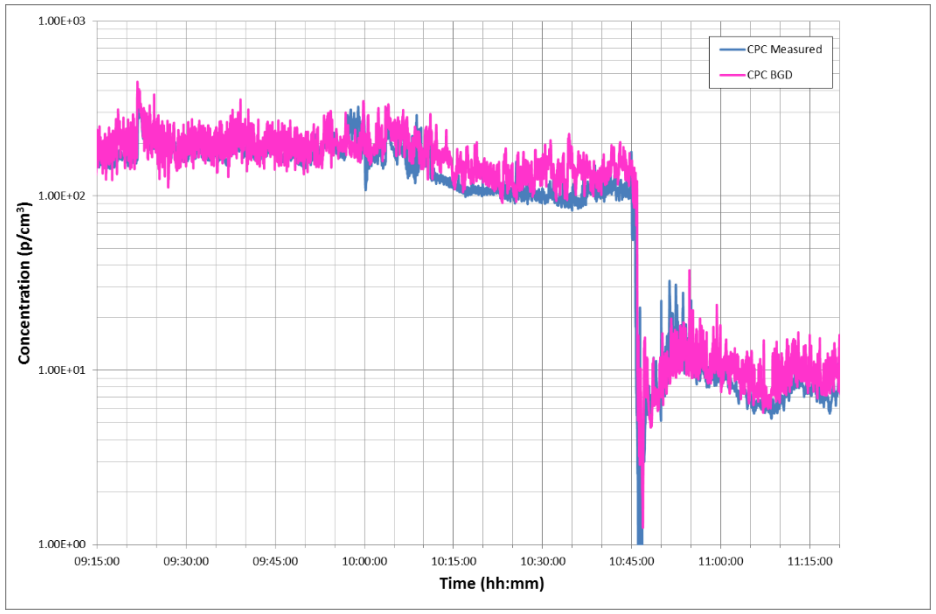


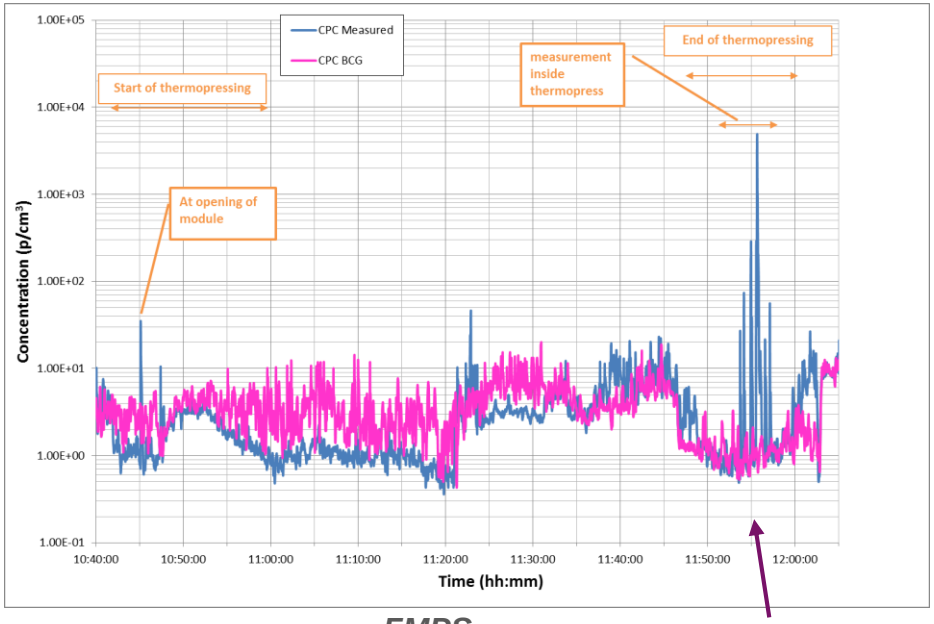
Emission measure

- *Process performed in clean room => low background*
- *The most emissive phase was not expected and not directly related to the manufacturing process => manipulation of graphite material*

VCCS ON NANO-ENABLED THERMOELECTRIC GENERATORS







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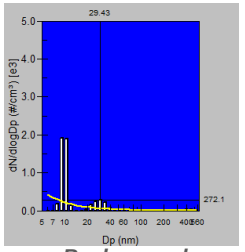

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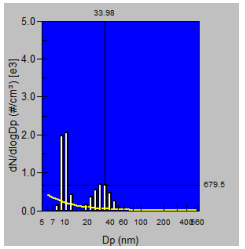
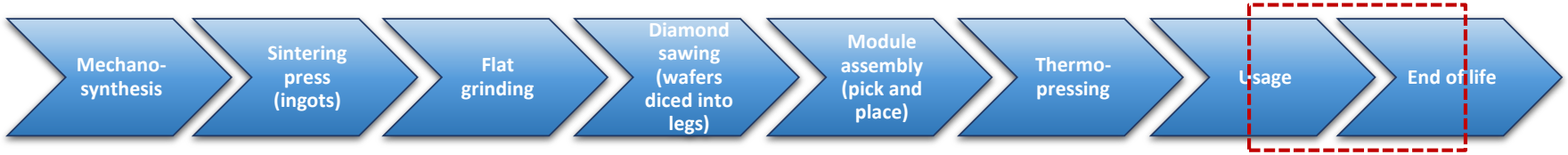
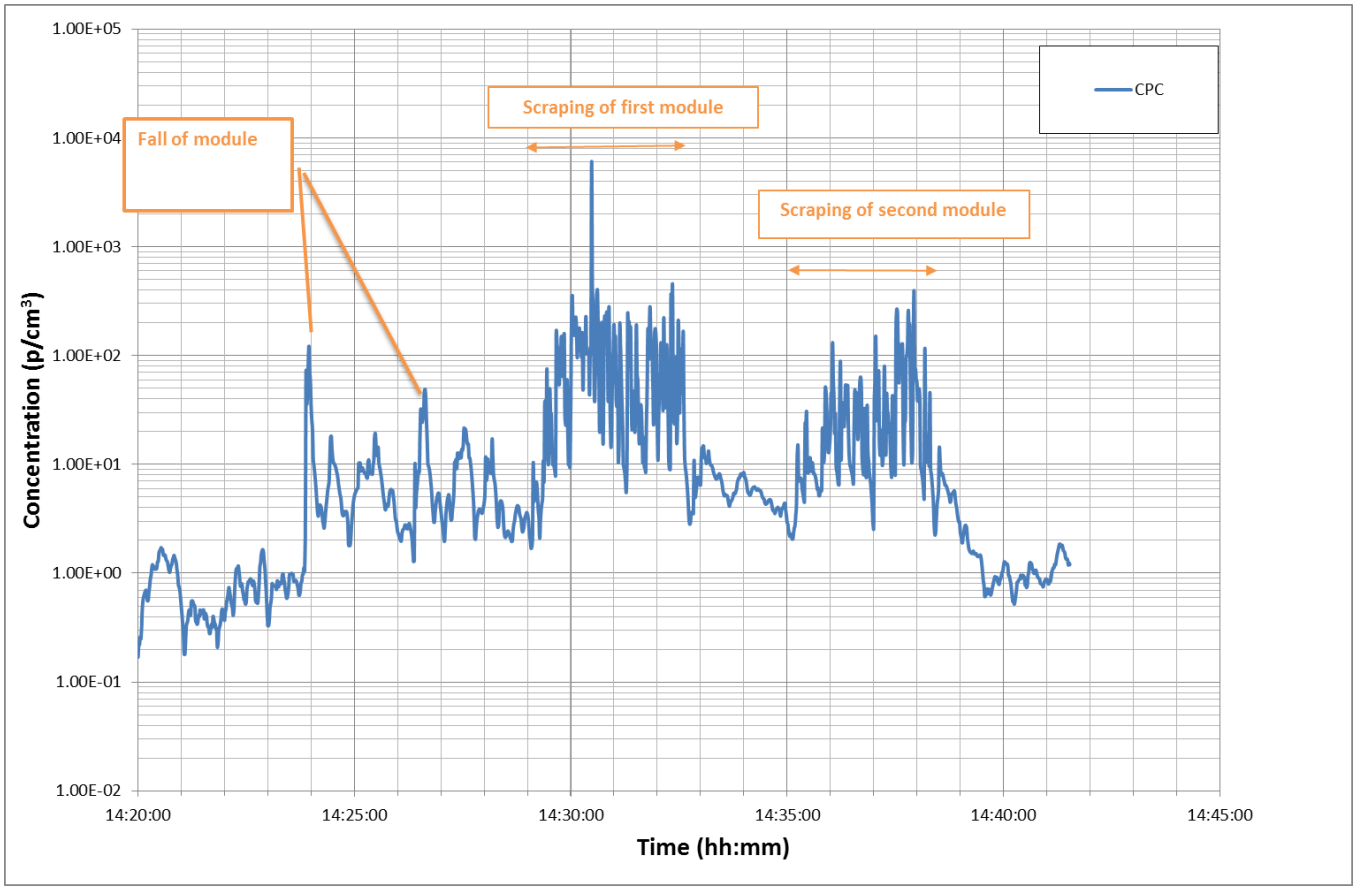


Emission measure

- ***No significant release was observed during the two stages monitored except artifacts and thermal effects***

VCCS ON NANO-ENABLED THERMOELECTRIC GENERATORS



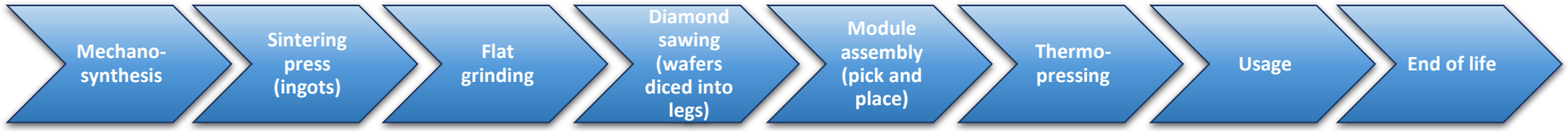


Evaluation of the potential release of excess of sintered silver lacquer

- ***Mechanical shocks releases reduced amounts of NOAA (50 to 100 p/cm³)***
- ***Manual abrasion and scratching releases more significant amounts (up to 6000 p/cm3) of micronic and submicronic particles containing Si, Ge, Ag***

A simple encapsulation of the modules could prevent that release during the use phase.

VCCS ON NANO-ENABLED THERMOELECTRIC GENERATORS



- Except the mechanosynthesis step (bowl milling) which was not monitored, the other VC stages are **not emitting significant amounts of NOAA**
- The first **sintering step tends to aggregate** (fuse) the particles and therefore their subsequent release is unfavoured
- The manipulation of **graphite material emitted** NOAA unexpectedly

- Even the high energy process such as **sawing and grinding are not emitting** airborne aerosols in the vicinity of the equipements. This is certainly due to the **liquid / lubricants used** during the process that prevents the emission in air of the released material. Extra care should be taken during maintenance steps when the liquids and the associated filters are manipulated

- **CPE** and **PPE** at workplace seem adequate in order to protect the operator

- **Mechanical sollicitation** on the devices showed that in some cases the excess of silver lacquer could be partly removed and **released minute amounts** of airborne particles. A simple **encapsulation** of the modules could prevent that release during the use phase.

CONCLUSION AND PERSPECTIVES

Release, emission and exposure:

- Early stages of the VC case studies: **Powder handling** and **transferring** releases airborne NOAA
- High energy mechanical processes: **wet processed** (if possible) are **preferred**
- Use: **encapsulation strategies** and **sintering steps** when relevant reduces the potential release of NOAA and their subsequent emission
- **End-of-life stage**: high energy processes and potentially less trained and informed workers on the risks associated with ENMs requires more **attention and care**

EHS good practices already in place or that could be implemented:

- Good **confinement** prevents (or reduces) the emission of airborne NOAA: **wet processes** or **integrated suction** to the tool used as close as possible to the source are recommended
- Worn **PPE** seems appropriate and are recommanded (nitrile gloves and disposable forearms, non-woven fabric worksuit and disposable headware, FPP3 masks, safety glasses)
- **Training** sessions to make **aware workers of the risks** associated to NOAA

Thank you for your attention !

The research leading to these results has received funding from the European Research Council under the European Union's FP7 Grant Agreement n.604602 (FutureNanoNeeds project) and Grant Agreement n.310584 (NANoREG project) .

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Direction de la Recherche Technologique
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L2N - PNS

Description of the instruments used

Real time monitoring

Counters

CPC, GRIMM

3 nm to 3 µm

+ rapid

- only part. coutns

Granulometers

FMPS

5 to 560 nm

+ rapid

- sensitivity to low concentration

SMPS

5 to 350 nm

+ sensitivity and accuracy

- Requires 3 min stability of events

Fidas

180 nm to 18 µm

+ large range

- saturation occurs