Behaviour of nanoparticles during high temperature treatment (Incineration type)

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Abstract. The treatment of waste containing nanoparticles (NP) will become a matter of first importance being given the increasing production and use of engineered NP. At present no specific end of life treatment is planned for such waste and most of the time it follows the path of conventional waste in incineration plants. The study of the behavior of NP at high temperature may help to define dedicated procedures and eventually lead to new regulations. This work deals with the set up of an incineration mounting at a laboratory scale. This assembly tested on NP samples shows significant results and interesting trends.

1. Introduction
In a global context of reduction and follow-up of the atmospheric particle emissions, limiting the release of NP when submitted to waste incineration is a non negligible element. This subject is growing while the implementation of end of life solutions under control are put in place, as a necessary continuation of the growth in the manufacturing and use of engineered NP.

Nowadays waste containing nanomaterials are most of the time treated by elevated temperature (from 850°C to 1100°C) like classical waste in incineration plants. There is not much information about the behaviour of NP during incineration to establish which fraction stays in the slag and which percentage becomes airborne and is released outside the plant. However, some studies have reported the problem [1] and on-line analysis were performed [2-3] to characterize concentration and size distribution of NP released from municipal waste incinerators.

Measuring and especially understanding NP release when submitted to end of life high temperature processes is one of the topics of the NanoSafety Platform at CEA Grenoble. The first step of this fundamental study has been to develop a specific bench test including a laboratory furnace connected at its exhaust to NP analysis tools. Different NP samples were subjected in this way to incineration tests to validate our assembly.

2. Experimental setup and methods

2.1. Samples
The choice was made to focus the study on starting samples entirely at a nanometric scale. Another option would have been to conduct the incineration tests on waste containing NP. However, the NP concentration in waste being usually very low (around one part per thousand), we were not sure to be
sensitive enough to measure any release of NP (the ones included from the start) when heating such samples. Indeed, our goal was to avoid measuring NP potentially released from the macroscopic part of the waste. Three samples were selected: silver, tin and nickel. For each incineration trial, around 600 mg of NP are used.

2.2. Furnace
The incineration tests are performed using a benchtop tubular furnace. As seen on Fig. 1, the furnace is made of different parts with the most important element of the assembly being the quartz tube. On the right side of this tube, the NP sample is being held in a crucible waiting to be introduced in the central heating part once the chosen temperature is reached. The incineration trials are conducted at 850°C and 1100°C which are the usual temperatures used in waste incineration. On the opposite end of the quartz tube, all the emitted particles are collected and measured using various on-line particle sizing techniques described in next section. It is important to point out that after the sample being positioned in its ceramic crucible and waiting to be carried in the central heating portion, the furnace is isolated from the outside environment. Clean air filtered with an HEPA filter is then sent all along the tube at an adequate flow rate during the rest of the experiment. By this manner, no NP are added from the outside while the flow rates needed by the analytical equipments are matched. The experiment is then started when the background noise count is showing no NP along the furnace.

![Figure 1. Schematic of the furnace](image)

2.3. Analytical equipments
To measure NP liable to be released during incineration, we used several techniques to characterize particles aerosol in terms of volume concentration and size distribution:

Particles counting is performed using a water-based Condensation Particle Sizer (CPC 3785) manufactured by TSI Inc [4] operating on the principle of enlarging small particles using a condensation technique to a size allowing optical detection. The CPC detects particles in the size range from 5 nm to 3 µm and provides measurements over a particle concentration range from $0$ to $10^7$ p.cm$^{-3}$ with time resolutions in the order of one second.

We also used a GRIMM 5.416 Scanning Mobility Particle Sizer (SMPS) [5] consisting of a particle neutralizer (Am241), a short-column Differential Mobility Analyzer (DMA) and a CPC. In such a configuration, the SMPS provides the size distribution of NP in the range 5-350 nm up to a concentration of $10^7$ p.cm$^{-3}$ with time resolution of around three minutes.

Finally, we performed real-time measurements by using a Fast Mobility Particle Sizer (FMPS) [6]. The FMPS 3091 from TSI measures the particle mobility diameter in the range 5.6-560 nm with a time resolution of 1 s this time.
For solid samples characterization, before and after heating, we used a Scanning Electronic Microscopy (SEM) 5500 from HITACHI. The high resolution of this tool allows the visualization of the nanoparticles for size measurement and shape determination.

3. Results
An example of CPC profile recorded when a NP sample is introduced and kept in the hot furnace is given on Fig. 2. We can first notice that before the test (when the furnace is empty), no particle emission is measured. This point proves that our setting equipped with adequate filters is in conformity with our need of a background noise count close to zero before any heating of the sample. The second point is that a substantial emission of NP is measured when the sample is heated. As seen on Fig. 2, at the maximum of emission, a concentration around $1.5 \times 10^5$ p.cm$^{-3}$ is reached. It is important to notice that the amount of sample being heated and the sizing of our furnace lead to timescales of few minutes. For this reason, the SMPS having a too long sampling time was replaced by the FMPS very early in our study. Finally, we see that the particle emission is not an endless process. The concentration value goes back to the same level as before the start of the experiment while the sample is not yet removed from the heating section. Our setup being ready to use and giving consistent results, we extended the tests to NP comparisons.

![Figure 2. CPC data – NP sample heated at 850°C](image)

For nickel and tin NP, the number of particles emitted per cm$^3$, at 850°C and 1100°C, is reported on Fig 3. The first information coming out from those data is that the number of particles released from the sample is significantly higher when the temperature is set at 1100°C. The maximum of concentration peaks are around 7 times higher at 1100°C compared to 850°C. One can also see that the process of emission is much shorter when the temperature is low. For both two samples, the duration of emission at 850°C is around one third of the 1100°C one.
Figure 3. FMPS data – Tin and Nickel NP samples heated at 850°C and 1100°C

For silver NP, the number of particles emitted per cm$^3$ at 850°C and 1100°C is reported on Fig 4. For this sample, the temperature level seems to have a very low impact on the emission process as the results are very close. Although, the number of particles emitted at 1100°C is slightly higher than at 850°C, the length of the emission processes is very similar.

Figure 4. FMPS data – Silver NP samples heated at 850°C and 1100°C

Concerning the size of the released particles, as seen on Fig. 5 for tin NP, we can associate small size particles to low incineration temperature and higher sizes to high temperature. Indeed, very small NP of diameter lower than 50 nm are released at 850°C while at 1100°C, NP of diameter 100 nm and higher are measured. Although the results are not presented here, the same behaviour is found for nickel. One explanation is that at 850°C, the smallest “elementary” particles from the starting NP sample are released whereas at 1100°C, high size NP and aggregates are likely to be emitted. This assumption is illustrated on figure 6, on a Tin NP starting sample.
Figure 5. FMPS data (Sizes vs. time) – Tin NP heated at 850°C and 1100°C

Figure 6. SEM Picture- Initial Sn NP- Potential NP release at 850°C and 1100°C

For silver NP (see Fig. 7), the behaviour is similar with tin and nickel at 850°C. At 1100°C, the behaviour is somewhat different as NP close to 100nm are first released before a size decrease.
This specific behavior of the silver sample has to be linked to the fact that melting starts even at 850°C, which is not the case for other samples. Indeed, a SEM picture of the silver residue, collected from the crucible after a 850°C heating (see Fig.8), shows that melting already occurred. This point highlights the fact that physical properties of the samples at the incineration temperature are parameters of first importance for NP release.

**Figure 8.** SEM Pictures – Silver NP before heating (left) and residue collected from the crucible after heating at 850°C (right)

4. **Conclusion**

The study of the incineration of NP at a laboratory scale is possible. We were able to develop an installation and a protocol that gives interesting results. Preliminary data show that release of NP from an initial sample at a “nano” scale is significant and measurable with our mounting. Differences between samples and global trends were identified. For instance, correlations were established between incineration temperatures, concentrations and sizes of NP released. Moreover, the position of the incineration temperature with respect to the melting temperature of the initial NP sample seems to be one of the critical points that control the properties of NP release. Future studies will deal with adjustments that can be undertaken with our mounting and our incineration methodology. In addition this study will be extended to other type of NP samples.
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