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INCINERATION OF A COMMERCIAL COATING WITH NANO CEO₂

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Abstract. The potential environmental risk arising from the incineration of waste containing nanomaterials is a new field which deserves further attention. Some recent studies have begun to focus on this topic but the data are incomplete. In addition, there is a need to consider real life waste.

The present study gives some insight into the fate and behavior of a commercial coating containing a commercial additive (7% w/w) based on nano-CeO₂ (aggregates of 10 to 40 nm, with elemental particles of 2-3 nm). The tests have been conducted with a system developed in the frame of the NanoFlueGas project. The test protocol was designed to respect the regulatory criteria of a good combustion in incineration plants (temperature around 850°C, highly ventilated combustion, at least 2 s residence time for the combustion gas in a post-combustion chamber at 850°C, and high oxygen/fuel contact).

Time tracking by electric low pressure impaction (ELPI) shows that the incineration produces aerosol with number concentration dominated by sub-100 nm particles. Cerium is observed by TEM and EDS analysis but as a minor compound of a sub-group of particles. No nanoCeO₂ particles have been observed in the aerosol.

ICP-MS analysis indicates that the residual material consists mainly of CeO₂ (60% of the mass). Observation by TEM establishes that this material is in the form of aggregates with individual particle of 40-200 nm and suggests that sintering occurred during incineration.

As a conclusion, the lab scale incineration study led mainly to the release of nano-CeO₂ in the residual material, as the major component. Its size distribution is different than the one of the nano-CeO₂ observed in the initial sample before incineration. Additional research is needed to improve the understanding of nanoCeO₂ behavior, and to integrate experiments at lab and real scale.



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1. Introduction

Nanomaterials (NMs) are more and more widely studied and produced. Part of these trendy materials are expected to end up in incineration waste plants due to the lack of specific recovery procedures. It seems necessary to address the issue of the fate of nano-objects during the incineration: are they destroyed, do they undergo changes in the incinerator furnace, and where are they released? To answer these questions, more and more studies investigate the behavior and the fate of nano-objects during thermal disposal at lab-scale [3, 4, 5, 6, 2, 7, 8], at pilot scale [9] and at real scale [1, 9, 10]. However, regarding the very large number of nano-objects and products, the data are far to be complete and more studies are needed to fully determine the risks related to the incineration of waste containing NMs.

The case study of nano-CeO₂ appears interesting since it is the only nano-object for which the incineration has been studied at the intermediate scale [10] and real scale [2, 9, 10]. Both studies conclude that incineration plants with state-of-the art gas cleaning systems can treat efficiently nanostructured metal oxides such as Ceria. These results are also consistent with the results of the NanoFlueGas project [2].

In that context, the aim of the present study is on the one hand to enlarge the data base by considering a product available in the market, and on the other hand to support the comparison between the lab scale and the larger scales (pilot and real scale) by testing a product containing nanoCeO₂.

This case study investigates the behavior and the fate of nano-CeO₂ during incineration of a commercial coating containing nanoCeO₂ and gives insights on potential exposure and environmental risk related to the incineration of waste containing nano-CeO₂.

Incineration tests have been performed at lab-scale using a specific tubular furnace, with the purpose to characterize the combustion residues and the combustion aerosol. The results are discussed regarding the studies at intermediate and real scale.

2. Materials and methods

In this study, imagery on the sample (prior to the incineration tests), the aerosol and the residues was carried out using transmission electronic microscope (Philips CM12 TEM 120 kV, and JEOL JEM 1400 Plus), and elemental analysis was performed using Energy Dispersive Spectroscopy (EDS). A commercial coating (colours lasure 4ans 11 in color code 101805 Groupe V33, Castorama – wood coating), has been enriched with 7% w/w of a commercial nanostructured additive Nanobyk 3810, which is a “Nanoparticle dispersion (cerium oxide) for long-term UV protection in aqueous system”. It has been applied on a clean and hard surface. Later the dry residue of that coating has been sampled. Incineration tests have been performed on 250 mg samples.

Laboratory scale incineration tests were performed using a specific tubular furnace fully described in a previous study [3]. The combustion conditions (within both the combustion and post-combustion zones) were controlled to satisfy the key operational parameters that govern an incineration process, *i.e.*: temperature (850 °C in the combustion and post combustion-zone), residence time (at least two seconds in the post combustion zone at 850 °C), air-excess (never below 11 % of oxygen) and turbulence (a good mix between combustible and oxygen). As illustrated in Figure 1 the “combustion chamber” is maintained at 850 °C (at least) and air cross flows penetrate and mix with the combustibles. Then, the “post-combustion chamber” is the furnace zone where the combustion aerosol stays for 2 s at 850 °C (at least). Finally, the combustion released gases and the aerosol particles were conveyed to the measurement line for on-line (an Electrical Low Pressure Impactor, Dekati (ELPI) was used downstream of a Fine Particle Sampler dilutor (FPS, Dekati)) and off-line analyses (particles

from the combustion aerosol were collected on a TEM grid with a MPS ® (Mini-Particle-Sampler, Ecomesure) [11]).

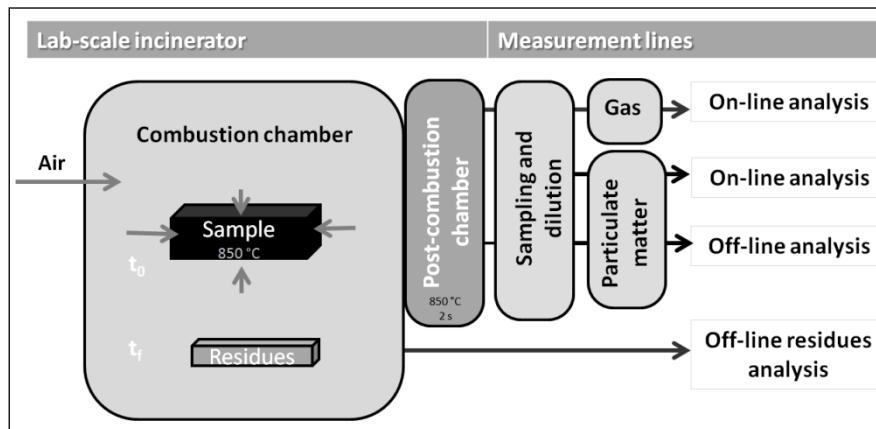


Figure 1. Lab scale incinerator and its measurement lines

A multi-gas analyzer (Portable Gas Analyzer PG-250 Horiba) was used to measure the consumption of O₂ (%vol.) and the production of CO₂ (%vol.) and CO (ppm_{vol}).

The residues have been crushed, dispersed in 2 mL ultrapure water (ultra-waves). 2 µl have been deposited on a TEM grid, and dried.

3. Results and discussions

3.1. Characterization of the sample

The sample was characterized prior to the incineration tests, by TEM imagery coupled with elemental analysis (EDS). The nanostructure of the CeO₂ was observed. It is composed of aggregates of 10 to 40 nm, with elemental particles of 2-3 nm (Figure 2, 3). In addition, elemental analysis was performed and showed that the sample contains carbon, oxygen, cerium, sodium and sulfur (Figure 4).

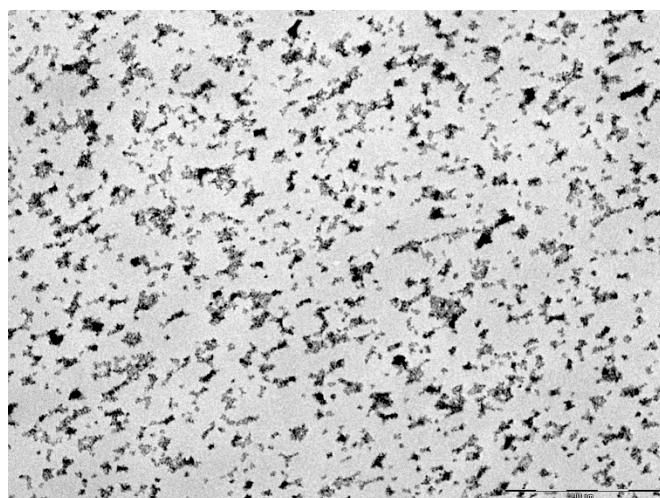


Figure 2. TEM image of the dry coating – scale 200 nm

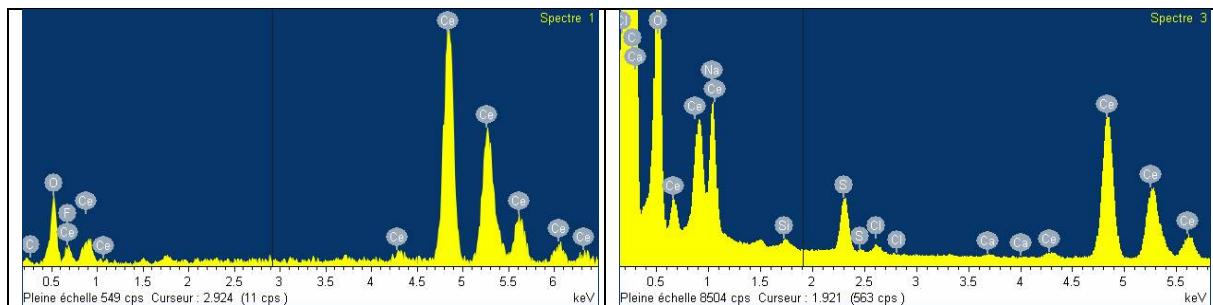


Figure 3. EDS spectrum of an example of individual particle

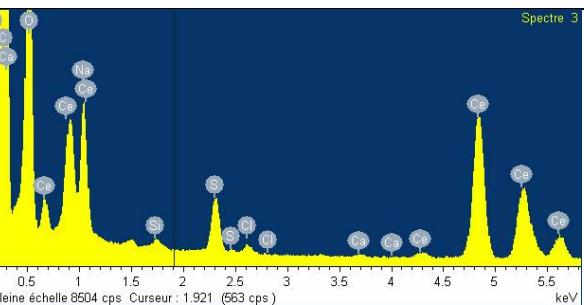


Figure 4. EDS spectrum showing the average composition of the dry coating

3.2. Time Tracking of gas and aerosol

The graphs describing the concentrations evolution during the incineration test are given in Figure 5. The two verticals delimit the time range with more than 5 % O₂ consumption from the baseline. This was named Area Of Interest “AOI” and it is considered as the time range when the combustion conditions are the closest to incineration conditions. The averages of three runs are presented with the associated standard deviation.

Ignition was observed at the beginning of the test during a period of 19 s; this could be related to the release and the combustion of volatile organic compounds (VOCs) commonly used in painting formulation.

Before the AOI, from 0 to 29 s, O₂ consumption is low, CO₂ and CO are produced, and particles are emitted at a high emission rate with a domination of PN0.1-1 (in the range of 0,1 to 1 µm) in terms of particle number. After this initial peak dominated by 0,1 – 1 µm, particles emission of particles smaller than 0,1 µm increases and becomes predominant in number concentration.

During the AOI, from 29 s to 75 s, oxygen consumption is maximal. PN0.1 becomes the most important contributor to the total number concentration.

The peak of emission of CO₂ and O₂ are not synchronized while it would be expected, as observed for instance in a previous study by Ounoughene et al. [3]. As a result, additional experiments will be needed to study further this point.

After the AOI, from 75 s to the end, O₂ reaches its baseline and gases are less and less emitted. Until the end of the test high particle concentration levels are observed. This phenomenon needs also to be studied further.

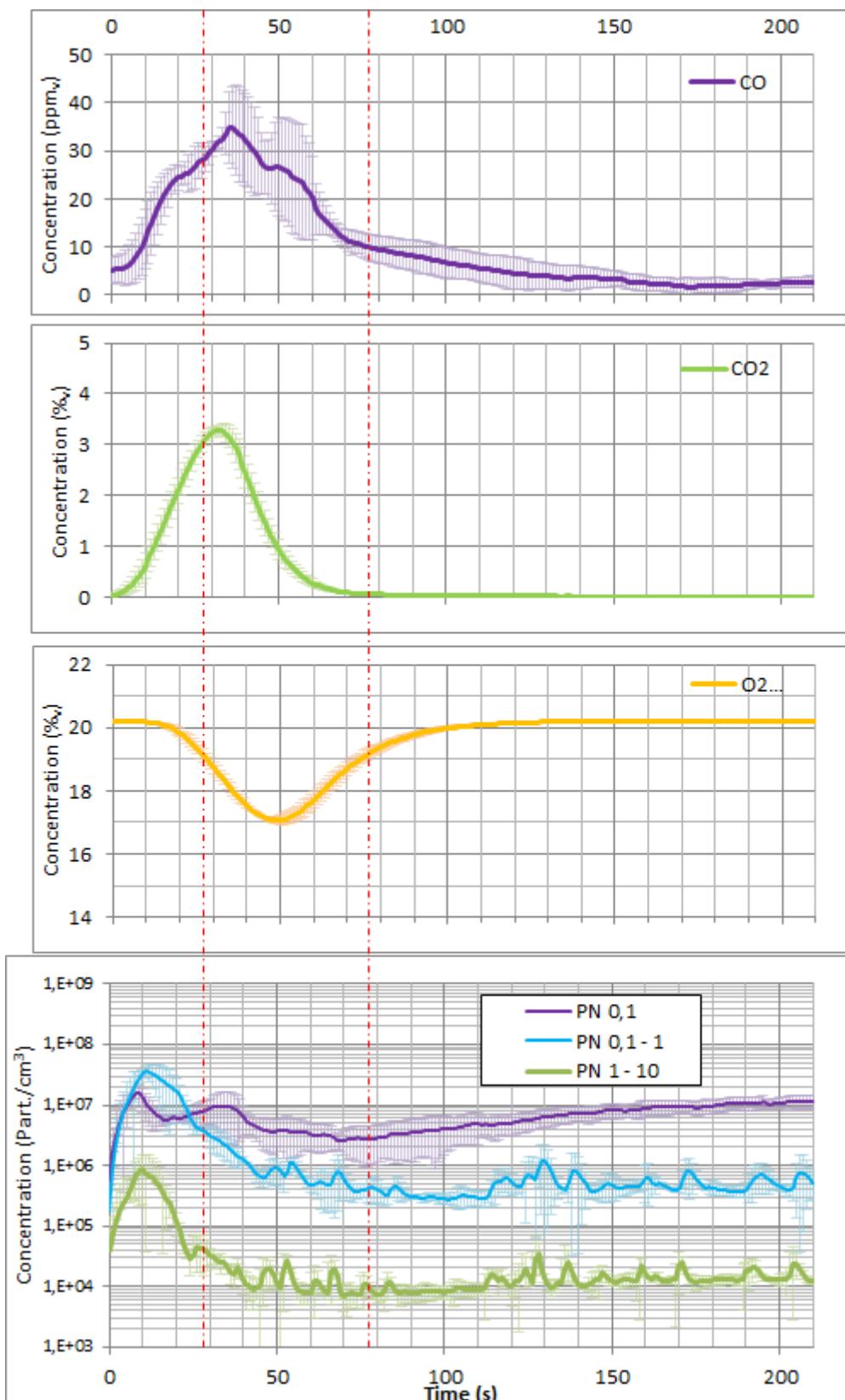


Figure 5. Time tracking for coating incineration: gas concentration (CO, CO₂, O₂) and particle number concentration. Average of three experiments.

3.3. Fate of nano-objects from the incineration of the nanowaste

The results from imagery provide qualitative information on the composition of the aerosol emitted during combustion and of the residues.

3.3.1. Analysis of the aerosol

Figure 6 shows examples of particles collected on a TEM grid during incineration. Different shapes and amount of particles have been collected (e.g soot aggregates, spherical or acicular particles, etc.), with some changes versus time. Some traces of cerium have been detected in some spherical particles mainly composed of oxygen, silica and sodium (ex. Figure 7 – a and b). Very rarely, CeO₂ particles are visible inside of some of these spherical particles (cf. Figure 7 – c and d). No free nanoCeO₂ particles have been observed.

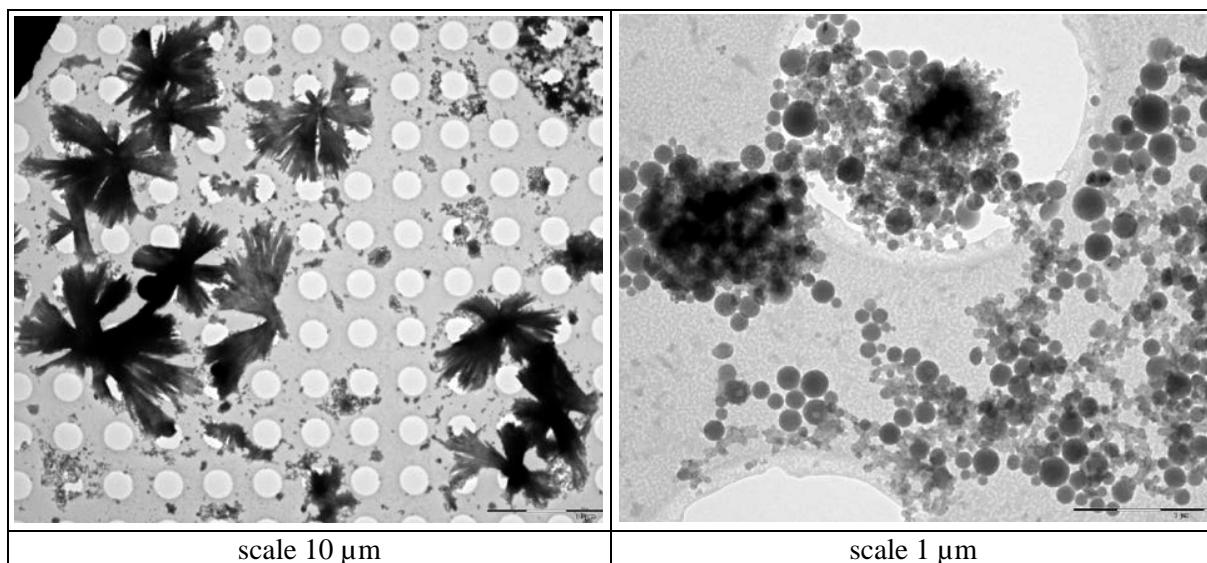


Figure 6. examples of combustion aerosol collected on TEM grid

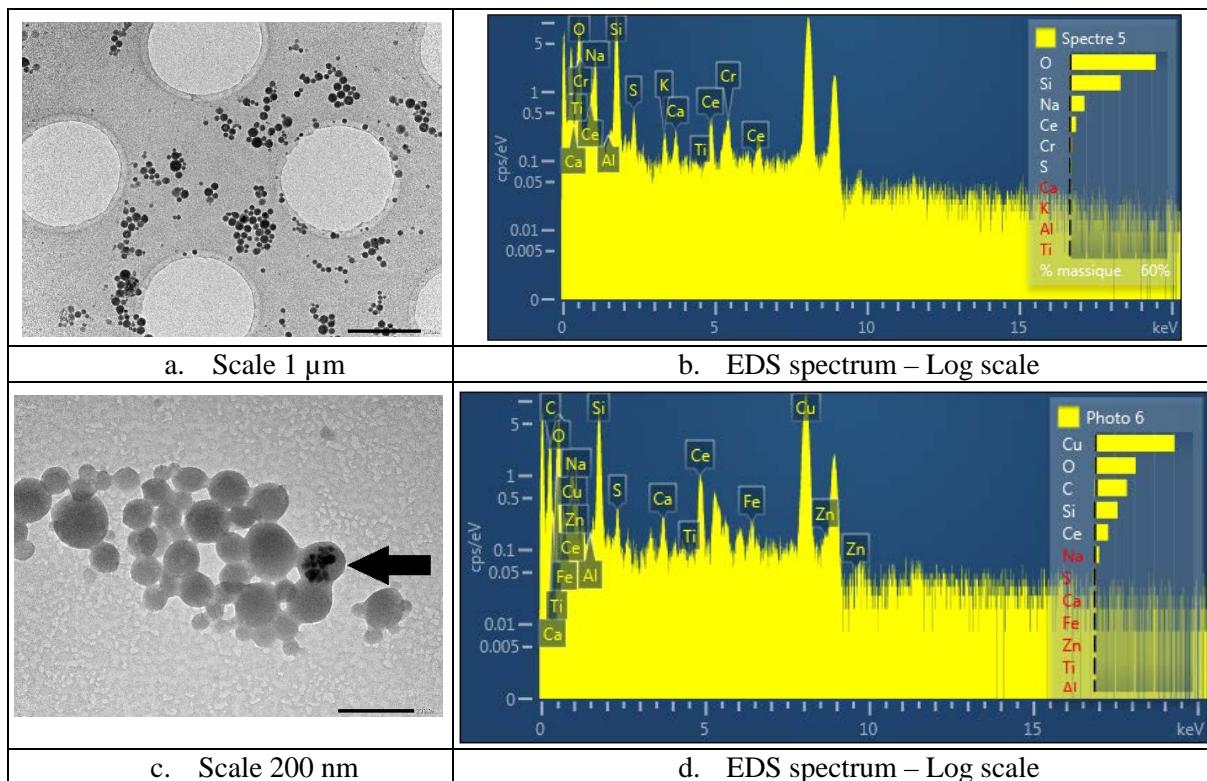


Figure 7. spherical particles containing some traces of cerium

3.3.2. Analysis of the residues.

The residues represent about 6% of the sample mass before incineration. According to ICP-MS analysis, the residual material consists mainly of CeO_2 (60% of the mass).

TEM (coupled with EDS) imagery performed on combustion residues reveals that the residues consist mainly of aggregates with elemental nanoparticles of 40-200 nm (Figure 8).

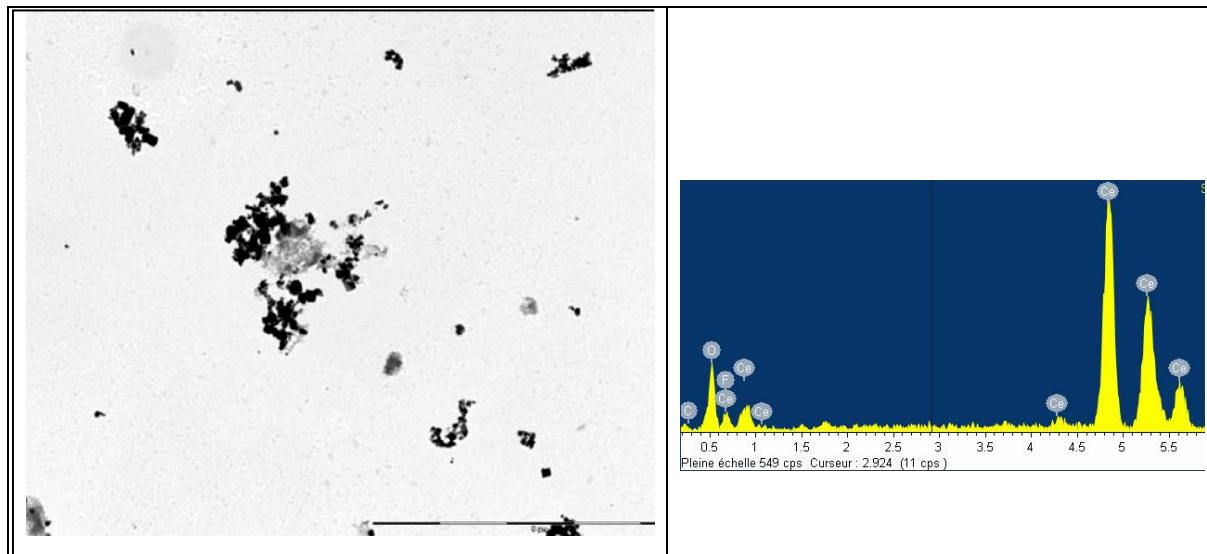


Figure 8. combustion residues analysed by TEM (scale 5 μm) and EDS

4. Discussion

4.1 Fate of nano-CeO₂ (qualitative)

In the current study, a significant mass of cerium has been observed to remain in the residues, which is consistent with Walser et al. 2012 who found the majority of the recovered cerium in the solid combustion residues.

The contribution of Paur et al. [9, 10] is not considered here for comparison because the ceria nanoparticles have been introduced downstream, in the post-combustion chamber.

4.2 Evolution of the size distribution of the CeO₂ nanoparticles

In the frame of Paur et al. study [10], in the case of the combustion of coal, “Ceria nano-particles were mainly found in the particles size range of 1 – 10 µm”, “due to the fast agglomeration with fly ash”. In the case of gas as a fuel “less agglomeration was observed and the Ceria NP were in the particles size range below 1 µm.” They also observed in a premixed propane flame that the nano-CeO₂ of 65 nm partly evaporates forming a new particle mode at 15 nm.

These results show that the size distribution of the CeO₂ particles can change very significantly, depending on various factors as the type of fuel, the temperature of combustion, the properties of the initial CeO₂, etc.

In the present study, the initial CeO₂ was in the form of agglomerates of very small elemental particles of 2-3 nm. Because of its high-developed surface, the NM is more reactive than the corresponding bulk material, as suggested by Luo et al. 2011 and Attarian et al. 2007 [13, 14]. So it can be supposed that, under heating at high temperature, the initial nanomaterial will undergo thermal changes, via sintering for instance which could be the case here for the residues.

5. Conclusion

Here is reported a study dedicated to the small scale incineration of a commercial coating with nano-CeO₂. The results have been discussed and compared to intermediate scale and a real scale studies on incineration of nano-CeO₂.

In a qualitative point of view, this leads to the conclusion that during incineration, nano-CeO₂ is distributed between the combustion aerosol and the residues.

In a semi-quantitative point of view, a significant amount of cerium has been observed in the residues of combustion. Only traces of cerium have been observed in the aerosol, always as a minor compound of the particles.

Further studies and technical developments on the lab-scale pilot are needed to provide quantitative information.

Based on this study and previous works by Walser et al. and Paur et al., it is supposed that a series of phenomena can take place such as sintering, evaporation, agglomeration with fly ash, etc. These phenomena seem to be strongly influenced by the composition of the combustible fraction and the temperature at which incineration takes place. Very small elemental particles (e.g. 2-3 nm in this study) would be especially affected by these potential transformations. As a result, additional research is needed, both at lab scale and real scale in order to better understand the link between the combustion conditions and the fate of nanoCeO₂.

As suggested by Ounoughene et al. [3, 12], this leads to the conclusion that in any case, both flue gas and bottom ashes will contain nanoCeO₂. Hence, risk assessment should be performed to better estimate the risks associated with the potential release of nanoCeO₂ during their thermal processing. Precautions may need to be taken to avoid exposure of workers, populations or environment to nanoCeO₂ particles.

Acknowledgements

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