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## **Lab-scale characterization of emissions from incineration of halogen and sulfur containing nanowastes by use of a tubular furnace**

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## **Abstract**

Many solid materials contain nanoparticles to enhance their functionalities. The question of whether they may release nanoparticles at different moments of their life cycle is raised. Lifecycle includes waste management. There is therefore a need to determine the fate of nanoparticles when the materials they are incorporated in are incinerated. The present study aims at shedding light on these issues. In this context, three real life wastes selected for their specific compositions were combusted in a lab-scale furnace under incineration conditions. The first two wastes contained nanoparticles, namely silica and titanium dioxide. The third waste was purposely nanoparticle free. In addition, the waste containing titanium dioxide did contain chlorine and the nanoparticle free material was partly made of sulfur. Disposal of halogen and sulfur -containing garbage implies an incineration temperature of 1100 °C. This complex waste composition was seen as an opportunity to assess possible interactions between nanoparticles and hazardous elements such as chlorine and sulfur during the combustion. Most of the analyses were supported by electronic microscopy imaging after having sampled particles in the fumes and in the bottom ashes. Eventually, three mechanistic scenarios were drawn from these experiments. Focus was made on the evolution of the nanostructure. It was observed to be preserved for the first waste. It disappeared both from the aerosol and the residue for the second waste. The third material, though not initially nanostructured, led to the formation of a nanostructure in the aerosol.

**Keywords:** incineration, halogen- and sulfur- containing nanowastes, nanoparticles, lab scale tubular furnace, 1100 °C

## 1. Introduction

Global nanotechnology market is growing at a rapid pace. According to market forecast reports, it is expected to reach \$ 2,231 billion by 2025 (Tewari and Baul 2019). Within the European Union, nanotechnology has been designated as a key enabling technology and its development is seen essential for Europe and the rest of the World. Nanostructured materials and nanoparticles display properties allowing designing new objects and products with advanced functionalities and/or with improved performances. All sectors of economy benefit from the developments of nanotechnology. The sectors of energy, cosmetics, automotive, plastics, electronics, health to name but a few are all impacted by this revolution. However, the effects that nanostructured materials and nanoparticles may have on human health and the environment are not well known yet (Wilson 2018; Giese et al. 2018; Sajid et al. 2015; Ray et al. 2009). Correlatively, limited scientific papers presenting cutting-edge results in the field are appearing in the open literature. Therefore, concerns are growing about the potential adverse effects nanostructured materials may display (Kessler 2011). The question about the potential noxious effects that nanomaterials may have on human health and the environment spans the whole life cycle of the nanoproducts, including end-of-life. Waste disposal of nanostructured products may indeed be problematic and could necessitate an appropriate treatment. From the 2016 OECD report (OECD report 2016) dealing with nanomaterials in waste streams, it was also established that 22% of these wastes were eventually incinerated. However, though many nanoproducts are likely to end up in an incineration plant, their fate is not well documented and still raises many questions (Ounoughene et al. 2017). A global insight of limited progress achieved so far in the field has been established and reported in table 1, based on articles retrieved from the open scientific literature. From the examination of this table, no clear extrapolations of these results are yet allowed to predict the fate of a given nanocharge in a given housing matrix when incinerated in given conditions. Many conclusions have been drawn from incineration conditions in the order of 850°C, a rather low temperature to reflect actual temperature incineration conditions. Even some contradictory conclusions appear in the literature about the potential release of nanoparticles in the fly ash. Besides, very limited information appears about interaction between physical aspects of nanoparticles of the nanofillers and the chemistry aspect of the housing matrices.

The OECD document (OECD Report 2016) reports that the building and plastics sectors were found to be the major providers of nanowastes. The bibliographic search underlines the necessity to put to incineration tests different materials containing nanoparticles. The fate of nanoparticles remains an open question and cannot be generalized from only a few examples. Tendencies already observed need to be confirmed through additional experiments.

To summarize the current issue faced by concerned stakeholders, it must be stated that current knowledge regarding the fate of plastic nanowastes or regarding nanostructures potentially emitted during thermal treatment of polymeric wastes keeps today far beyond the requested level of understanding necessary to adapt incineration technology and optimize operation conditions in a reliable manner to achieve satisfactory performances. Indeed, conventional issues like in-situ capture of gaseous pollutant species arising from the presence of sulfur and chlorine in common plastic wastes, are largely complexified by both increasing levels and ever-expanding diversity of embedded nanostructures and make the technical equation yet unsolved.

In order to bring a further step towards a solution to this problem, we have investigated the fate of the nanocomponents embedded in halogen- and sulfur- containing nanowastes treated by incineration in a lab scale tubular furnace operating at 1100°C. Such high temperature is commonly used for thermal processing of hazardous wastes in real incinerators. The experiments were designed to mimic at laboratory scale the combustion in an incineration plant. Three real world wastes originating from the plastics sector were selected. Two of these wastes contain chlorine and sulfur. The influence of high temperature on particulate emission was investigated by comparing the combustion of nanowastes at 850 °C (temperature used for municipal waste incineration) and at 1100 °C (a temperature less studied in the literature). The influence of the S and Cl hazardous elements on particle emission was investigated as well. The question of whether the S and Cl elements were part of the composition of the particles was examined. Determining the fate of the nanoparticles required a thorough examination of the bottom ashes. These were therefore carefully analyzed. Finally, the incineration of the mixture of the three wastes was examined as well. Eventually, the observations made led to outline three different scenarios regarding the fate of the nanocomponents of the material. Based on these observations, a few recommendations have been proposed.

## **2. The test samples**

Three real world waste materials of which two contained chlorine and/or sulfur were supplied, characterized and used as test samples in these experiments. These samples presented themselves as follows. The composition of the first waste sample was a Polydimethylsiloxane (PDMS) polymer matrix with embedded mineral nanocharges. The neat PDMS chemical structure contained silicon, in addition to the C, H, O elements. In addition to the silicon embedded in its polymeric chain, this waste contained silica nanoparticles. The detailed characterization of this waste is available in Tran et al. (Tran et al. 2016). The second test sample was a Polyvinyl chloride (PVC) based plastic. Neat PVC contained chlorine originating from its chemical formulation. In our PVC based waste plastic sample, titanium dioxide particles were also contained in the matrix, of which a fraction was in nanometric size.

The Transmission Electron Microscopy (TEM) analysis was made resorting to ultramicrotomy to identify the titanium dioxide (TiO<sub>2</sub>) particles. The third test waste was an organic resin incorporating the sulfur element. This last sample was free of nanoparticles. This was checked resorting to ultramicrotomy and Transmission Electron Microscopy analysis as well. The list of all the elements found in the three wastes is presented in table 2. The elemental analyses of the three wastes were made according to the CEN/TS 15407 standard for C,H,N,S,O and NF EN 13657 standard for the other elements. In table 3, the elements of interest (namely Si, Ti, Cl and S) targeted in the analyses made in these experiments are summarized for each waste.

### **3. The experimental set-up and protocol**

#### **3.1 Experimental setup**

The experimental setup is presented in figure 1. This setup was used in previous work (Ounoughene et al. 2019; Ounoughene et al. 2015, LeBihan 2017). In this paper, the originality lies in the fact that the temperature was raised to 1100°C. The furnace is 150 cm long with an inner diameter of 95 mm. The samples were introduced in an Inconel-made meshed holder (diameter of 30 mm and 25 mm height). The sample holder is meshed to allow for air diffusion into the sample during the combustion process. For activating the incineration process of the test sample, the sample holder was pushed through the furnace center to assure incineration of its content. As indicated in figure 1, dried air was flowed through the furnace with a flowrate of 12 L/min. The flow rate was set to assure fully oxidative combustion in incineration mode. The accurate conditions that were defined to assure proper incineration are indicated hereafter. The inner furnace temperature was set to 1100°C, a residence time of two seconds in the post-combustion zone was assured. Turbulence conditions were met in the furnace so that a good mix between combustible gases and oxygen and a high excess of oxygen concentration was reached. These four rules are usually applied in incinerator plants. Several instruments were implemented to monitor gas and particulate emissions:

A gas analyzer Horiba PG350 allowed monitoring the temporal evolutions of the O<sub>2</sub>, CO<sub>2</sub> and CO concentrations. The combustion phases could therefore be identified monitoring the temporal evolution of these gases.

A particle sizer DMS500 Cambustion was utilized for real-time particulate emission monitoring. With this instrument, charged particles enter a cylindrical classification section with a radial electric field. The particles are then deviated toward electrometers according to their aerodynamic drag/charge ratio. It allowed to determine particle size distributions and concentrations for sizes ranging from a few nanometers to 1 µm.

Particle sampling on TEM grids was assured with a Mini Particle Sampler (MPS supplied by Ecomesure) (R'Mili et al. 2013). Post-processing particle analysis was performed using a JEOL JEM 1400 Plus Transmission Electron Microscope. The possibilities offered by such instrument include imagery (morphology, size) and elemental analysis of large areas of the grid integrating several particles or of single particles (minimum size of 10 nm) using the Energy Dispersive X-ray (EDX) technique.

A Scanning Emission Microscope (SEM, model FEI Quanta 400) was used to make imagery and EDX analysis of the residue.

Real-time monitoring of gases such as hydrochloric acid (HCl) and sulfur dioxide (SO<sub>2</sub>) was achieved by use of Fourier Transform InfraRed Spectroscopy (FTIR).

Quantitative measurements of HCl and SO<sub>2</sub> cumulative gas fluxes were made after sampling and collecting solutes in a bubbler. The solutions of the bubbler containing the trapped gases were analyzed with the Inductively Coupled Plasma / Mass Spectrometry (ICP/MS) technique.

### **3.2 Protocol**

For each waste studied, the measurements were repeated three times. For each measurement, a sample mass of around 200 mg was introduced in the Inconel-made meshed holder. For the incineration test of the mixture of the three wastes, one third in mass (66,7 mg) of each waste was sampled for the experiments with a total mass of 200 mg. All the tests were performed in the same furnace. The furnace and all the pipes were cleaned up when switching from one sample to the other.

The MPS grids were sampled according to time delays and time durations set by reference to oxygen consumption history. The time delay corresponds to the time elapsed between the moment oxygen consumption starts and the beginning of TEM grid sampling. The time duration spans TEM grid sampling time. For the PDMS and the waste mixture samples, time delays and durations were of about 20 seconds and 5 seconds respectively. A time delay of 20 seconds and a time duration of 20 s were selected for the resin and the PVC samples. The sampling time was reduced for the PDMS and the mixture given that preliminary experiments showed that these two wastes were particularly emissive in particulate matter. Higher time durations led to high particle loading thus preventing the analysis of the grids. The sampling time was therefore not higher than 5 seconds.

The residue of the combustion (what is left after combustion) was analyzed both with SEM and TEM. TEM analysis required preparation. The solid residue was put in a mixture of alcohol and water and sonicated in an ultrasonic bath. Then a drop of the solution was deposited on TEM grid and dried prior to analysis. Before

depositing the drop on the TEM grid, the latter was rendered hydrophilic by use of a plasma device to treat its surface.

## **4 Results**

### **4.1 PDMS sample**

#### *4.1.1 Real-time gas and particle emissions*

In figure 2 are shown the temporal evolutions of oxygen, carbon dioxide, carbon monoxide and particle emission. Four vertical lines are drawn in this figure. The two mauve lines mark respectively 5% and 95% of the overall oxygen consumption. The dashed green lines delimit the beginning and the end of the incineration. The green line on the left marks the moment when the sample is introduced in the furnace and therefore when the oxygen level drops and incineration begins. The green line on the right shows the oxygen level back to its initial value thus designating the end of the combustion. Figure 2 evidences that oxygen consumption and particle emission are well synchronized. During the tests, blanks were made to check that particle emission was negligible without samples in the meshed holder. The meshed holder was therefore emptied and pushed through the furnace while particle emission was being monitored. The curves in red represent the blanks and they can barely be seen in figure 2. There are two curves for two size ranges, namely 10-100 nm and 100-1000 nm. These curves in red clearly show that particle emission under these conditions is negligible and therefore insignificant compared to that observed during incineration of the samples. Examination of the temporal evolutions of particle emission shows that particles in the size range of 100-1000 nm dominate. These curves also show that particle emission is not completely stopped when the consumption of oxygen ends, namely when the combustion is over.

#### *4.1.2 Analysis of the aerosol*

Images of the particles sampled when incinerating the PDMS sample are presented in figure 3. On these pictures, there are two categories of particles. The first category ((1) in figure 3) is made of bead-shaped particles (larger than 100 nm). The second category ((2) in figure 3) corresponds to agglomerates of aggregates of nanometric-sized particles. The EDX analyses made on several particles and focused on single particles of the two categories reveal the presence of two elements, namely silicon and oxygen. The relative abundances of these two elements strongly suggest that these particles are made of silica. A sample of PDMS was also incinerated at a temperature of 850°C. Figure 4 shows a comparison between the particles sampled when incinerating PDMS at 850°C and those collected from the same material undergoing incineration at 1100°C. EDX analyses reveal that these particles

are all made of silica. There is a difference though between incineration at 850°C and 1100°C. In the latter case, bead-shaped particles can be observed. Their presence may be explained by one hypothesis. A sintering process may be involved and explain the presence of bead-shaped particles.

#### *4.1.3 SEM and TEM Analyses of the residue*

The silicon (Si) and oxygen (O) elements were found in the residue using the EDX analysis of the SEM. Their relative abundances suggest that the residue is mainly composed of silicon dioxide (SiO<sub>2</sub>), an assumption that is supported by Holder and coworkers (Holder et al 2013). The same compound was observed in the aerosol. The residue was also analyzed by TEM following the protocol defined in section 3.2. The particles composing the residue can be seen in figure 5. A fraction of these particles is in nanometer size (particle diameter < 100 nm). The residue could be concluded to be nanostructured, if more than 50 % of the particles were in nanometer size. It remains however difficult to tell whether more than 50 % of these particles are nanometric in size. The residue contains therefore nanometric-sized particles in agglomerates but the conclusion as to its nanostructure is difficult to draw.

## **4.2 PVC sample**

### *4.2.1 Real-time gas and particle emissions*

Real-time particle and gas emission are presented in figure 6. Like previously presented for the PDMS sample, four vertical lines have been drawn with a meaning identical to that described in section 4.1.1. Particle and gas emission are well synchronized. Particle emission starts when oxygen consumption begins indicating the beginning of the combustion. As previously reported, blank emission was recorded along with other recordings. The blank is seen in figure 6 as the red graph. Like previously, blank emission is seen to be far less emissive than the emission observed when the combustion of the sample takes place. Figure 6 shows that the size fraction 10-100 nm dominates particle emission, by contrast to the PDMS sample case. As the PVC nanowaste contains the chlorine element, its combustion was very likely to release hydrochloric acid, as the major chlorinated species issuing the incineration process (Chivas et al, 2006, Lu et al 2019)). It was indeed easily detected in real time by the FTIR as may be seen in the graphs of figure 6 and the overall quantity of chlorine emitted as HCl in the flue gas has been assessed to represent 70% of chlorine input from PVC (see table 3). The peak of HCl release was also found to be synchronized with oxygen consumption.

#### 4.2.2 Analysis of the aerosol

The analysis of the TEM grid (figure 7) showed three categories of particles. The first category ((1) in figure 7) is made of micrometric-sized beads. The EDX analysis showed that they were made of titanium, calcium and oxygen. The relative abundances of these elements suggest that the particles could be made of both titanium dioxide ( $\text{TiO}_2$ ) and calcium Titanate ( $\text{CaTiO}_3$ ). The second category (2) is made of nanometric-sized particulates ( $d < 100\text{nm}$ ) and the third (3) of submicrometric sized particles ( $100\text{ nm} < d < 1\mu\text{m}$ ). The analysis of the second and third categories of particles reveals that these are formed from other elements contained in the soft PVC. The chlorine element as part of undetermined inorganic compound present in the aerosols is also detected from EDX analysis integrating several sorts of particles. The analysis was found consistent with the composition of this waste. Particles made of zinc chloride ( $\text{ZnCl}_2$ ) could also be formed (Jones et al. 2013). The hypothesis of the formation of compounds such as calcium chloride ( $\text{CaCl}_2$ ) for instance may be retained as well.

#### 4.2.3 SEM and TEM Analyses of the residue

EDX analyses of the residue using SEM reveals that it is mainly composed of Calcium (Ca), titanium (Ti) chlorine (Cl) and oxygen (O). Several EDX analyses are performed on the sample and the same ratio of Ca, Ti and O elements was found. The relative abundances of these three elements suggests that the residue could be made of calcium titanate ( $\text{CaTiO}_3$ ). As presented for the previous waste, the residue was also analyzed using Transmission Electron Microscopy. The corresponding images are presented in figure 8. The EDX analysis leads to results identical to those found when resorting to Scanning Emission Microscopy (SEM). Titanium, Calcium, chlorine and oxygen were found to compose the residue. Here again, the relative abundances of the different elements suggest that the residue is made of calcium titanate. The EDX analyses also indicated that almost 40% of the residue was made of chlorine. Therefore, from a more global viewpoint, integrating differences in mass flows of gases, residues and aerosols and potential HCl condensation on its way to the analyser, the overall trend observed regarding the fate of chlorine seems to be quite consistent to the relating review recently published in the matter by Lu and coworkers (Lu et al, 2019). Using EDX elemental analysis, only hypotheses may be made as to the compounds formed in the residue. Thus, compounds such as  $\text{CaCl}_2$  for instance may be found in the residue.

## **4.3 The resin**

### *4.3.1 Real-time gas and particle emissions*

Temporal evolutions of particle and gas emission obtained when incinerating the resin are shown in figure 9. In this case again, particle and gas emission are found well synchronized. Here again, the emission of the blank is found much lower than emissions observed when incinerating the resin. Particles in the size range of 10-100 nm dominates the overall emission. As indicated in section 2, the resin contains the sulfur element. Sulfur dioxide emission was consequently observed in the course of the combustion in significant quantities as may be seen in figure 9. Its emission seems synchronized with the main peak of oxygen consumption.

### *4.3.2 Analysis of the aerosol*

The grid used when incinerating the resin is presented in figure 10. Three categories of particles were identified on these grids. The first category (1) is made of micrometric-sized bead-shaped particles. The other two categories ((2) & (3)) are sub-micrometric and nanometric in size. The EDX analysis integrating many particles shows the presence of the iron, calcium and Sulphur elements. This analysis is consistent with the composition of the resin which happens to contain these elements. When focusing on the bead-shaped particles, the analysis showed that they contained iron (Fe), Sulphur (S), calcium (Ca) and oxygen (O). The other two categories proved to be made of iron (Fe) Sulphur (S) and oxygen.

### *4.3.3 SEM and TEM Analyses of the residue*

No residue was found when incinerating the resin, which was found consistent on the fact that the resin waste contained much less inorganics, as compared to the other wastes studied.

## **4.4 The mixture**

### *4.4.1 Real-time gas and particle emissions*

Like previously described for the three wastes, here again are the temporal evolution of particulate emission and oxygen consumption well synchronized (figure 11). Particle emission is still active even after the end of the combustion. But it tends to stop after a few minutes.

#### 4.4.2 Analysis of the aerosol

The aerosol sampled on TEM grids when incinerating the mixture is presented in figure 12. The examination of the grid shows that it is filled with agglomerates of aggregates. The aggregates are made of particles nanometric in size ( $d < 100$  nm). Both global and local EDX analyses of the grid yield the same results. The particles are made of Si and O elements. Their relative abundances strongly suggest that these particles are made of  $\text{SiO}_2$  in consistency with observations made with single PDMS sample. Eventually, only a subset of particles not representative of the three wastes, can be seen on the TEM grid. Emission of  $\text{SiO}_2$  corresponds to the incineration of the PDMS waste. This result suggests that the PDMS is far more emissive in aerosol than the other wastes and dominates the emission when incinerating a mixture.

#### 4.4.3 TEM analysis of the residue

Pictures of particles corresponding to the residue are presented in figure 13. The vast majority of the particles are micrometric in size. EDX analysis shows that they are made of the Ca, Ti and O elements. Here again, the relative abundances suggest that these particles may be made of calcium titanate  $\text{CaTiO}_3$  (without excluding possible co-presence of some micrometric  $\text{TiO}_2$ ). Non-nanometric silica particles are also observed.

### 5. Discussion

The combustion of the PDMS sample leads to the production of silica particles. In addition, it is important to note that these particles are mostly and partly nanostructured respectively for the aerosol and the residue. The silicon element can be found both in the polymer and in the nanoparticles embedded in the polymer. Combustion of PDMS has already been studied in the literature (Ounoughene et al. 2019). The silica particles observed in the aerosol come both from the PDMS decomposition and from the nanoparticles embedded in the matrix. As explained in Ounoughene's article, it is quite difficult to differentiate the particles originating from the nanoparticles from those stemming from the decomposition of the PDMS. Ounoughene et al. surmised that the finer particles observed on the TEM grids could originate from the nanoparticles initially incorporated in the PDMS. This distinction cannot be made in the framework of the experiments described in this article. In their article, Ounoughene et al. have also observed that the residue was made of silica particles. Identical observation was made in this work. But only a fraction of the particles (fraction close to 50 % in number) was found to be nanostructured.

As indicated in section 2, the PVC sample contains  $\text{TiO}_2$  particles. A fraction of these particles is nanometric in size. Eventually,  $\text{TiO}_2$  nanoparticles were not found neither in the aerosol nor in the residue. In addition, EDX

analysis suggests that at least part of the titanium atoms recombine with calcium and oxygen to form calcium titanate. Similar observations were made by Massari et al. (Massari et al. 2014) from their incineration tests of solid paint wastes. They also found in this context that most of the titanium was no longer in titanium dioxide form but in calcium titanate form in the residue. They explain that the  $\text{TiO}_2$  is likely to react with  $\text{CaO}$  during the incineration process. The aerosol only displays nanoparticles made of elements other than titanium and oxygen. As indicated in section 2, the resin does not contain nanoparticles. In addition, there are no bottom ashes left after combustion. However, the combustion of this compound generates nanoparticles found in the aerosol.

Eventually, three incineration scenarios may be outlined. With the incineration of the PDMS waste, the nanostructure of  $\text{SiO}_2$  is preserved. Indeed, the waste contains  $\text{SiO}_2$  nanoparticles. These are found in the aerosol and the residue and originate both from the nanoparticles initially present in the waste and from the polymer matrix decomposition. When incinerating the PVC, the nanostructure of  $\text{TiO}_2$  disappears.  $\text{TiO}_2$  nanoparticles are not found neither in the aerosol nor in the residue. Nanoparticles are found in the aerosol, but they are not made of titanium. The resin proved not to contain nanoparticles. In that case, nanoparticles however appear, as a thermochemical consequence from the incineration process. Like in the case of PVC, nanoparticles formed are made of different elements contained in the resin. The three scenarios are summarized in table 4.

Quantitative assessment of gas fluxes could be made owing to gas sampling and trapping in the bubbler and post analysis of the solutions by ICP/MS. Knowing the initial mass of the sample put in the meshed holder (and water content), the initial mass of sulfur and chlorine in the sample could be determined using table 2. The mass of chlorine and sulfur in the fumes could easily be inferred from the measurements with the bubbler. The proportion of chlorine and sulfur elements released respectively as  $\text{HCl}$  and  $\text{SO}_2$  in the fumes could therefore be easily calculated.

These measurements showed that about 60 % of sulfur could be found in  $\text{SO}_2$  gas form in the fume stream. The rest of the sulfur must therefore essentially be found in the aerosol. EDX analysis revealed that sulfur seemed to be part of the composition of the particles. One hypothesis is that it could be found as inorganic metallic salts (mainly iron II or III sulfates and some calcium sulfate, according to presence of these metals in the resin waste (see again table 2)). Around 70 % of chlorine was found in the fume stream in  $\text{HCl}$  form when incinerating the PVC. The rest of the chlorine should essentially be found (as inorganic metallic salts) both in the residue and the aerosol as suggested by the EDX analyses. The proportion of each element in the aerosol and the residue remain difficult to determine. The fate of the elements of interest (Si, Ti, Cl and S) contained in each waste is summarized in table 3.

Eventually, what recommendations can be drawn from these observations? The following remarks may be made bearing in mind that they are limited to the wastes presented in this article for the time being.

Chlorine and sulfur are both part of particle composition. Chlorine is found in the residue. Consequently, the particle filters of the filtration system of an incineration plant and the residues should be disposed of with care. In section 4.1.2, incineration of the PDMS waste was presented at both 850 and 1100°C. It seems that there is an influence of the temperature on the nanostructure of the aerosol. A sintering process was evidenced leading to the reduction of the nanostructure. Thus, though this result may not be generalized, it seems that high temperatures (below the fusion temperature of the waste) could favor sintering and therefore lead to the reduction of the nanostructure.

In section 4.4; the incineration of the mixture of the three wastes was presented. The results do not exhibit an influence of the mixture on the incineration of the wastes. Neither catalytic nor inhibitory effects were detected. No influence of the mixture was observed on the evolution of the nanostructure of the aerosol. There is therefore no specific recommendation to make when incinerating such mixture.

## **6. Conclusion**

A lab-scale, purpose-built experimental tube furnace was primarily used to bring one further contribution to the current understanding of the fate of nano-charges and nanostructured elements included in waste streams processed by incineration. Additionally, the influence of the presence of hetero-atoms commonly found in organo-wastes like sulfur and chlorine on nanoscale potential emissions was also studied. Results obtained from the treatment of three representative samples of polymeric wastes show that the nanostructure may be preserved, destroyed or even created out of the incineration process. Most of the chlorine and sulfur elements (more than 50%) were detected in the gas stream. The rest was found in the aerosol and the ashes. It was also observed that high temperature of combustion seems to favor the reduction of the nanostructure through sintering. Though the obtained results remain essentially qualitative, the observations made on both the aerosol and the ashes using electron microscopy provide a better insight on the fate of nano-wastes in the course of incineration. Based on only two types of nano-charges in our waste samples, these results also clearly illustrate the potential complexity of possible scenarios to be faced by incineration plants in soon future. A challenging issue is rising for the concerned industry, considering predictable regular increase in both loads and variety of nanofillers and nano-charges used in innovative materials, which certainly warrants further dedicated research for the resilience of the efficiency of gas and particle cleaning units.

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## Figures

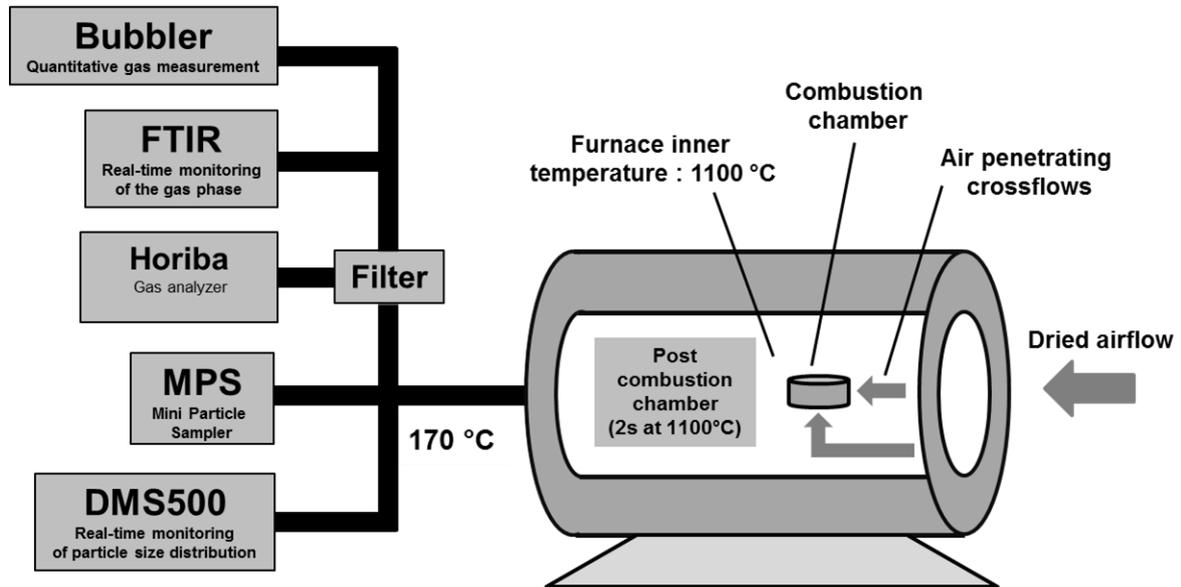


Figure 1. Experimental setup

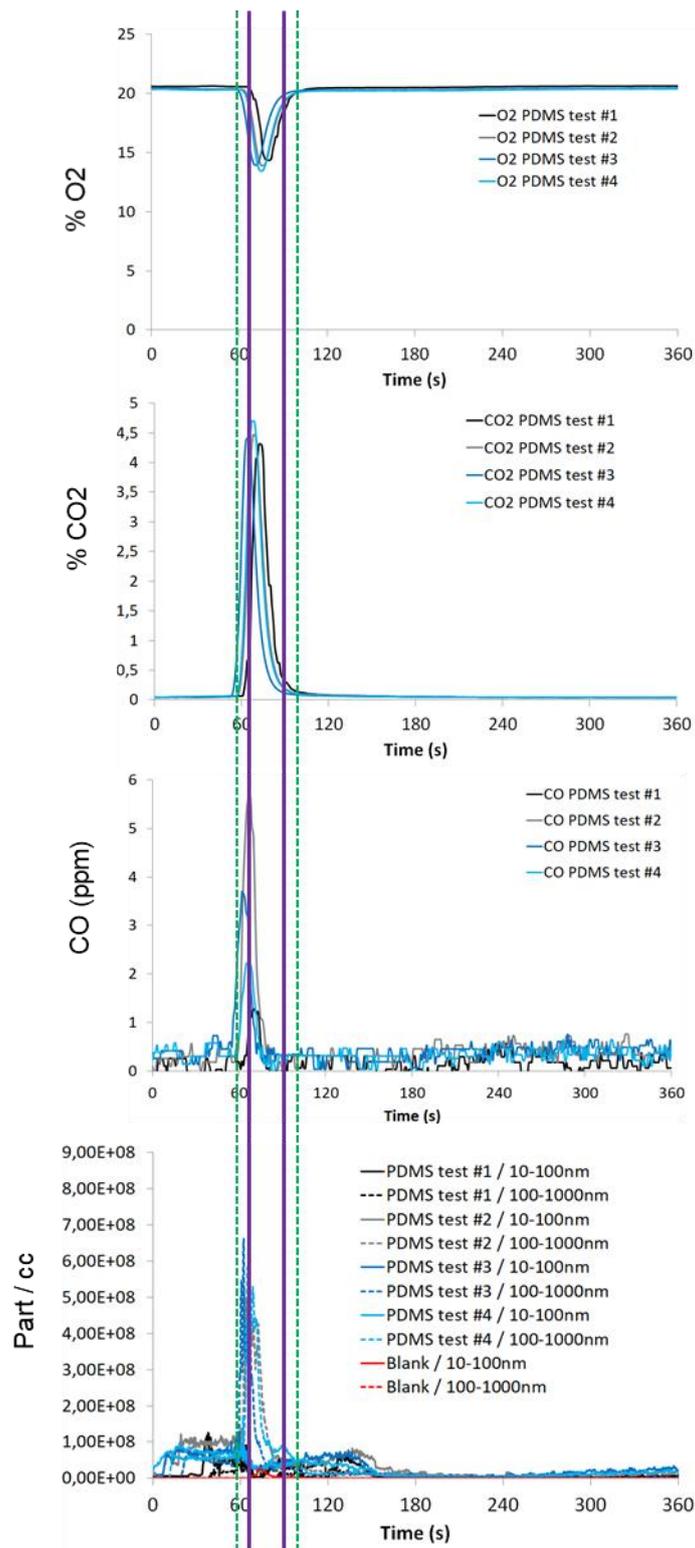


Figure 2. Temporal evolution of the different gases (O<sub>2</sub>, CO<sub>2</sub>, CO) and of particle emission when incinerating the PDMS waste.

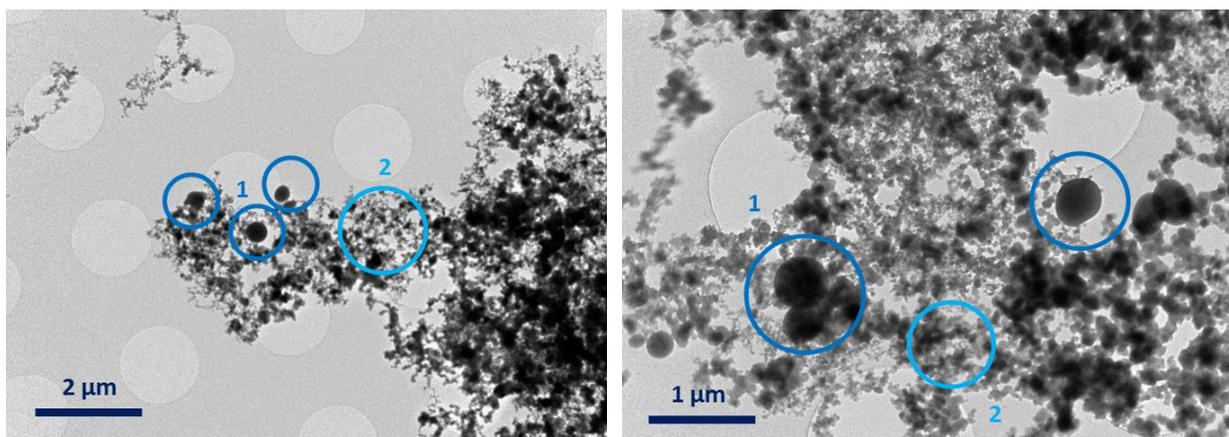


Figure 3. TEM analysis of the aerosol generated when incinerating the PDMS waste. Two categories of particles were identified.

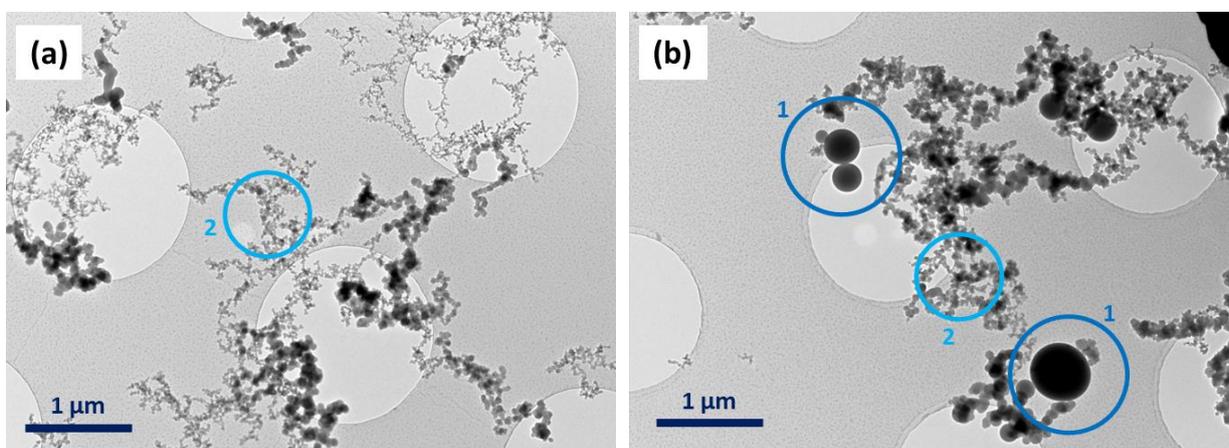


Figure 4. TEM analysis of the aerosol generated when incinerating the PDMS waste with two different temperatures: 850 °C (a) and 1100 °C (b). Two categories of particles were identified.

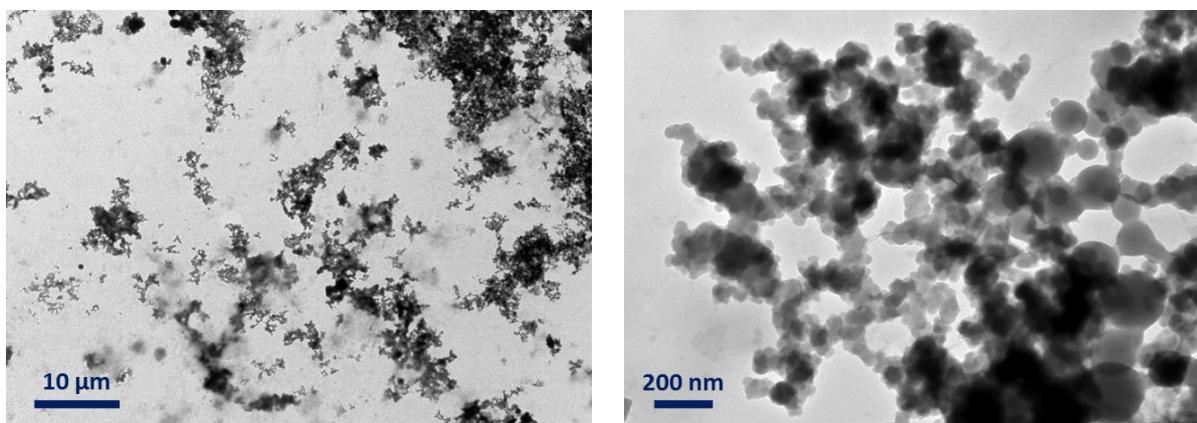


Figure 5. TEM analysis of the combustion residue of PDMS. The residue was mixed with water and alcohol and a droplet was deposited on TEM grid prior to analysis.

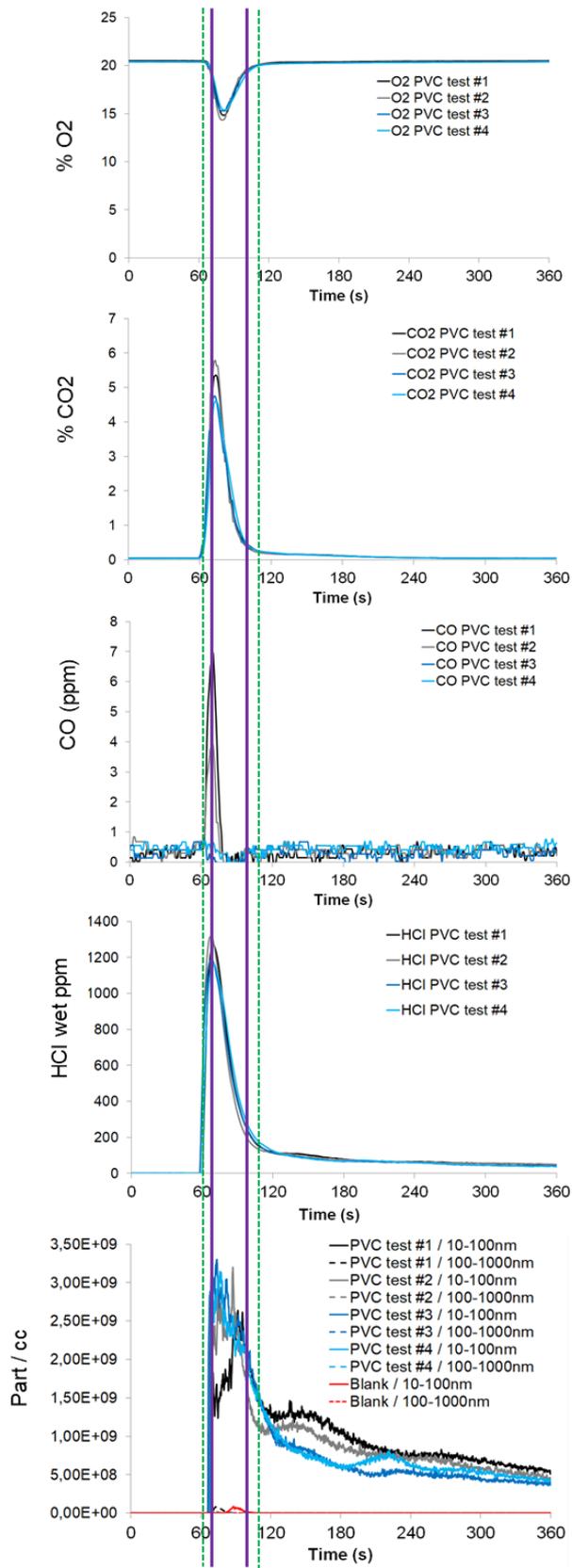


Figure 6. Temporal evolution of the different gases (O<sub>2</sub>, CO<sub>2</sub>, CO and HCl) and of particle emission when incinerating the PVC waste.

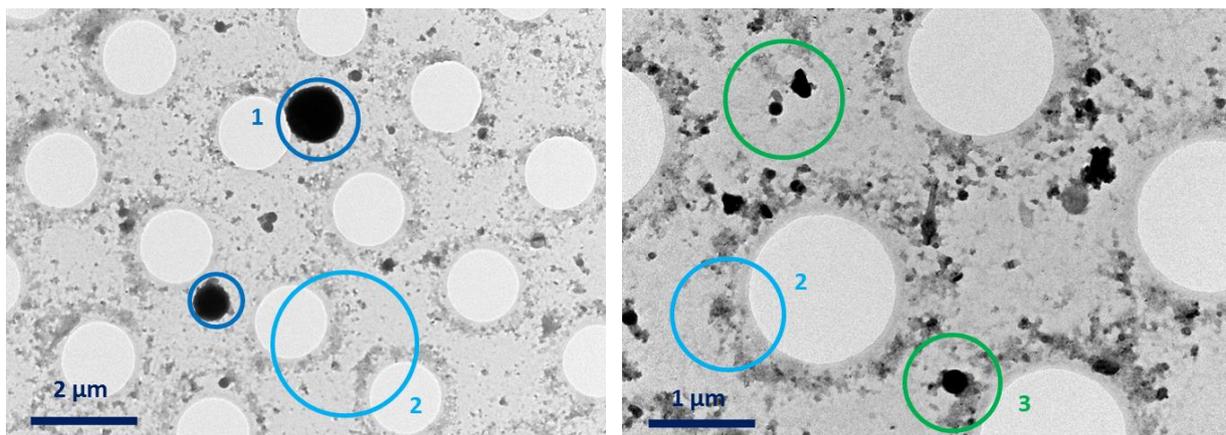


Figure 7. TEM analysis of the aerosol generated when incinerating the PVC waste. Three categories of particles were identified.

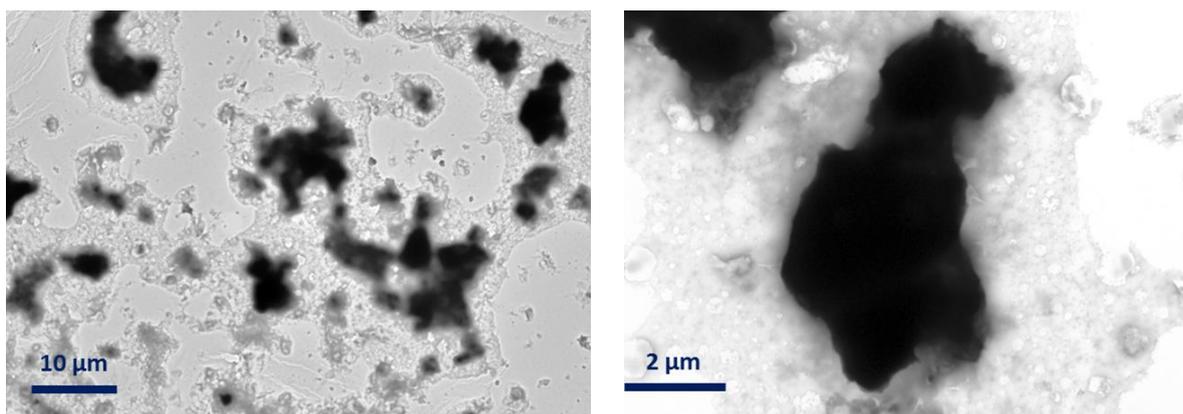


Figure 8. TEM analysis of the combustion residue of the PVC. The residue was mixed with water and alcohol and a droplet was deposited on TEM grid prior to analysis.

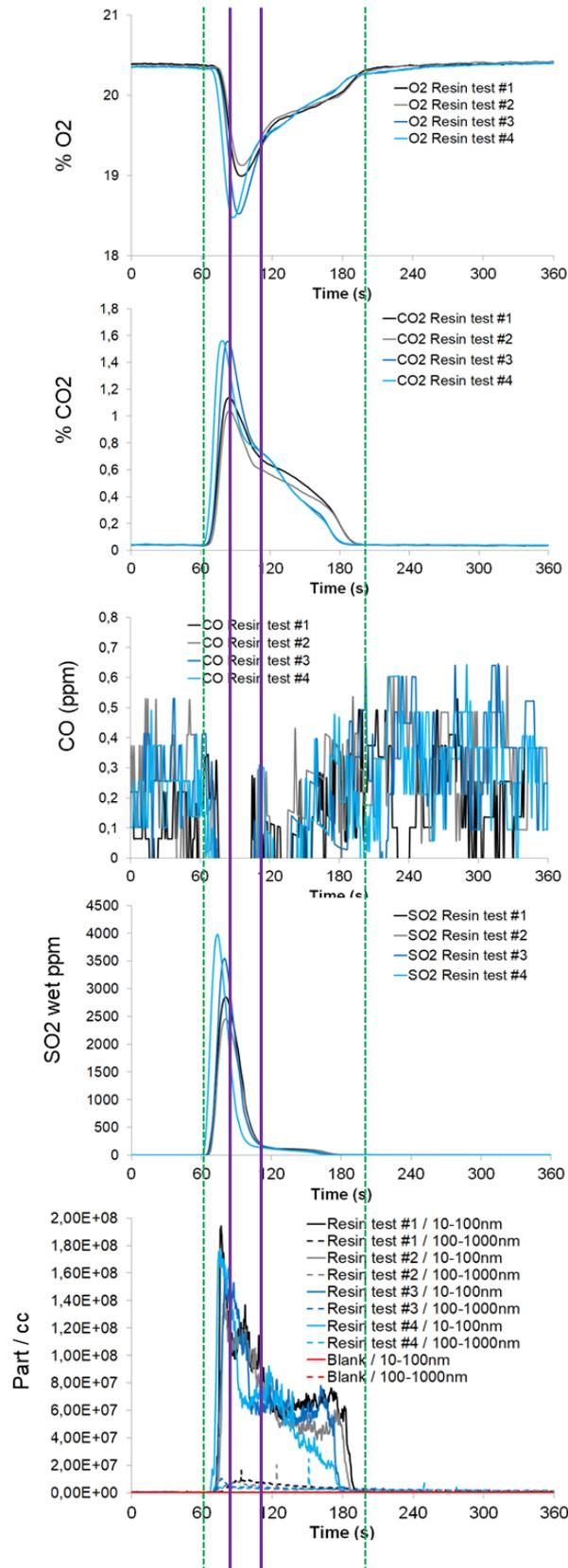


Figure 9. Temporal evolution of the different gases (O<sub>2</sub>, CO<sub>2</sub>, CO and SO<sub>2</sub>) and of particle emission when incinerating the resin waste.

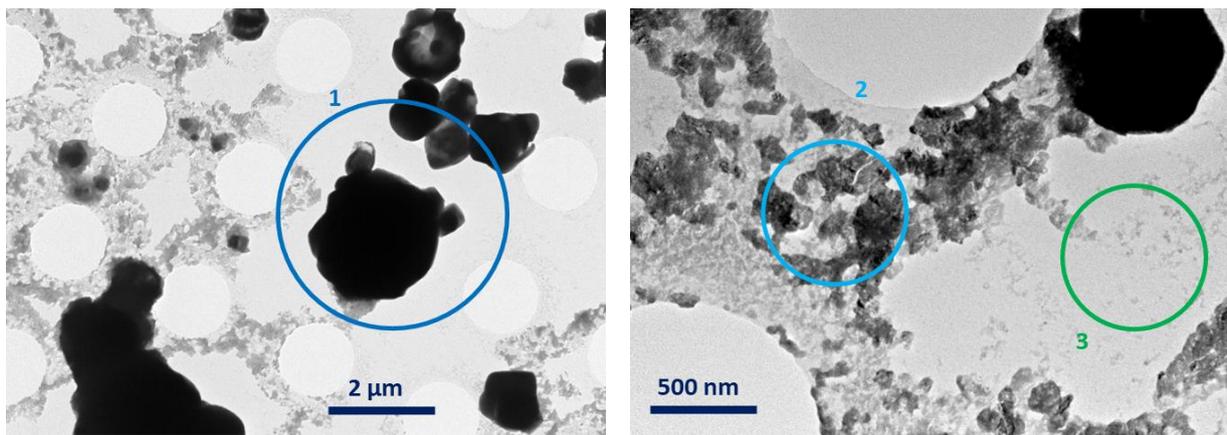


Figure 10. TEM analysis of the aerosol generated when incinerating the resin waste. Three categories of particles were identified.

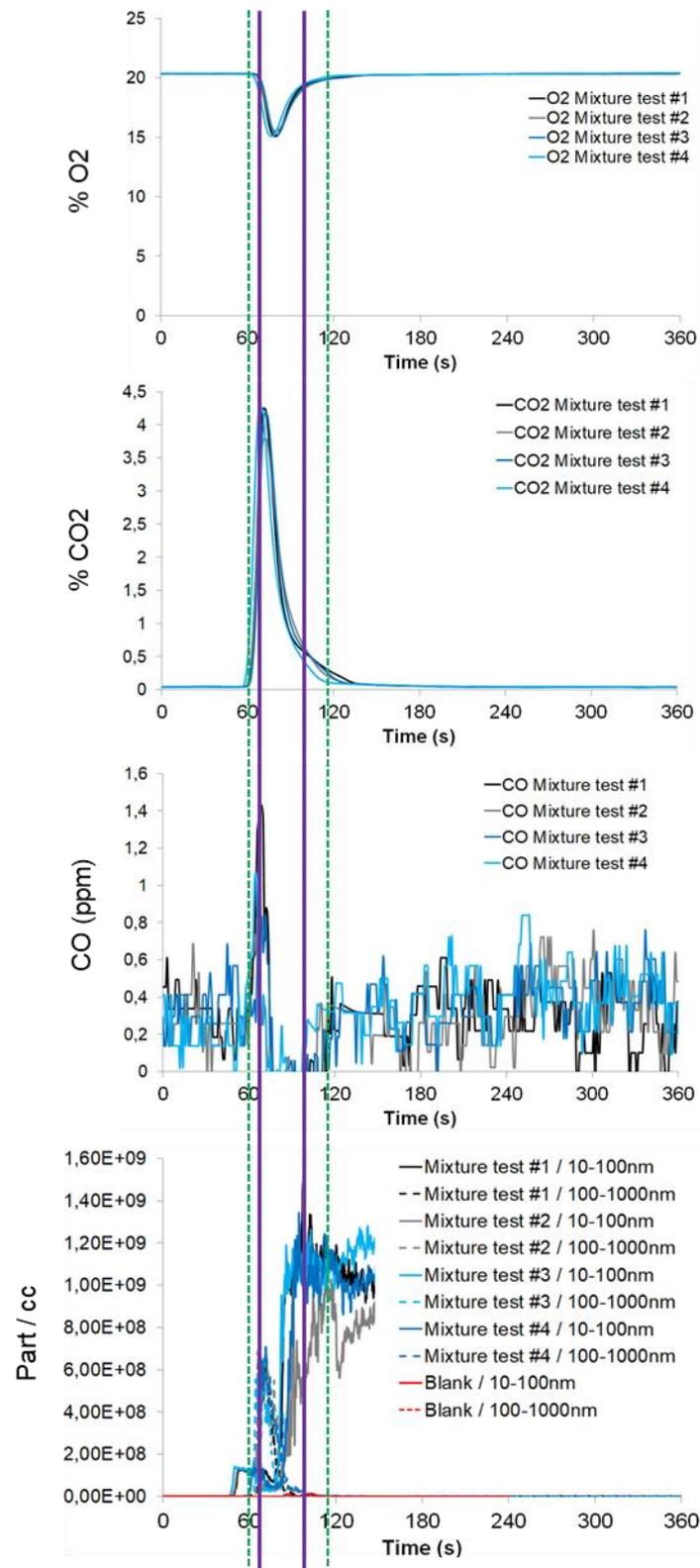


Figure 11. Temporal evolution of the different gases (O<sub>2</sub>, CO<sub>2</sub>, CO) and of particle emission when incinerating the mixture.

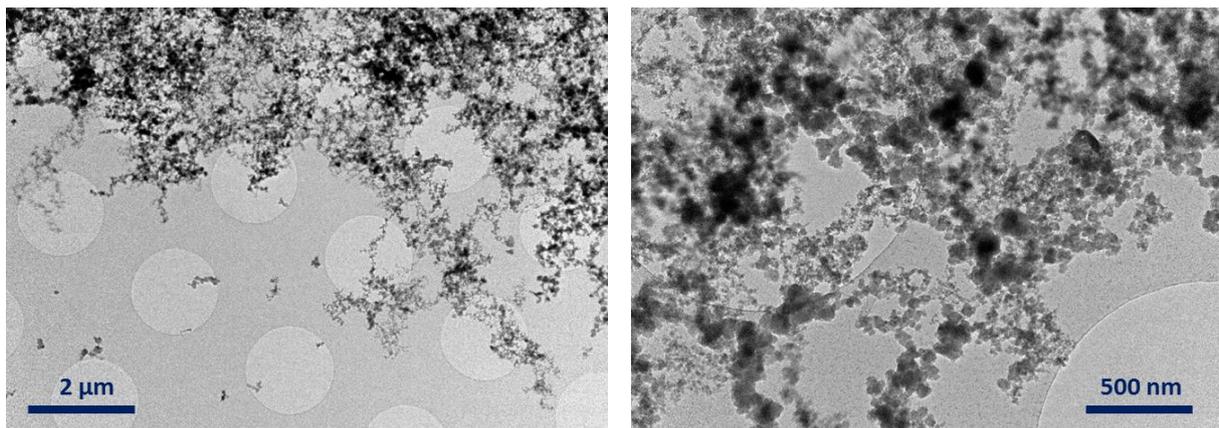


Figure 12. TEM analysis of the aerosol generated when incinerating the mixture of the three wastes.

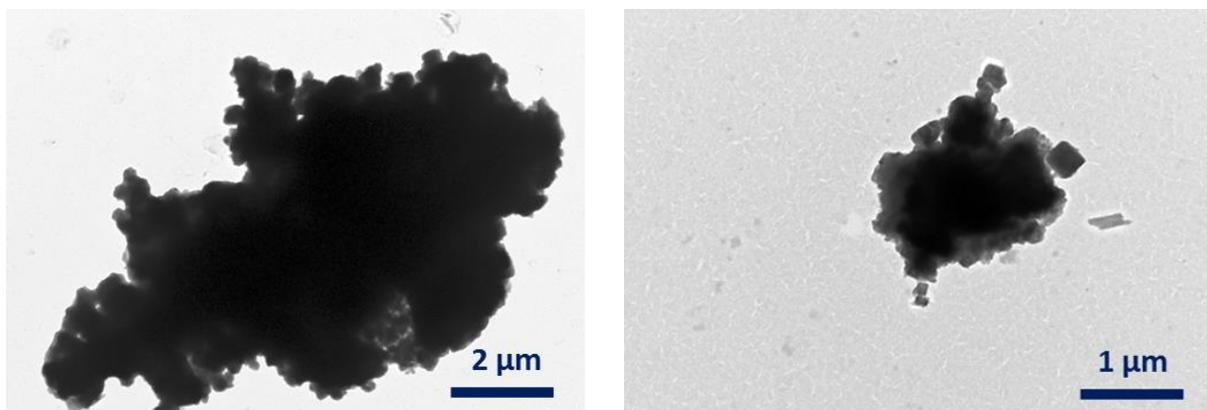


Figure 13. TEM analysis of the combustion residue of the mixture of the three wastes. The residue was mixed with water and alcohol and a droplet was deposited on TEM grid prior to analysis.

Tables :

References	Type of nanoparticles	Incineration conditions	Major outcomes / breakthroughs
<b>Baumann et al. 2017</b>	Ceria (CeO <sub>2</sub> ) nanoparticles	Lab-scale burner, tube furnace, KIT combustion plant BRENDA / variable temperatures	Sintering for the particles (metal oxides) in the flame when the temperature increases. Nanoparticles were shown to interact with the fly ash in the waste incineration plant.
<b>Chivas-Joly et al. 2019</b>	Aluminum (Al) -based nanofillers	Lab-scale incineration at 850°C	Nanoparticles may become toxic due to a chemical modification after incineration process.
<b>Fujimori et al. 2020</b>	Carbon nanomaterials	Laboratory scale electric furnace at 850°C	Carbon nanomaterials have a strong potential to generate polychlorinated dibenzo p dioxins, furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) during incineration with sodium chloride (NaCl) and trace copper.
<b>Holder et al. 2013</b>	Many nanoparticle types are presented in this review	Incineration plant (850- 1200°C)	A portion of nanomaterials may persist through the combustion zones. The use of control technologies is expected to remove nanoparticles from the effluent. Nanomaterials may become enriched in fly ash and bottom ash and may require special handling and disposal to prevent release in the environment.
<b>Le Bihan et al. 2017</b>	CeO <sub>2</sub> nanoparticles	Lab-scale furnace at 850°C	Both fly ash and bottom ash contain CeO <sub>2</sub> nanoparticles. Only traces of CeO <sub>2</sub> nanoparticles were found in the aerosol. A significant amount of CeO <sub>2</sub> was found in the bottom ash.
<b>Massari et al. 2014</b>	Titanium dioxide (TiO <sub>2</sub> ) nanoparticles in solid paint wastes	Lab scale incineration furnace at 950°C	TiO <sub>2</sub> was not found in the aerosol but in the bottom ash. Titanium was found in calcium titanate form (CaTiO <sub>3</sub> ) in the bottom ash.
<b>Ounoughene et al. 2015</b>	Nanoparticles of silica (SiO <sub>2</sub> ) in polydimethylsiloxane composite	Lab scale furnace at 850°C	Silica nanoparticles were found in the fly ash and the bottom ash.
<b>Ounoughene et al. 2019</b>	Halloysite Nanotubes (HNTs) in polyamide 6 (PA6)	Lab scale furnace at 850°C	Mineral nano-objects are found in the fly ash and the bottom ash.
<b>Part et al. 2018</b>	Many nanoparticle types are presented in this review	Small- and large-scale studies - 850-1100°C	Inorganic nanoparticles end up in the bottom ash. They can retain their original form or be changed either chemically or physically. Airborne nano-objects can be effectively separated by existing flue gas cleaning systems because of their tendency to agglomerate / aggregate.

References	Type of nanoparticles	Incineration conditions	Major outcomes/ breakthroughs
<b>Paur et al, 2107</b>	CeO <sub>2</sub> , TiO <sub>2</sub> and SiO <sub>2</sub> engineered nanoparticles	Bench scale Flame reactor (1160-1340°C) and tube furnace (up to 1800°C) Old waste incinerator converted to co-combustion (coal-biomass) facility	Access to some fundamental trends of non-combustible nanoparticles under strong thermal stress: sintering of metal oxides nanoparticles. Trend to agglomeration of nanoparticles within fly ash confirmed by making use of CeO <sub>2</sub> nanoparticles as a tracer.
<b>Pourchez et al 2018</b>	5 types of Al and silicon (Si) based nanofillers in Ethylene Vinyl Acetate (EVA) polymer matrix	Ventilation controlled cone calorimeter tentatively targeting incineration conditions (Temperature < 850°C)	No presence of nanoparticles in the fly-ash from any of the 5 tested nanofillers; all forms of nanofillers recovered at trace levels in residual ash (bottom slag).
<b>Roes et al 2012</b>	Most engineering particles associated to industrial activity	Purely desktop (paperwork) study not combined with validation experiments	General risk assessment approach to estimate potential release of nanoparticles as aerosols from theoretical considerations of thermal impact of main steps of incineration of polymer nanocomposites. The study concluded a significant risk for many of the nanoparticles considered, requiring experimental confirmation.
<b>Singh et 2016</b>	Carbon nano tubes (CNTs) as 5% filler in polyethylene (PE) and polypropylene (PP) TiO <sub>2</sub> in various proportions in EVA elastomer matrix	So called 'Integrated Exposure Generation Platform' Temperatures 400°C and 800°C based on estimates of thermoplastics decomposition Temperature range	From the tested engineered nanoparticles, the findings provide some tentative fundamental clearing into what parameters that might govern the nano-release and morphological properties of by-products.
<b>Singh et al 2019</b>	SiO <sub>2</sub> , copper oxide (CuO) and iron oxide (Fe <sub>2</sub> O <sub>3</sub> ) and diketopyrrolopyrrole (DPP) Red (organic pigment) in Nano-enabled coatings (NECs) acrylic coatings	So called 'Integrated Exposure Generation Platform' 4 incineration related Thermal Decomposition scenarios selected (final temperatures ranging from 500°C to 850°C)	Several influencing parameters identified (nanofiller composition, size and mass loading in the NEC matrix, incineration conditions) on the fate of nanoparticle emissions as aerosols. The study also warrants further studies targeting synergistic interaction between released by-products, their fate and relating environmental issues.
<b>Surendhiran et al 2020</b>	Many nanoparticle types are presented in this book	See for example Ounoughene et al. 2015	General overview on the routes of dissemination of engineering nanoparticles, including waste incineration and review of current knowledge on the impact of the various ecosystems (waters, soils).

References	Type of nanoparticles	Incineration conditions	Major outcomes/ breakthroughs
<b>Vejerano et al 2014</b>	Seven nanoparticles dispersed in solvent then loaded into surrogate waste (mocking up medical/laboratory waste)	Cylindrical furnace at 850°C with 1 L/min air flow	Low contribution to Particulate Matter (PM) to be expected at chimney emission according to this study, which concludes that the main environmental issue to be considered is the need to carefully dispose of bottom ash in which nanoparticles mostly agglomerate, while keeping their original size.
<b>Vejerano et al 2020</b>	Same 7 nanoparticles in previous study from the same team; subsequently similar surrogate waste	Lab-scale incinerator operated at 850°C at 1.8 air excess ratio (1 L/min of particle free/organic free air)	Polyaromatic hydrocarbons (PAHs) and PCDD/Fs visibly increased by nanoparticles impregnated surrogate wastes. Results on the fate of nanoparticles studied announced in a companion paper not yet published at time of submission of present work.
<b>Walser et al 2012</b>	CeO <sub>2</sub>	Testing campaign in actual incineration plant (up to 1200°C), 2 scenarios for NPs introduction in the plant (either sprayed on waste, or direct spray in furnace)	For the tested nanoparticles, findings are that dedusting system of the plant is efficient enough to retain nanoparticles driven PM in released flue gas. Nanoparticles bind to bottom slag, in a loosely way, which may be an environmental issue for landfills.
<b>Walser &amp; Gottschalk 2014</b>	CeO <sub>2</sub>	None in this paperwork study. Reference to incineration conditions prevailing in Walser et al 2012 study	Probabilistic fate analysis results from dynamic modeling of flows, based for validation on single experiment reported in Walser et al 2012 study. Prediction of the fate of CeO <sub>2</sub> nanoparticles in various outlet flows when incinerated as a load in waste matrix in good agreement with measurements from study of 2012 by Walser et al.

Table 1. Bibliography related to nanomaterials and incineration.

	<b>Elemental analysis of waste samples</b>		
	<b>Mass content %</b>		
	<b>PDMS</b>	<b>PVC</b>	<b>Resin</b>
<b>C</b>	29.8 ± 0.3	45.5 ± 0.3	46.6 ± 0.2
<b>H</b>	7.4 ± 0.1	6 ± 0.1	5.8 ± 0.2
<b>N</b>	< DL*	< DL	0.5 ± 0.01
<b>O</b>	2.5 ± 0.2	5.7 ± 0.3	13.9 ± 0.1
<b>Al</b>	< DL	< DL	< DL
<b>Ca</b>	< DL	5.86 ± 0.05	0.9 ± 0.01
<b>Cl</b>	< DL	31.71 ± 0.01	< DL
<b>Cr</b>	< DL	< DL	< DL
<b>Cu</b>	< DL	< DL	< DL
<b>Fe</b>	0.06 ± 0.01	< DL	2.95 ± 0.04
<b>K</b>	13.02 ± 0.05	< DL	< DL
<b>P</b>	0.67 ± 0.09	0.13 ± 0.01	1.06 ± 0.02
<b>S</b>	1.20 ± 0.17	0.38 ± 0.03	28.25 ± 0.01
<b>Si</b>	45.35 ± 0.33	< DL	< DL
<b>Sr</b>	< DL	0.042 ± 0.01	< DL
<b>Ti</b>	< DL	4.5 ± 0.02	< DL
<b>Zn</b>	< DL	0.21 ± 0.01	< DL

Table 2. Elemental composition of the three wastes (dried waste samples). (\*DL = Detection Limit) Three replicates were made for the measurement of the C, H, N, O, S elements and two replicates for the other elements.

<b>Incineration</b>				
	<b>Initial product</b>	<b>Aerosol</b>	<b>Residue</b>	<b>Gas</b>
<b>PDMS</b>	Nano-SiO <sub>2</sub>	Nano-SiO <sub>2</sub>	Nano-SiO <sub>2</sub> (about 50% in number)	---
<b>PVC</b>	Nano-TiO <sub>2</sub>	Non nanometric TiO <sub>2</sub> and CaTiO <sub>3</sub>	Non nanometric CaTiO <sub>3</sub>	---
	Cl	% Cl unknown	% Cl unknown	70 % Cl in HCl form
<b>Resin</b>	S	40 % S in the aerosol	No residue	60 % S in SO <sub>2</sub> form

Table 3. Fate of the elements of interest (Si, Ti, Cl and S) contained in the three wastes.

	<b>Nanostructure</b>		
	<b>Initial product</b>	<b>Aerosol</b>	<b>Residue</b>
<b>PDMS</b>	<b>Yes</b>	<b>Yes</b>	<b>Partly nanostructured</b>
<b>PVC</b>	<b>Yes</b>	<b>No*</b>	<b>No</b>
<b>Resin</b>	<b>No</b>	<b>Yes</b>	<b>No residue</b>

Table 4. Summary of the three scenarios for each waste with a special focus on the evolution of the nanostructure (\* the nanostructure of TiO<sub>2</sub> is destroyed but the incineration of the PVC generates other nanoparticles)