



INCINERATION: PARADIGM FOR NANOWASTE DISPOSAL

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ARTICLE INFO

Article History:

Received 17th April, 2018
Received in revised form
26th May, 2018
Accepted 16th June, 2018
Published online 30th July, 2018

Key Words:

Nanowaste, Incinerating Nanowaste,
Nanoparticles Incineration,
Combustion behaviour,
Cerium Oxide Nanoparticles.

ABSTRACT

Engineered nanoparticles (ENMs) are extensively used in varied consumer products. Along the period of usage for nano-enabled products, these nano particles can be released into the environment and get accumulated in the waste streams. Accidental or deliberate release of nanoparticles in the environment results into a new type of waste which is termed as nanowaste. In the framework of this review paper, details about nanowaste, challenges encountered during nanowaste management, Incineration as a method of ultimate disposal, Behaviour of Cerium oxide nanoparticles during incineration and post incineration strategies are summarized. Suitable analytical methods for characterization of nanowaste form the backbone of the nanowaste management system. Various methods for nanowaste sampling, separation and quantification are used according to the nature of the nanomaterial. Incineration can be used for most of the nanomaterials, but not for all, due to varied behaviour of nanoparticles under the incinerating conditions. Behaviour of nanoparticles constituting the nanowaste must be analysed before subjecting it to incineration. As per the incineration outcomes, post incineration steps may be required for ultimate disposal. With full regard of the current developments in this field, further work must be conducted for apposite characterization of the nanoparticles and appropriate incineration techniques. Moreover, improvement of the current disposal methods, to minimize hazards and disposal costs is essential along with development of new methods.

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Citation: Chirag R. Ratwani, 2018. "Incineration: Paradigm for nanowaste disposal", *International Journal of Development Research*, 8, (06), 21568-21573.

INTRODUCTION

Invention on nanomaterials dates back to late 1980s, but it wasn't until early 2000s when the use of nanoparticles was started in varied applications. Nanostructured materials are designed to use in fields like controlled drug delivery, semiconductors, optronics, catalysis, photovoltaic cells, to name a few. As their use flourished, waste in the form of nanoparticles (NP) was also generated. Harmful effects and the problems caused by these particles, when exposed to environment was unknown earlier. But as the technology has advanced, disposal of nanomaterials (NM) after their usage has become an arduous task (Musee N, 2010). These new unique forms of waste streams, that contain residue nanomaterials, may pose challenges to the current waste management practices and technologies.^[A] These new forms of waste streams are generically referred herein as nanowastes. Research in the field of Nanowaste Management gained momentum early in the decade of 2010 with the realization of

the fact that nanoparticles possessed some serious threats to the living beings. Nanowaste as shown in Figure 1, is generically defined as the waste streams containing NMs or synthetic by-products on nanoscale dimensions or the waste streams resulting from the end of lifespan of formerly nanotechnologically-enabled materials and products, and even the items contaminated by NMs such as pipes, personal protection equipment, etc are considered to be nanowaste (Musee, 2011).

Challenges faced during Nanowaste Management:

Behaviour of nanoparticles is quite different from their bulk counterparts as they tend to be more chemically active and toxic than the ordinary, regular sized particles. This problem is further enhanced due to the dynamic transformation of the particles during their entire lifetime. Such transformation influences the fate and behaviour of these materials in different environments owing to nanostructures intrinsic properties (e.g. surface chemistry, aggregation, agglomeration, adsorption or absorption properties, etc.), and the environmental factors (pH, presence or absence of oxidants, complexed ions, zeta

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potential, effects of macromolecules, presence of other chemicals, etc). Due to this, predicting the behaviour of particles under different conditions is a herculean task and this unpredictability poses serious troubles in material handling. Varied companies ranging from small scale start-ups to large global entities which are involved in nanomaterial production, produce wide variety of nanoparticles which have different sets of properties. This renders nanowastes management quite challenging task – and unless universal principles and technologies of managing these wastes are developed urgently – a case-by-case approach recommended presently may prove uneconomically viable, laborious, and even impractical considering the number and types of NMs as well as the nanoproducts. Moreover, the rate at which the development in nanoproducts takes place is exorbitant when compared to the rate at which the NMs detection systems have advanced, especially in the soil systems and free water bodies. This makes it improbable to detect, monitor, and develop remediation protocols to mitigate possible nanopollution in the soil environments. Nanowaste is notoriously difficult to contain and monitor; due to its small size, it can spread in water systems or become airborne, causing harm to human health and the environment. Trace analysis and quantification of nanoparticulate species is also very challenging because of the variety of ENM types that are used in products and low concentrations of nanowaste expected in complex environmental media. Adding to the trouble, there is paucity of toxicity data and its relationship to the physicochemical properties of NMs, incoherency of few reported toxicity data and lack of universally agreed units of expressing the NMs toxicity. As nanotechnology-based products enter into widespread use, many will end up in disposal waste streams. Disposal is the phase in the product life cycle at which most nanomaterials are predicted to enter the environment. However, this topic has gained recent attention with several life cycle analyses and reviews specifically addressing nanomaterial release through different disposal pathways (Musee, 2011). There are four methods for treatment of nanowaste to convert them into harmless, simpler molecules. The methods are incineration, landfilling, recycling and organic treatment. Incineration being one of the major methods for ultimate disposal, is discussed here (Allan, 2009).

Incineration: Incineration is a key waste treatment technique with great potential for modifying nanomaterials and either controlling them effectively or releasing them to the environment. Nanomaterials may enter waste streams that will be incinerated through several different pathways: disposal of consumer products as municipal solid waste (MSW), wastes generated from nanotechnology research and development, hazardous wastes, medical and infectious wastes, and sewage sludge from wastewater treatment plants (WWTP) handling nanomaterial laden water. Although plastics account for a small amount of the waste, they have the potential to be a large source of nanomaterials. Nanomaterials are frequently incorporated into polymer matrices to form nanocomposite plastics, and the volume of nanomaterials is expected to increase as novel applications emerge. Almost all types of nanomaterials can be incorporated into polymers. Clay, SiO₂, and TiO₂(Al-kattan, 2013) nanoparticles as well as carbon nanotubes (CNT) are used as fillers to improve the mechanical, electrical, magnetic, and thermal properties of polymers. Nanocomposites containing TiO₂ and nanoclay incorporated in polyethylene terephthalate (PET) bottles are used for high barrier packaging to minimize oxygen penetration. Nanoscale

metal and metal oxides have been incorporated into plastics and packaging materials as pigments or to prevent colour degradation. Another potentially large source of nanomaterials in the waste incineration stream is scrap tires. Tires may incorporate nanoscale amorphous silica, carbon black, clay, and CNT26 and are often processed into rubber crumb and used as fuel in cement kilns, utility boilers, pulp and paper mills, industrial boilers, and dedicated scrap tire-to-energy facilities.

Conditions required for Incineration: Incineration can be used to remove highly toxic organic wastes, reduce the volume of wastes, and potentially recover some of the energy stored in wastes. Incineration facilities burn hazardous wastes at high temperatures (850–1200 °C) in oxidative environments to ensure complete combustion of the waste before release to the atmosphere. There are various types of incinerators, including water-wall, modular, multiple hearth, catalytic combustion, waste-gas flare, direct-flame, liquid injection, fluidized bed, rotary kiln, and grate incinerators (moving and fixed). The choice of incinerator type depends on the type, volume, and hazard of the waste to be destroyed. Moving grate incinerators are the most common type in the US and account for 90% of the MSW incinerators in Europe. Moving grate incinerators can handle large volumes of waste with heterogeneous composition and calorific value. Rotary kiln incinerators are commonly used because they can combust various types of wastes, including solid, liquids, and sludge, with minimal processing. Fluidized bed incinerators are also common due to their high combustion efficiency and low emissions compared to other incinerator types. Since the majority of incinerators used for MSW are grate types, the details of the processes in them that may alter, destroy, and form new nanomaterials are presented in greater detail.

Incineration Operation: A typical incinerator operation (Buonanno *et al.*, 2009) shown in Figure 1 includes four general processes: pre-treatment, combustion, energy recovery, and flue gas cleaning. If needed, pre-treatment includes shredding and sorting. The waste is then introduced to the combustion chamber by moving grates. First, wastes are dried by heating at 100°C, and air is injected to remove as much moisture as possible. As the drying stage wanes, the wastes are heated at 250°C under pyrolytic conditions, which causes some components to outgas. Oxygen is supplied to the incinerator and the gases ignite. During this process, the wastes are burned at lower temperature (450 °C), and easily oxidizable solid wastes volatilize and decompose. More oxygen (primary and secondary air) is introduced to the combustion chamber, and the environment becomes highly oxidizing, with temperatures reaching around 1100–1200 °C. In most cases, the large amount of heat produced during combustion is recovered for energy use. After much of the combustible materials and gases are oxidized, the incineration process enters the last phase—burn-out—and the non-combustible materials subsequently cool (Holder *et al.*, 2013). The bottom ash from the primary combustion chamber, which typically accounts for 15–25% of the waste by weight, is sent to a land-fill. Flue gases containing combustion by-products and PM are routed to air pollution control devices where fly ash (i.e., PM) and other combustion by-products are treated or removed, and the cleaned gas is released into the atmosphere. The most common pollutants released from waste incineration include acid gases such as hydrogen chloride (HCl) and sulfur dioxide (SO₂); nitrogen oxides (NO_x); heavy metals such as mercury, lead,

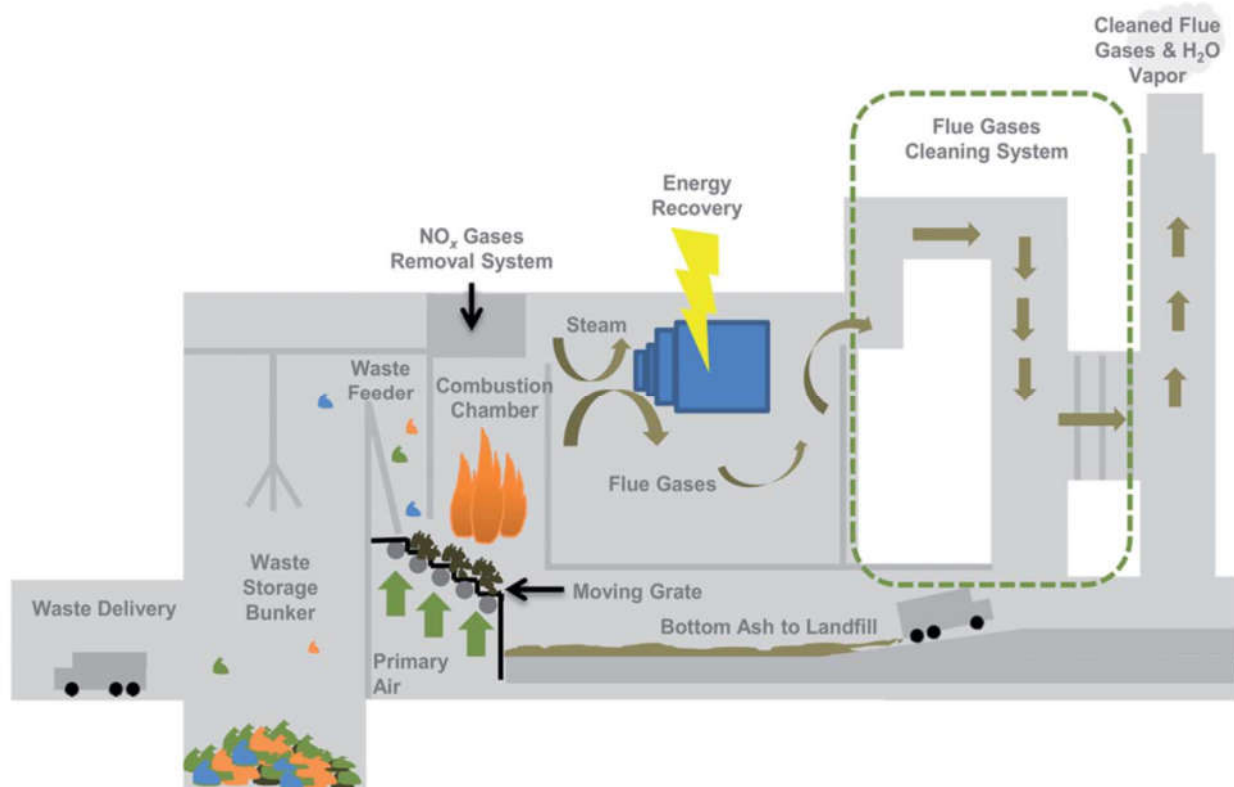


Fig. 1. Schematics of Grate Incinerator Operation

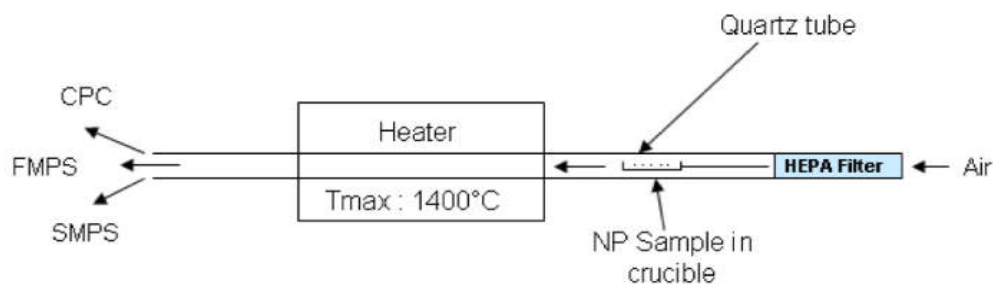


Fig. 2. Schematics of the Furnace

and cadmium; PM; polycyclic aromatic hydrocarbons (PAH) and other semi-volatiles; and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). While incinerators typically operate at higher temperature to increase pollutant destruction efficiencies, some zones in the combustion region, as well as in the post combustion region, facilitate pollutant formation. A portion of NO_x (thermal NO_x) is formed at higher temperatures (>1450 °C) in the combustion zone. At lower temperatures (150 °C to 400 °C), PCDD/F are formed, primarily from wastes containing chlorine (e.g. PVC).

Constituents of Incineration operation

- Samples:** The choice is made to focus the study on starting samples entirely at a nanometric scale. Another option is 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, goal is to avoid measuring NP potentially released from the macroscopic part of the waste.

- Furnace:** The incineration tests are performed using a benchtop tubular furnace. As seen on Figure 2, 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 a High efficiency particulate air (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 equipment are matched. The experiment is then started

when the background noise count is showing no NP along the furnace.

- **Analytical equipment:** To measure NP liable to be released during incineration, Derrough *et al.*, 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 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 107 p.cm with time resolutions in the order of one second. Sometimes, Scanning Mobility Particle Sizer (SMPS) consisting of a particle neutralizer, a short-column Differential Mobility Analyzer (DMA) and a CPC is also used. In such a configuration, the SMPS provides the size distribution of NP in the range 5-350 nm up to a concentration of 107 p.cm with time resolution of around three minutes.

Behavior of Nanoparticles in the incinerator

The fate of ENMs in the MSWI is considerably influenced by redox conditions, the temperature in the waste bed and the post combustion chamber. These aspects thereby influence the possible emission of ENMs from the MSWI. Five opportunities exist for the (re-)formation or destruction of ENMs during incineration:

- ENMs are destroyed due to combustion (for example CNT to CO_2)
- ENMs are not destroyed or incinerated but captured by the flue gas treatment system (for example metal oxides). These ENMs can be detected afterwards in the fly ash or other residues.
- Certain types of ENMs may not be destroyed during combustion. However, they react with other substances and form new particles (e.g. CaCO_3 to CaO and CO_2 or $\text{ZnO} + \text{HCL}$ give $\text{ZnCl}_2 + \text{H}_2\text{O}$).
- Bigger particles decompose and turn into new, smaller particles or even ENMs. (Roes *et al.*, 2012) describes how ENMs can be destroyed and, converted into other ENMs or left unchanged during incineration.
- Agglomeration of ENMs to bigger particles may occur, therefore, those particles lose their "nano" status.

Case Study: Behavior of Cerium Oxide particles during incineration

In 2012, a survey was published by OECD which focused on the incineration of ENMs in real waste incineration plants. They analyzed the behavior of cerium oxide (hydrodynamic average 80 nm) during incineration. Two cases were considered: in the first case, ENMs were introduced by spraying them onto the waste. In the second case, ENMs were injected directly into the furnace. The mass balance of the first case showed that nearly 81% of ENMs were transferred into the slag, nearly 19% into the fly ash, 0.02% into the quench water and only 0.0004% into clean flue gas. In the second case 53% of ENMs were found in the slag, 45% in the fly ash and 1.7% in the quench water. It was concluded that electrostatic precipitators, in combination with a wet flue gas purification system, can effectively remove nanosized oxides from the flue gas Nanomaterials in Waste Streams. These studies were

evaluated for just a few particle types; and hence the conclusions drawn were specific to the particular nanomaterial investigated and hence extension to other nanomaterials is a question. Current understanding from the patchwork of studies on the behavior of nanomaterials in combustion systems or at high temperatures provides a glimpse of the possible fate of nano- materials in waste incinerators. (OECD, 2016)

Possible pathways describing the fate of nanomaterials within waste incinerators

Fig 3 (DTU Environment, 2015) describes the possible pathways that a nanoparticle, or nanotube or other shape, can follow inside the incinerator system. Nanoparticles may exist in the waste as free particles (i.e., a powder), dispersed in a liquid, or embedded in a solid material. This initial state is likely to be an important determinant of whether the particle will become aerosolized, which largely dictates its fate in the combustion zone. Based on the behavior of nanoparticle fire retardants and nanofluids, we hypothesize that nanoparticles contained within a solid or liquid system are more likely to aggregate. These larger aggregates may or may not burn depending upon the local conditions in the combustion chamber. Chemical composition is also likely to play an important role in determining the fate of nanomaterials. Particles that are already oxidized, especially those with high melting points, like the CeO_2 used in the full-scale incinerator study and as a fuel- borne catalyst in diesel engines may exit the combustion zone essentially unchanged. Alternatively, reduced nano-particles, such as aluminum, will combust given high enough temperatures, as was seen with the nanofluid fuels and energetic nanoparticles. However, complete combustion may depend on the particle size and aggregation state. For example, the super micron aluminum particles suspended in hydro-carbon fuels and the CNT added to polymers did not fully combust. It was also found that nanomaterials partition into the ash at the bottom of the incinerator but interestingly, it was observed that presence of nanomaterials influenced the combustion efficiency and the composition of the emissions. For Example, Metal oxide nanomaterials were found to increase the efficiency of combustion and decrease the formation of toxic Polycyclic Aromatic Hydrocarbons (PAHs). Meanwhile, silver nanoparticles decreased combustion efficiency and increased PAHs emissions (Holder, 2013). In the post-combustion region, aerosolized nanoparticles that persisted through the flame zone are mixed with other particles produced inside the combustion zone. Particle aggregation may occur, shifting the original size distribution toward larger diameters. Additionally, other species may condense on the nanoparticle, changing its composition, which may increase the health hazard of these particles, as was the case with nanoscale sorbents. All of these changes may impact the effectiveness of particle control technology at removing these nanoparticles. Fabric filters are expected to be most effective among existing control technologies at removing nanoparticles and larger aggregates, regardless of particle composition. (Holder, 2013)

Behavior of common nanomaterials during incineration

Table 1 summarizes combustion behavior for several common nanomaterials. To provide some context on how important each nanomaterial may be within incineration systems, the nanomaterials are categorized by their global production levels.

Table 1. Combustion behavior of common Nanomaterials (Holder, 2013)

Sr. No.	Nanomaterial	Production Level	Combustible	Fire Retardant	Persist through combustion zone	Increases Pollutant Emissions
1	SiO ₂	High	No	Yes	Yes	Unknown
2	TiO ₂	High	No	Yes	Yes	Yes
3	CNT	Medium	Yes	Yes	Yes	Unknown
4	CeO ₂	Low	No	Yes	Yes	Yes
5	Ag	Low	Unknown	Unknown	Unknown	Yes
6	Fullerene	Low	Yes	Unknown	Unknown	Yes

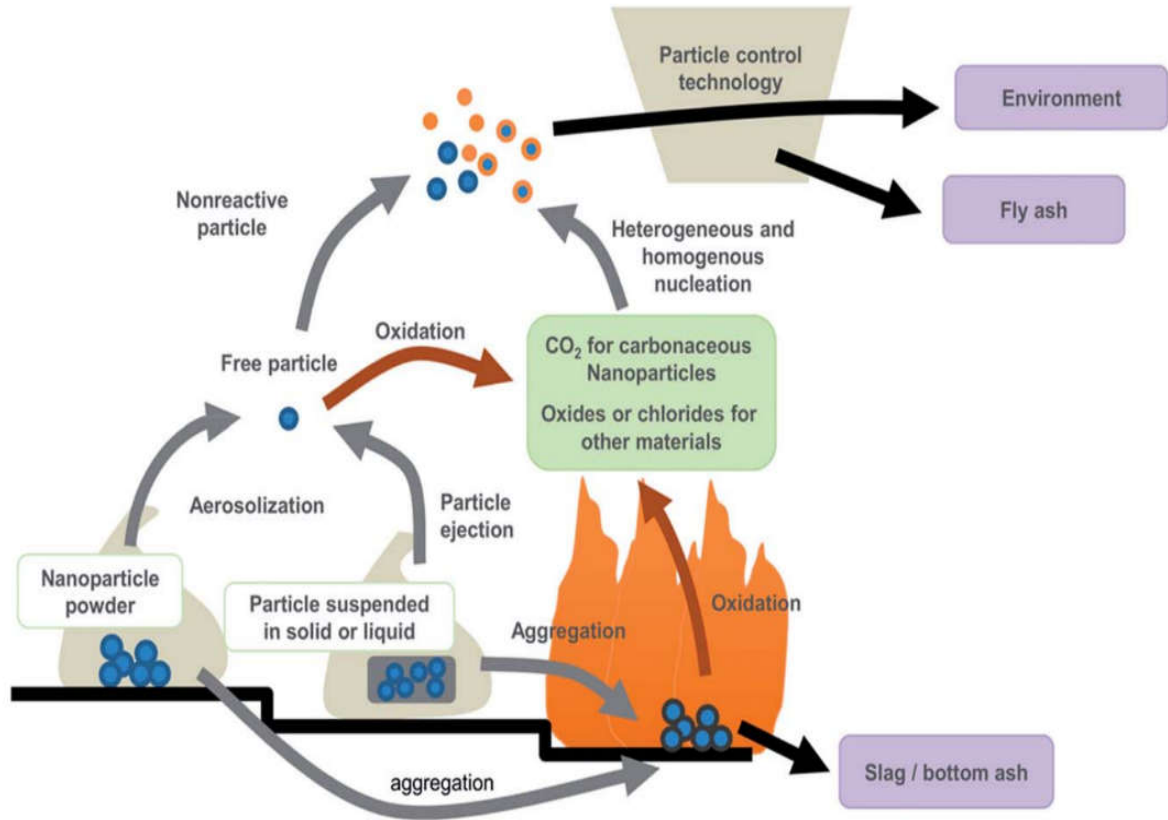


Fig. 3. Possible Pathways describing the fate of nanomaterials within the waste incinerators

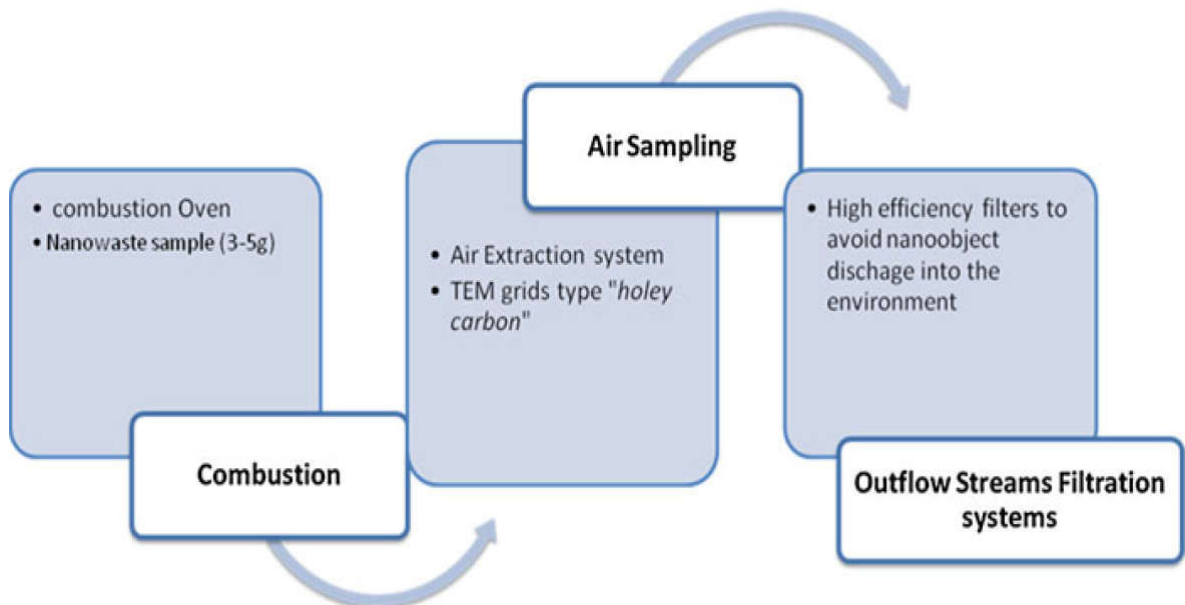


Fig. 4. Functional block diagram for Post Combustion analysis of released substances (Bouillard, 2015)

For most nanomaterials the amount incinerated is likely to be a small fraction of that produced, and the amount for CNT is slightly higher due to their prevalence in polymer material (Derrough *et al.*, 2013). The two nanomaterials with highest production levels (TiO₂ and SiO₂) are not combustible, likely persist through the combustion zone, and may impact pollutant formation. This suggests that nanomaterials produced in the largest quantities may impact the incinerator system and require greater scrutiny to limit releases to the environment (Vejerano *et al.*, 2014).

Post Incineration Process

Figure 4 shows the post incineration process which is composed of 3 building blocks. Gas phase emissions of nanoparticles and/or nanofibers that are originally present in nanocomposites can be characterized through TEM measurements. A high-performance filtration system allows for the exhaust release of gas mixtures from the combustion reactors to meet the environmental compliance requirements. Two techniques were used during these experiments to characterize the particles released during the combustion test: An online particle size measurement using an Electric Low-Pressure Impactor (ELPI) technique and an aspiration-based TEM grid sampler based on aspiration through holey TEM grids for off-line TEM analysis. Special attention should be paid with regard to inhalation risks to people engaged in disposing of such polymers by combustion, and that special care should then be taken while handling filtration systems used in energy vaporization processes to limit potential environmental risks due to potential CNT releases. Disposal of wastes through incineration produces hazardous pollutants. Among them, polycyclic aromatic Hydrocarbons (PAH), chlorinated dioxins and furans are of concern as some can induce cancer, some can cause mutation in genetics and can interfere with proper functioning of the hormones. In addition to that, these materials stay in the environment for a long time and due to their small size, can be transported to large distances from the original place of their generation. (Bouillard, 2015)

Summary

Nanomaterials have found varied application in the fields of packaging, clothing, disinfectants, Food industry, electronic devices, catalysts etc and their use is increasing at a burgeoning rate. Due to their uncontrolled production and usage, it is a herculean task to manage them in the environment. Waste generated during their production, usage

or disposal is termed as Nanowaste, which is one of the major environmental concerns in waste management. Incineration cannot be used for a wide variety of materials due to their unpredictable behavior at higher temperatures. Generation of Air pollution is a major concern while disposing waste by incineration. Hence care should be taken to prevent the nanomaterials from escaping to the environment while incineration. Analysis of the incineration behaviour is mandatory before subjecting it to the heat treatment.

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