Working Party on Resource Productivity and Waste

INCINERATION OF WASTE CONTAINING NANOMATERIALS

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FOREWORD

The OECD and the German Federal Ministry of the Environment jointly held a workshop on the Safe Management of Nanowaste in May 2012 in Munich, Germany. The workshop was attended by 35 experts from 12 OECD countries, non-member countries and private sector experts, trade unions, NGOs, and members of the scientific community.

The objectives of the workshop included:

- to achieve a better understanding of the potential exposure involved in waste containing nanomaterials (WCNM), and

- to identify that which OECD and member countries could contribute towards the safe management of WCNM.

Against the backdrop of participants’ discussions, it was agreed that an environmentally sound management of WCNM is essential. Knowledge gaps in potential exposure were identified. One challenge is to find methods to identify the potential risks which accompany various waste management options (e.g. incineration, recycling, use of sewage sludge in agriculture) (OECD, 2012). An OECD expert group on nanowaste is currently focusing on filling the above-mentioned knowledge gaps.

This draft paper is one of four reflection papers that discuss the possible release of nanomaterials from waste treatment operations, i.e. recycling, incineration, landfiling and wastewater treatment. It has been developed using the same structure as the other reflection papers and aims to point out the knowledge gaps and areas where further research is needed. Within that context, this short reflection paper was developed to attempt to improve the knowledge base and achieve progress on the discussion concerning the environmentally sound management of WCNMs.
INCINERATION OF WASTE CONTAINING NANO MATERIALS

1. Introduction

The aim of this document is to provide an overview of the emerging scientific findings on the behaviour and exposure of engineered nanomaterials (ENMs) during the waste incineration process and to identify knowledge-gaps regarding specific aspects of the disposal of waste containing nanomaterials (WCNMs).

This document briefly explains the relevance of nanotechnology in section 2, provides information on definitions, quantities and main sources of ENMs in section 3, describes waste incineration processes and applicable standards in section 4, investigates the fate and behaviour of ENMs in section 5, and concludes in section 6.

The report concludes that in order to estimate the quantities of ENMs in waste, the availability of information on ENM containing products on the market is crucial. Moreover, little knowledge is available about the influence and behaviour of ENMs throughout the waste incineration process and currently available literature and findings on incineration of WCNMs are mostly contradictory. Therefore further research is needed. At the current stage, in order to prevent harm for human health and the environment, all waste incineration plants should be equipped with a flue gas treatment system as, for instance, described in the European Union BREF document. In addition, the treatment and disposal of solid residues from waste incineration also require further research.

2. Relevance of nanotechnology

Nanotechnology is a relatively new and promising field of applications and tasks. ENMs are used for pharmaceuticals, cosmetics, batteries, paints, coatings or as additives in construction materials or other products in order to improve certain properties. The advent of nanotechnology into our everyday lives should therefore not be underestimated. Current research into effects on the environment and human health of the most commonly used ENM shows that some ENMs may be hazardous to human health and the environment, but no nano-specific statement could be made and, thus, exposure evaluation through a case-by-case approach is still recommended (SCENIHR, 2009).

ENMs may also enter the environment at the end-of-life of the products containing them. As nanotechnology is an emerging field, the disposal of WCNMs has raised little attention thus far. Therefore, it is still unclear if an environmentally sound management of WCNMs can be achieved. Consequently, experts fear that ENMs could be released from products and may enter different environmental compounds.

The present report focuses on one waste treatment option – incineration, and the issues surrounding waste containing nanomaterials therein. It includes:

- a brief summary of the scientific information available on the behaviour of ENM during the waste incineration process;
- an overview of the ENMs of highest relevance in municipal solid waste incinerators (MSWI);
• a short description of the best available techniques (BAT) of waste incineration and the techniques meant to retain or destroy hazardous substances;
• a short discussion of the existing hypotheses and suspected ways how ENMs may pass through existing pollution control devices.
3. Information on waste containing nanomaterials (WCNMs) (quantity, composition)

This section provides some necessary background to the discussion of ENMs in waste incinerators, including definitions, quantities of ENMs, the sources of ENMs and the amount of nanomaterials that enter municipal solid waste incinerators (MSWI).

3.1. Definitions

The definitions of nanomaterials and other related terminology are shown in box 1 below. This paper focuses on engineered nanomaterials (ENMs) to distinguish them from naturally occurring ubiquitous nanomaterials.

<table>
<thead>
<tr>
<th>Box 1. Definitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>• <strong>Best available techniques (BAT):</strong> the definition of BAT refers to the European Directive 2010/75/EU: &quot;best available techniques means the most effective and advanced stage in the development of activities and their methods of operation which indicates the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and, where that is not practicable, to reduce emissions and the impact on the environment as a whole”.</td>
</tr>
<tr>
<td>• <strong>Best available technique REFerence document (BREF):</strong> Result/product of an information exchange about BAT for selected industrial sectors organised by the European Commission.</td>
</tr>
</tbody>
</table>
| • **Nanomaterials:** The following definition of nanomaterials by the International Organization for Standardization (ISO) is used in this paper:  
  - **Nanoscale:** Size range from approximately 1 to 100 nm.  
  - **Nanomaterial:** Material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale.  
  - **Engineered nanomaterial (ENM):** Nanomaterial designed for a specific purpose or function. |
| • **Waste containing nanomaterials (WCNM)** – The term "waste containing nanomaterials" means typical municipal solid waste, which includes commercial similar to domestic waste and household waste containing nanomaterial. The term "nanowaste" is used in the context of specific waste containing nanomaterials, generated by nanomaterial production or even preparations of products. WCNM can be generated during the use phase, during the repair of products or in particular the disposal of products at the end of their lifecycle. |

3 ISO/TS 80004-1:2010
3.2. Quantities

The number of waste incineration plants has been increasing over the last few years. According to the OECD (2014), nearly 658 million tonnes of municipal solid waste were generated in the OECD and 145 million tonnes (22%) of those were incinerated in 2012. More detailed figures on the disposal routes of municipal solid waste in Europe are presented in the Annex.

As mentioned above, the number of products containing ENMs is steadily increasing. Some studies have indicated that, in 2010, TiO$_2$, ZnO, SiO$_2$, FeO$_x$ and AlO$_x$ dominated the global ENM market by mass flow, mainly used in coatings, paints, pigments, electronics and optics, cosmetics, energy and environmental applications, and as catalysts (Keller et al., 2013). Table 1 shows the production quantities of some ENMs worldwide, in Europe, the US and Switzerland. These ENM products become waste when they reach their end-of-life status. For instance, Musee (2011) found that 5000 t/a TiO$_2$ were produced from 2006 to 2010 and nearly 10 000 t/a between 2011 and 2014. A large, but unknown quantity of these ENMs will end up in waste incineration plants.

<table>
<thead>
<tr>
<th>ENM</th>
<th>Worldwide (t/year)</th>
<th>Europe (t/year)</th>
<th>US (t/year)</th>
<th>Switzerland (t/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median and 25/75 percentile</td>
<td>Median and 25/75 percentile</td>
<td>Range</td>
<td>In brackets values extrapolated to Europe</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3 000 (550-5 500)</td>
<td>550 (55-3 000)</td>
<td>7 800-38 000</td>
<td>435 (38 000)$^a$</td>
</tr>
<tr>
<td>ZnO</td>
<td>550 (55-550)</td>
<td>55 (5.5-28 000)</td>
<td></td>
<td>70 (6 100)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>5 500 (55-55 000)</td>
<td>5 500 (55-55 000)</td>
<td></td>
<td>75 (6 500)</td>
</tr>
<tr>
<td>FeO$_x$</td>
<td>55 (5.5-5 500)</td>
<td>550 (30-5 500)</td>
<td></td>
<td>365 (32 000)</td>
</tr>
<tr>
<td>AlO$_x$</td>
<td>55 (55-5 500)</td>
<td>550 (0.55-500)</td>
<td></td>
<td>0.005 (0.4)</td>
</tr>
<tr>
<td>CeO$_x$</td>
<td>55 (5.5-550)</td>
<td>550 (0.55-2 800)</td>
<td>35-700</td>
<td></td>
</tr>
<tr>
<td>CNT</td>
<td>300 (55-550)</td>
<td>550 (180-550)</td>
<td>55-1.101</td>
<td>1 (87)</td>
</tr>
<tr>
<td>Fullerenes</td>
<td>0.6 (0.6-5.5)</td>
<td>0.6 (0.6-5.5)</td>
<td>2-80</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>55 (5.5-550)</td>
<td>5.5 (0.6-55)</td>
<td>2.8-20</td>
<td>3.1 (270)</td>
</tr>
</tbody>
</table>

The median and the 25/75 percentile are rounded to two significant numbers.

$^a$ The values in brackets for Switzerland have been extrapolated using the population of Switzerland (6.9 Million) and applied to Europe (593 Million)

Source: (Piccinno, et al., 2012; Hendren, et al., 2011; Schmid and Riediker, 2008)

3.3. What are the main sources of WCNMs?

There are two main sources from which ENMs enter MSWI. The first one is municipal solid waste (including some residues from manufacturing of ENM containing products). The second source is sewage sludge (SS), if it is incinerated.

Limited information has thus far been made available on products containing ENMs or the quantities such products contain. However, products (e.g. food packaging, cleaning products) containing ENMs have to be disposed of reaching their end-of-life and then enter MSWIs. The same applies to residues from the production of ENMs (Health Council of the Netherlands, 2011).
According to Musee (2011), it can be assumed that 95% of all nanoscale materials contained in cosmetics end up in the wastewater stream. Kuhlbusch and Nickel (2010) verified the release of nanosilver during washing of clothes and textiles containing said ENMs. If wastewater is treated in wastewater treatment plants, the ENMs are transferred mostly into the sewage sludge and therefore in the waste stream. Burkhardt et al. (2010) showed that 93 to 99% of nanosilver is bound in sewage sludge.

Leakage of ENMs into the soil is possible if sewage sludge is used as a fertilizer. In case of energy recovery from sewage sludge, ENMs can enter the incineration plant on that pathway.

3.4 How much Nano enters municipal solid waste incinerators (MSWIs)?

Roes et al. (2012) calculated the amounts of ENMs released in MSWI off-gas treatment for 1t of municipal waste, assuming that the content of ENMs in nanocomposites is between 1 wt-% and 10 wt-%. The assumed average content of plastics in municipal solid waste is 12%, of which 7% are nanocomposites. However, it needs to be considered that the average of composites in the MSWI-input can vary strongly depending on local infrastructure and specific waste streams entering the respective MSWI plant.

4. Waste treatment option: waste incineration

4.1. Technical description of a representative MSWI

Most municipal waste incineration plants are equipped with a bunker for waste storage, which usually is a concrete bed. The waste from the bunker is well mixed to enable an effective burnout and is then fed the incineration device. The most common technique for waste incineration is the grate firing system. Thereby a hot and highly-polluted flue gas is produced. This flue gas stream passes through a steam generator for electricity generation. The flue gas then enters the flue gas cleaning system where dust, acids and other harmful substances are eliminated via chemical processes or separated from the flue gas via mechanical processes. The clean flue gas then exits to the atmosphere via a tall chimney, thereby possibly releasing a small amount of ENMs. The residues from the incineration process, called bottom ash, can be used for road construction and other applications in some countries like Germany or have to be landfilled. The residues from the flue gas cleaning system (fly ash), containing ENMs as well, are usually landfilled.

4.2. BAT in the OECD and the EU

The use of BAT in waste incineration plants is a complex issue, due to the wide variety of plant constructions, the local and climate circumstances etc. To address this issue, the European Commission has established an information exchange to describe the BAT for various industrial sectors, including waste incineration. The result of this information exchange is the so-called BREF document (best available technique reference document).

According to the BREF document, to prevent harm to human health and the environment, all waste incineration plants should be equipped with a flue gas treatment system. Furthermore, all waste incineration plants in Europe are equipped with a flue gas cleaning system in order to fulfill the requirements of several directives (e.g. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control, IPPC), ABl. L 334 of 17.12.2010, p. 17). Moreover, the Directive (2010/75/EU) sets emission limit values and monitoring requirements for gaseous pollutants like dust, nitrogen oxides (NOx), sulphur dioxide (SO2), heavy metals, dioxins, furans and others. The Directive sets requirements on the release of polluted wastewater leaving the flue gas cleaning facilities. The BREF document on waste incineration, however, does not include any regulations concerning ENMs. It, therefore, can only be used as reference for high quality flue gas treatment in general and standards described within the BREF documents need to be reviewed for their effectiveness removing ENMs. At a subsequent stage, once reliable data is available
concerning ENM removal from flue gas of MSWI, the BAT for ENM removal may be included in the BREF-document.

So far only few studies investigated the ENM emissions from MSWI. According to those a high end flue gas treatment system may be able to remove most ENMs from the flue gas. However, this was only shown for certain materials or calculated on a model base.

Therefore, the German Federal Environment Agency/German Federal Ministry of Environment and the German Federal Ministry of Research have already started research projects to study possible emissions of nanoparticles from the incineration process in more detail. However, results are not yet available.

However, still many countries do not implement BAT standard technologies for flue gas treatment. In order to ensure proper flue gas treatment not only with respect to ENMs but all emissions, national governments should enforce high standards for all waste incineration plants.

5. Fate and behaviour of engineered nanomaterials (ENMs) in waste incineration plants

The fate of ENMs in the MSWI is considerably influenced by redox conditions, the temperature in the waste bed and the post combustion chamber (Roes et al., 2012). 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:

1) ENMs are destroyed due to combustion (for example CNT to CO₂) (Mueller et al., 2013).
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.
3) Certain types of ENMs may not be destroyed during combustion. However, they react with other substances and form new particles (e.g. CaCO₃ to CaO and CO₂ or ZnO + HCL give ZnCl₂ + H₂O).
4) 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.
5) Agglomeration of ENMs to bigger particles may occur, therefore, those particles lose their “nano” status.

The present paper focuses on the first two cases. In order to fill the knowledge gaps about the fate of ENMs in waste incineration plants more research is necessary. The German Federal Environment Agency has commissioned a study analysing the fate of nanoscaled TiO₂ within a waste incinerator and a sewage sludge incineration plant. Within this study, a mass balance will be conducted. Results will be available in 2015. France has also launched two research projects in order to assess the emissions from incinerating WCNMs and the effectiveness of flue gas treatment systems. Results will be available in due course.

In 2012, a survey was published which focused on the incineration of ENMs in real waste incineration plants. Walser et al. (2012) analysed the behaviour of cerium oxide (hydrodynamic average 80 nm) during incineration.

This considered two cases: 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.

Walser et al. (2012) concluded that electrostatic precipitators, in combination with a wet flue gas purification system, can effectively remove nanosized oxides from the flue gas stream. Therefore, no nano-CeO₂ will be emitted from waste incineration plants equipped with such a flue gas treatment.

In contrast Roes et al. (2012) stated that the removal efficiency for particles from the flue gas is very high for particles larger than 100 nm. For particles smaller than 100 nm the removal effectiveness is supposed to be reduced significantly. ENMs smaller than 100 nm are partially removed by fabric filters and wet scrubbers, but a significant amount (up to 20%) may pass through such devices. The ENMs captured by the scrubbing system end up in the residues (bottom ash and fly ash). Roes et al. (2012) concluded that leaching from these residues should be prevented. However, it should be mentioned that the efficiency depends on the filter technique as well as on the filter material and can vary from plant to plant. Moreover, this study included no experiments and results are based on theoretical considerations only.

Mueller et al. (2013) found that the majority of ENMs enter bottom ash during incineration and end up in landfill sites as part of bottom ash. Other residue flows, such as fly ash, are of a smaller magnitude than bottom ash.

Mueller et al. (2013) concluded that waste incineration can have an important influence on some ENMs. Most ENMs are supposed to end up in the incineration residues and thus mostly in landfills but carbon nanotubes (CNT) for example may behave differently as models indicate that they may be burnt with an efficiency of 94% due to their chemical nature. However, some of the available data indicates that carbon nanomaterials may not incinerate as efficiently as expected (Vejerano et al. 2014).

Mueller et al. (2013) also estimated a total of 80 000 t/a of fly ash that are produced in waste and sludge incineration plants in Switzerland. According to their measurements, a fraction of only 0.00058 wt-% of the sludge and waste incineration fly ash is smaller than 100 nm corresponding to a total of 464 kg per year. Differing from that, results from the calculation model used by Mueller et al. (2012) in a different study are nearly 50 times higher: 22 t/a TiO₂, 0.8 t/a ZnO, 160 kg/a Ag and 4.9 kg/a of CNT. Similarly, Buha et al. (2014) investigated five waste incineration plants in Switzerland with electrostatic precipitators or bag-house-filters and reviled that a range of 0.00009% to 0.07% of the fly ash in mass based volumes were identified as nanomaterials. They also suggested that ENMs may form a decent proportion of nanomaterials found in the flue gas through comparison with modelling results. The reason given for the discrepancy between measured and modelled values is that ENMs tend to agglomerate and quickly form bigger particles of several hundred nanometres. Therefore, they are no longer ENMs, according to the recommendation of the European Commission.

The European Commission declared that the open burning of textiles containing CNTs could emit such ENMs. It is assumed that only incineration above 850°C can eliminate CNTs. Therefore, incineration in modern and well-operating waste incineration plants is necessary, where such high temperatures can be reached (European Commission DG Environment, 2009).

The Health Council of the Netherlands (2011) noted that although MSWI emit ultrafine particles they are negligible in comparison to the emissions from road traffic. The concentration of fine particles are reduced by a factor of one thousand after scrubbing the flue gas, but still a high number of fine particles may not be captured by scrubbing and, thus, emitted to the air. The Council concluded that it is quite plausible, based on such a limited body of evidence, that the waste incineration process releases ENMs.
6. Summary and outlook

The number of products containing ENMs will probably increase in the future. As a result, the amount of waste containing ENMs will also increase. Information about the influence of the ENMs embedded in products is scarce. In order to estimate the quantities of ENMs in waste, the availability of information on ENM-containing products on the market is crucial.

Moreover, little knowledge is available about the influence and behaviour of ENM size throughout the waste incineration process. The available literature and the findings on incineration of WCNMs are mostly contradictory. On the one hand, there are studies reporting that measurements in a waste incinerator show no emission of ENM; on the other hand, model calculations find that ENMs can pass through cleaning devices. Therefore, further research is needed and has partly been started.

However, in order to prevent harm for the human health and the environment, all waste incineration plants should be equipped with a flue gas treatment system as described in the BREF document. From the only studies available at the moment it can be assumed that, if a plant is equipped with a BAT flue gas treatment system, the majority of ENMs will be captured by the treatment system. However, this was only shown for nano-CeO$_2$; all other estimations were based on theoretical considerations. Additionally, all incineration parameters such as temperature, residence time or oxygen level should be taken into consideration in order to achieve a high level of ENM destruction and ideal conditions for ENM removal.

Unfortunately, there are still a large number of waste incineration plants worldwide that do not have adequate flue gas treatment systems, not only concerning ENMs but all other emissions as well. National governments should therefore ensure high standards in flue gas treatment systems of MSWI plants in general.

The understanding of ENM behaviour during municipal solid waste incineration and how ENMs are released into the environment is at an early stage. In order to learn more about this and to improve data availability, a more detailed survey of different ENMs in various waste incineration plants and co-incineration plants is necessary. Such studies should include determining the conditions that enable the efficient removal of ENMs from MSWI flue gas. Furthermore, the fate of ENMs in the solid residues from waste incineration plants also needs further research and should not be disregarded.
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ANNEX

Annex Figure 1. Disposal routes of municipal solid waste in the EU 27 in 2010