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Energy Procedia 120 (2017) 705–712

Energy Procedia

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INFUB - 11th European Conference on Industrial Furnaces and Boilers, INFUB-11

# Behaviour of engineered nanoparticles in a lab-scale flame and combustion chamber

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## Abstract

Nanostructured materials are widely used to improve the properties of consumer products such as tires, cosmetics, light weight equipment etc. Due to their complex composition these products are hardly recycled and thermal treatment is preferred. In this study we investigated the thermal stability and material balance of nanostructured metal oxides in flames, in a pilot scale combustion plant and an industrial hazardous waste incinerator. We studied the size distribution of nanostructured metal oxides ($CeO_2$, $TiO_2$, $SiO_2$) in a flame reactor and in a heated reaction tube. In the premixed ethylene/air flame, nano-structured $CeO_2$ partly evaporates forming a new particle mode. This is probably due to chemical reactions in the flame. In addition sintering of agglomerates takes place in the flame. In the electrically heated reaction tube however only sintering of the agglomerated nanomaterials is observed. Ceria has a low background in waste incinerators and is therefore a suitable tracer for investigating the fate of nanostructured materials. Low concentrations of Ceria were introduced by a two-phase nozzle into the post-combustion zone of a waste incinerator. By the incineration of coal dust in a burning chamber the Ceria nanoparticles are mainly found in the size range of the fly ash (1 – 10 µm) because of agglomeration. With gas as a fuel less agglomeration was observed and the Ceria nanoparticles were in the particle size range below 1 µm.

Peer-review under responsibility of the organizing committee of INFUB-11

*Keywords:* engineered nanoparticles; combustion chamber; waste incineration

## 1. Introduction

The amount of consumer products containing engineered nanomaterials is constantly growing. Cosmetics, plastics, paints, fuel catalysts, UV-coatings, textiles and electronics are only a few product groups in which nanoparticles like

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10.1016/j.egypro.2017.07.194

Titania, Ceria and CNTs are used to improve their properties [1]. As these products reach their end of life they often end up in the waste incineration (Figure 1). Till now only few data are published concerning a possible release of nanoparticles (NP) into the environment [2, 3, 4]. In the Institute for Technical Chemistry (ITC) at the Karlsruhe Institute of Technology (KIT) this topic is analysed in fundamental investigations of NP behaviour in lab-scale flames [5, 6], in technical investigations at a 2.5 MW combustion chamber at the KIT [7] and in large-scale investigations at an industrial hazardous waste incineration plant in the chemical industry. Since 2005, landfilling of municipal waste is no longer allowed in Germany and the only possible disposal routes are therefore recycling or thermal waste treatment (Figure 1). With every recycle step the product quality is decreasing and a thermal process is always the last possible treatment.

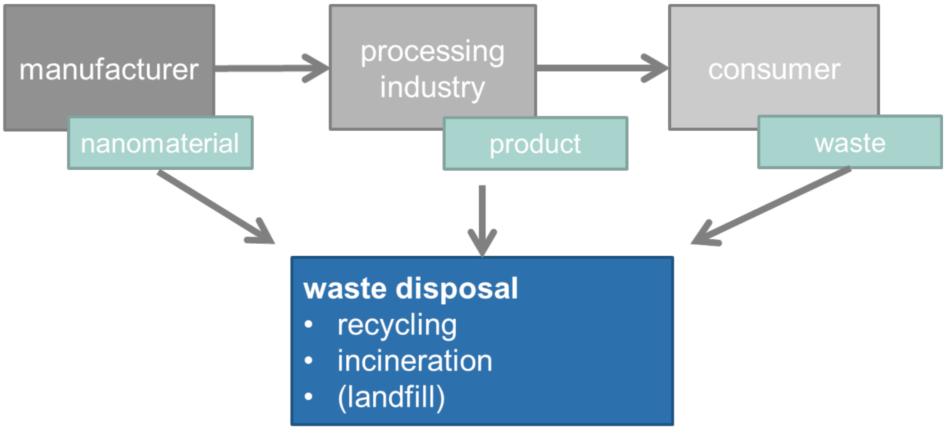

Figure 1: Life cycle of products including nanoparticles.

Figure 2 illustrates the flow sheet of a municipal waste incineration plant with possible paths of nanoparticle release. These can be the exhaust gas, the waste water or the solid residues. First investigations were concentrated on the release via the exhaust path and afterwards also other paths were studied including a mass balance of the incineration plant.

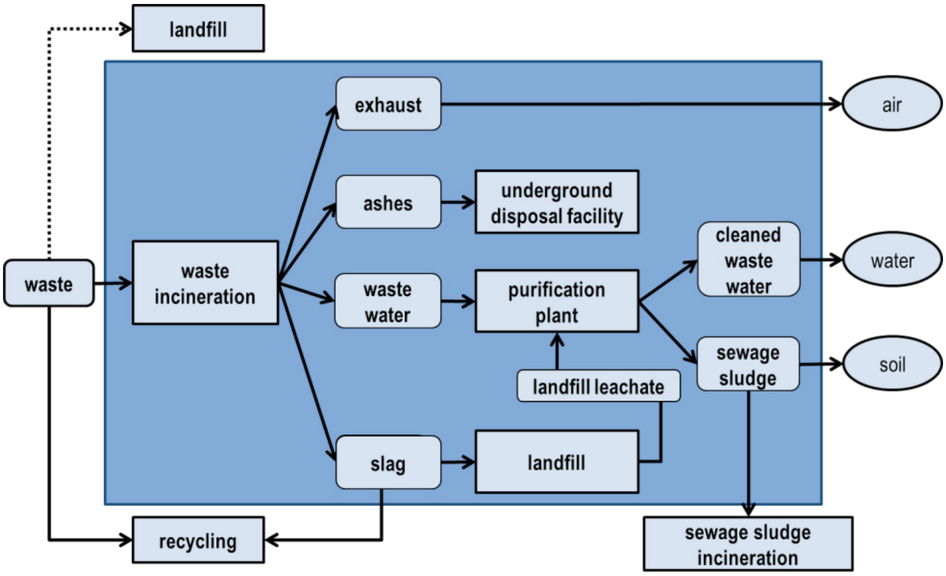

Figure 2: Flow sheet of a municipal waste incineration plant with possible paths of release of nanoparticles.

## 2. Experimental

### 2.1. Fundamental investigations on the thermal behaviour of nanoparticles

The fundamental investigations on the thermal behaviour of nanoparticles were carried out at a lab-scale burner and at a tube furnace. The used temperature in both systems is similar and the comparison of the results allows a differentiation between flame chemistry and temperature effect.

### 2.1.1. Material

The used Ceria suspension (Cerium(IV) oxide) is commercially available at Alfa Aesar (NanoTek CE 6082) and is specified as 18 m.-% Ceria in $H_2O$. The producer declares the primary particle size to be approximately 30 nm. The melting temperature of the bulk material is around 2000 °C and the density is 7.3 g/cm$^3$.

### 2.1.2. Lab-scale burner

For this study a so called McKenna burner was used, which provides a laminar premixed flame. The burner was operated with an Ethylene/Air-mixture and the flame is stabilized on a porous bronze plate. The burner is considered to be one-dimensional, therefore the flame properties only change with one coordinate, the height above burner (HaB). The laminar flame speed $v_L$ is supposed to be higher than the velocity of the cold gases $v_{cold}$, otherwise the flame would lift off. Through a centered tube in the porous plate it was possible to add cerium dioxide sprayed via an atomizer (Figure 3). The stoichiometry of the flame can be defined as C/O ratio, air number $\lambda$ or equivalence ratio $\Phi$. The temperature of the Ethylene/Air-flame was varied by changing either the C/O ratio or the cold gas velocity and the temperature profiles were recorded over the cross section of the burner plate in different heights above the burner. The burner was operated only with non-sooting conditions. The size distribution of the aerosol after passing the flame was measured with a scanning mobility particle sizer (SMPS) by sampling in different heights above the burner.

Figure 3: McKenna burner with centered tube (Holthuis & Associates) and installed measuring probe.

### 2.1.3. Tube furnace

In addition to the McKenna burner a tube furnace (Gero HTRH 100-600/18 with temperature controller Eurotherm Type 2408) was used. This furnace can reach up to 1800 °C. The tube material was $Al_2O_3$ with a heated length of 600 mm and an inner diameter of 30 mm. Either Air or Nitrogen can be used as carrier gas for the sprayed nanoparticle suspension. Additionally the humidity of the carrier gas could be varied via a bubbler system to adjust a similar water-content compared to the flue gas of the flame.

### 2.2. Investigation on the release of nanoparticles during waste incineration

#### 2.2.1. KIT combustion plant BRENDA

The pilot scale experiments are performed at the KIT combustion plant BRENDA which has a thermal output of 2.5 MW. BRENDA was formerly used as a hazardous waste incineration plant and is now operated for co-combustion of coal dust and different biomasses in the combustion chamber. BRENDA is a rotary kiln facility and has a combustion chamber equipped with a boiler for heat recovery and a flue gas cleaning system which complies with the German regulations of emissions (17. BImSchV). The pilot plant BRENDA (Figure 4) provides the opportunity to work on different topics like optimization of hazardous waste incineration, the development of load and fuel flexible burner systems for pulverized fuels and investigations on the NP distribution in waste incinerators. Currently investigations have the focus on the increase of the load flexibility of power plants within the challenges of the German “Energiewende” in combination with fuel flexibility to reduce the carbon footprint. Ongoing projects will deal with the co-incineration with different biomass among themselves under transient conditions.

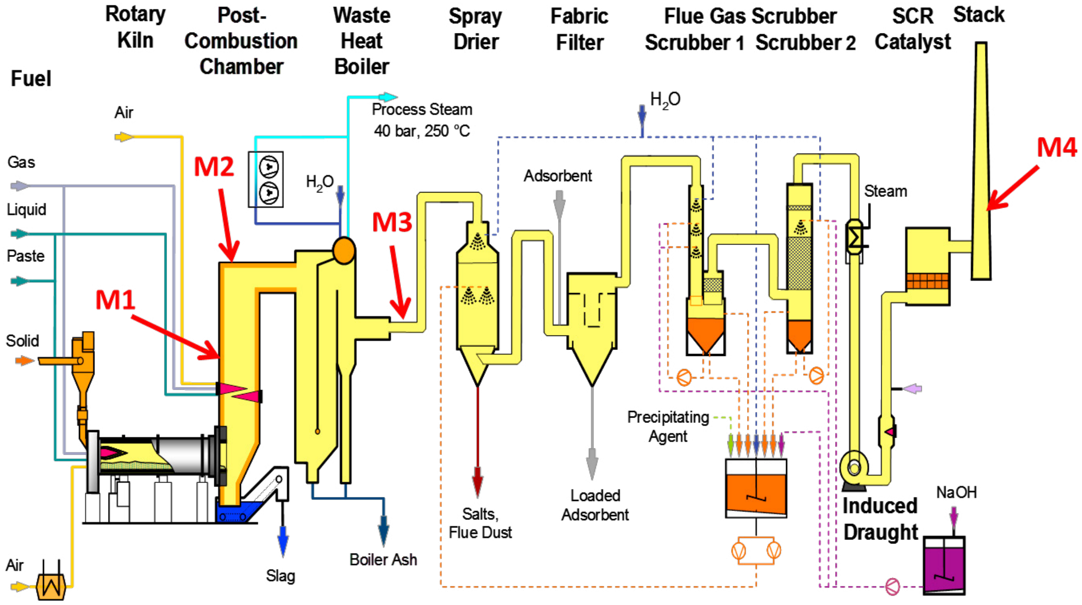

Figure 4: Schematic diagram of the rotary kiln incineration pilot plant BRENDA.

The combustion gases from the rotary kiln are fed into the post combustion chamber, which is equipped with one burner for gases and liquids and a second burner for pulverized fuels. The gas residence time in the post combustion chamber is depending on the load conditions between 4 and 9 s. The burners are staggered anti-parallel to each other and this configuration provides high turbulence and improved mixing of the combustion gases. The hot flue gas leaves the post-combustion chamber under standard operation conditions with a temperature of 1000 °C and enters the boiler. The boiler generates saturated steam of 40 bar and 250 °C. BRENDA is operated with a quasi-dry, waste-water-free flue gas cleaning system, containing spray dryer, fabric filter, scrubbers and an SCR reactor. The tracer ($CeO_2$) was dispensed into the combustion chamber via a two-phase nozzle and the tracer concentration along the furnace, boiler and flue gas cleaning system was analysed. The particle size distribution of the fly ash was measured with different methods like Low Pressure Impactor (DLPI), Electrical Low Pressure Impactor (ELPI), Scanning Mobility Particle Sizer (SMPS) and with Single Particle Light Scattering Spectroscopy (WELAS) downstream of the boiler. To determine the concentration of the tracer material along the exhaust path, filter and impactor (DLPI) samples were analysed via inductively coupled plasma – mass spectrometry (ICP-MS). The mass concentration of the fly ash was varied by combustion of either natural gas or hard coal.

### 2.2.2. Industrial hazardous waste incineration plant

Large-scale investigations were carried out at an industrial hazardous waste incineration plant with a rotary kiln and combustion chamber. This system can be operated with solid, liquid and gaseous waste. The flue gas temperature at the outlet of the combustion chamber is above 1000 °C and the energy of the hot flue gas is used to generate steam in the boiler. The cerium dioxide suspension was dispensed into the combustion chamber via a two-phase nozzle and the tracer concentration along the plant was measured at different points (M1-M4). The first measurement point in the flue gas was in the boiler and the second at the boiler outlet. The next behind the wet-wall electrostatic precipitator and the last measurement point was at the stack as tracer balance limit in the flue gas. In the boiler the flue gas temperature decreases from 1000 °C to the range of 350 °C. The particle concentration in the raw gas at the boiler outlet is very high and depends on the incinerated waste mixture. The hazardous waste incineration plant has a wet flue gas cleaning system and the first device is a quench, where the flue gas is cooled down to the water dew-point by injection of water. Subsequently two rotary scrubbers are installed, one acid and one alkaline scrubber. Downstream of the rotary scrubbers a wet-wall electrostatic precipitator is operated followed by a heating of the flue gas before it enters the selective catalytic reduction (SCR) to reduce the nitrogen oxide emission (Figure 5).

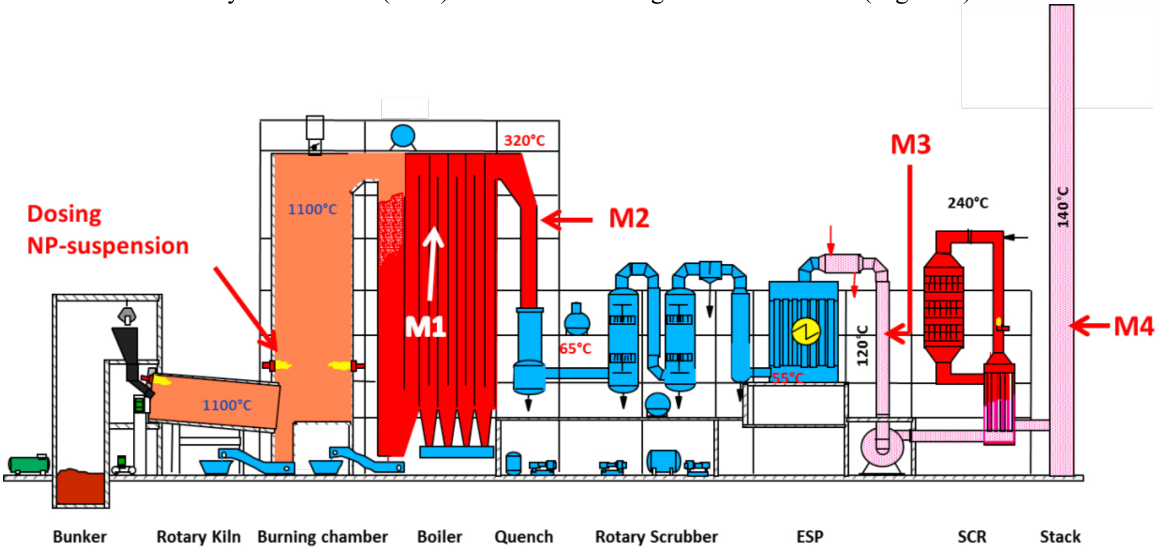

Figure 5: Flow sheet of the industrial hazardous waste incineration plant.

## 3. Results

### 3.1. Experiments at the lab-scale burner

The flame parameters cold gas velocity and stoichiometry can change the flame temperature and their influence on the morphology, size distribution, sintering behaviour, or new particle formation is investigated in different heights above the burner (HAB). The size distributions for 4 different cold gas velocities are shown in Figure 6 for $CeO_2$ nanoparticle injection. The red squares belong to the lowest cold gas velocity and therefore the lowest temperature and refer to the right axis. With increasing cold gas velocity and flame temperature a new particle mode around 10 nm starts to form.

Additionally TEM pictures were taken to compare the aerosol with and without passing the flame (Figure 7). The original aerosol (without flame) shows typical angular Ceria agglomerates, whereas the aerosol with flame consists mainly of very small single particles. This experiment was executed with a few metal oxides ($CeO_2$, $TiO_2$, $SiO_2$) and the same effect was observed. Only the starting temperature is material dependent and this effect was interpreted as an evaporation and nucleation of the nano-material, which was also found by other authors [8].

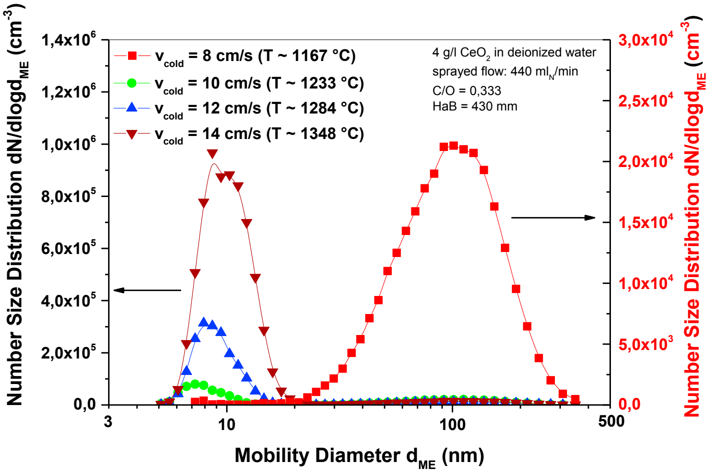

Figure 6: SMPS measurement of a Ceria suspension added to the McKenna burner via center tube. The red curve belongs to the right axis and the other curves to the left axis.

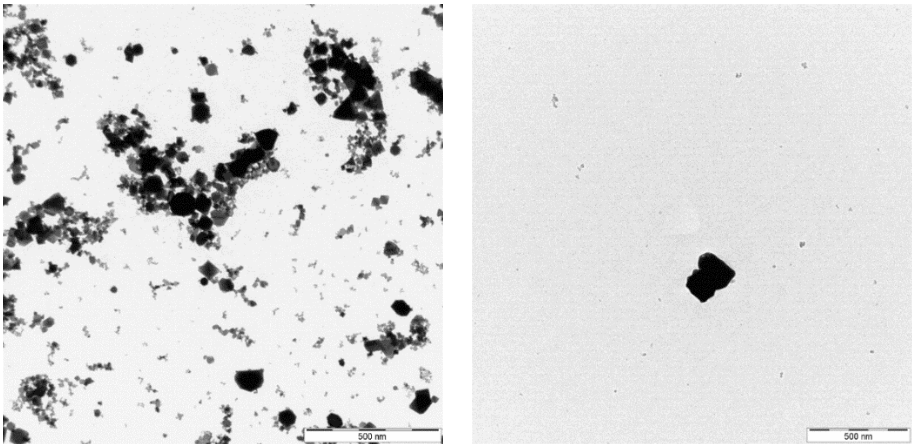

Figure 7: TEM pictures of a Ceria suspension added to the McKenna burner via center tube. Left: without flame, Right: with flame.

### *3.2. Experiments at the tube furnace*

Investigations in the tube furnace with similar temperature don’t show a new particle formation. The effect of particle formation in the flame does not only depend on temperature but depends on gaseous components in the flame, like $H_2O$ as well. The most promising component is water and it was possible to add water via a bubbler system to the carrier gas ($N_2$ or Air) so that the same humidity is adjustable in the tube furnace as in the flue gas of the burner. With this change in the experimental set up a new particle formation was observed. Literature research showed that it is possible for metal oxides to form hydroxides or oxyhydroxides in the presence of water vapour [9].

### *3.3. Experiments at the KIT combustion plant BRENDA*

The influence of the number concentration of fly ash particles on the size distribution of the nano sized tracer material was determined by analysing different impactor plates via ICP-MS. Ceria, which has a low background in waste incinerators, is a suitable tracer for investigating the fate of nanostructured materials. Low concentrations of Ceria were introduced by a two-phase nozzle into the post-combustion zone of a waste incinerator. We found that nanostructured Ceria agglomerates with the fly ash and is found in the size range of 1 – 10 µm. With gas as a fuel less agglomeration was observed and the Ceria NP were in the particle size range of 0.1 – 1 µm (Figure 8 and Figure 9). The removal efficiency of the flue gas cleaning system for the injected nano sized tracer is in the range of 99.99 %. Additionally the fly ash concentration was measured with gravimetric filter samples and the removal efficiency in the gas cleaning system was 99.99 % which is the exact same range as for the tracer.

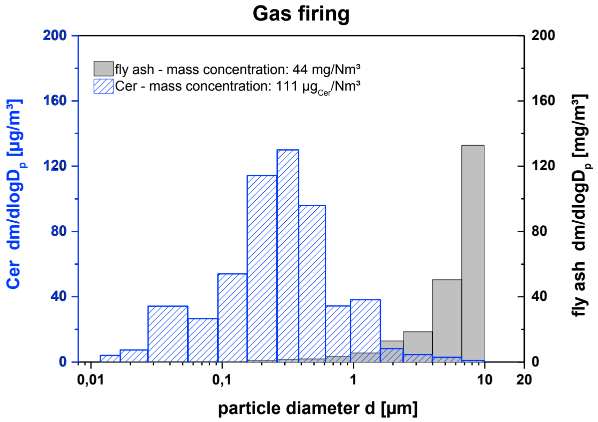

Figure 8: Fly ash and Ceria mass concentration in the off gas of an incinerator for gas firing (sampling upstream of the filter).

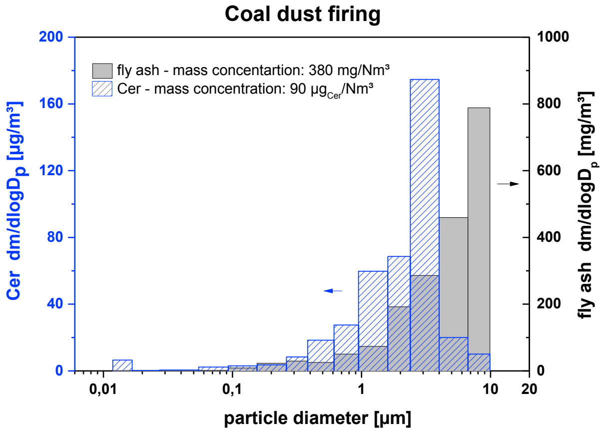

Figure 9: Fly ash and Ceria mass concentration in the off gas of an incinerator for coal dust firing (sampling upstream of the filter).

### *3.4. Experiments at industrial hazardous waste incineration plant*

At the industrial hazardous waste incineration plant the tracer material ($CeO_2$) was injected as a suspension into the post-combustion chamber. The size distribution of the fly ash was measured by ELPI+ at the boiler outlet. To determine the concentration of the tracer along the exhaust path, filters were sampled inside the boiler, behind the boiler, behind the wet-wall electrostatic precipitator and at the exhaust chimney and all samples were analysed via ICP-MS. Additionally all relevant material flows were sampled and also analysed via ICP-MS. The mass balance of the injected tracer at the industrial waste incineration plant shows that over 80 % could be retrieved and the largest amount with roughly 70 % is found in the acid scrubber effluent (Figure 10).

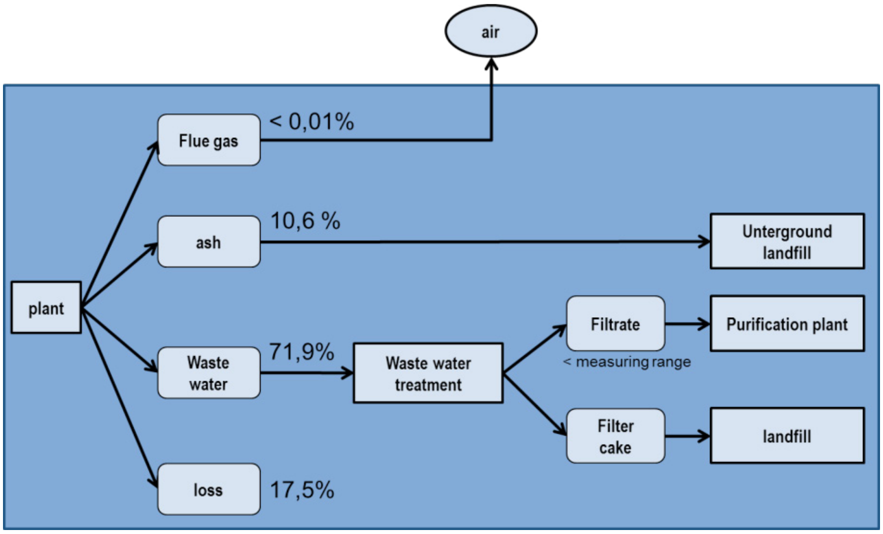

Figure 10: Mass balance of the injected tracer material at the industrial hazardous waste incineration plant.

## 4. Summary

Nowadays engineered nanoparticles are used in many products and at the end of their life cycle they often end up in the waste incineration. Therefore deeper knowledge about the behaviour of nanoparticles in thermal treatment is necessary. Basic investigations in a flame show a sintering of metal oxides. With increasing flame temperature the formation of a new particle mode around 10 nm was observed due to a partial evaporation of the material. This formation is not only temperature driven but also dependent on the gaseous components in the flame. The seen effect is independent of the burner type (McKenna, tube and slit burner), burning gases (Ethylene and Propane) and used materials ($CeO_2$, $TiO_2$ and $SiO_2$). Tracer investigations in a semi-technical combustion chamber show that the nano sized $CeO_2$ tracer interacts with the fly ash particles in the flue gas and the tracer was found in size fraction of the fly ash by ICP-MS analysis of impactor samples. These investigations were repeated on a large scale industrial hazardous waste incineration plant with the same result and measurements at the chimney show a tracer amount below 0.01 % of the injected tracer. Therefore the removal efficiency of the flue gas cleaning system is in the range of 99.99 %. By probing the different material flows of the incineration plant the mass recovery rate of the tracer material was found to be higher than 80 %.

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