

Thermal Stability and Material Balance of Nanomaterials in Waste Incineration

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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 and in an industrial 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 .

1. Introduction

The amount of consumer products containing engineered nanomaterials is constantly growing. As these products reach their end of life they often end up in the waste incineration. Till now only few data are published concerning a possible release of nanoparticles (NP) during combustion into the environment (Walser et al. 2012; Nowack et al. 2013; Andersen et al. 2014). In the Institute for Technical Chemistry at the Karlsruhe Institute of Technology (KIT) this topic is analysed in fundamental investigations of NP behaviour in lab-scale flames (Lang et al. 2015; Teuscher et al. 2016), in technical investigations at a 3 MW combustion chamber at the KIT (Scherrmann et al. 2016) and in large-scale investigations at an industrial hazardous waste incineration plant in the chemical industry. A new project 'ProCycle' concerning the behaviour and possible release of NPs by incineration of polymer nanocomposites started in 2015. 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 (see Figure 1). With every recycle step the product quality is decreasing and a thermal process is always the last possible treatment.



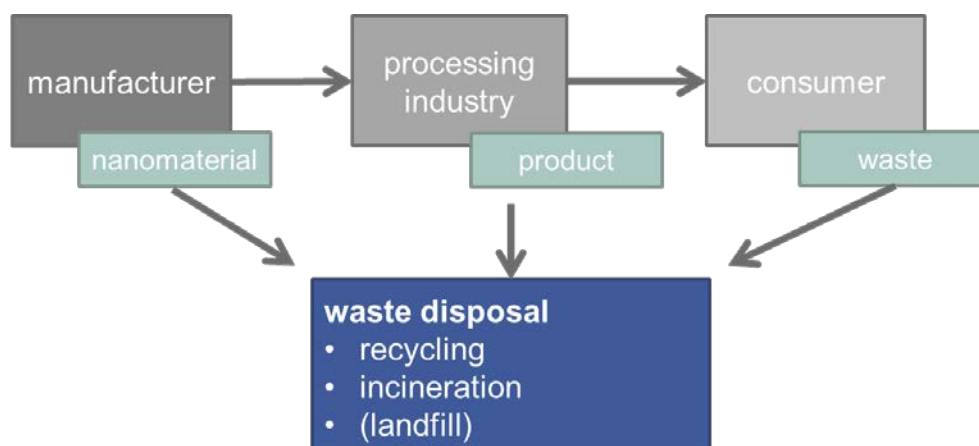


Figure 1: Life cycle of products including nanoparticles.

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.

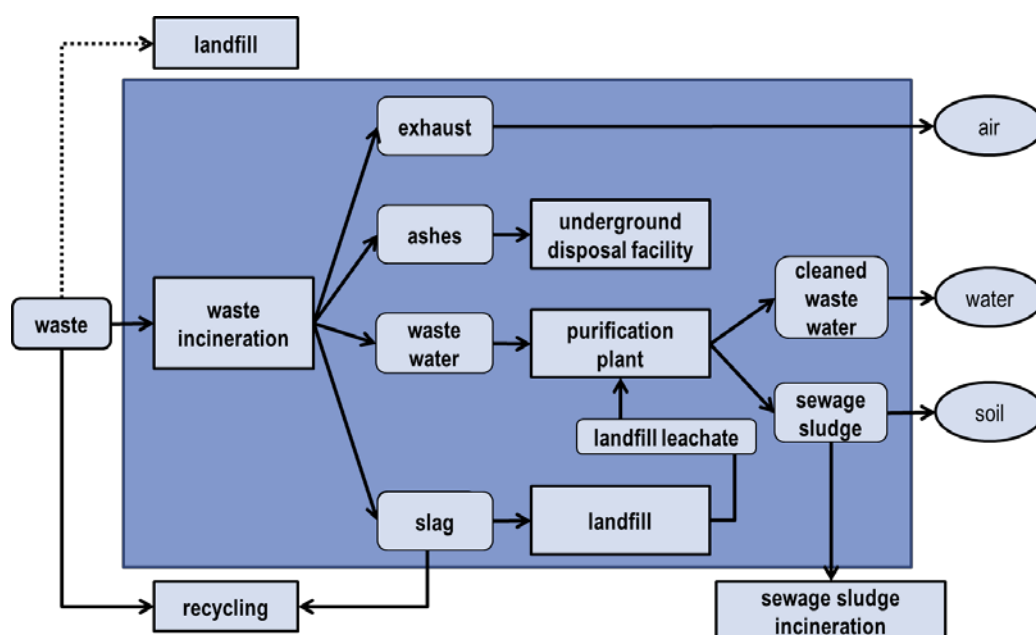


Figure 2: Flow sheet of a municipal waste incineration plant with possible paths of release of nanoparticles.

2. Lab-scale 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. The used Ceria suspension (Cerium(IV) oxide) is commercially available at Alfa Aesar (NanoTek CE 6082) and is specified as 18 m.-% Ceria in H₂O. 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/cm³.

2.1. Experiments at the 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 smaller 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 (see Figure 3). The temperature of the Ethylene/Air-flame was varied by changing either the C/O ratio or the cold gas velocity. The temperature profiles were recorded over the cross section of the burner plate in different HaB. 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).

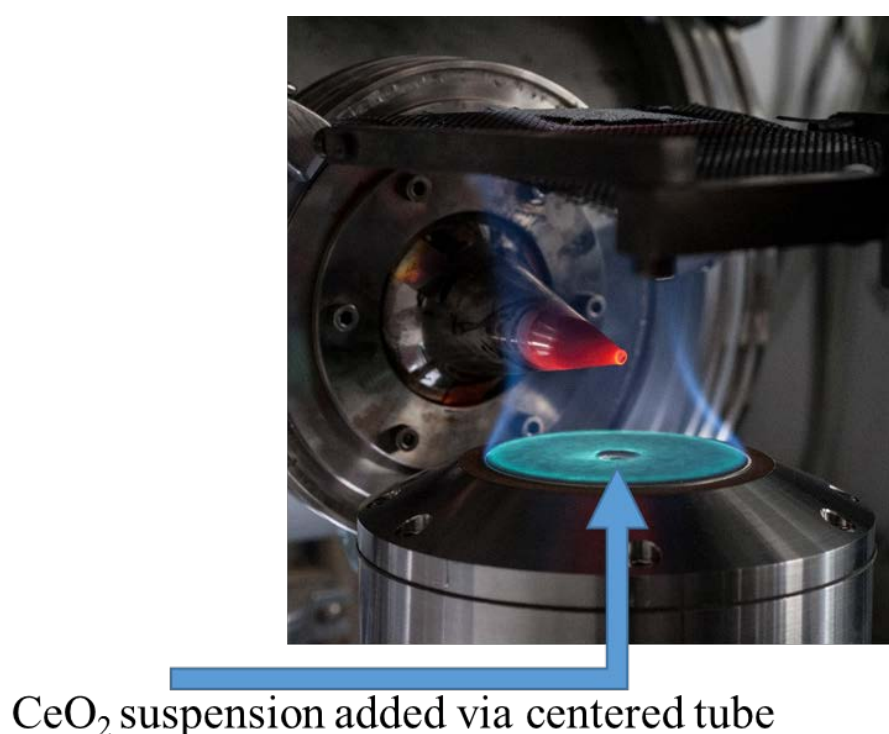


Figure 3: McKenna burner with centered tube (Holthuis & Associates).

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 HaB. The size distributions for 4 different cold gas velocities are shown in Figure 4 for CeO₂ 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.

This experiment was executed with a few metal oxides (CeO₂, TiO₂, SiO₂) 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 (Goertz et al. 2011).

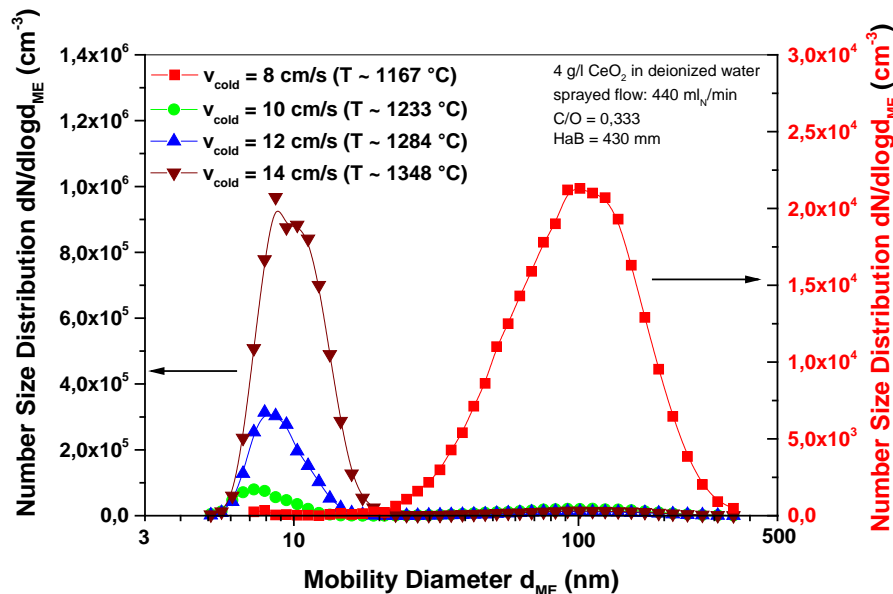


Figure 4: SMPS measurement of a Ceria suspension added to the McKenna burner via center tube.

The red curve belongs to the right axis and the other curves to the left axis.

2.2. Experiments at the tube furnace

In addition to the McKenna burner a tube furnace (Gero HTRH 100-600/18 with temperature controller Eurotherm Type 2408) was used. With this furnace temperatures up to 1800 °C were adjustable. 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.

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 (Golden and Opila 2016).

3. Investigation on the release of nanoparticles during waste incineration

3.1. KIT combustion plant BRENDA

The pilot scale experiments are performed at the KIT combustion plant BRENDA which has a thermal output of 3 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 (see Figure 5) provides the opportunity to work on different topics. A combined burner for gases and liquids and an atomizer lance for liquids are installed. Depending on the temperature in the rotary kiln (up to 1300 °C), the combustion residues may be either solid or molten.

The combustion gases from the rotary kiln are fed into the post combustion chamber which is equipped with two combined burners for gases and liquids and an air nozzle for secondary combustion air. The gas residence time in the post combustion chamber is around 9 s. The burners are staggered anti-parallel to each other and this configuration ensures high turbulence and improved mixing of the combustion gases. The post-combustion chamber is designed for gas temperatures up to 1300 °C. The hot flue gas leaves the post-combustion chamber under standard operation conditions with a temperature of 1000 °C and enters the boiler with a residence time of 22 – 25 s. 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, Electrical Low Pressure Impactor (ELPI+), SMPS and with Single Particle Light Scattering Spectroscopy downstream of the boiler. To determine the concentration of the tracer material along the exhaust path, filter and impactor 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. 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.

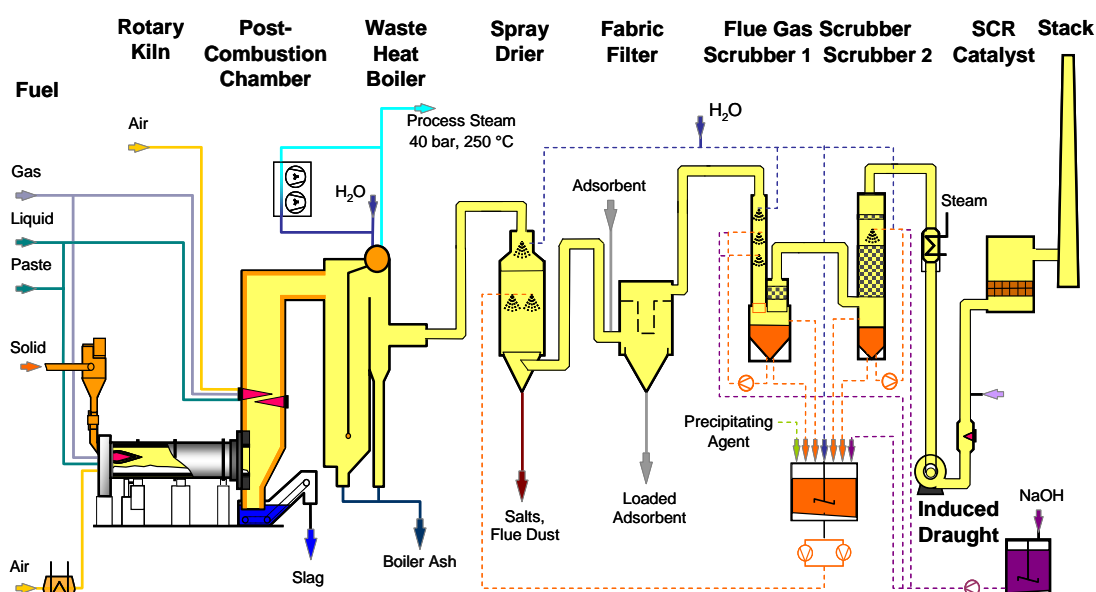


Figure 5: Schematic diagram of the rotary kiln incineration pilot plant BRENDA.

We found that nanostructured Ceria agglomerates with the fly ash, formed by combustion of coal. With gas as a fuel less agglomeration was observed and the Ceria NP were in the particle size range of 0.1 – 1 μm (see Figure 6). 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.

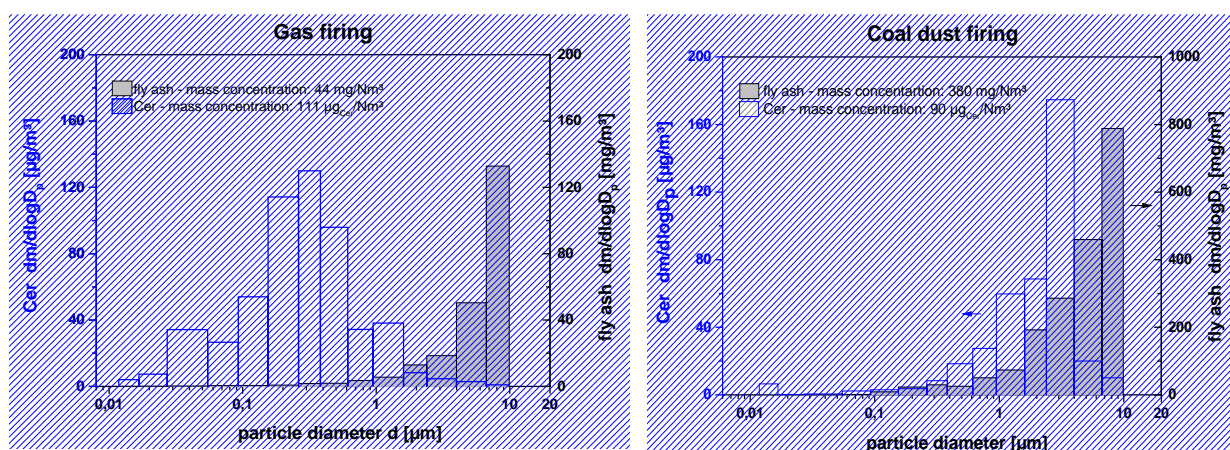


Figure 6: Fly ash and Ceria mass concentration in the off gas of an incinerator for gas and coal dust firing (sampling downstream of the boiler).

3.2. 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. 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 (see Figure 7).

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 (see Figure 8).

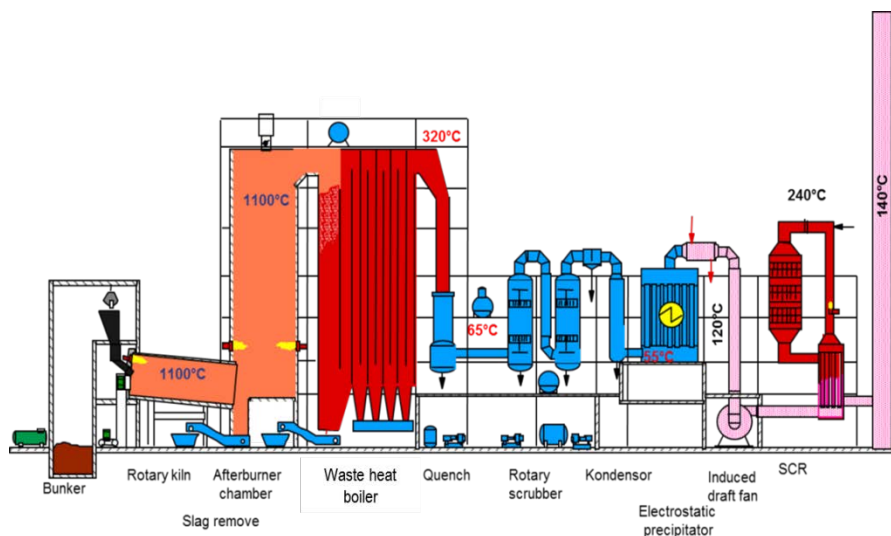


Figure 7: Flow sheet of the industrial hazardous waste incineration plant.

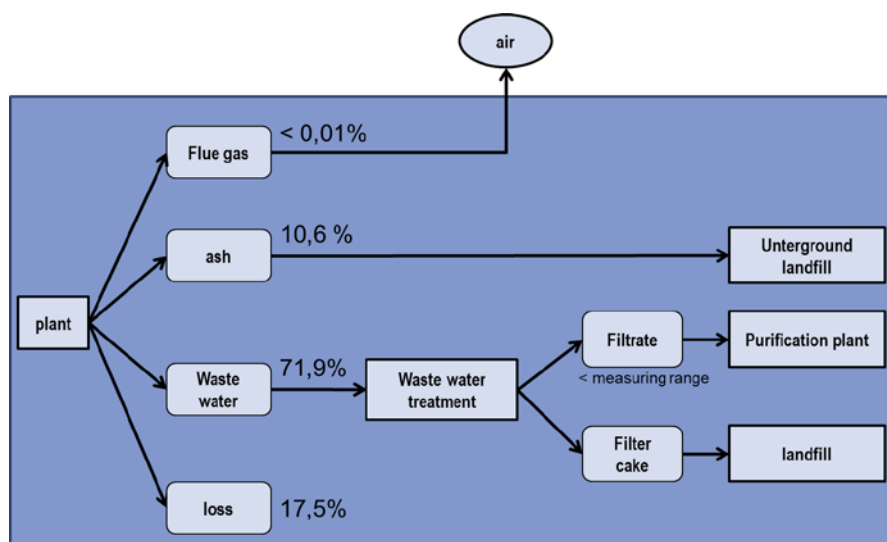


Figure 8: Mass balance of the tracer material at the industrial hazardous waste incineration plant.

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. 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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