MODELLING DE-NOVO FORMATION OF DIOXINS IN THE EFFLUENT GAS CLEANING TRACT OF A ZINC RECYCLING PROCESS

Hermann Nordsieck, René Peche

Bavarian Institute of Applied Environmental Research and Technology, Am Mittleren Moos 46, D-86167 Augsburg, Germany

Introduction

Dioxins as well as other chloroaromatics are an unwanted by-product of most metallurgical processes, both in primary metal production and in recycling, such as at the re-use of high-zinc steel dust, as obtained in the second steel melting process using in electric arc furnaces, by extracting the included zinc. For achieving this purpose, the steel dust is treated in a rotary kiln. This resulting zinc oxide is offered to metal working companies in form of fine powder where it is used for galvanizing of components, for example, or for converting the powder to pure metal.

In the framework of the MINIDIP-project (**Mini**mization of **Di**oxins in Thermal Industrial **P**rocesses: Mechanisms, Monitoring, Abatement) the formation of dioxins was studied as a function of temperature, time, oxygen, and inhibitor addition. The resulting kinetic data are introduced into a computational fluid dynamics (CFD) model, featuring geometric representations of the effluent gas cleaning tract components and the temperature and gas flow field as well as the trajectories and destination of particles different sizes are calculated. This CFD model is used to estimate the de-novo formation of dioxins from the moment the gas leaves the rotary kiln until its cleaning, in order to define the role of this part of the plant in the formation of dioxins, as well as the identification and extent of possibilities for minimizing dioxin emissions.

Method

For numerical modelling the commercial program FLUENT® is applied[1].

For simulation of formation of dioxins proceeding from the particles flight path it was necessary to program an User Defined Function (UDF) which can be dynamically linked with the FLUENT® solver. The UDF is only active for moving particles and depends on the particle temperature upon leaving a cell as well as on its residence time and concentration in a cell. The dioxin formation kinetics are based on measurements of *Forschungszentrum Karlsruhe.* On the assumption that the turn over is small and without detailed information on the influence of other flue gas components, the formation of dioxins is calculated on base of a pseudo zero order kinetics. It is common knowledge, that the formation rate also depends on the oxygen content in a large extent. Nevertheless, within the computational domain any changes in oxygen content can be neglected. The oxygen concentration is essentially constant in all three parts of the computational domain since the combustion of the carbon, which is admitted as reducing agent, takes place primarily in the rotary kiln, outside (upstream) of the computational domain. Therefore, the UDF for dioxin formation from entrained particles depends on the parameters:

- particle temperature upon leaving a cell,
- particle residence time in the cell and
- permanent number of particles (solid mass) in the cell.

Results and Discussion

The key component of the zinc recycling process is a rotary kiln, where a mixture of steel dust and various additives is treated at about 1200 °C. Due to the kiln inclination and rotation the mixture moves down through the rotary kiln with simultaneously drying and preheating by the counter current process gas. At a temperature of 850 °C metal oxides are reduced and zinc are volatilised. The excess of air in the kiln results in a back-oxidation of the zinc vapour while CO is converted into CO_2. The process gas loaded with dust leaves the rotary kiln into a following effluent gas cleaning tract , whereas the residual non-metallic slag is rapped off at the other end of the kiln. The process gas is cooled in a dust chamber and an evaporation cooler by an injection of spray water. The coarse dusts with low zinc content are separated in the dust chamber and transferred back into the rotary kiln. The separation of the fine dust with a high zinc content takes place in the evaporation cooler as well as in a following electrostatic precipitator.

The kinetic study of the 'de novo' formation of dioxins at a zinc recycling process leads to a computational domain that begins at the gas outlet of the rotary kiln and contains the dust chamber, the evaporation cooler and the electrostatic precipitator. Because of the limited number of cells in the CFD model this computational domain is divided in three parts, which are modelled separately.

The hot process gas enters the dust chamber (geometry cf. figure 1) at the interface to the rotary kiln. During the transport through the dust chamber, the process gas passes water nozzles, which are arranged in the ceiling at the interface of the connection chamber and the settling chamber 1, whereby the injected water cools the it by evaporation. In all hoppers as well as inside the settling chamber 2 recirculation areas occur with low flow velocities. Entrained particle with representative sizes between 10 and 140 µm are able to leave the dust chamber through the four hoppers as well as the connection pipe to the evaporation cooler. According to the particle calculations approx. 40 % of the defined particle mass flow leave the dust chamber through the gas outlet (predominately fine particles) and approx. 50 % through the hoppers of the settling chamber 1 (predominately coarse particles). The remaining particle mass flow can be found in the hoppers of the settling chamber 2.

In the dust chamber de-novo formation of dioxins is only possible in a small area near the injection points of cooling water because there the temperature is low enough to be within the dioxin formation

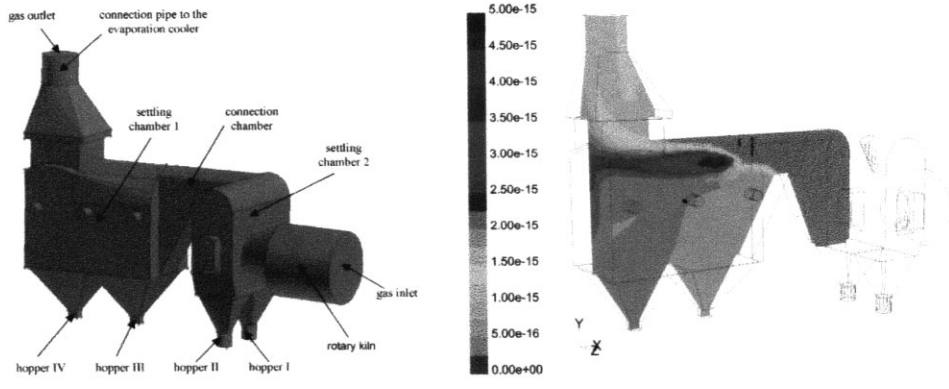

Figure 1. Geometry and nomenclature of the dust chamber (left) as well as distribution of the dioxin concentration in the middle of chamber 1 based on particles with a size of 10 µm (right)

window. Resulting of the small dimension of this area the calculated formation rates of dioxins from entrained particles are low. Therefore only 0.01 % of the total calculated formation of dioxins in the investigated effluent gas cleaning tract is calculated at the gas outlet (cf. figure 1).

After leaving the connection pipe as well as passing a second time nozzles with cooling water the process gas enters the evaporation cooler (geometry cf. figure 2), whereby the velocity is rapidly reduced because of the diffuser effect of the entrance into the cylindrical vessel. Inside the vessel, a main flow in the middle can be realised from where the velocity values decrease in wall direction. between the main flow and the vessel wall several local recirculation areas are formed. Furthermore, a presence of a small recirculation area can be assumed in the hopper where the process gas is turned around into a connection pipe to the gas divider. Inside the gas divider the process gas is linked in two almost identical volume parts which flow into two filtering units of the following electrostatic precipitator. All particle calculations in the evaporation cooler underline the dependency of the mass inertia on the particle size. Whereas fine particles can be found almost in the whole computational domain, coarse particles fly with clearly less fluctuation effects through the cylindrical vessel straight forward to the hopper. Only a third of the fine particles with sizes less than 25 µm leave the evaporation cooler through the hopper, whereas particles with a larger size are predominantly deposited in the hopper. No particle with a size above 140 µm do reach the connection pipe to the gas divider.

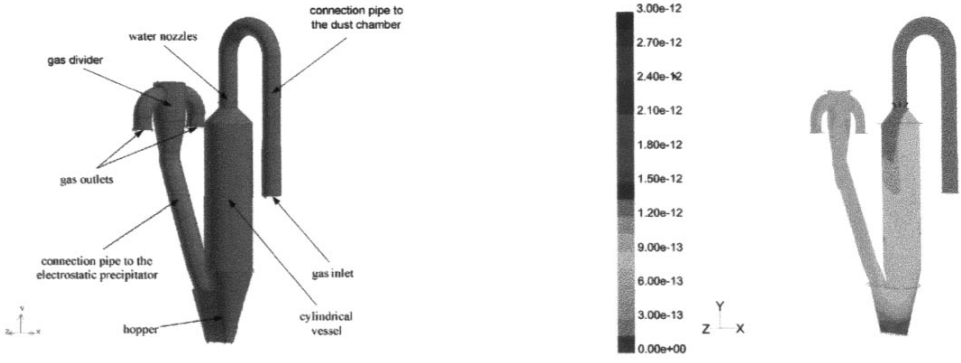

Figure 2. Geometry and nomenclature of the evaporation cooler (left) as well as distribution of the dioxin concentration in the middle of computational domain based on particles with a size of 25 µm (right)

The formation of dioxins by de-novo synthesis from particles with sizes of 10 µm and 25 µm is higher than from coarser particles as a result of the much higher defined mass flow and the different residence times in the evaporation cooler. At the gas outlets approx. 40 % of the total calculated formation of dioxins in the investigated effluent gas cleaning tract is calculated (cf. figure 2), predominantly formed by particles with a size of 10 µm.

The electrostatic precipitator system of the investigated zinc recycling process contains two separate filtering units (a scheme of one filtering unit is shown in figure 3). Because of the complexity of the physical processes for electrostatic precipitation of particles it was not possible integrate it into a CFD model. Therefore, only one gas distribution section, bordered by the gas inlet (corresponding to one gas outlet of the gas divider of the evaporation cooler) and the entrance into the first field of electrostatic precipitation, could be modelled.

Behind the gas distribution wall the incoming process gas is steered into a horizontal flow field with small vertical deflection and low velocity values. Only at the left and the right of the end of the

gas distribution wall and between the gas distribution wall and the outside wall the velocities are higher because of gaps respectively slits. Recirculation areas with low velocities are developed in the upper part in front of the gas distribution wall and in the hopper. Additionally, a so-called “dead zone” (an area with extremely small flow velocities) can be realized between the gas distribution wall and the entrance into the precipitation field 1.

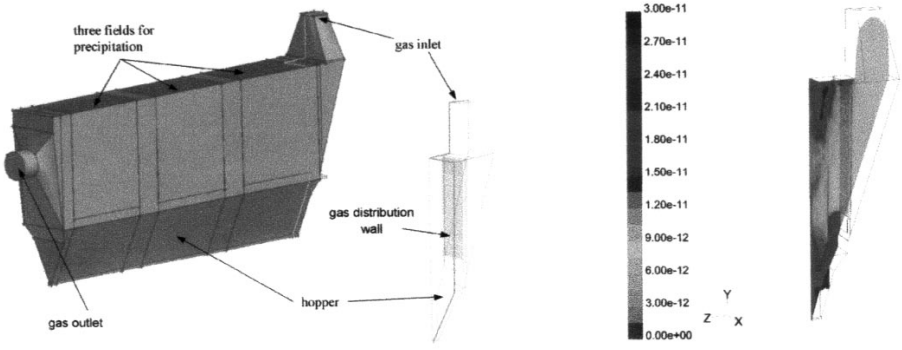

Figure 3. Scheme of one filtering unit of the electrostatic precipitator and geometry and nomenclature of the modelled gas distribution section (left) as well as distribution of the dioxin concentration at the gas outlet and in the middle of the computational domain based on particles with a size of 10 µm (right)

With the flow field entrained coarse particles fly from the gas inlet predominantly near the wall to the lower end of the gas distribution wall. Behind this wall, most of these particles enter the hopper immediately. Almost no coarse particle with a size between 50 µm and 100 µm are able to reach the precipitation field 1. Fine particles are found in the whole upper area of the computational domain between the gas inlet and the gas distribution wall. Behind the gas distribution wall, more than half of the fine particles enter the precipitation field 1, whereas the other part is found on the way to the hopper. Totalling approx. 95 % of the defined mass flow leaves the computational domain through the gas outlet, where approx. 60 % of the total calculated formation of dioxins in the investigated effluent gas cleaning tract is calculated (cf. figure 3).

An estimation of the formation of dioxins in the three fields of the electrostatic precipitator shows, that most of the dioxin is not contributed by the particle flying but by the particles precipitated. This depends on the long residence time of such particles at the precipitation walls (at least 5 minutes per field depending on the cleaning interval for the precipitation walls). From this it follows that minimum of 80 % of the total emission of dioxins is formed in the electrostatic precipitator, if only the de-novo-mechanism is regarded.

Acknowledgement

The authors are indebted to the E.U. Programme ‘Environment & Climate’ for funding the R&D-project with acronym ‘MINIDIP’ (cf. Introduction) and Prof. Buekens of the Vrije Universiteit Brussel (Faculteit Toegepaste Wetenschappen, Pleinlaan 2, B-1050 Brussel, Belgium), the co-ordinator of the project.

References

1. Fluent User´s Guide (1999): Version 5.5, FLUENTÒ Deutschland GmbH