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Modeling study of polychlorinated dibenzo-*p*-dioxins and dibenzofurans behavior in flue gases under electron beam irradiation

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HIGHLIGHTS

- Efficiency of electron beam dry scrubbing method as applied to PCDD/Fs was estimated.
- Decomposition of PCDD/Fs is the main channel of their transformation under EB irradiation.
- Production of PCDD/Fs at low concentrations of chlorinated phenols is insignificant.
- Further experiments are required to clarify mechanisms of PCDD/Fs transformation.

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ABSTRACT

The efficiency of the electron beam treatment of industrial flue gases for the removal of sulfur and nitrogen oxides was investigated as applied to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) using methods of mathematical modeling. The proposed kinetic model of the process includes mechanism of PCDD/Fs decomposition caused by their interaction with OH radicals generated in the flue gases under the electron beam (EB) irradiation as well as PCDD/Fs formation from unburned aromatic compounds. The model allows to predict the main features of the process, which are observed in pilot plant installations, as well as to evaluate the process efficiency. The results of calculations are compared with the available experimental data.

1. Introduction

The industrial flue gas contains a variety of harmful admixtures such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and others, which cause considerable environmental pollution. The most toxic representatives of VOCs are polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). The US EPA recommends an intake limit of PCDD/F for humans of 0.001 pg/kg bw/day in terms of the most toxic 2,3,7,8-TCDD for a lifetime additional cancer risk of 10^{-6} (Rodriguez et al., 2008). The problem of the environmental pollution by PCDD/F arose from the fact that noticeable amount of dioxins was found in the products of municipal solid waste incineration (MSWI) (Tuppurainen et al., 1998). However, these compounds are formed in almost all processes associated with the combustion of organic fuels in the presence of various chlorine compounds, namely, industrial and domestic coal combustion, medical waste incineration, sinter plants, cement industry, ferrous and non-ferrous metallurgy, motor transport, etc. (Kulkarni et al., 2008).

At the present time, there are a number of technologies for cleaning of the MSWI flue gases from PCDD/Fs (Liu et al., 2012). The electron-beam dry scrubbing (EBDS) process for the removal of SO_2, NO_x, and VOCs from industrial flue gas is the most intensely developed area of radiation technology application to solve environmental problems (Chmielewski, 2007; Sun and Chmielewski, 2012). This cleaning method has a number of advantages over traditional ones, namely, the simultaneous removal of harmful admixtures, the simplicity and reliability in operation, low capital and operation costs, the possibility of by-products utilization, etc. (Frank, 1995). Originally developed in pilot-scale conditions (Kawamura et al., 1981; Jordan, 1988), it has been implemented at

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full-scale in industrial plants (Doi et al., 2000; Chmielewski et al., 2004).

Problems of PCDD/Fs destruction under the electron beam (EB) irradiation were experimentally investigated at various process conditions (Paur et al., 1998; Hirota et al., 2003). Theoretical description of the process is based on the model of polycyclic aromatic hydrocarbons (PAHs) decomposition in gas-phase reactions with OH radicals produced by the irradiation of flue gases (Gerasimov, 2007). The presence of active species (atoms and radicals) in the irradiation zone and their reactions with unburned gaseous and condensed aromatic compounds can result in an opposite effect, namely, the formation of PCDD/Fs in considerable amounts (Khachatryan et al., 2003). The concentration of these compounds under certain process conditions can exceed their initial concentration. In this study, an attempt was made to evaluate the overall efficiency of the EBDS process as applied to the PCDD/Fs removal from the MSWI flue gases.

2. Kinetic model of radiation-induced PCDD/Fs transformation

The EBDS process is based on the oxidation of major admixtures in the flue gases, SO_2 and NO_x, into corresponding acids under the influence of active species (ions, atoms, and radicals) generated during the EB irradiation of multi-component gas system. The acids are converted into salts by the addition of neutralizing species (e.g. ammonia, NH_3), and removed from the flue gases by dry electrostatic precipitators. The presence of PCDD/Fs in the irradiation zone has slight influence on the kinetics of SO_2 and NO_x oxidation since their concentrations in the MSWI flue gases is negligible. In these conditions, the concentration of active species that are responsible for the conversion of PCDD/Fs molecules depends on the set of chemical processes related to the oxidation of SO_2 and NO_x.

2.1. Specifics of the EBDS process

The operating principle of the EBDS method consists in the irradiation of a swirling gas flow by a scanning beam of accelerated electrons, which ensures uniform radiation energy absorption in a flow volume (Kawamura et al., 1981). The interaction of accelerated electrons with macro-components of the flue gases (N_2, O_2, H_2O, and CO_2) results in their ionization, dissociation, and excitation followed by charge components transformation in charge transfer and neutralization reactions. The simplified scheme of this radiolytic process can be represented as:

$$(N_2, O_2, H_2O, CO_2) \xrightarrow{EB} \left(N_2^+, O_2^+, H_2O^+, CO_2^+, N^+, O^+, e^-, N, O, H, OH\right),$$

$$\left(N_2^+, O_2^+, CO_2^+, N^+, O^+\right) \xrightarrow{H_2O} H_2O^+ \xrightarrow{H_2O} H_3O^+ + OH,$$

$$O_2 \xrightarrow{e^-} O_2^- \xrightarrow{NO_2} NO_2^- \xrightarrow{H_3O^+} NO_2 + H_2O.$$

The reaction scheme of gas phase SO_2 oxidation is simple. It can be represented as the following sequence of reactions that lead to the formation of sulfuric acid vapor:

$$SO_2 \xrightarrow{OH} HSO_3 \xrightarrow{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4.$$

The group of reactions that describe the formation and conversion of nitrogen containing components has a more branched structure. The main sequence of NO_x oxidation reactions can be represented as:

$$NO \xrightarrow{OH} HNO_2 \xrightarrow{OH} NO_2 \xrightarrow{OH} HNO_3.$$

These sequences of reactions show that the hydroxyl radicals OH are important in the gas-phase oxidation of SO_2 and NO_x.

The typical temperatures of the EBDS process are in the range from 60 to 85 °C. At these temperatures, the conditions of bulk binary condensation of water vapor and sulfuric acid one, which is formed in gas-phase chemical processes, are realized (Paur and Jordan, 1988). The formation of small droplets is accompanied by dissolution therein of some gaseous components, such as SO_2, NH_3, OH etc. This gives rise to liquid phase SO_2 oxidation that plays a significant role in the EBDS process (Yermakov et al., 1992; Calinescu et al., 2013).

The details of the mathematical model, which was used in this study for description of the EB induced PCDD/Fs transformation in the MSWI flue gases, are given earlier (Gerasimov et al., 1996; Gerasimov, 2015). The computational procedure is based on the widely used CHEMKIN code (Kee et al., 1996) that was modified to include equilibrium and liquid phase reactions associated with SO_2 oxidation in droplets. The calculations are carried out in the approximation of an adiabatic process at a constant pressure.

2.2. PCDD/Fs decomposition under irradiation

The OH radicals, which are formed in the flue gases under the EB irradiation and play an important role in radiation induced oxidation of main harmful admixtures in wet gaseous mixture, are also the main active components responsible for decomposition of PCDD/Fs molecules (Atkinson, 1991; Kwok et al., 1995). Brubaker and Hites (1998) have carried out experiments to measure the OH radical rate constants k_{OH} for polycyclic aromatic hydrocarbons and dioxin congeners. According to their results, the addition of the OH radical into the PCDD molecule under atmospheric conditions should be more favorable than the substitution or H abstraction. The magnitudes of the rate constants were in good agreement with the room temperature structure-reactivity calculations of Atkinson (1991) and Kwok et al. (1995) based on the electrophilic constants. At elevated temperatures (500 K < T < 1000 K), the OH radicals react with aromatic compounds initially through H abstraction rather than OH addition into the benzene ring (Atkinson, 1986). Nevertheless, there is no experimental evidence for a change in reaction mechanism from OH addition to H abstraction for PCDD molecules at elevated temperatures (Taylor et al., 2005).

Theoretical study using density functional theory calculations can provide sufficiently accurate predictions for the atmospheric oxidation mechanism of PCDD/Fs initiated by OH radical (Lee et al., 2004; Wang and Tang, 2012; Sun et al., 2012). The oxidation of the PCDD molecule is initiated by OH addition predominantly to the C_γ and non-chlorinated C_β sites, while the addition to C_α and chlorinated sites are negligible. The PCDD-β-OH adducts react with O_2 to form PCDD-β-ols, while PCDD-γ-OH adducts undergo fused-ring C-O rupture with formation of substituted phenoxy radicals. The gas-phase oxidation products for the 2,3,7,8-PCDD are the substituted

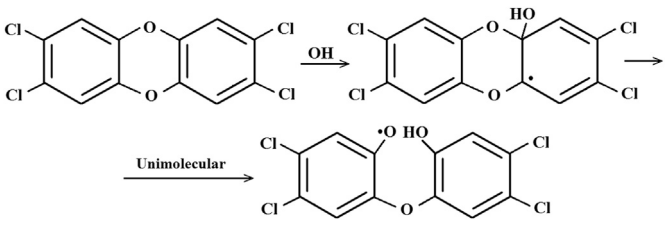

Fig. 1. Simplified scheme of the 2,3,7,8-TCDD oxidation mechanism.