

NUMERICAL SIMULATION OF DIOXIN FORMATION IN A STOKER-TYPE FURNACE

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Introduction

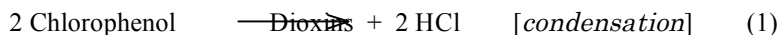
Dioxin formation in solid waste incinerator was brought by two processes, that is, the condensation of precursors in furnaces and the “de novo” process in the post-furnace region. The former process contains condensation of precursors such as chlorophenols, and the combustion of dioxin and precursors. The latter contains the reaction between unburned hydrocarbons and chlorine from hydrogen chloride with catalysts via Deacon reaction.

The reaction mechanism of the condensation process was proposed by Shaub and Tsang[1]. Kinetic data for dioxin formation under in-furnace conditions were obtained using chlorophenols [2,5], chlorobenzenes[3], and PCBs[4] precursors.

The authors construct the numerical simulation model including devolatilization of chlorophenol precursor, condensation of chlorophenol to dioxin, and combustion of them. The model is applied to a stoker furnace of 150ton/day scale.

Methods

Rate constant : Overall rate constants of condensation of chlorophenols and combustion was calculated assuming the following consecutive condensation-combustion schemes. The rate expressions are assumed in first order to reactants for simplification. The rates of combustion are independent on oxygen concentration because that of oxygen is high compared with dioxin and chlorophenol.



Rate constants of reactions (1) to (3) are shown in Table 1. It is assumed that the rate constant of chlorophenol combustion is equal to that of dioxin combustion.

Table 1 Rate Constants of Dioxin Formation and Combustion

reaction	rate constant	temperature	ref.
Dioxin formation	$63.6 \exp[-83600/RT]$	783 – 923K	[2], [3], [4]
Dioxin combustion	$431 \exp[-46600/RT]$	673 – 1023K	[5]
Chlorophenol combustion	$431 \exp[-46600/RT]$	673 – 1023K	[5]

Simulation model : The simulation model used the 3-dimensional turbulence(k-epsilon) model with reactions. The compositions of CO/CH₄/H₂ in pyrolyzed gas evolved on stokers is calculated using elemental compositions of solid wastes. The temperature of gas phase in each element is calculated with heat of combustion and amounts of burned CO/CH₄/H₂ using conventional rate expression. Solid wastes on the stokers are heated by radiation from gas phase to evolve volatiles. Solid wastes contain chlorophenol at certain portion of chlorides. Evolution rate of chlorophenol from solid wastes on stokers is calculated with vapor pressures of chlorophenol and gas flow rates.

Results and Discussion

Distributions of chlorophenol and dioxin in the furnace is calculated under the conventional conditions varying air flow rate and humidity of wastes. An example of contour maps of the concentration of chlorophenol and dioxin is shown in Figure 1. Evolution of chlorophenol occurs on the second stage of stokers. Dioxin formation occurs consecutively at the upper parts of the chlorophenol evolution. Profiles of concentrations of dioxin and chlorophenol indicate that the consecutive combustion of dioxin and chlorophenol. Calculated concentrations at furnace exit of dioxin and chlorophenol are averaged along cross sectional elements of furnace exit.

Concentrations of chlorophenols and dioxins in flue gas were reported in the literatures[6-9] at some incineration plants in Japan. Gas sampling sites were located from exit of furnace to exit of dust collector. Sum of concentration from dichlorophenol to pentachlorophenol and sum of concentration of PCDDs (tetra- to octa-) and PCDFs(tetra- to octa-) are plotted along horizontal and vertical axes, respectively, in Figure 2. It is found that concentrations of chlorophenol and dioxin shows broad band correlation. The calculated concentrations of chlorophenol and dioxin at furnace exit are also plotted in the same figure.

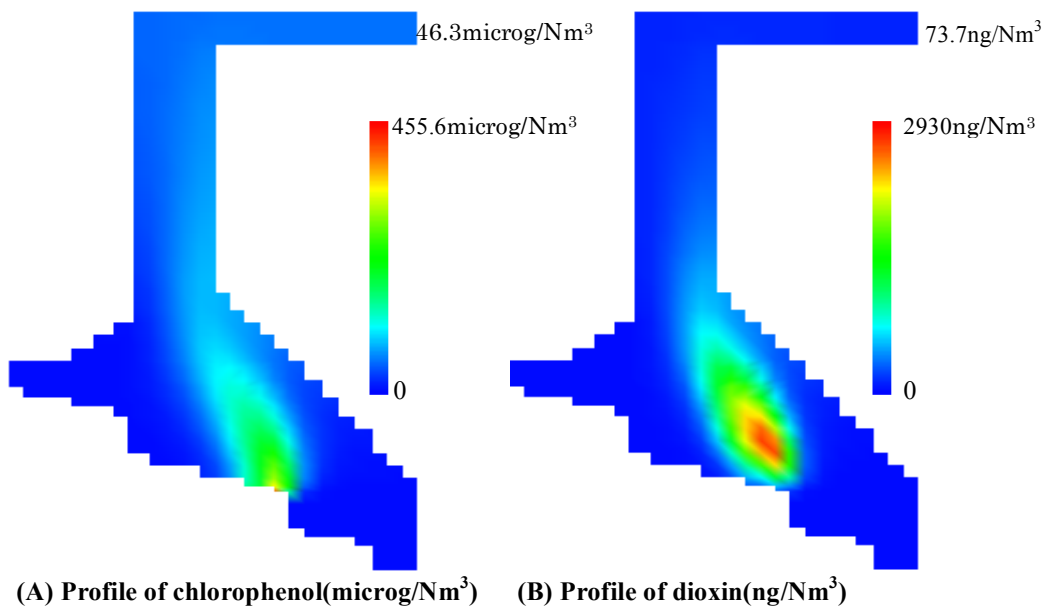


Figure 1 Contour maps of chlorophenol and dioxin in a stoker furnace

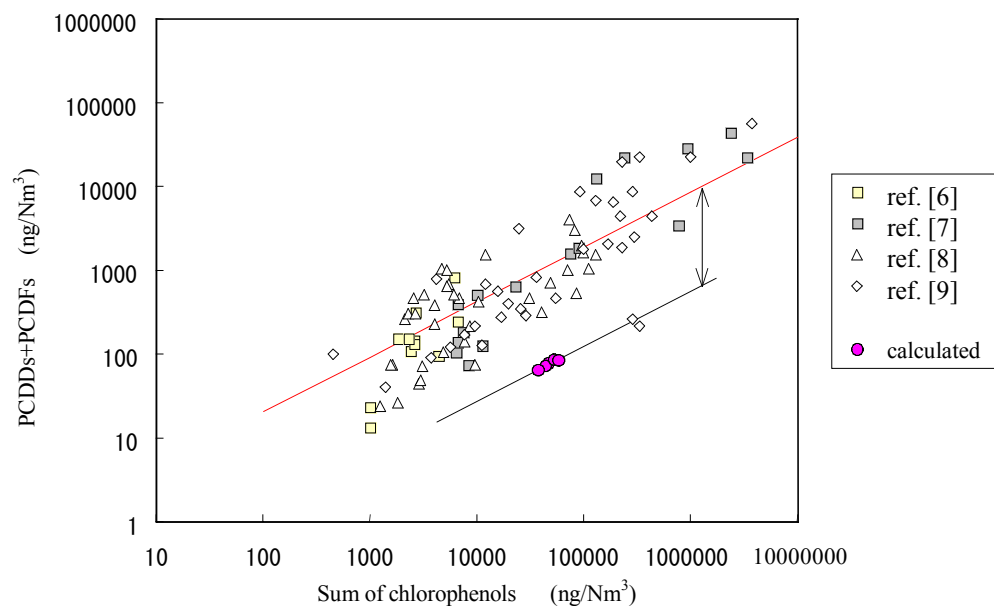


Figure 2 Correlation of chlorophenol and dioxin in stoker furnaces

As shown in Figure 2, calculated concentrations of dioxin at the furnace exit are lower than that of observed concentrations. Almost of observed values are measured at entrances and exits of dust collectors, so they contain dioxin synthesized by “de novo” process certainly. It is plausible that the differences between observed and calculated concentrations are attributed to “de novo” synthesis.

The rates of dioxin formation in “de novo” region(473 – 573K) through the condensation of chlorophenol is calculated by the extrapolation of the rate constant listed in Table 1. They are too small(less than 1/100) compared with the differences shown in Figure 2. Chlorination of hydrocarbons containing Deacon reaction is predominant in “de novo” process, so it is necessary to evaluated the chlorination of particular hydrocarbons such as dibenzofuran for complete understanding of dioxin formation in waste incinerators.

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Acknowledgements

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