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INVESTIGATION OF DIOXIN FORMATION IN MUNICIPAL SOLID WASTE INCINERATION BASED ON CHEMICAL EQUILIBRIUM

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Introduction

In this paper, the governing mechanisms of dioxin generation are discussed based on multi-phase chemical equilibrium in regard to a multi-element system of H/C/N/O/Na/Si/Al. The results suggest that dioxins are likely to be generated at temperatures below 700 K. It was also shown that dioxin generation from the incineration of municipal solid waste is caused by the heterogeneity of components in the combustion field. Furthermore, it is pointed out that in addition to organic chloride, an inorganic chloride such as NaCl is a likely Cl source in dioxin generation.

Thermodynamic data and calculation methods

The thermodynamic behavior of dioxins has not as yet been adequately determined. Shaub¹ estimated the thermodynamic data of dioxins using the groupadditivity method, which Benson proposed. Koester calculated the thermodynamic data using the semi-empirical molecular orbital method with MNDO². Recently, Adriaens³ and Saito⁴ estimated the thermodynamic function of dioxin in the gas phase using the semi-empirical molecular orbital method with PM3. Okamoto⁵ proposed a formation mechanism of a few isomers of dioxin in the gas phase from their precursors using the hybrid-density functional theory method with B3LYP as an ab initio study. The values reported in the studies mentioned above, however, differ somewhat from those reported in. In the present study, the thermodynamic data for gaseous dioxin reported by Shaub are used. Thermodynamic data for polychlorinated phenol and polychlorinated benzene have been estimated by CHETAH⁶, a program for evaluating thermodynamic properties. For all other species, JANAF thermodynamic data are used. As thermodynamic data relating to solid and liquid phases of PCDDs have not been reported, the Gibbs' free energy for the condensed phase of dioxins was estimated from the vapor pressure. Vapor pressure was estimated using Rordorf's method⁷.

A multi-phase chemical equilibrium calculation has been carried out using the computer code ECAT version 5, based on the free energy minimization method⁸. Carbon graphite was excluded from the equilibrium composition. Although carbon graphite or soot is stable, its formation is controlled kinetically and proceeds gradually under the carbon rich conditions of the combustion processes. Therefore, equilibrium calculations without graphite yield more realistic compositions.

Results and Discussion

To elucidate the conditions of dioxin formation in a municipal solid waste incinerator, equilibrium compositions were calculated under various temperatures and excess-air ratios. The

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calculations were based on the assumptions that the system is perfectly homogeneous. The results show that dioxin emission is very low, even in fuel rich conditions. This indicates that dioxins are not generated even in fuel rich conditions, as long as the solid waste reacts homogeneously. In other words, the generation of dioxins in a municipal solid waste incinerator is a result of the heterogeneity of components in a combustion field. Water vapor, chlorine and hydrocarbon volatilize sequentially in the process of incinerating solid waste according to the temperature history. Therefore, the atomic ratio of the reactants is likely to be heterogeneous in the area local to a combustion field.

Dioxin generation is discussed in relation to this premise. Figures. 1 (a) and (b) show contour lines of the mole fractions for TCDD (2,3,7,8) and OCDD, respectively, on a plane of temperature T and excess-air ratio λ , for an atomic ratio of the reactants of C:H:Cl=1:1:1. The mole fraction of TCDD and OCDD is the sum of the gas and condensate phases. It can be seen that considerable TCDD is formed at temperatures below 600 K and excess-air ratios below 0.75. However, the equilibrium concentration of OCDD reaches a maximum at slightly higher temperatures than that of TCDD. This shows that OCDD is more likely to form before TCDD during the cooling process. It is well known that in a practical incinerator dioxin forms mainly during cooling of the flue gas, at temperatures between 550 ~ 750 K. The present results are consistent with this practical knowledge⁹. As the rate of chemical reaction becomes slow at lower temperatures, dioxin formation proceeds extremely slowly at lower temperatures near 300K, where the equilibrium concentration of TCDD is high.

Polychlorinated benzene (CBs) and polychlorinated phenol (CPhs) are thought to be the precursors of dioxin and hence the formation of these species is discussed. Figures. 2 (a) and (b) show equilibrium concentrations of CBs, CPhs, MCDD, TCDD, and OCDD at excess-air ratios of $\lambda=0.25$ and 0.5, respectively. It should be noted that highly chlorinated CBs and CPhs are much more stable. This trend is also exhibited by dioxins because the concentration of non-chlorinated

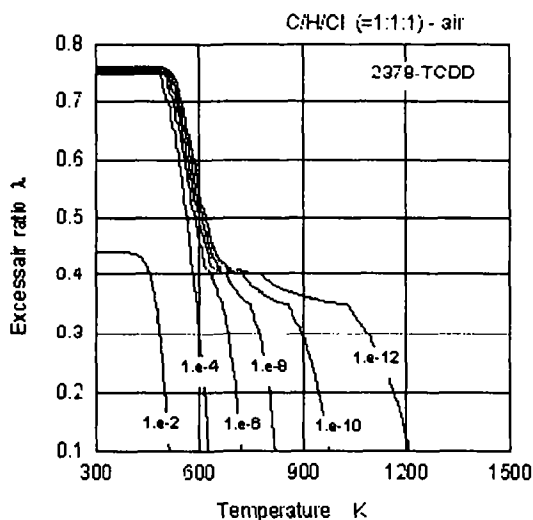


Fig.1 (a) Contour line for mole fractions of 2,3,7,8-TCDD

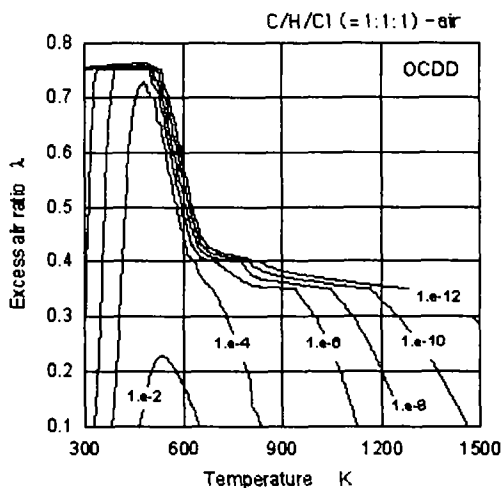


Fig.1 (b) Contour line for mole fractions of OCDD

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and mono-chlorinated dioxin is much lower than that of TCDD and OCDD. In the figures, the level of non-chlorinated dioxin is smaller than the minimum scale. It can also be seen that the formation trends of CBs and CPhs are similar to those of dioxins.

A considerable amount of inorganic chloride such as NaCl and CaCl₂ is contained in municipal solid waste. It has been discussed, in this section, whether inorganic chloride, in particular NaCl, is a possible source of dioxin in municipal solid waste incinerators. It is observed from the Gibbs' free energy of formation for major compounds including sodium, that the compounds of sodium and silica and/or those of sodium and alumina are much more stable than NaCl. Although NaCl is stable, chlorine in salt may dissociate if silica and/or alumina are present in the system. Figure. 3 shows the equilibrium concentrations of HCl and some related species in heating NaCl and hydrocarbon, with and without silica and/or alumina. From the figure, HCl concentration can be seen to become about 20 times higher if the system includes silica and/or alumina. As HCl is stable, Cl released from NaCl will bond to H, released from hydrocarbons and H₂O for instance, to form HCl. With an atomic ratio of H:Cl=1:1, HCl is a possible source of dioxin under the carbon-rich conditions shown in Figs. 1 (a) and (b). Therefore, it is concluded that dioxins are likely to form in when NaCl is in the presence of silica and/or alumina in a practical incinerator. The present results are consistent with this practical knowledge⁹.

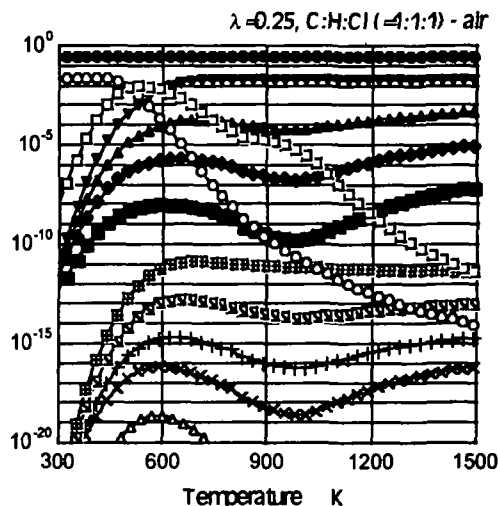
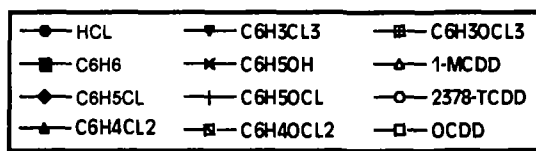


Fig.2(b) Equilibrium concentration at $\lambda=0.5$

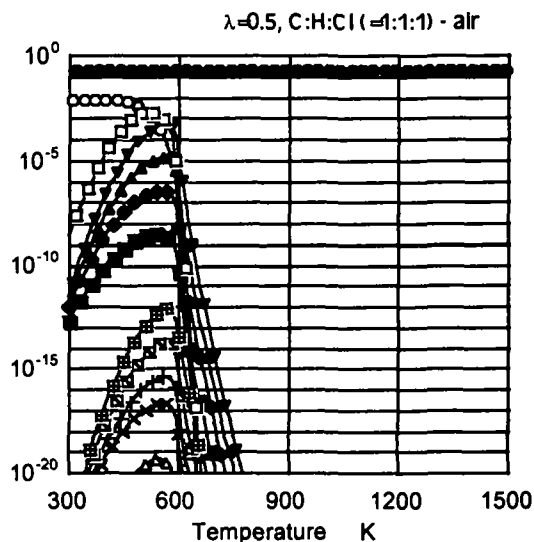


Fig.2(b) Equilibrium concentrations at $\lambda=0.5$

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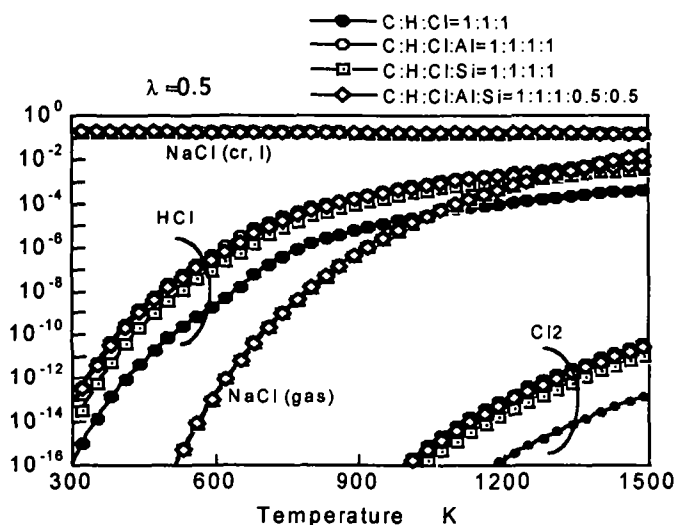


Fig.3 HCl generation from NaCl with silica and/or alumina

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