

FORMATION AND SOURCES I -POSTER

FORMATION OF PCDD/Fs FROM THE COMPOSITE OF GRAPHITE AND CHLORIDE

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Introduction

The kind and form of chlorides coexisting with residual carbon in the thermal process appear to govern the dioxins emissions not only in the solid waste incineration but also some recycle/manufacture processes of metals, *e.g.*, electric arc furnaces (EAF) for steelmaking, sintering of iron ores and zinc recovery processes from EAF dusts. Such a residual carbon particle is often called "soot" and typically existed in the fly ashes discharged from incinerators. A numbers of studies have been made to examine *de novo* synthesis of dioxins on the actual/model fly ashes. However, they have been conducted under rather complex conditions in terms of coexisting metals, metallic chlorides/oxides and the forms of (hydro-) carbons. In this study, *de novo* synthesis on the carbon particles will be systematically investigated. The existing state and form of metal and chlorine in/on the carbon and their effect on the formation rate of dioxins will be examined. The present paper reports the results on the composites of graphite and some metallic chlorides prepared by different methods.

Materials and Methods

Graphite powder of reagent grade was preliminarily rinsed twice by distilled water and acetone, respectively, and was dried out at 100°C. Then, KCl- or CuCl₂- bearing graphite samples was prepared by the following manners:

[KCl-1]: Graphite and KCl powders are well hand-mixed.

[KCl-2]: Graphite and KCl powders are mixed-ground by using a planetary ball mill (inside volume of the pot is 30 cm³) for 30 min at 700 rpm.

[CuCl₂-1 to 4]: Acetone solution of CuCl₂·2H₂O (0.016mg/ml) is added to the graphite powder and well hand-mixed. Then, acetone in the mixture was dried out at 100°C.

[KCl-3]: Hand-mixed of KCl and graphite powders is press-shaped into a disk tablet. Then, it was put in a

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graphite crucible and heated at 800°C for 1h in Ar atmosphere.

[KCl-4]: Same procedure as [KCl-3], but heated at 1100°C.

The obtained powders were crushed and press-shaped again into disk tablets. Then they were crushed and sieved between 1 and 2 mm in granule size. Chlorine concentrations of the samples are listed in Table 1. Chlorine concentration of [KCl] samples was set at 10000 ppm and that of [CuCl₂] was varied from 1000 to 10000 ppm.

Schematic diagram of the experimental apparatus is illustrated in Fig. 1. 10 g of each obtained granulated sample was packed in a reaction tube made of a Pyrex glass (27 mm in inside diameter) and the tube was placed in an electric furnace. The gas mixture of Ar and O₂ (2.5 mol%) was flowed through the sample bed with the rate of 58.2 mm/s. Then, it was heated up to 300 °C. It takes approximately 15 min to obtain a steady-state temperature of the sample bed. The bed temperature and the gas flow rate were kept constant

Table 1. Chlorine concentrations of the samples

Sample	Concentration of Cl (ppm)
[KCl-1~4]	10000
[CuCl ₂ -1]	1000
[CuCl ₂ -2]	2500
[CuCl ₂ -3]	5000
[CuCl ₂ -4]	10000

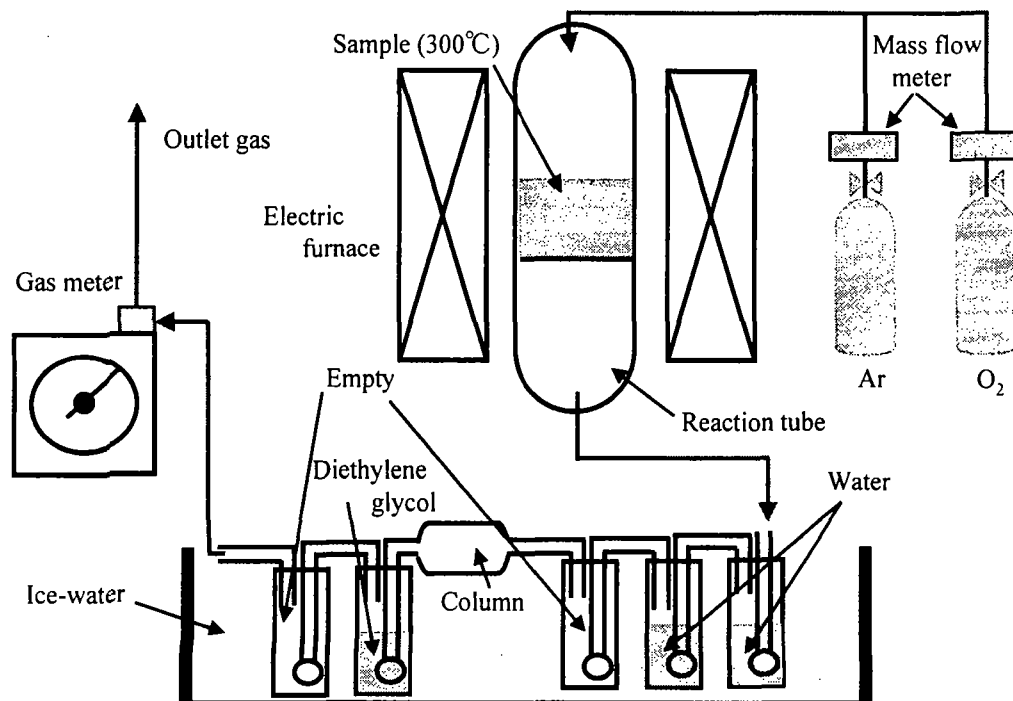


Fig. 1. Schematic diagram of the experimental apparatus

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for 120min. During the experiment, outlet gas was passed through the ice-cooled gas traps. Five impingers and one XAD-2 resinous column were used for PCDD/Fs sampling. After the experiment, the amounts of mono- to octa-chlorinated homologues of PCDD/Fs in the gas traps and remaining in the solid sample were determined, respectively. The dichloromethane for washing the inside of tubes and gas connectors after the experiment is included to the analysis of the gas traps.

Results and Discussions

Figure 2 shows the relation between CuCl_2 concentration (indicated on the basis of Cl) of the sample and the amounts of PCDD/Fs detected in the gas traps and solid sample, respectively. Both increase with increase in the concentration of CuCl_2 , while the amounts of PCDD/Fs in the solid samples are remarkably larger than those in gas traps. It means that a large proportion of formed PCDD/Fs stably remains on the surface of the graphite sample.

The total amounts of PCDD/Fs obtained by the [KCl] samples are shown in Fig. 3. The hand-mixed sample [KCl-1] gives an extremely small value. However, mixed-ground [KCl-2] and heat-treated samples [KCl-3 and 4] show considerably large values. It suggests that such pretreatments significantly change the composite state of KCl in graphite and promote PCDD/Fs formation. Mixed-grinding mechanically progresses not only the size reduction of ground materials but also the enlargement of contact area between different materials, e.g., through formation of a lamellar structure. Further, it sometimes leads to a solid-phase reaction at the interface of the materials, namely “mechanochemical” reaction. The heat-treatment causes partial vaporization of KCl in the sample. Then, KCl will repeat the volatilization/condensation during heat treatment and homogeneously dispersed on the surface of graphite particle. It may partly leak from the graphite crucible during the

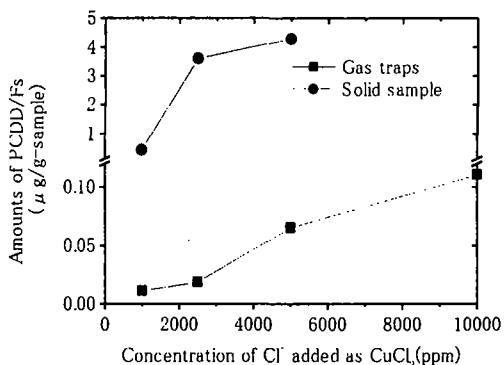


Fig. 2. The amounts of PCDD/Fs in the gas traps and solid sample.

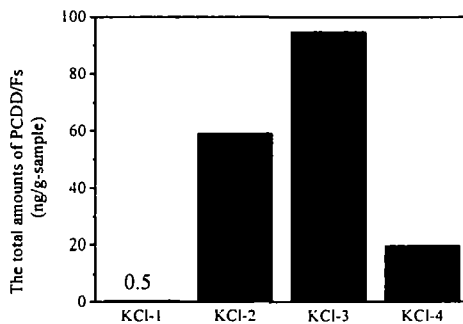


Fig.3. The total amounts of PCDD/Fs in the [KCl-1~4] samples.

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heat-treatment although a cap is used on it. The leakage loss of KCl was about 40 % for the case of the treatment at 1100 °C.

The above results show that the formation of PCDD/Fs strongly depends on the existing state of chlorine. For example, many chlorides can easily intercalate to the graphite structure and form intercalation compounds. Although KCl does not recognized to form an intercalation compound¹⁾, potassium can form that of KC_8 ²⁾. In this case, Cl may remain as a "residue compound" in the graphite structure. From such point of view, XPS, XRD and FT-IR observations have been tried to examine the changes in the composite states of carbon with other substances induced by the pretreatments. However, clear results have not yet obtained. It is a future subject and will give significant information on the mechanism of *de novo* synthesis as well as the behavior of residual (hydro-) carbons in actual fly ashes.

The ratios of the amounts of PCDD/Fs detected in the solid sample and gas traps are compared in Fig. 4. The solid samples give remarkably higher ratios for the $[CuCl_2]$ comparing to $[KCl]$. This appears to suggest the differences between both samples in the number of the site where PCDD/Fs can be stably adsorbed. The kind of chloride possibly affects the condition of graphite surface. In addition, higher temperature treatment $[KCl-4]$ shows a smaller ratio. To clarify these complex phenomena, further study will be continued by analyzing the composite structure of carbon and chlorides, and also considering its effect on the oxidation rate of carbon.

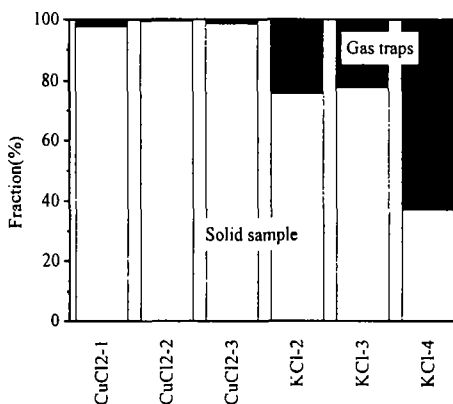


Fig.4. The ratios of the amounts of PCDD/Fs detected in the solid sample and gas traps.

Acknowledgements

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