

**FORMATION OF PCDD/Fs ON IRON OXIDES
FROM CHLOROBENZENE AND CHLOROPHENOL**

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Introduction

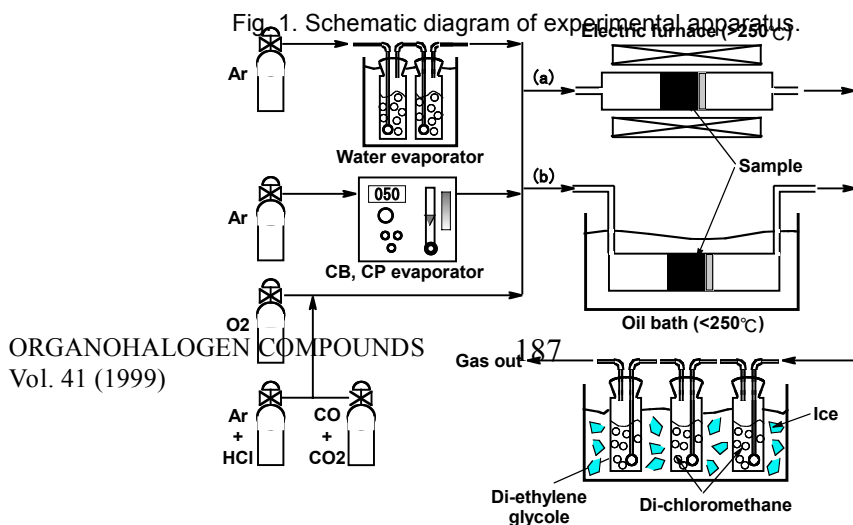
Municipal and industrial waste incinerators have been pointed out as major emission sources of PCDD/Fs in Japan. However, the amount of emissions from the incinerators are remarkably decreasing by applying the advanced emission controls and disusing the old facilities. On the other hand, such reduction of the emissions relatively enlarges the share of emissions from other emissions, *e.g.*, metallurgical industries. In such sources, PCDD/Fs also form in high temperature processes for recycle and/or pretreatment of secondary resources, *e.g.*, scraps, dusts and sludge. These secondary resources generally contain various kinds of metals/metallic oxides with complex phases. Among these oxides, iron oxides and hydroxides occupy major fraction.

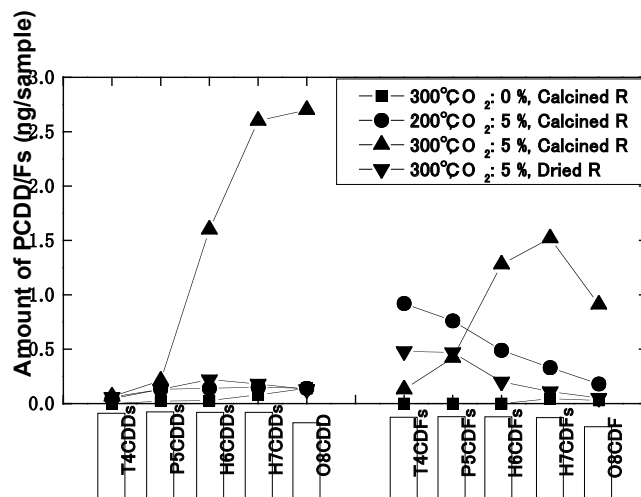
The present study aims to examine the formation of PCDD/Fs on the surfaces of iron oxides or hydroxides from chloro-benzenes (CBs) and chlorophenols (CPs) which are used as precursors. The effects of temperature, properties of iron oxide particles and co-existing gases are examined.

Table 1. Composition of iron ore R used (mass%).

T. Fe	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃	LOI*
58.0	0.25	0.55	5.17	0.27	2.58	9.15

* Loss on ignition (combined water)





Materials and Methods

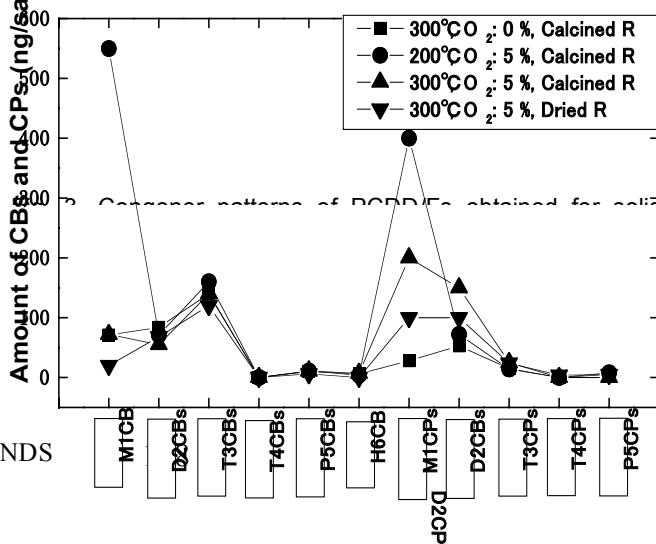
Iron ore R from Australia was used for a catalyst sample.

This is called as pisolitic goethite ores which consists of hematite (Fe₂O₃) and goethite (FeOOH) and other gangue minerals (see Table 1). The ore was crushed and sieved to the size range between 0.5 and 1.0 mm. Then, It was dried at 100 °C (D-R), and part of ore was calcined at 500 °C (C-R). Specific surface areas (SSA) of D-R and C-R are 9.9 and 33.1 m²/g, respectively. The ore sample of 20 g was set on the disk filter made of silica in a fused silica tube and hold by silica wool. The silica tube, disk filter and wool, and the ore samples were washed well with acetone and toluene of high purity before use.

Figure 1 shows the outline of the experimental apparatus. Heating apparatus was oil bath for the reaction temperature less than 250 °C and electric furnace for that over 250 °C. Main gas introduced through the sample bed was argon (Ar). CB and/or CPs were added to the introduced gas by using an evaporator.

Concentration of oxygen (CO, CO₂ and HCl in some cases) was controlled by a precise mass flow controller. Outlet gas from the reaction tube was passed through the ice cooled gas traps. They contains about 100 cm³ of dichloromethane and

Fig. 2. Congener patterns of CBs and CPs obtained for solid sample by introducing M1CB.

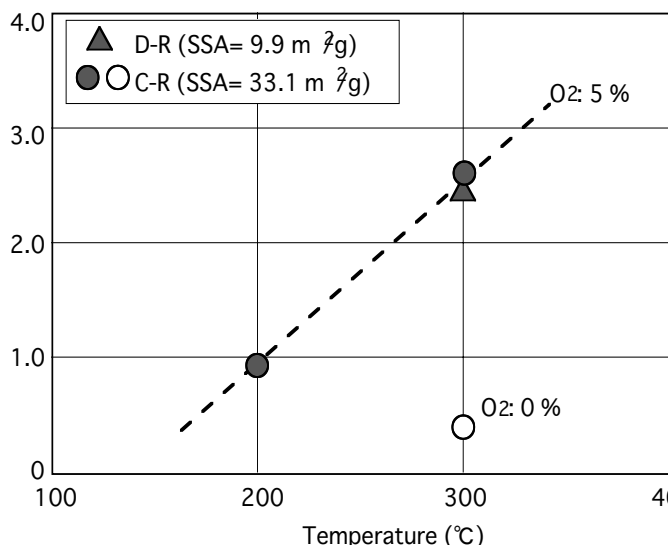


diethyleneglicole. After the experiment, the formed/remaining amounts of PCDD/Fs, CBs and CPs in both the sample bed and traps were quantitatively determined.

Results and Discussions

Figure 2 shows the con-gener patterns of CBs and CPs quantified for the sample bed after the reaction for 30 min. In this experiment, total gas flow rate was 1.0 Nl/min. Monochlorobenzene (M1CB) was added by the rate of 15.3 $\mu\text{g}/\text{min}$. This makes its concentration to be 3.04 ppm. Reaction temperature was set at 200 or 300°C, and oxygen concentration was zero or 5 mol%. At the lower temperature, 200°C, a larger amount of M1CB is held in the bed of C-R which has a larger SSA. Considerable amount of M1CP also forms. All the other experiment conditions resulted in similar patterns except for the formed amounts of M1CP and D2CP. These congeners tend to form more at higher temperature and oxygen potential.

The congener patterns of PCDD/Fs obtained for the same experiment are shown in Fig. 3. These are total values of solid samples and liquids in the gas traps. Large amounts of dioxins with higher numbers of chlorines, *i.e.*, H6-, H7- and O8- CDDs are obtained for the sample C-R heated at 300°C with 5 mol% O₂. The amount of PCDFs with lower numbers of chlorines are greater for the lower reaction temperature. For the sample D-R, the quantities of PCDFs are smaller than C-R under the same condition. Highly chlorinated furans, *i.e.*, H6-, H7- and O8- PCDFs, tend to form more for the sample C-R heated at 300°C with 5 mol% O₂. Only a quite small amount of PCDFs forms for the case of 5 mol% O₂. From these results, both reaction temperature and surface area of the hematite seem to significantly influence the PCDD/Fs formation



The rate of PCDD/Fs formation per unit surface area of the sample ore R can be calculated based on the above results. Figure 4 shows the plot of the formation rate against the reaction temperature. Although the number of data is too few to discuss it in detail, a clear increase in the rate with increasing temperature can be found. Further, it is noteworthy that the rates for the two samples (D-R and C-R) having

different SSA agree fairly well under the same condition.

The results obtained for the other oxide materials, e.g., silica and alumina, under various conditions will be also discussed.

Fig. 4. Temperature dependence of the rate of PCDD/Fs formation on the hematite ore R.

Conclusions

The conversion of PCDD/Fs on the surfaces of iron oxides from chlorobenzenes (CBs) and chlorophenols (CPs) are examined under various experimental conditions. Formation amounts of PCDD/Fs are larger at the higher temperature, 300°C, than 200°C. They hardly form without oxygen addition. Highly chlorinated PCDD/Fs tends to form at the higher temperature when using calcined hematite/goethite ore. The formation rates of PCDD/Fs on the dried and calcined ores seem to give similar values on the basis of their surface area.

Acknowledgements

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