



Effects of inorganic chlorine source on dioxin formation using fly ash from a fluidized bed incinerator

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Abstract

Chlorine source is indispensable for polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) formation during municipal solid waste (MSW) incineration. Inorganic chlorine compounds were employed in this study to investigate their effects on PCDD/F formation through heterogeneous synthesis on fly ash surfaces. A fly ash sample obtained from a fluidized bed incinerator was sieved to different size fractions which served as the PCDD/F formation sources. The capability of different metal chlorides which facilitate the formation of PCDDs/Fs was found to follow the trends: Na < Mg < K < Al < Ca, when two particle fractions of >177 μm and 104–125 μm were used in the experiments. However, the capability of NaCl, MgCl₂ and KCl did not seem much different from each other, whereas CaCl₂ and AlCl₃ were much more active in PCDD/F formation. NaCl and MgCl₂ were relatively effective to produce more PCDDs, while KCl, AlCl₃ and CaCl₂ generated more PCDFs during heterogeneous reactions occurring on fly ash. 2,3,7,8-TCDF was the most significant contributor to the toxicity of the PCDDs/Fs formed from inorganic chlorine sources. Decreasing the sizes of fly ash particles led to more active formation of PCDDs/Fs when NaCl was used as inorganic chlorine in the experiment. The highest PCDDs/Fs produced from particles with size <37 μm , while the lowest PCDDs/Fs produced from particles with size >177 μm . The toxicity generally increased with decreasing size of the fly ash particles. The formation of PCDDs was mainly facilitated by the two size fractions, 104–125 μm and <37 μm , while the formation of PCDFs was favored by the two other size fractions, >177 μm and 53–104 μm .

Key words: fly ash, inorganic chlorine source, PCDDs/Fs, heterogeneous synthesis

Introduction

In the post-combustion zone of a municipal solid waste (MSW) incinerator, polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) formation via heterogeneous synthesis on fly ash surfaces seems to be one of the most important pathways for PCDD/F emissions (Altwichker, 1996; Hagenmaier *et al.*, 1987). When catalyzed by metal chlorides at flue gas cooling temperatures from 200 to 400°C, PCDDs/Fs can be formed via two routes on solid surfaces, either from precursors such as chlorophenols and chlorobenzenes, or from elemental carbon, oxygen, and chlorine, the so called *de novo* synthesis (Addink *et al.*, 1995; Stanmore, 2004). Experimental and theoretical studies have showed that PCDD/F formation by catalytically heterogeneous synthesis on fly ash surfaces is the main source of PCDDs/Fs emitted in flue gas (Huang and

Buekens, 1996), and the range from 250 to 450°C is the most active temperature window for PCDD/F formation (David, 1996).

Chlorine is the indispensable component for PCDD/F formation. In MSW incineration process, the main input chlorine sources are organic chlorine such as polyvinyl chloride (PVC), and inorganic chlorine such as NaCl. Part of the input chlorine is emitted as HCl or Cl₂, other part is deposited in combustion residues or fly ash as metal chlorides. The emitted gaseous chlorine can react with aromatic hydrocarbons to produce gas phase precursors or even PCDDs/Fs. And in the heterogeneous system it can also chlorinate the residual carbon remaining in fly ash, which then be disintegrated into PCDD/F precursors. The chlorine deposited in fly ash can be transformed in the chlorination process through heterogeneous catalytic reactions by metal ions to produce PCDDs/Fs.

The analytical data of fly ash components implicated that, besides Cu and Fe, metal elements such as Na, Mg, Al, Ca, and K etc. are also existed at a certain ratio (Chris and Donald, 1999). The fly ash samples from thirteen American MSW incinerators have been investigated for

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their physical and chemical characteristics that affecting the low-temperature synthesis of polychlorinated dioxins (Hinton and Lane, 1991). It was found that S, Cl, Na, K, and Zn played a positive role in the formation of dioxins, whereas Si, Al had negative effect. Moreover, the granularity distribution of the fly ash did not seem to affect the formation.

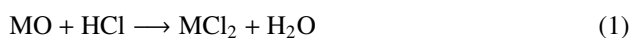
In this study, inorganic chlorine compounds such as chlorides of Na, Mg, Al, Ca, and K were employed separately to serve as the chlorine source, and fly ash obtained from an incinerator co-firing MSW and coal was used as the reaction medium for dioxin formation experiments. The goal of the research is to evaluate the relative impact of different metal chlorides on the formation of dioxins when fly ash functions as reactive surface, which has not been thoroughly understood. At the same time, we also investigated the effect of fly ash granularity distribution on the heterogeneous dioxin synthesis using inorganic chlorine sources.

1 Chlorination in solid phase during PCDD/F formation processes

The solid-phase chlorination occurring in the process of dioxin formation mainly includes two pathways. The first one is medium- or low-temperature heterogeneous catalytic synthesis. It occurs when HCl/Cl₂ and small organic molecules in the gas phase are firstly absorbed on the fly ash, then directly chlorinated to form C–Cl bond or CuCl₂, FeCl₃ etc., and they are finally chlorinated to PCDDs/Fs via the catalytic effect of transition metals. The other one is de novo synthesis. Organic C–Cl bond in the solid phase is transformed to dioxins or dioxin precursors via isomeric reactions. Under the conditions which contain water, oxygen, and silica or aluminum oxide, part of the inorganic chlorides contained in the fly ash is converted to transition metals such as Cu, Fe etc., which tend to participate in the catalytic reactions, and subsequently accelerate the oxidation and chlorination of small organic molecules.

1.1 Chlorine transformation in fly ash

Apart from gas phase, chlorine in the fly ash mainly comes from the reaction of inorganic chlorine sources and fly ash, its transformation ratio to HCl is relatively low. The extent of NaCl transforming to HCl at less than 700°C in the presence of water is less than 0.25%. The mechanism of the transformation from other typical chlorine sources to HCl is almost the same as that from NaCl. Transition metals in the fly ash may present as both chlorides and oxides. It may react with the transformed HCl as follows:



Small amount of chlorine reacts with metals via Reaction (2) shown below. It may also be transformed to HCl first, and then Reaction (1) occurs.



where, M represents metal atoms, mainly Cu and Fe.

1.2 Chlorination of inorganic chlorine sources forming PCDDs/Fs via de novo synthesis

Chlorine sources involved in the de novo synthesis are mainly from inorganic chlorides, which are deposited in the fly ash due to decreasing temperature after volatilization, except for extremely little organic C–Cl bond in fly ash. Those inorganic chlorides include NaCl, KCl, CaCl₂, AlCl₃, and MgCl₂ etc., and also those that have better catalytic effect such as CuCl₂ and FeCl₃. It has been suggested that it is impossible for NaCl³⁷ to form dioxins via direct chlorination (Addink and Altwicker, 2001), and its chlorine may exchange with Fe or other metal ions (e.g. Cu) first, and the exchange rate is slower than that of the chlorine in those metal chlorides transferring into carbon and dioxin structures. Even though C–Cl bond has already existed, the water-soluble metal chlorides are necessary in the process of dioxins formation. Dioxin formation from residual carbon remaining in the fly ash and inorganic chlorine sources has been investigated (Addink *et al.*, 1998). Between 250–350°C the increase in temperature could promote the formation of PCDDs/Fs, while the formation efficiency decreased as the concentration of NaCl increased. When the oxygen content in atmosphere is between 6%–21% and chlorine concentration is 4 wt%, the change of oxygen content will promote the formation of PCDDs/Fs, and the change of reaction time does not affect the average levels of chlorination. Furthermore, the optimal temperature will maintain at about 300–325°C and it will not change when NaCl is used as chlorine source.

2 Experimental materials and methods

2.1 Preparation of materials

The fly ash sample was obtained from the shutter precipitator of a fluidized bed incinerator (150 t/d) co-firing MSW and coal located in Hangzhou. The ash was sieved into 6 different fractions (i.e., <37 μm, 37–53 μm, 53–104 μm, 104–125 μm, 125–177 μm, >177 μm) by using a shaker equipped with standard meshes.

Fig.1 describes the size distribution characteristics of the sieved particles, it is clear that when using fluidized bed as the combustion mode, the granularity distribution of fly ash tends to big granularity distribution, in which >177 μm particles occupy 46.7%, and 125–177 μm 16.2%, while 104–125 μm 27.3%, and others only 9.80%. The material used in the bed of a fluidized bed incinerator may be the main reason for causing such particle size distribution.

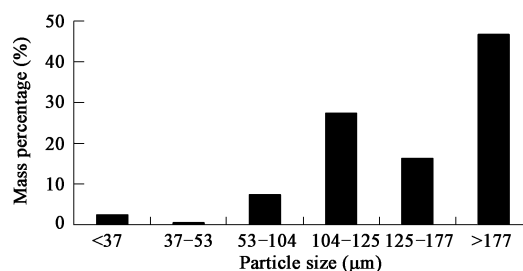


Fig. 1 Distribution of different size fractions of the fly ash sample.

Furthermore, the fly ash sample was obtained from the inertial shutter precipitator which is used to separate the fly ash particles with large sizes from the stack gas, so the small size particles are much fewer in the sample.

On the basis of the mass proportion of granularity distribution, particles $>177\ \mu\text{m}$ and $104\text{--}125\ \mu\text{m}$ are the two biggest fractions which were first selected to investigate the impact of chlorine sources on the formation of dioxins via heterogeneous synthesis on the fly ashes of two size fractions. Then fly ashes of multi-granularity were selected to investigate the formation of dioxins under the conditions of organic (PVC) and inorganic (NaCl) chlorine sources.

Table 1 lists the X-ray diffraction (XRD) analytical result of the particles $>177\ \mu\text{m}$ and $104\text{--}125\ \mu\text{m}$. From the table, it can be seen that the fly ash contains small amount of chlorine (0.9%–1.5%), and metal elements such as K, Ca, Na, Mg, Al selected for study in the experiments exist as metal oxides. In the experiments, chlorides of K, Ca, Na, Mg, Al also took part in the *de novo* synthesis reactions. The calculation of chlorine content of the experimental reactants should include both the original chlorine contained in the fly ash and the additional chlorides. However, the impact of original metal chloride in fly ash on experimental results was little reported (Stieglitz *et al.*, 1989), thus such impact was omitted in this study.

2.2 Experimental equipment and methods

Each fly ash fraction was heated for 2 h at 500°C . The content of residual carbon in each fly ash fraction was about 2.1%. One gram of each fly ash fraction was mixed with 0.5 g of activated carbon made from wood, which contain 58.6% carbon and 25% moisture. Chlorine source (4 wt% NaCl, KCl, MgCl_2 , AlCl_3 , and CaCl_2) was mixed together with fly ash. The experimental equipment schematic refers to Fig.2. The mixed materials were put in the middle of a quartz tube and plugged by glass wool, then heated in an oven set to 340°C for 30 min. A flow (300 ml/min) of gas mixing nitrogen and oxygen (9:1) with 18% moisture was introduced into the tube at the same time. The moisture content of the reaction environment was adjusted

by adding hot water, and the moisture content in the gas flow for all the experiments was maintained at about 18%.

The flue gas was sampled by using XAD-2 as the adsorbent and two impinged bottles of toluene. In each test run, XAD-2, reactant residues, toluene and quartz tube rinsed solvent was collected and mixed as one sample to follow the standard PCDD/F analysis procedures.

2.3 Sample pretreatment and PCDD/F analysis

The sample pretreatment method employed for this study was USEPA method 8280B. All analyses were performed on a low resolution mass spectrometer (LRMS, Finnigan Voyager) coupled with a high-resolution gas chromatograph (HRGC). Chromatographic separations were carried out on a 60 m DB-5 quartz capillary column. The temperature program for GC oven was: initial temperature 100°C , held for 2 min; $100\text{--}200^\circ\text{C}$ at $25^\circ\text{C}/\text{min}$; $200\text{--}280^\circ\text{C}$ at $3^\circ\text{C}/\text{min}$; 280°C held for 20 min; carrier gas: helium (99.999%), 1 ml/min; splitless sample injection. Mass spectrum condition: electron impact ionization 70 eV; electron multiplier voltage 420 V; ion source temperature 220°C ; interface temperature 250°C ; SIM (selected ion monitoring) mode. All the isotope standards used for the PCDD/F analysis were purchased from Wellington Laboratories, Canada.

3 Results and discussion

3.1 Impact of different inorganic chlorine sources on PCDD/F formation using two fly ash fractions

Na, K, Mg, Ca, Al are important metal elements of fly ash components. The calcium chloride content could be relatively higher due to the addition of calcium for flue gas dechlorination and desulfurization. Some researchers reported that the chlorine, which is needed in the heterogeneous catalytic reaction to form dioxins on the fly ashes surfaces, originated from fly ashes themselves. It has been reported that the above metal chlorides could be the chlorine sources for the formation of dioxins (Addink *et al.*, 1995). Although Hinton and Lane (1991) concluded that S, Cl, Na, K, Zn, Si, Al etc., were able to produce passive or negative impact on the heterogeneous formation of dioxins in the fly ashes. Their relative reaction capability with chlorine remained to be identified when the chlorine content is maintained constant in the *de novo* synthesis. Therefore, those fly ashes with higher percentage, $>177\ \mu\text{m}$ and $104\text{--}125\ \mu\text{m}$, were selected to investigate the impact of inorganic chlorine sources on the formation of dioxins, and also to make us get a deeper understanding on the mechanism of the heterogeneous-phase catalytic reaction of dioxins.

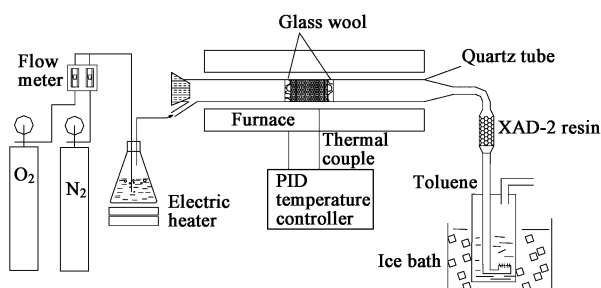


Fig. 2 Schematic of the tubular reaction and sampling system.

Table 1 Ultimate analysis of fly ash samples (wt%)*

Fly ash fraction	Al	Si	S	Cl	K	Ca	Ti	Fe	Cu	Zn	Others
104–125 μm	5.3	17.3	4.4	1.5	2.4	37.8	3.0	19.5	4.9	3.6	0.3
$>177\ \mu\text{m}$	7.7	22.9	2.4	0.9	4.4	27.3	6.5	20.7	3.9	3.2	0.1

*In the XRD analysis of fly ash, the weight percentage data of the small molecular weight elements including H, C, N, O and etc. could not be obtained because of the instrument limitation. So the data in this table are the comparative weight percentage.

Fig.3a shows the characteristics of total PCDDs/Fs, 2,3,7,8-PCDDs/Fs and I-TEQ (International toxicity equivalence quantity) emissions when different chlorine compounds were employed for experiments using the two major fly ash fractions, $>177\ \mu\text{m}$ and $104\text{--}125\ \mu\text{m}$, respectively. Generally, the capability of different metal chlorides to facilitate the formation of PCDDs/Fs was ranked as follows: $\text{Na} < \text{Mg} < \text{K} < \text{Al} < \text{Ca}$. The reaction capability of chlorides of Na, Mg, and K was almost the same for different sizes of fly ash particulates according to formation of PCDDs/Fs: $0.93\text{--}7.07\ \text{ng/g}$ (Fig.3a) and $1.01\text{--}4.57\ \text{ng/g}$ (Fig.3b). However, the chlorides of Al and Ca could obviously boost the reaction. The emission factors were $24.12\ \text{ng/g}$, $33.31\ \text{ng/g}$ in Fig.3a, and $48.51\ \text{ng/g}$ and $76.60\ \text{ng/g}$ in Fig.3b, respectively. It also could be implied from Figs.3a and 3b that the smaller the size of the fly ash particles, the more favorable to heterogeneous formation of PCDDs/Fs. The profile of the 2,3,7,8-substituted PCDDs/Fs was almost the same as total PCDDs/Fs. It could be found that the quantities of total PCDDs/Fs and 2,3,7,8-substituted PCDDs/Fs formed from Na, Mg, and K chlorides was almost the same, while that for Ca and Al chlorides was completely different from them. For the case of I-TEQ emission, those formed from Na, Mg, and K chlorides were close to each other, while Ca and Al chlorides produced much higher levels of I-TEQ. In Fig.3b, the I-TEQ emissions were almost the same formed from Ca and Al chlorides. The above results

strongly suggest that the Ca-based adsorbents injected into the furnace or flue gas could possibly promote the emissions of PCDDs/Fs in flue gas and fly ash via heterogeneous reactions, although they serve as SO_2 and HCl adsorbents in flue gas.

Fig.4 shows the homologue profiles when different chlorine compounds were employed for experiments using the $104\text{--}125\ \mu\text{m}$ fly ash as an example. It seems that dioxins were the main products when NaCl and MgCl_2 were used as chlorine source, whereas furans were the dominant products when KCl, AlCl_3 and CaCl_2 were used. The homologue profiles were completely different for different metal chlorides. Results shown in Fig.4 suggest that NaCl and MgCl_2 tend to produce more dioxins, while KCl, AlCl_3 and CaCl_2 produce more furans from the heterogeneous reactions on fly ash surfaces. It appears that different chlorine sources may produce different PCDD/F products. Thus we might conclude that there was a selective characteristic of inorganic chlorine sources to facilitate the PCDD/F formation on the fly ash surfaces.

Fig.5 shows the toxicity distribution of PCDDs/Fs when different inorganic chlorine sources were employed in the experiments. In Fig.5 it seems that for NaCl, OCDD contributed the most toxicity; for KCl the most toxicity contributors were 2,3,7,8-TCDF and 1,2,3,4,7,8-HxCDF; for MgCl_2 they were 1,2,3,7,8-PeCDD and 1,2,3,7,8,9-HxCDD; for CaCl_2 they were 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF and OCDD;

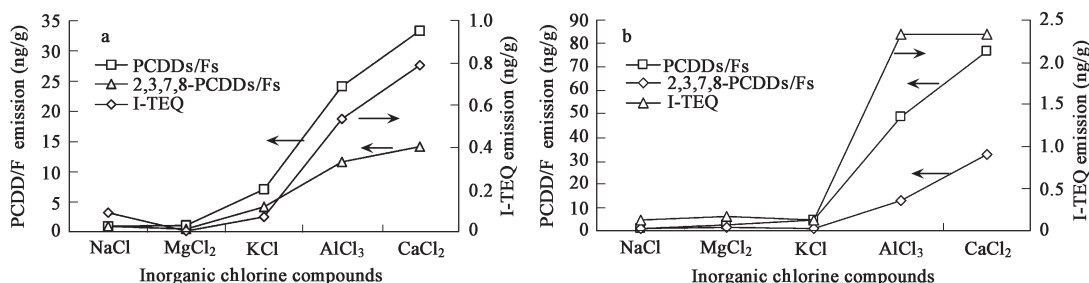


Fig. 3 PCDD/F formation from different inorganic chlorine compounds on $>177\ \mu\text{m}$ (a) and $104\text{--}125\ \mu\text{m}$ (b) fly ash. I-TEQ (International toxicity equivalence quantity).

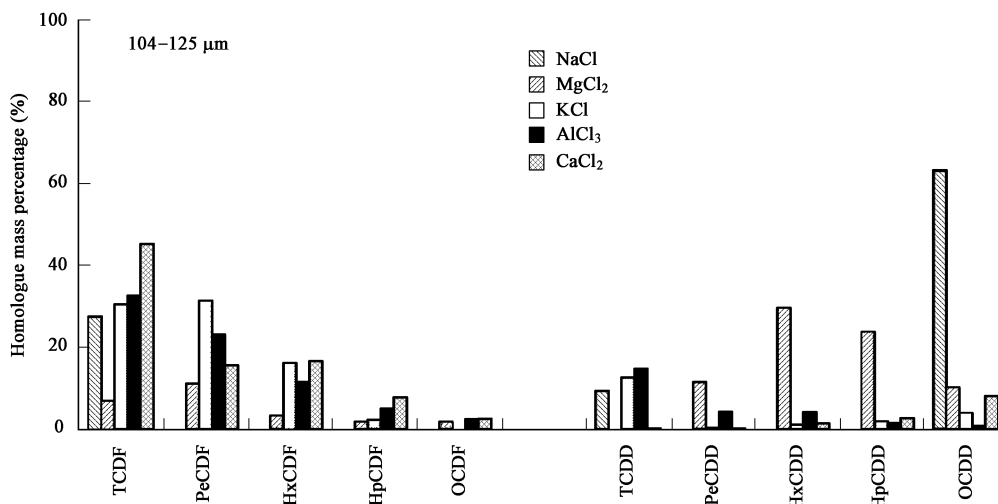


Fig. 4 Homologue profiles when using different inorganic chlorine compounds on $104\text{--}125\ \mu\text{m}$ fly ash.

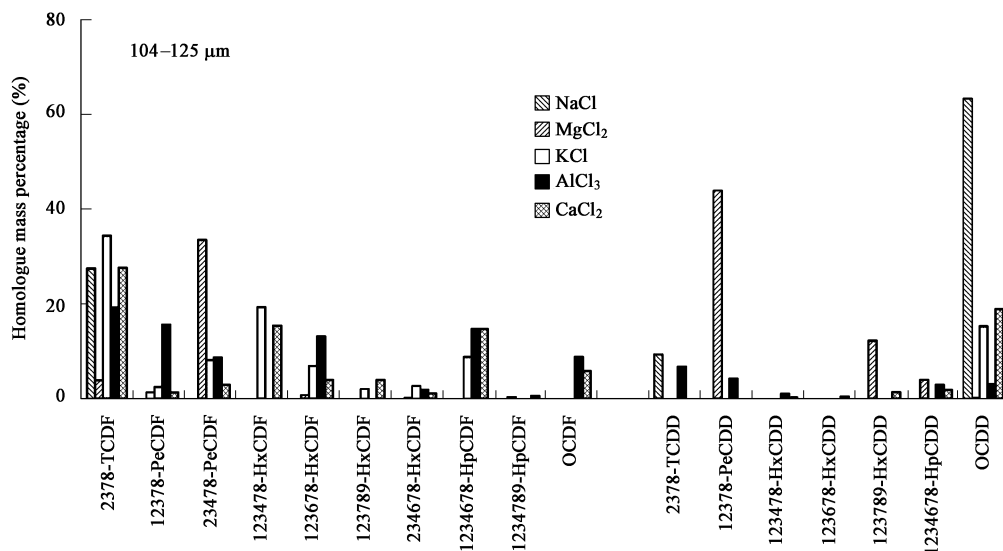


Fig. 5 Distribution pattern of 2,3,7,8-PCDDs/Fs for different inorganic chlorine sources.

for AlCl_3 they were 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, OCDD and OCDF. Therefore, it could be concluded that in the PCDD/F formation from inorganic chlorine sources 2,3,7,8-TCDF was more important contributor than others to the toxicity, and during the formation from chlorides of Na, K, Mg, Al on the surface of bigger-size fly ashes, OCDD played a relative significant role in the toxicity contribution. In the process of heterogeneous synthesis of PCDDs/Fs with inorganic chlorine sources on the fly ash surfaces, except for MgCl_2 , the furans formed from the other chlorine sources were the most toxicity equivalent contributors. Furthermore, NaCl and KCl mainly depended on four and five chlorines substituted furans while CaCl_2 and AlCl_3 depended on high chlorine substituted furans such as four, six, seven, or eight chlorines substituted furans, but the amount of five chlorines substituted furans were very little. This conclusion generally consisted with the result of Chang and Chung (1998).

3.2 Impact of fly ash fractions on PCDD/F formation using NaCl as inorganic chlorine source

The inorganic chlorides in the combustible waste materials usually present as NaCl, CaCl_2 , and MgCl_2 . Most NaCl will be transformed to gas phase at high temperatures (its melting point 801°C), and deposit on the fly ash in the

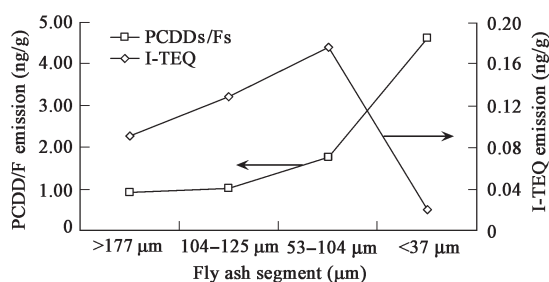


Fig. 6 PCDD/F emission factors when NaCl was employed on four flash fractions.

flue gas cooling process to become the chlorine contributor for dioxin formation. It has been reported that when no other chlorine sources presented in fly ash, NaCl would act as the chlorinating source for dioxin formation (Addink *et al.*, 1998). The NaCl content in the fly ash is often at approximately 1.9%–5.2%(wt) which would cause no negligible impact on the dioxin formation. Fig.6 shows the impact of fly ash fractions on PCDDs/Fs and I-TEQ emissions when NaCl was used as the inorganic chlorination source. It seems that the total PCDD/F emissions increased when fly ash particle size decreased, where the maximum reached at the particle size less than $37\ \mu\text{m}$ (4.62 ng/g), and the minimum was at the largest particle size interval $>177\ \mu\text{m}$ (0.93 ng/g). The profile of PCDD/F formation indicated that smaller particles of fly ash can facilitate more formation of PCDDs/Fs. This result is consistent with that from Chang and Chung (1998). One explanation for the above results is that small size fly ash particles have more active surface sites and thus can easily absorb reaction intermediates or catalysts to promote the heterogeneous reactions. The resulting I-TEQ emission profile was different from that of Chang *et al* (1998), which had reported that I-TEQ concentration in particles $<37\ \mu\text{m}$ was the highest. However, our experiment indicated that the I-TEQ produced from the experimental reaction using particles $<37\ \mu\text{m}$ was dramatically low, even its total PCDD/Fs emissions reached the maximum. That meant less toxic PCDDs/Fs formed in our experiment using particles $<37\ \mu\text{m}$ even though the amount of total PCDDs/Fs increased. This could be explained by the significantly different properties of the two fly ash samples. Generally, smaller sizes of fly ash led to more active formation of PCDDs/Fs when NaCl was used as inorganic chlorine in above serial experiments.

Fig.7 shows the homologue distribution of PCDDs/Fs when fly ash of different sizes was employed. It seems that fly ash samples $>177\ \mu\text{m}$ and $53\text{--}104\ \mu\text{m}$ produced more furans than dioxins. The $104\text{--}125\ \mu\text{m}$ fly ash fraction produced more dioxins, the ratio of PCDDs to PCDFs was

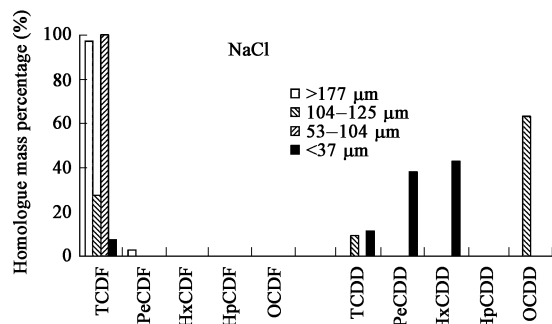


Fig. 7 Homologue distribution of PCDDs/Fs with different fly ash size fractions.

2.64, and the main dioxin product was OCDD, while the major furans produced were TCDFs. The ash of size <37 μm , shown in the Fig.7, mainly promoted the formation of dioxins, including TCDDs, PeCDDs, HxCDDs, and only very little TCDFs were formed as furans. Therefore, fly ash of smaller sizes led to more active formation of PCDDs/Fs when NaCl was used as inorganic chlorine in this experiment. The highest concentration of PCDDs/Fs formed from particles with size <37 μm , while the lowest concentration formed from particles with size >177 μm . The toxicity concentration increased as the rise of size of the fly ash. PCDD formation was mainly facilitated on fly ash fractions of 104–125 μm and <37 μm , while PCDF formation was favored by the two size fractions >177 μm and 53–104 μm . It showed that in the heterogeneous reactions employing NaCl as chlorine sources, fly ash of different sizes could be more capable to facilitate the formation of furans (TCDFs).

4 Conclusions

In this study, we measured PCDD/F formation from mixtures of fly ash fractions and different inorganic chloride salts. The experimental results suggested a strong correlation between inorganic chloride source and PCDD/F formation. It was found that smaller sizes of the fly ash led to more active formation of PCDDs/Fs when NaCl was used as inorganic chlorine in the experiments. The capability for different metal chloride facilitating formation of PCDDs/Fs could be ranked as follows: Na < Mg < K < Al < Ca. Further work is needed to investigate the possible connections or pathways between the inorganic chlorides and PCDD/F formation.

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