

# MECHANISM OF THE FORMATION OF CHLORINATED ORGANIC COMPOUNDS IN THE IRON ORE SINTERING PROCESS

Sun Y<sup>1\*</sup>, Liu L<sup>1</sup>, Fu X<sup>1</sup>, Zhu T<sup>1</sup>

School of Chemistry and Environment, Beihang University, Beijing 100191, China

## Introduction

Dioxins are a generic group of polycyclic chemicals, composed of polychlorinated dibenzofurans (PCDFs), dibenzo-p-dioxins (PCDDs) and biphenyls (PCBs), and earmarked by the Stockholm Convention as Persistent Organic Pollutants (POPs)<sup>1</sup>, compounds capable of causing great harm to human health and the environment. Dioxins are hypertoxic substances with a half lethal dose(LD50) of  $10^{-5}$ - $10^{-6}$ g/kg. Dioxins are mainly a consequence of human activities, such as combustion, incineration, and thermal metallurgical processes.

Steel smelting, Solid waste incineration and cement production process are the three main sources of dioxins. In the 1990s, dioxins from solid waste incineration accounted for the most part of total emissions. Developing countries controlled strictly the emissions of solid waste incineration so as to this resource of dioxins becoming less significant. Instead, dioxins from metal smelting, typically steel smelting, occupied more and more proportion. Nevertheless, there was not technical dispose aimed at the emissions treatment of steel industry, and dust removal, desulfurization and denitration were the only way to reduce a small number of dioxins. In consequence studying dioxins from integrated iron and steel industry and also steel mills came to be the focal point of pollution abatement. In iron and steel industry, dioxins mainly originated in iron ore sintering. According to data released by European environment council, during 1993~1995, 18% of the total dioxins were discharged from Iron ore sintering process. In 1995, dioxins from sintering process accounted for 95% of total emissions of iron and steel industry and approximately 10% of the national total emissions in China<sup>2</sup>. Now Iron ore sintering process was the leading source of dioxins rather than solid waste incineration. In 2004, dioxins discharged by steel and other metal smelting industries reached 4666.90g/a, about 46% of dioxin total emission load a year<sup>3</sup>. At the same year, dioxins from steel sintering process was 1523.4g-TEQ, the annual emissions into the atmosphere and the annual total emissions were both the top of 28 countries investigated. And the total dioxin amount discharged by iron and steel sintering process was Estimated to 1847.26g-TEQ in 2005<sup>4</sup>, and 1850g-TEQ in 2007<sup>2</sup>.

The mechanisms of dioxin formation are complex, varied, and incompletely understood. Two main pathways have been identified<sup>5</sup>. The precursor pathways propose dioxins formation from structurally similar precursors, such as chlorophenols, chlorobenzenes, and diphenyl ethers. The de novo synthesis explains the formation of dioxins from carbonaceous and polycyclic aromatic structures by their low-temperature (300-350 °C) partial oxidation in the presence of chlorides or chlorine and metal catalysts (Cu, Fe etc.)<sup>6</sup>. Dioxins formation in sintering process shows typical de novo synthetic characteristics. Cokes is a rich carbon source, chlorides derive from ores, and metal catalyst in the raw materials of sintering. The gases arising in the high-temperature sintering zone, while cooling, pass through the optimum temperature window (300-350°C) for dioxin formation. In addition, the presence of volatiles derived from cokes and volatilized salts, and oxygen also provides the necessary conditions for dioxin formation. Metal catalysts reduce the temperature required for carbon oxidation and promote the various reactions such as oxidation and chlorination of carbonaceous structures, related to the dioxin formation, and chlorides of Cu and Fe have a significant catalytic effect. The physical and chemical properties of the carbon sources, the speciation of metals and the transfer of chlorine to organic compounds also influence dioxin formation. Consequently, clarifying the mechanism has particular significance to controlling dioxin emission.

## Materials and methods

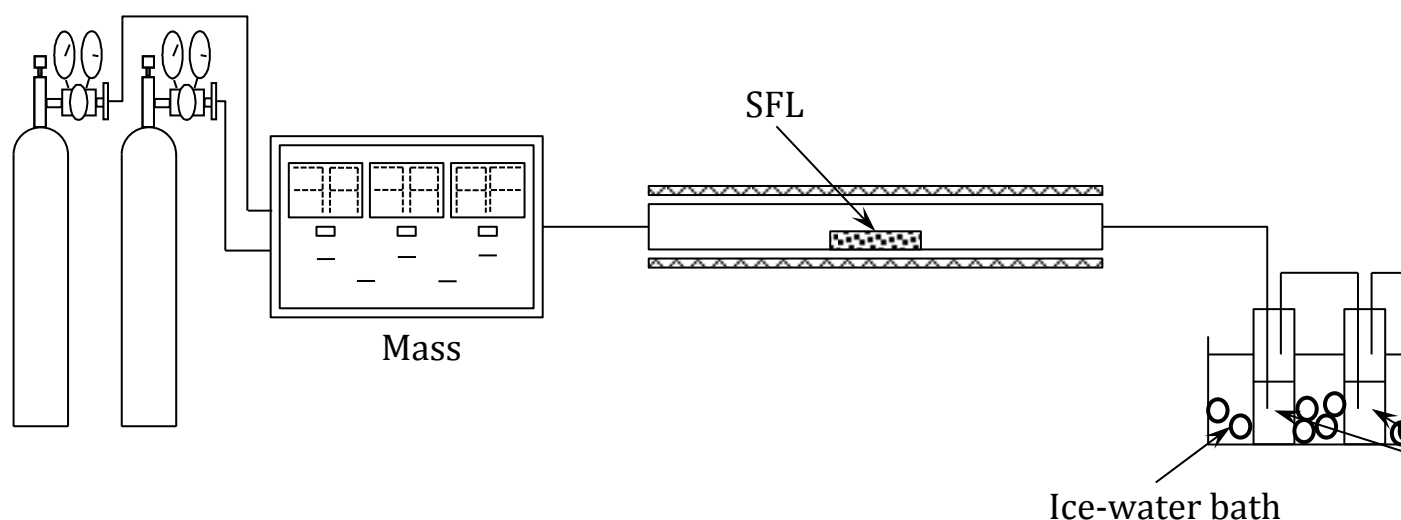
### Influence of Carbon Concent and Temperature During Iron Sintering Process

This research aimed to investigate the influence of different operating conditions and raw materials to the formation of chlorinated organic compounds which is the precursor of dioxins. Simulative fly ash (SFL) was used in this research as a replacement of the actual fly ash from iron sintering process. The carbon contents and operating temperature were two main elements investigated in this study.

Under the condition of different carbon content in SFL of 0%, 2%, 5%, 10% and 20%, SFL was burned in an electric furnace which has two furnaces, one of them could shift. With the optimal temperature of 300°C, the production of chlorinated organic compounds was measured by GC/MS. To surveying the impact of the operating temperature, it was set as 250°C, 300°C, 350°C, 400°C, 450°C and 500°C respectively. In addition to this, the sintering raw materials used in this survey were prepared according to the real fly ash with Fe<sub>2</sub>O<sub>3</sub> (35%Fe) active carbon (4%C) , KCl (7%Cl) and matrix SiO<sub>2</sub>.

### Simulated the sintering process

The simulated sintering system is shown in Fig 1. Simulative fly ash was placed in the heating zone of a tube furnace with a temperature control system. Mixed air with a total flow rate of 100 ml/min (21% O<sub>2</sub> and 79% N<sub>2</sub>) was sent to the furnace by a mass flow meter controlling the flow. The gaseous products were absorbed by toluene which was held in impingers placed in ice-water bath. The solid product in burned fly ash was extracted using toluene by Soxhlet extraction apparatus for 24 hours.



### Chlorinated organic compound analysis and calculation

The sample pretreatment method employed for this study was USEPA method 8280B. Chlorobenzene (CBzs) and polychlorinated biphenyl (PCBs) were analyzed in this study. All analyses were performed on a low resolution mass spectrometer (LRMS, Finnigan Voyager) coupled with a low-resolution gas chromatograph (LRGC).

Chromatographic separations were carried out on a 60 m DB-5 quartz capillary column. The temperature program for GC oven was: For CBzs: initial temperature 150°C, held for 2 min; 150–180°C at 20°C/min; 180–245°C at 2°C/min; 245°C -290°C at 6°C/min; 290°C held for 10 min; carrier gas: helium (99.999%), 1.0 ml/min; splitless sample injection. For PCBs: initial temperature 80°C, held for 2 min; 80–116°C at 20°C/min; 116–122°C at 1°C/min; 122°C -270°C at 10°C/min; 270°C held for 20 min; carrier gas: helium (99.999%), 1.0 ml/min; splitless sample injection. Mass spectrum condition: electron impact ionization 70eV; electron multiplier voltage 420 V; ion source temperature 220°C; interface temperature 250°C; SIM (selected ion monitoring) mode.

Calculating the concentration of target objects by using internal standard method, prepare the standard solution using the standard and internal standard substance weighed accurately. Inject standard solution and samples to be tested with internal standard substance into GC/MS. Record their chromatogram respectively. the concentration of target objects can be calculated as follows:

$$C_x = \frac{A_s \times A_{ist} \times C_{st}}{A_{st} \times A_{is}} \quad (1)$$

In Eq. (1),  $C_x$  is the concentration of target objects in samples to be tested;  $A_s$  is the area of target object chromatographic peak in samples to be tested;  $A_{st}$  is the area of target object chromatographic peak in standard solution;  $A_{is}$  is the area of internal standard substance chromatographic peak in samples to be tested;  $A_{ist}$  is the area of internal standard substance chromatographic peak in standard solution;  $C_{st}$  is the concentration of target objects in standard solution.

## Results and discussion

### Influence of carbon contents

In the carbon oxidation process of simulative fly ash with different carbon contents, various kinds of organic compounds generated in the existence of active carbon, chlorine source, metal catalyst and appropriate conditions. In this survey, only the production of Chlorobenzene (CBzs), polychlorinated biphenyl (PCBs) and  $CO_x$  was focused on since they have consanguineous relationship with the formation of dioxins. The yields of Chlorobenzene (CBzs) and polychlorinated biphenyl (PCBs) are shown in Fig 1(a). As can be seen, the yields of CBzs and PCBs have the same trend. They both increase rapidly from a nethermore value with the augment of carbon contents as the carbon contents less than 10%. When reaching a 10% carbon content in the simulative fly ash, either CBzs or PCBs reach a maximum peak, 827.02ng/g fly ash for CBzs and 1018.84 ng/g fly ash for PCBs. Nevertheless, with carbon contents increasing further, the production of both CBzs and PCBs have a sharp drop. Every test with a carbon content was repeated twice to ensure that the standard deviations are all below 20%.

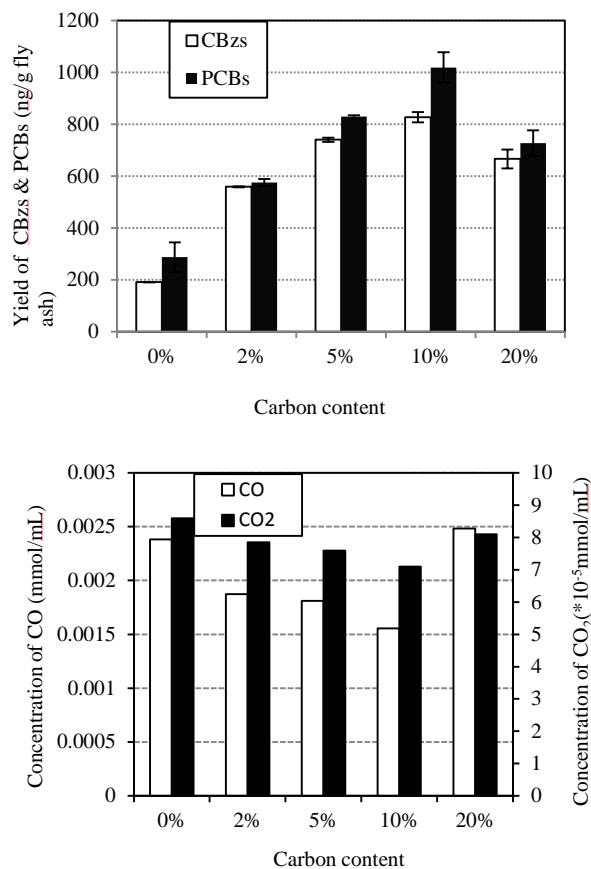
(a)

Moreover, the results about the concentration of CO<sub>x</sub> generated in the carbon oxidation process of simulative fly ash with different carbon contents are shown in Fig 1(b). The concentration of CO and CO<sub>2</sub> have similar tendency dramatically. They both decrease rapidly with the augment of carbon contents as the carbon contents less than 10%. When reaching a 10% carbon content in the simulative fly ash, either CBzs or PCBs reach a minimum peak,  $1.56 \cdot 10^{-3} \text{ mmol} \cdot \text{mL}^{-1}$  for CO and  $7.10 \cdot 10^{-5} \text{ mmol} \cdot \text{mL}^{-1}$  for CO<sub>2</sub>. The production of both CO and CO<sub>2</sub> increase contrarily with carbon contents increasing. As can be seen in Fig 1, the yield of CBzs&PCBs and CO<sub>x</sub> have completely opposite trend with the increasing of carbon content. It is absolutely casual. There are necessary contact between the formation of chlorinated organic compounds and CO<sub>x</sub>, even the formation of dioxins.

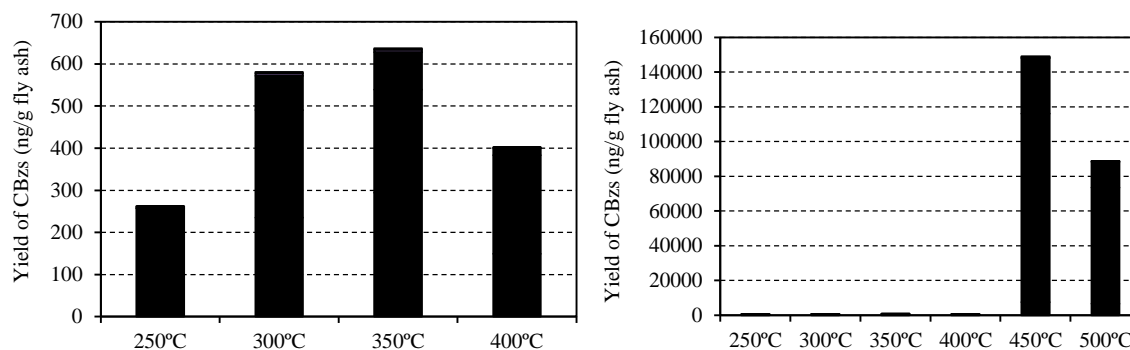
#### Influence of temperature

Optimal operating conditions are key element of the formation of chlorinated organic compounds and even dioxins. Above all, temperature is one of the main conditions investigated in this research. The simulative fly ash used in this survey were prepared according to the real fly ash with Fe<sub>2</sub>O<sub>3</sub> (35%Fe) active carbon (4%C), KCl (7%Cl) and matrix SiO<sub>2</sub> (other). It was heated in the tube furnace under different temperature (250°C, 300°C, 350°C, 400°C, 450°C and 500°C). The yields of CBzs and PCBs are also shown in Fig 2 and Fig 3.

It can be seen from Fig 2 that in the range of 250°C to 400°C, the yield of CBzs increases primitively and reaches a maximum peak of 637 ng/g fly ash at 350°C, then it fleetly drops to 402 ng/g fly ash when the temperature reaches 400°C. In addition, as the temperature increases further to 450°C, a huge transition occurred to the production and the maximum of CBzs generated is 149098 ng/g-fly ash which is more than 200 times of the production at 350°C. When the temperature then increases to 500°C, the production of CBzs decreases instead. During the whole temperature range, the yield of CBzs presents regular fluctuations and has two production peak at 350°C and 450°C respectively. 350°C is the optimum temperature of *de novo* formation which is confirmed by other researchers. Nevertheless, 450°C is another optimum temperature at which the production is much higher than 350°C.



(b)



**Fig 2** Yield of Chlorobenzene (CBzs) in the carbon oxidation process of simulative fly ash with different operating temperature(250°C, 300°C, 350°C, 400°C, 450°C and 500°C)

Moreover, the results about the yield of PCBs are shown in fig 3. We can conclude that the production of PCBs reaches a maximum of 73 ng/g-ash at 300 °C , as the temperature increases further to 350°C, the production gets to a minimum of 40 ng/g-ash, and the yield of PCBs increases gradually with the temperature go through from 350°C to 500°C.

#### Acknowledgements

The authors are grateful to National Natural Science Foundation of China (Project No. 21277010), the National Science and Technology Support Program of China (No. 2010BAC66B04) for providing financial assistances.

#### References:

1. UNEP, (2002); *A Guide to the Stockholm Convention on Persistent Organic Pollutants*.
2. Jia H, Song C, Dai Z, Gao B. (2008); *Sintering and Pelletizing*. 01:25-30.
3. Olie K, Vermeulen P, Hutzinger O. (1977); *Chemosphere*. 6(8): 455-459.
4. Yu Y, He X, Li X. (2009); *World Iron & Steel*. 9(6): 1-6.
5. Karasek F. (1995); *Organohalogen Compounds*. 23(2): 315-319.
6. Ooi TC, Lu L.(2011) *Chemosphere*. 85(3): 291-299.