# PCDDs/PCDFs EMISSION FROM FERROUS METAL INDUSTRY

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### *Introduction*

Iron and steel foundries produce gray or white iron and steel castings, which are molten solid of iron, carbon, and various alloying materials. The castings are produced from scrap iron, pig iron, and foundry returns from melting, alloying, and molding works. The major operations include: 1) raw material preparation, 2) metal sintering, 3) metal melting, and 4) casting and finishing (Figure 1).

First, raw materials require blending prior to the sintering operation. This can involve layering the raw materials on prepared area into the precise quantities required by the sintering process. Some flux material can be added at this stage with recycled materials from downstream operations. Ore blend is recovered from the beds and transferred to storage pit. In the mixing stage other additives can be added to the ore blend. These additives include limestone, colleted dust from sintering and melting processes, and recycled sinter in the size of less than 5 mm from sinter screening. In the sintering process, the blended fine iron ore is melted into lump iron by the heat (1,300~1,500 ) of burning coke breeze (<5mm). A sintering furnace, which is operated as down draft sintering on a continuous basis, is a planar steel plate open at the top and equipped with traveling grate with slots at the bottom. Combustion air is introduced downwards through the layer of materials to be sintered by induced-draft (ID) fan. Due to the coke combustion and the poor supplement of air, emissions released from the sintering furnaces include the high levels of particulate matter, carbon monoxide, sulfur dioxide, nitrogen oxide, and small quantities of chlorine compounds. Thus, the sintering process has been indicated as a emission source of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs)[1, 2].

The metal melting process is primarily accomplished in blast furnace, which is the major metal melting furnace, and to a lesser extent in electric arc or induction furnace. The blast furnace is typically a vertical and cylindrical shell with refractory-lined inner wall. The sintered metal, coke and fluxes are charged into the furnace, and pure oxygen or air to burn off the iron-bearing carbon is injected through tuyeres at the base of furnace. The heat produced by burning coke melts the iron, which flows down and is tapped from the bottom of the furnace. The emission gas is all recycled as a fuel for power plant. In Korea, about 70% of all iron castings are produced using blast furnaces, while about 30% of those rely on electric arc or induction furnaces. Scrap metal melting is performed almost at the electric arc or induction furnace in Korea. In an electric furnace, which is operated as sequence-batch basis, electric current flows from the cathode to anode through the scrap charge. Since the electrical resistance of the charge causes the charge to heat up and become molten. The molten iron is poured into the crucible by tilting the electric furnace. Fugitive dust is controlled by enclosing the barrel furnace in a hood system and by ducting the emission to a fabric filter. Principally, though no combustion process is occurred in electric furnace, scrap metal melting processes have been also indicated as a emission source of PCDDs/PCDFs because of the partial combustion of chlorine-containing plastics or liquids that can provide the conditions required for the formation of chlorinated compounds.

Although electrostatic precipitator or bag filter is commonly used to control emissions from the sintering and melting processes, emissions released from these processes can include the high levels of carbon monoxide, sulfur dioxide and nitrogen oxide, and the small quantities of particulate matter, organic compounds, and chlorine and fluorine compounds. Therefore, this study was performed in order to investigate the emission level of PCDDs/PCDFs in the sintering and melting processes in Korea.

***Material and Methods***

Four iron-ore sintering furnaces, thirteen steel melting furnaces, and three alloy melting furnaces were selected from eighteen plants in iron and steel foundries of Korea. PCDDs/PCDFs samplings were achieved two times at the stacks of each furnaces by using a sampling train, which consisted, in order, of a probe, a cylindrical filter, two impingers (one was filled with 250 ml of distilled water, and the other was empty), a sorbent (XAD-2) trap, and two impingers (one was filled with 150 ml of ethylene glycol, and the other was empty). After sampling, the collected PCDDs/PCDFs samples were extracted and pretreated, according to the Korean Standard Testing Method for Dioxins and Furans[3], and were also analyzed by HRGC/HRMS (high resolution gas chromatograph/high resolution mass spectrometer: Micromass Co., Autospec Ultima) above 10,000 resolution with an SP-2331 column of 60m × 0.32mm ID × 0.25um. Toxic equivalents, expressed as 2,3,7,8-TeCDD (TEQ) values, were all calculated by using the international toxicity equivalency factor (I-TEF) without the correction by oxygen concentration in flue gases.

***Results and Discussions***

**In the iron-ore sintering furnace,** PCDDs/PCDFs emissions were in the range of 0.333 to 1.342ng-TEQ/Nm$^3$, and averaged 0.615ng-TEQ/Nm$^3$ from eight measurements. Like the PCDDs/PCDFs emission pattern of municipal solid waste (MSW) incinerator, flue gas contained four times or more PCDFs than PCDDs, showing that the ratio of PCDDs to PCDFs was 18:82 on average. The most abundant 2,3,7,8-congener was 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 51.7% and 8.5% of total TEQs, respectively. The most toxic 2,3,7,8-TCDD was detected at the level of less than 5% of total TEQs. Currently, the problems of sintering furnace are the facts that it has emitted one million or more normal cubic meters of off-gases per hour, and has released many and much higher pollutants such as particulate matter, carbon monoxide, sulfur dioxide and nitrogen oxide into the atmosphere. In particular, the off-gases released contain about 1.6% of carbon monoxide, thus it is necessary to properly control the emissions of pollutants including PCDDs/PCDFs.

**In the electric steel-melting furnaces,** which were all electric arc or induction furnaces, PCDDs/PCDFs emission were in the range of 0.014 to 0.558 ng-TEQ/Nm$^3$, and averaged 0.097 ng-TEQ/Nm$^3$ from twenty six measurements. Like the sintering furnaces, PCDFs showed an approximately four times higher concentration than PCDDs, showing that the ratio of PCDDs to PCDFs was 22:78 on average. The most abundant 2,3,7,8-congener was also 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 44.5% and 9.7% of total TEQs, respectively. 2,3,7,8-TCDD was detected at the level of less than about 6% of total TEQs. Compared to sintering furnaces, electric furnaces have released slightly lower levels of PCDDs/PCDFs than sintering furnaces, but the emission amounts of off-gas were up to about one and a half million normal cubic meters per hour, depending on the numbers of electric furnace in a plant. Due to sequence-batch operation of electric furnace, the building is totally enclosed in order to minimize dust and gaseous emissions, thus off-gases contain very high concentration of oxygen (20.5%) and carbon monoxide (410ppm) on average.

**In the electric alloy-melting furnaces,** PCDDs/PCDFs emission were in the range of 0.001 to 0.052 ng-TEQ/Nm$^3$, and averaged 0.024 ng-TEQ/Nm$^3$ from six measurements. Like the sintering and melting furnaces, PCDFs showed an approximately four times higher concentration than PCDDs, showing that the ratio of PCDDs to PCDFs was 20:80 on average. The most abundant 2,3,7,8-congener was also 2,3,4,7,8-

PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 47.2% and 8.5% of total TEQs, respectively. 2,3,7,8-TCDD was detected at the level of 7.8% of total TEQs. Similarly to steel-melting furnaces, off-gases also contain 20.1% of oxygen and 5,011ppm of carbon monoxide on average.

**Table 1. PCDDs/PCDFs emissions of sintering and melting furnaces in the iron and steel foundries**

(Unit: ng TEQ/Nm$^3$)

| 2378-PCDD/DF | Sintering Furnace | | Electric Furnace | | | |
|---|---|---|---|---|---|---|
| | Iron (n=8) | | Steel (n=26) | | Alloy (n=6) | |
| 2,3,7,8-TCDD | 0.022 | 3.64 | 0.006 | 5.68 | 0.002 | 7.75 |
| 1,2,3,7,8-PeCDD | 0.052 | 8.48 | 0.009 | 9.71 | 0.002 | 8.45 |
| 1,2,3,4,7,8-HxCDD | 0.007 | 1.14 | 0.001 | 1.11 | 0.000 | 0.70 |
| 1,2,3,6,7,8-HxCDD | 0.013 | 2.10 | 0.003 | 2.72 | 0.001 | 2.11 |
| 1,2,3,7,8,9-HxCDD | 0.010 | 1.55 | 0.002 | 1.58 | 0.000 | 0.70 |
| 1,2,3,4,6,7,8-HpCDD | 0.005 | 0.75 | 0.001 | 0.75 | 0.000 | 0.70 |
| OCDD | 0.001 | 0.08 | 0.000 | 0.04 | 0.000 | 0.00 |
| **PCDDs** | **0.109** | **17.74%** | **0.021** | **21.59%** | **0.005** | **20.42%** |
| 2,3,7,8-TCDF | 0.036 | 5.82 | 0.009 | 9.67 | 0.002 | 8.45 |
| 1,2,3,7,8-PeCDF | 0.015 | 2.46 | 0.004 | 3.91 | 0.001 | 2.82 |
| 2,3,4,7,8-PeCDF | 0.318 | 51.69 | 0.043 | 44.49 | 0.011 | 47.18 |
| 1,2,3,4,7,8-HxCDF | 0.024 | 3.84 | 0.004 | 4.15 | 0.001 | 4.23 |
| 1,2,3,6,7,8-HxCDF | 0.047 | 7.63 | 0.007 | 6.75 | 0.002 | 7.75 |
| 2,3,4,6,7,8-HxCDF | 0.050 | 8.12 | 0.007 | 6.75 | 0.002 | 7.75 |
| 1,2,3,7,8,9-HxCDF | 0.007 | 1.16 | 0.001 | 0.75 | 0.000 | 0.00 |
| 1,2,3,4,6,7,8-HpCDF | 0.008 | 1.34 | 0.001 | 1.30 | 0.000 | 1.41 |
| 1,2,3,4,7,8,9-HpCDF | 0.001 | 0.20 | 0.000 | 0.28 | 0.000 | 0.00 |
| OCDF | 0.000 | 0.00 | 0.000 | 0.04 | 0.000 | 0.00 |
| **PCDFs** | **0.506** | **82.26%** | **0.076** | **78.41%** | **0.019** | **79.58%** |
| **PCDDs+PCDFs** | **0.615** | **100%** | **0.097** | **100%** | **0.024** | **100%** |

Note: The figures in shaded areas represent the compositional percentiles of each 2,3,7,8-congeners to total TEQs.

***Conclusions***

The emission pattern of PCDDs/PCDFs from sintering and melting furnaces in iron and steel foundries could be summarized as follows:

1) PCDDs/PCDFs emission levels were in the range of 0.024 to 0.615ng-TEQ/Nm$^3$ on average.
2) PCDFs showed an approximately four times higher concentration than PCDDs, showing that the ratio of PCDDs to PCDFs averaged approximately 20:80.
3) The main contributor to total TEQs was 2,3,4,7,8-PeCDF, and its TEQ values were in the range of 44% to 52% of total TEQs.

***References***

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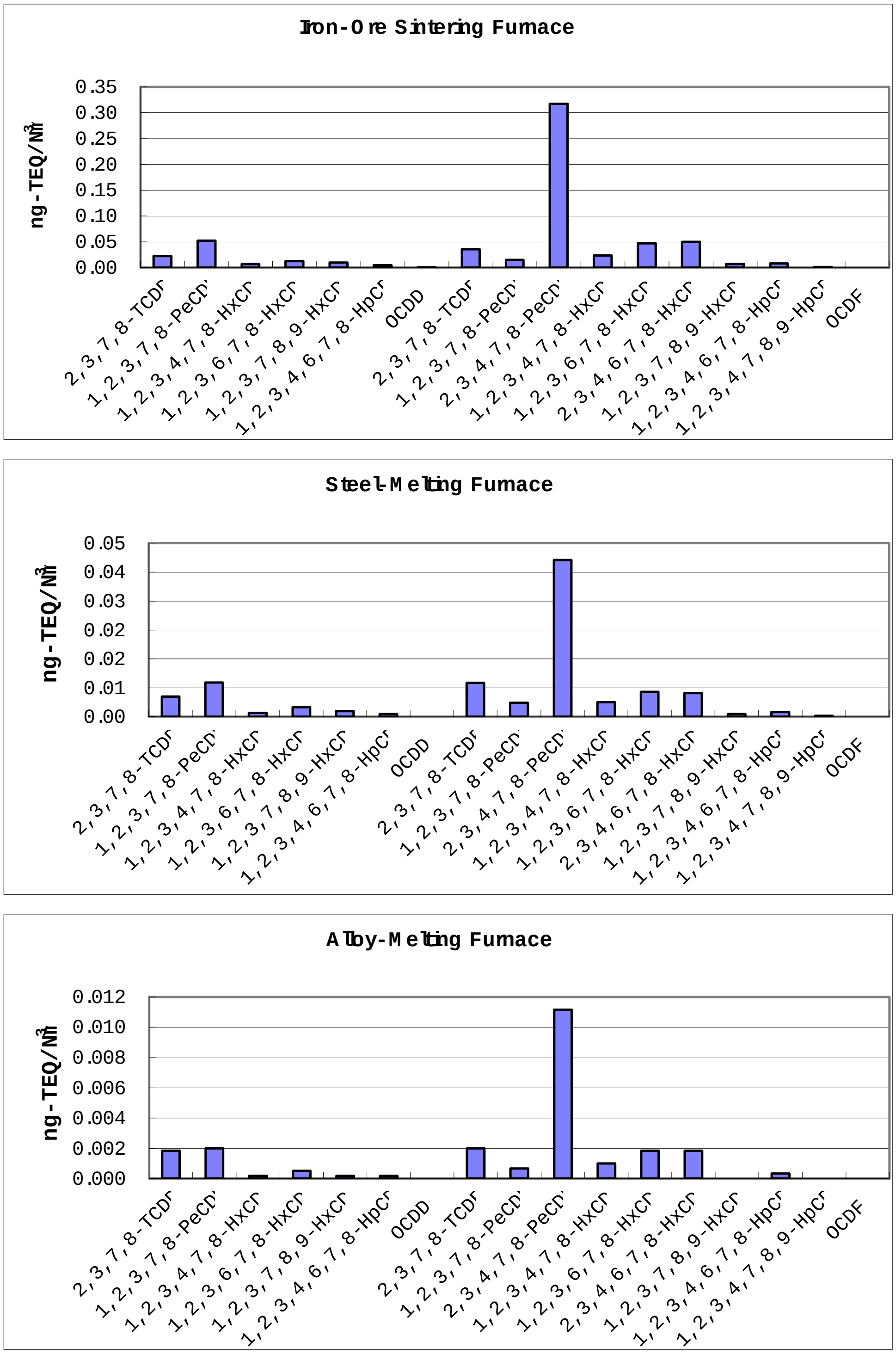


**Figure 2. Congener profiles in sintering, steel-melting and alloy-melting furnaces**.