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Emission Characteristics of PCDDs/PCDFs from Nonferrous Metal Foundry

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Three lead-smelting furnaces, one of which was primary and two of which were secondary, and two zinc-melting furnaces, one was primary and the other was secondary, were selected from five plants in nonferrous metal foundries. PCDDs/PCDFs samplings were achieved two times at the stacks of each furnace to investigate emission characteristics of PCDDs/PCDFs from both primary and secondary smelting processes of lead and zinc. From a total of ten measurements, PCDDs/PCDFs emission levels averaged 0.074 ng-TEQ/Sm^3 and 0.022 ng-TEQ/Sm^3 in lead- and zinc-smelting processes, respectively. Secondary smelting furnaces emitted about three to five times higher levels of PCDDs/PCDFs than primary smelting furnace. PCDFs showed approximately 1.5 to 3 times higher concentrations than PCDDs, revealing that the ratios of PCDDs to PCDFs averaged 40:60 and 23:77 in lead- and zinc-smelting processes, respectively. The main contributor to total TEQs was 2,3,4,7,8-PeCDF, and its TEQ values were in the range of 32% to 37% of total TEQs.

Key words: PCDDs/PCDFs, nonferrous metal, lead, zinc, smelting furnace

1. Introduction

Nonferrous metals include lead, zinc, copper, and aluminium, which are the major four nonferrous metals in Korea. In nonferrous metal smelting and refining, various thermal processing technologies are applied according to physicochemical properties of nonferrous metals[1].

In primary lead smelting, lead ores such as galena (PbS), cerusite ($PbCO_3$) and anglesite ($PbSO_4$), of which grades are about 50% or more by weight after mineral dressing, are smelted through roasting, sintering, and reducing processes. In roasting process, the lead ores, mainly galena, are oxidized into lead oxide (PbO), emitting sulfur dioxide[2]. Prior to entering the sintering process, silicate, limestone ($CaCO_3$) and recycled ore from sintering process are added into oxidizing ore, and then palletized into proper sizes for sintering.

In the sintering process, roasted ore with additives are sintered and further desulfurized. The lumped sinters are charged into the smelter with coke, and lead oxide is reduced chemically by coke to produce elemental lead in the smelter. Blister lead is further refined to increase the purity of lead.

Similarly, in the primary zinc smelting, zinc ores such as zinc blend (ZnS), marmatite ($ZnS \cdot FeS$), calminel ($Zn_4SiO_8 \cdot H_2O$), smithsonite ($ZnCO_3$), and zincite (ZnO), of which grades are about 50% more or less by weight after mineral dressing, are in order smelted through roasting, sintering, and reducing processes[3,4]: zinc sulfide is oxidized into zinc oxide, and then chemically reduced into elemental zinc by coke as a reducing agent. Blister zinc is further refined to increase the purity.

In secondary smelting, nonferrous metals and alloys are recovered from new and used scraps and dross. Some nonferrous-metal scraps and wastes contain organic components such as plastics, cutting oils, paints, and solvents[5,6]. Thus, combustion of these components could result in the formation of PCDDs/PCDFs (polychlorinated dibenzo-*p*-dioxins/polychlorinated diben-

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zofuran), which have been reported in some stack emission tests[7-9].

The secondary lead smelting produces elemental lead through the chemical reduction of lead compounds in a high temperature furnace (1,200 to 1,260°C)[2]. Smelting is performed in rotary, blast, electric, and reverberatory furnaces. Blast and reverberatory furnaces are the most common types of smelting furnaces. Furnace charge materials consist of lead-bearing raw materials and slag, fluxes, and coke. Motor vehicle battery scraps are 90% of lead-bearing raw materials in Korea. Fluxing agents consist of silica sand and limestone or coke. Coke is used as fuel in blast furnaces and as a reducing agent in rotary and reverberatory furnaces. Secondary zinc smelting produces zinc ingot from shredder and electric furnace dusts, of which grades are less than 10% or 10% to 30% as zinc, respectively. These dusts are oxidized into blister zinc oxide, and upgraded up to 50% to 55% as zinc at Waelz kiln or melting furnace. Blister zinc oxide is produced as zinc ingot by further thermal treatment.

As a point view of feed materials, it could be expected that secondary smelting processes produce more pollutants and PCDDs/PCDFs than primary smelting processes[5,6]. So far, many papers[10-16] have indicated the emission possibility of PCDDs/PCDFs from secondary smelting of nonferrous metal so that some data have been reported on secondary smelting, but very few data on primary smelting of nonferrous metal. Thus, this study was carried out in order to investigate the emission characteristics of PCDDs/PCDFs from both primary and secondary smelting processes of lead and zinc.

2. Methods and Materials

Three lead-smelting furnaces, one of which was primary and two of which were secondary, and two zinc-smelting furnaces, one was primary and the other was secondary, were selected from five plants in nonferrous metal foundries of Korea.

PCDDs/PCDFs samplings were achieved two times at the stacks of each furnace by using a sampling train: which consisted, in order, of a probe, a cylindrical filter assembly allowed insertion of a thermocouple (silica fiber thimble, 90 mm in length and 25 mm outside diameter, Whatman: at least 99% efficiency on 0.3 μm dioctyl phthalate smoke particles), three impingers (two of which were filled with 150 ml of distilled water, and one of which was empty), a sorbent (XAD-2) module allowed insertion of a thermocouple, and two impingers (one of which was filled with 150 ml of ethylene glycol, and the other was empty).

After spiking 2 ng of $^{37}Cl_4$-2,3,7,8-TCDD to the sorbent, two traverse-point sampling over the respective cross sections was iso-kinetically (isokinetic factor of 95~105%) done at the stack for about 5 hours. During the sampling, the cylindrical filter was kept below 120°C with cooling water, and sorbent trap was kept below 30°C by chilling the impingers with ice water.

After sampling, the PCDDs/PCDFs samples were divided into two portions: one is solid portion (cylindrical filter and sorbent) and aqueous portion (impinger water, ethylene glycol, probe-rinsed solvent). An internal standard cocktail, 2 ng of $^{13}C_{12}$-PCDDs/PCDFs was added to each portion of samples as internal standards prior to extraction. Then, each portion of samples was separately extracted with toluene: Soxhlet extraction for solid portion and liquid extraction for aqueous portion. Toluene extracts were combined into one and cleaned up by 5 ml of concentrated sulfuric acid 4 or 5 times, followed by silica gel column cleanup eluting 150 ml of n-hexane, and basic alumina column cleanup eluting 100 ml of 2% dichloromethane in n-hexane (this portion was discarded) and then 150 ml of 50% dichloromethane in n-hexane. Final eluate was concentrated to a volume of 1 ml, and further concentrated to about 50 μl after spiking 2 ng of recovery standards.

Concentrated eluates of the samples were analyzed by high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). The HRGC/HRMS setup consisted of a Hewlett Packard 6890 GC coupled with Autospec Ultima (Micromass Co.) with OPUS quantification programme. Selected ion monitoring with electron impact of 36 eV was performed above a resolution of 10,000 with an SP-2331 column of 60 m ×

0.32 mm ID × 0.25 μm [120°C (3 min) → 10°C · min^{-1} to 200°C (3 min) → 3°C·min^{-1} to 265°C (15 min)]. The eluates were introduced in splitless mode with a flow rate of 2.5 ml · min^{-1} helium, and temperatures of injector and ion source were 260°C and 270°C, respectively.

Toxic equivalents (TEQs), expressed as 2,3,7,8-TeCDD values, were calculated without correction of oxygen concentration in flue-gas stream by using the international toxicity equivalency factor and OPUS quantification programme. All processes mentioned above, including sampling, sample preparation, and HRGC/HRMS analysis, were performed according to the Korean Standard Testing Method (KSTM) for Dioxins and Furans[17].

3. Results and Discussion

In the lead-smelting furnaces, the volumes and temperatures of emission gases, shown in Table 1, were in the range of 145~938 Sm^3/min (average 590 Sm^3/min) and 25~38°C (average 30°C), respectively. In particular, the primary lead smelting emitted much lower volume of off-gases per ton of product than secondary smelting: which averaged about 3,000 Sm^3/ton in primary, whereas about 23,000 Sm^3/ton in secondary smelting furnace. Emission concentrations of oxygen and carbon monoxide in off-gases also showed the considerable differences: oxygen and carbon monoxide averaged 12.2% and 2.6 ppm in the primary smelting process, while 19.95% and 7,029 ppm in the secondary smelting process.

Like this, the emission gases from a few of lead-smelting plants showed the high oxygen concentrations and temperatures similar to ambient air inside the plants. This was mainly because most of lead-smelting plants used the canopy hoods, and such an aspiration by canopy hoods led to the low temperature and high oxygen concentration of emission gas similar to those of ambient air inside plant.

PCDDs/PCDFs emissions were in the range of 0.001 to 0.041 ng-TEQ/Sm^3, and averaged 0.174 ng-TEQ/Sm^3 from six measurements. The secondary smelting furnaces emitted about five times higher levels of PCDDs/PCDFs than the primary smelting furnace by showing 0.046 ng-TEQ/Sm^3 and 0.289 ng-TEQ/Sm^3 in primary- and secondary-smelting processes on average, respectively.

Off-gases contained one and a half times more PCDFs than PCDDs, showing that the ratio of PCDDs to PCDFs was 40:60 on average. This ratio was the slightly different value of 20:80 of the ferrous-metal melting furnaces18,19). The most abundant 2,3,7,8-congener was 2,3,4,7,8-PeCDF same as ferrous-metal melting furnaces followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 32.4% and 17.1% of total TEQs, respectively (Table 2, Fig. 1). The most toxic 2,3,7,8-TCDD was detected at the level of 7.4% of total TEQs.

In the zinc smelting furnaces, PCDDs/PCDFs emissions were in the range of 0.001 to 0.063 ng-TEQ/Sm^3, and averaged 0.022 ng-TEQ/Sm^3 from four

Table 1. General description of non ferrous metal smelting furnaces

Plant Name		Emission Process	APCD	E. Gas (Sm^3/min)	E. Gas/Pro. (ton/day)	E. Gas Temp. (°C)	PCDDs/PCDFs (ng-TEQ/Sm^3)		
							1st	2nd	Mean
Lead	D1	SF	BF	938	3,002	26	0.090	0.001	0.046
	D2	SF	BF	145	21,979	38	0.128	0.247	0.188
	D3	SF	BF	686	22,973	25	0.410	0.168	0.289
	Average			590	5,057	30	0.074 (s = 0.142)		
Zinc	E1	SF	EP	760	1,140	29	0.001	0.021	0.011
	E2	SF	BF	524	12,579	15	0.063	0.002	0.033
	Average			642	1,812	22	0.022 (s = 0.029)		

<Note> SF: Sintering Furnace, APCD: Air Pollution Control Device, EP: Electrostatic Precipitator, BF: Bag Filter

Table 2. PCDDs/PCDFs emission pattern of nonferrous metal melting furnaces

2,3,7,8-PCDDs/PCDFs	Electric Furnace (ng-TEQ/Sm^3)			
	Lead Smelting (n = 6)		Zinc Smelting (n = 4)	
2,3,7,8 TCDD	0.013	7.38	0.001	3.45
1,2,3,7,8 PeCDD	0.030	17.05	0.002	8.05
1,2,3,4,7,8 HxCDD	0.004	2.30	0.001	2.30
1,2,3,6,7,8 HxCDD	0.009	5.27	0.001	4.60
1,2,3,7,8,9 HxCDD	0.009	4.98	0.001	2.30
1,2,3,4,6,7,8 HpCDD	0.005	2.68	0.001	2.30
OCDD	0.000	0.19	0.000	0.00
PCDDs	**0.069**	**39.85**	**0.005**	**22.99**
2,3,7,8 TCDF	0.009	5.36	0.000	1.15
1,2,3,7,8 PeCDF	0.004	2.39	0.000	1.15
2,3,4,7,8 PeCDF	0.056	32.38	0.008	37.93
1,2,3,4,7,8 HxCDF	0.006	3.64	0.001	5.75
1,2,3,6,7,8 HxCDF	0.011	6.03	0.003	11.49
2,3,4,6,7,8 HxCDF	0.012	6.70	0.003	13.79
1,2,3,7,8,9 HxCDF	0.002	0.96	0.000	1.15
1,2,3,4,6,7,8 HpCDF	0.004	2.11	0.001	4.60
1,2,3,4,7,8,9 HpCDF	0.001	0.48	0.000	0.00
OCDF	0.000	0.10	0.000	0.00
PCDFs	**0.105**	**60.15**	**0.017**	**77.01**
PCDDs+PCDFs	**0.174**	**100.00**	**0.022**	**100.00**

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

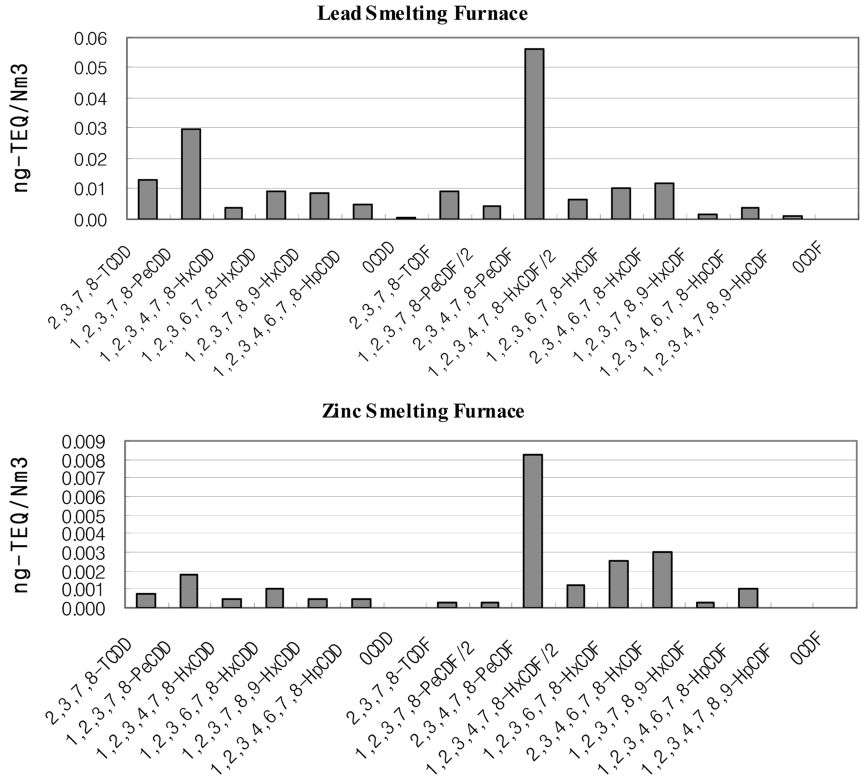

Fig. 1. Congener profiles of lead and zinc smelting furnaces in nonferrous foundries.

measurements. The secondary smelting processes emitted about three times higher levels of PCDDs/PCDFs than primary smelting process by showing 0.011 ng-TEQ/Sm^3 and 0.033 ng-TEQ/Sm^3 in primary- and secondary-smelting processes, respectively. Off-gases contained approximately three times or more PCDFs than PCDDs, showing that the ratio of PCDDs to PCDFs was 23:77 on average. This ratio was slightly different value of 40:60 mentioned above in lead-smelting case. The most abundant 2,3,7,8-congener was the same 2,3,4,7,8-PeCDF as lead-smelting furnace followed by 2,3,4,6,7,8-HxCDF, and their TEQ values constituted 39.9% and 13.8% of total TEQs, respectively. The most toxic 2,3,7,8-TCDD was detected at the level of 3.5% of total TEQs.

In particular, the emission pattern of 2,3,7,8-PCDDs/PCDFs was very similar to that of municipal-solid-waste incinerator[20-22] in a fact that three major 2,3,7,8-congeners were 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF and 1,2,3,6,7,8-HxCDF, and their compositional percentile was about 60% to total TEQs. The zinc-smelting furnace also emitted relatively much lower amounts of off-gases, which were in the range of 760 Sm^3/min to 524 Sm^3/min and averaged 590 Sm^3/min, than iron-and-steel melting furnaces[18,19]. The emission levels of oxygen and carbon monoxide in off-gases showed considerable differences: oxygen and carbon monoxide were 6.5% and 0.5 ppm in the primary smelting process, while 20.9% and 15.1 ppm in the secondary smelting process on average.

4. Conclusions

Three lead-smelting furnaces and two zinc-smelting furnaces were selected from five plants in nonferrous-metal foundries of Korea. PCDDs/PCDFs samplings were achieved two times at the stacks of each furnace to investigate the emission characteristics of PCDDs/PCDFs from both primary and secondary smelting processes of lead and zinc. Results were summarized as follows:

1. From a total of ten measurements, PCDDs/PCDFs emission levels averaged 0.074 ng-TEQ/Sm^3 and 0.022 ng-TEQ/Sm^3 in lead- and zinc-smelting process.

2. The secondary smelting furnaces emitted about three to five times higher levels of PCDDs/PCDFs than the primary smelting furnace.

3. PCDFs showed approximately 1.5 to 3 times higher concentrations than PCDDs, revealing that the ratios of PCDDs to PCDFs averaged 40:60 in lead smelting and 23:77 in zinc smelting process.

4. The main contributor to total TEQs was 2,3,4,7,8-PeCDF in all cases, and its TEQ values were in the range of 32% to 37% of total TEQs.

5. The emission patterns of 2,3,7,8-PCDDs/PCDFs in all cases were very similar to that of municipal-solid-waste incinerator in a fact that three major 2,3,7,8-congeners were 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF and 1,2,3,6,7,8-HxCDF, and their compositional percentile was about 60% to total TEQs.

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