PCDDs/PCDFs EMISSION FROM NONFERROUS METAL INDUSTRY

Kim Sam-Cwan, Na Jin-Gyun, Choe Sung-Hun, Lee Jung-Hee, Kim Yeon-Ho, Hwang Seung-Ryul,
Joo Chang-Han[1], Jung Dong-Hee[1], You Jae-Cheon[1], Lee Sang-Won[1], Jeon Sang-Eun[1]

NIER (National Institute of Environmental Research), Environmental Research Complex,
Kyungseo-Dong, Seo-Ku, Inchon, 404-170, Republic of Korea

[1]Analytical Research Center, Environmental Management Co., Boondang-gu Hasanwoon-dong
Mt. 26-4, Sungnam City, Kyonggi Do, 463-430, Republic of Korea

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 the physico-chemical properties of nonferrous metals.

In the primary lead smelting, the 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 the roasting process, the lead ore, mainly galena, is oxidized into lead oxide (PbO), emitting sulfur dioxide. Prior to entering the sintering process, silicate, limestone and recycled ore from sintering process are added into oxidized lead ore, and then pelletized into a proper size 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, where elemental lead is produced from lead oxide, which is chemically reduced by coke as a reducing agent. Blister lead produced is further refined to increase the purity of lead. Similarly, in the primary zinc smelting, zinc ores such as zinc blend (ZnS), marmatite (ZnS-FeS), calminel (Zn_4SiO_8 H_2O), smithsonite ($ZnCO_3$), and zincite (ZnO), of which grades are about 50% by weight after mineral dressing, are smelted through roasting, sintering, and reducing processes in order: zinc sulfide is oxidized into zinc oxide, and then chemically reduced into elemental zinc by coke as a reducing agent. Blister zinc produced 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. Thus, combustion of these components could result in the formation of PCDDs/PCDFs (polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofuran), which have been reported in some stack emission tests[1]. The secondary lead smelting produce the elemental lead through the chemical reduction of lead compounds in a high temperature furnace (1,200 to 1,300). Zinc smelting is performed in rotary, blast, electric, and reverberatory furnaces. Of the 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. Currently, 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 furnace and as a reducing agent in rotary or reverberatory furnaces. Secondary zinc smelting produce zinc ingot from shredder and electric-furnace dusts, of which grades are less than 10% and 10% to 30% as zinc, respectively. These dusts are oxidized into blister zinc oxide, and upgraded 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 expected from feed materials, it can be thought that secondary smelting processes produce more pollutants and PCDDs/PCDFs than primary smelting processes. So far, researchers have indicated the emission possibility of PCDDs/PCDFs from secondary smelting of nonferrous metal so that some data have been reported on secondary smelting[1], but very few data are available on primary smelting of nonferrous metal. Thus, this study was carried out to investigate the emission characteristics of PCDDs/PCDFs from both primary and secondary smelting processes of lead and zinc.

Methods and Materials

Three lead smelting furnaces, one of which was primary and two of which were secondary, and two zinc smelting furnaces, one of which was primary and the other of which 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 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[2], 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 lead smelting furnace, PCDDs/PCDFs emissions were in the range of 0.001 to 0.041ng-TEQ/Nm^3, and averaged 0.174ng-TEQ/Nm^3 from six measurements. Compared primary to secondary lead smelting furnace, secondary smelting furnace emitted about five times higher level of PCDDs/PCDFs than primary smelting furnace, showing 0.046ng-TEQ/Nm^3 in primary smelting and 0.239ng-TEQ/Nm^3 in secondary smelting. 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 slightly different value of 20:80 of ferrous metal melting process. The most abundant 2,3,7,8-congener was the same 2,3,4,7,8-PeCDF as ferrous-metal melting process followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 32.4% and 17.1% of total TEQs, respectively. The most toxic 2,3,7,8-TCDD was detected at the level of 7.4% of total TEQs. In particular, primary lead smelting emitted much lower volume of off-gas per ton of product than secondary smelting: which averaged about 3,000Nm^3/ton in primary, whereas about 23,000Nm^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 2.6ppm in primary smelting process, while 19.95% and 7,029ppm in secondary smelting process.

In the zinc smelting furnaces, PCDDs/PCDFs emissions were in the range of 0.001 to 0.063ng-TEQ/Nm^3, and averaged 0.022ng-TEQ/Nm^3 from four measurements. Compared primary to secondary zinc smelting furnace, secondary smelting furnace emitted about three times higher level of PCDDs/PCDFs than primary smelting furnace, showing 0.011ng-TEQ/Nm^3 in primary smelting process and 0.033ng-TEQ/Nm^3 in secondary smelting process. Off-gases contained approximately three times 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 melting 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 levels of 3.5% of total TEQs. In particular, emission pattern of 2,3,7,8-PCDDs/PCDFs was very similar to that of municipal solid waste incinerator in the 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[3], and their compositional percentile was about 60% to total TEQs. Similarly to lead smelting case, primary zinc smelting furnace emitted much lower volume of off-gas per ton of product than secondary smelting: which averaged about 1,140Nm^3/ton in primary, whereas about 12,600Nm^3/ton in secondary smelting furnace. Emission concentration of oxygen and carbon monoxide in off-gases showed a considerable difference: oxygen and carbon monoxide were 6.5% and 0.5ppm in primary smelting process, while 20.9% and 15.1ppm in secondary smelting process on average.

Table 1. PCDDs/PCDFs emission pattern of nonferrous metal melting furnaces

(Unit: ng-TEQ/Nm^3)

	Electric Furnace			
2378-PCDD/DF	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%**	**0.022**	**100%**

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

Conclusion

The emission pattern of PCDDs/PCDFs from primary and secondary smelting processes of lead and zinc could be summarized as follows:

1) PCDDs/PCDFs emission levels averaged 0.074 ng-TEQ/Nm^3 in lead smelting and 0.022

ng-TEQ/Nm^3 in zinc smelting process.

2) Secondary smelting furnace emitted about three to five times higher level of PCDDs/PCDFs than primary smelting furnace.
3) PCDFs showed approximately 1.5 to 3 times higher concentration than PCDDs, showing 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, and its TEQ values were in the range of 32% to 37% of total TEQs.

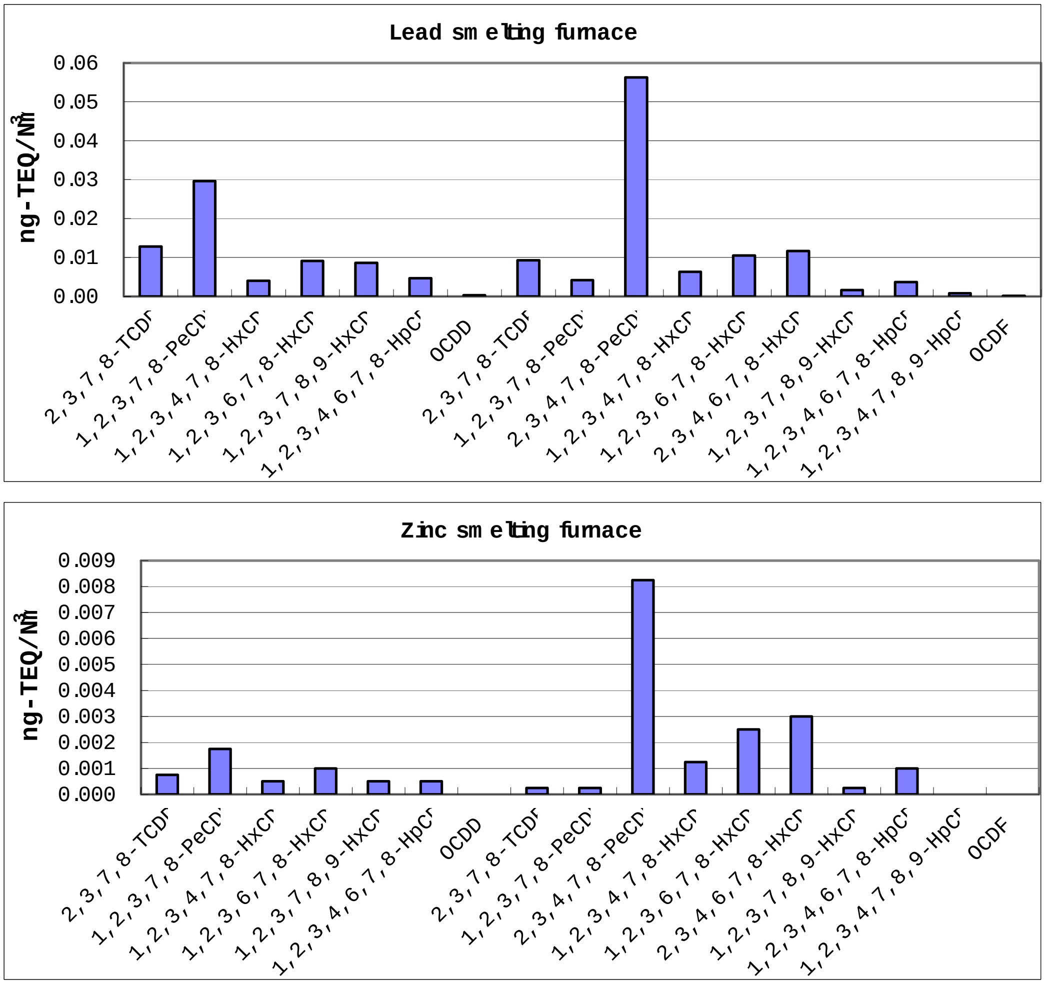

Figure 2. Congener profiles in nonferrous metal melting furnaces.

References

1. US EPA; (1997) EPA-454-/R-97-003.
2. Ministry of Environment, Republic of Korea; (1996) The Korean Standard Testing Method for Doixins and Furans.
3. Kim Sam-Cwan, et al.; (2001) Chemosphere 43 (2001), 701-707.