EMISSION INVENTORY OF PCDD/Fs FROM ELECTRIC ARC FURNACES IN TAIWAN

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Introduction

Electric arc furnaces (EAFs) have been widely used in the production of steel in Taiwan. Scrap and ferrous alloys act as major iron component, which are melted by electrical energy. EAFs have been identified as the main source of dioxin in several countries [1]. Scrap containing oil, plastic and chlorides leads to potential PCDD/F formation [2-3]. In January 2002, Taiwan government set 5.0 ng-TEQ/Nm^3 as the PCDD/F emission limit for existing EAFs starting from January 2004. In this study, PCDD/F concentrations and emission factors in stack gas from EAFs producing different types of steel were evaluated.

Materials and Methods

Raw materials and electric arc furnace process

Currently 18 EAF steel plants (3 for stainless steel and 15 for carbon steel) and 25 EAFs are in operation in Taiwan. The type of feed material used in the arc furnace melting process depends on the steel product. The main characteristic of the stainless steel is that they contain chromium, molybdenum and nickel elements to enhance the corrosion resistance of stainless steel. The scraps used for smelting include recycled waste car, boat, industrial waste and import of scrap steel. Scrap pretreatment includes manual sorting, shredding, and magnetic separation.

The melting procedure includes stages of feeding, charging, melting, oxidation, reduction and steel discharge. The raw materials -scraps, alloying agents and fluxes - were fed into the furnace. The capacity of EAFs ranges from 20 to 130 tons and 3~5 cans of scraps are fed per batch. Duration of a typical steel-making batch is about 50~130 min, depending on the type of steel produced (stainless steel takes longer). The temperature of furnace off-gas varies largely from 200 to 1600℃ during the steel-making process.

Off-gas treatment systems of EAFs

A typical EAF off-gas treatment system consists of (1) a direct evacuation system and (2) a secondary emission system [4] (Fig. 1). The former is used to induce the hot gas from the furnace. As the off-gas from the furnace contains high concentration of CO, CO converter (combustion chamber) was applied to convert CO to CO_2 and the hot gas is cooled through a water-cooled duct. The flow rate of the direct evacuation is about 1,500~2,000 Nm^3/min for 50 tons EAF. The secondary emission system has the canopy hood above the furnace and which was used to ventilate the off-gas during the steel discharge. As indoor air diluted the secondary flue gas, the temperature at the canopy hood inlet was between 80-120℃. If the direct evacuation system mixed into the secondary emission system and emission via a direct evacuation blower, this is called the mixed exhaust system. The flow rate of the mixed exhaust system is about 10,000 ~12,000 Nm^3/min with a 50 tons EAF. If the direct evacuation and secondary emission system have their own dedusting system and blowers prior to being discharged into the environment, this is called the separation system. All EAFs use baghouse as major de-dust system in Taiwan. Due to the high raw gas flow rate, some EAFs in Taiwan adopted shutter system (positive pressure operation) for flue gas emission and other EAFs use stack systems (Fig. 1).

PCDD/F sampling and analysis

The sampling campaign was undertaken during the steel-making operating period. The flue gas sampling was conducted with Graseby Anderson Stack Sampling System complying with the USEPA Method 23. Due to the characteristics of the shutter system, the sampling method adopted follows the standard sampling procedure (NIEA A807.73C) [3]. The gas-phase sample was collected by XAD-2 resin whereas the particle-bound portion was collected by the fiber glass filter and by rinsing of the sampling probe thereafter. The samples collected were analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners with high-resolution gas chromatography/high resolution mass spectrometer (HRGC/HRMS) (JEOL JMS 700D) equipped with a DB5-MS capillary column (60m × 0.25mm × 0.25 μm film thickness).

Results and Discussion

1. PCDD/F emission concentrations

The PCDD/F concentrations in the stack flue gas from the EAFs investigated ranged from 0.004 to 6.30 ng-TEQ/Nm^3, with an average of 0.68 ng-TEQ/Nm^3 in 2005 (Table 1). Previous study indicates that PCDD/F from EAFs was 0.08~1.33 ng-TEQ/Nm^3 in Japan [5] and 0.32~0.61 ng-TEQ/Nm^3 in Thailand [6], respectively. The types of steel and off-gas emission system applied affect the PCDD/F concentration from EAFs. The mean PCDD/F emission concentration was 0.08 ng-TEQ/Nm^3 (n=18) for those producing stainless steel, which was lower than that measured for the EAFs producing carbon steel (0.87 ng-TEQ/Nm^3, n=51) in 2005. The variable "n" represents the number of total flue gas samplings. It is attributed the fact that the raw materials and the scraps (high-grade) used for stainless steel were strictly selected and were much cleaner than that for carbon steel. The EAFs producing carbon steel usually buy the low-grade scrap and scrap pretreatment only includes manual sorting, stripping, shredding, and magnetic separation. Oil, plastic and chlorides in scrap cannot be removed. Table 2 lists the PCDD/F concentrations of different types of off-gas system. The average PCDD/F concentrations were 2.00 ng-TEQ/Nm^3 (n=6) for direct evacuation system, 0.26 ng-TEQ/Nm^3 (n=6) for the secondary emission system, and 0.49 ng-TEQ/Nm^3 (n=54) for the mixed exhaust system, respectively. The PCDD/F concentration for direct evacuation was 7.7 times higher than that for secondary emission. Due to the variation of operating temperature of the EAF and it could not keep in a stable condition, the direct evacuation flue gas contains high concentration of CO and dioxins. Comparatively, the secondary exhaust gas was the mixed gases of diluted air and hot gas escaping from the furnace. As it was diluted with large amounts of indoor air, the dioxin concentration became lower. In the mixed exhaust system, the direct evacuation hot gas was diluted with the secondary emission gas and the temperature of the mixed gas was cooled down to 80 ~120℃. At this condition, large amounts of gaseous dioxins will transfer or adsorb on the particulate matters as the solid-phase dioxins. Solid-phase dioxins predominate in the mixed flue gas and can be effectively captured by the baghouse. Gaseous dioxins will penetrate the filter and emit via the stack or the shutter system. The PCDD/F concentration of the mixed exhaust system was between that of the direct evacuation and the secondary emission system. The average dioxin concentrations measured for stack system and shutter system are close (Table 3).

2. PCDD/F congener profiles

The most abundant congeners for carbon steel include 2,3,4,7,8-PeCDF (16.4%), 1,2,3,4,6,7,8-HpCDF (10.2%), and 1,2,3,7,8-PeCDF (10%). The ratio of PCDF/PCDD is 5.1. However, the most abundant congeners for stainless steel include 2,3,7,8-TeCDF (20%), 2,3,4,7,8-PeCDF (14%) and OCDD (13%). The ratio of PCDF/PCDD is 3.7.

For the direct evacuation system, PCDF accounts for 70% of PCDD/F while 1,2,3,4,6,7,8-PeCDF (13%) and OCDD (12.8%) are the main congeners. However, PCDF accounts for 58% of PCDD/F while OCDD (37%) and OCDF (31%) are the main congeners in the secondary emission system. The congener profiles of two kinds of exhaust systems (the stack and the shutter) were similar.

3. PCDD/F emission factors and annual emission

PCDD/F emission factor based on the average of all stack tests. The average emission factors were 7.09 μg-TEQ/ton for carbon steel and 1.18 μg-TEQ/ton for stainless, respectively. The total annual emission for carbon steel was 49.3 g-TEQ (94%) and 2.9 g-TEQ for stainless steel and other steel (6%). The average emission factor for 25 EAFs in Taiwan was 6.06 μg-TEQ/ton. Emission factor of 12 μg-TEQ/ton was reported in Thailand [6].

The annual operational time of the EAF plants was between 320 and 340 days in 2005. Total amounts of steel production were 8,219,000 tons in 2004 and 8,621,000 tons in 2005, respectively. Total annual emissions from this source in Taiwan were estimated as 36.6 g-TEQ in 2004 and 52.2 g-TEQ in 2005 based on this study, respectively. Taiwan government will tighten the PCDD/F emission limit to 0.5 ng-TEQ/Nm^3 for existing EAFs starting from January 2007 and sets the emission target of 17.2 g-TEQ in 2008.

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Table 1 The PCDD/F concentrations of stack gas from EAFs.

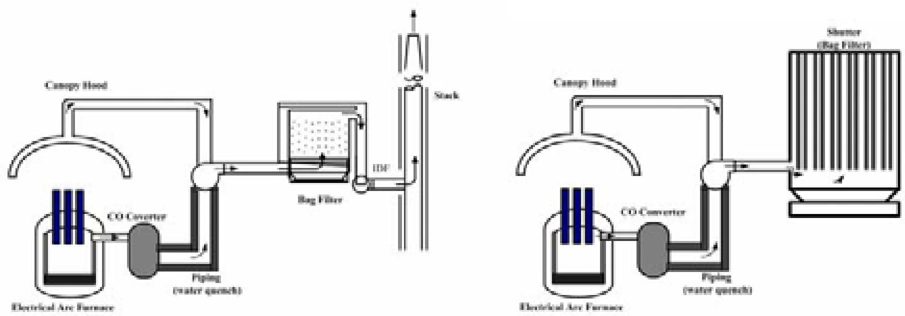
	Year	(n)	PCDD/F (ng-TEQ/Nm^3)		
			Min.	Max.	Average
EAFs	2004	81	0.04	2.66	0.52
	2005	75	0.004	6.30	0.68
EAFs for carbon steel	2004	57	0.04	2.66	0.64
	2005	51	0.01	6.30	0.87
EAFs for stainless steel	2004	12	0.06	0.38	0.19
	2005	18	0.004	0.38	0.08

Table 2 The PCDD/F concentrations of different type of off-gas system of EAFs.

Type		(n)	PCDD/F (ng-TEQ/Nm^3)		
			Min.	Max.	Average
Separated exhaust system	Direct evacuated duct	6	1.33	2.66	2.00
	Secondary emission duct	6	0.09	0.43	0.26
Mixed exhaust system		54	0.04	1.33	0.49

Table 3 The PCDD/F concentrations of different exhaust system of EAFs.

Type	(n)	PCDD/F (ng-TEQ/Nm^3)		
		Min.	Max.	Average
The stack system	18	0.21	0.95	0.47
The shutter system	15	0.09	1.06	0.41



(a) stack system (b) shutter system

Fig. 1 Off-gas treatment systems of the EAFs (the mixed exhaust system)