Evaluation of PCDD/F Emissions from Waelz Process for Zinc Dust Recycling

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Introduction

Previous study indicates that PCDD/F emission from metallurgical processes is even higher than that from municipal waste incinerations (MWIs) in some countries (European Union On-Line, 2001). The Waelz process is a classic method for treating EAF dusts containing zinc and lead. In most cases, the feeding material is heavily contaminated with organic and inorganic components, resulting in high potential of PCDD/F formation. As a result of the thermal treatment of the residues, PCDD/Fs are liberated on the flue gas, requiring the installation of additional air pollution control devices (APCDs) (Mager, 1998). The need to reduce PCDD/F emissions poses a serious challenge for secondary metallurgical smelting facilities. This paper is of a series detailed study on the emission and vapor/solid phase partitioning of PCDD/Fs from non-ferrous (zinc production) metal production process. Toward this aim, it is necessary to examine all aspects of the distribution and the removal efficiencies of PCDD/Fs with cyclone (CY) and bag filter (BF) in the Waelz plant investigated.

Experimental

The Waelz plant investigated in this study started to operate in 2002. It is a rotary typeacid-kiln and has the capacity of 12 tons per hour. Typical feeding material includes 15% sand (SiO_2), 20% coke and 65% EAF dust. The Waelz plant investigated is equipped with venturi cooling tower, cyclone (CY) and bag filters (BF) for controlling particulate matter emissions. The flue gas samples were collected by Graseby Anderson Stack Sampling System complying with USEPA Method 23. The vapor-phase sample was collected with XAD-2 resin while the particle bound samples were collected with glass fiber filter. Ash samples were collected at intervals when the corresponding stack sampling was conducted. The flue gas and ash sampling points are schematically shown in Figure 1. The samples collected were analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners with high resolution gas chromatography /high resolution mass spectrometer. The mass spectrometer was operated with a resolution greater than 10,000 under positive EI conditions, and data were obtained in the selected ion monitoring (SIM) mode.

Results and discussion

Figure 2 shows the PCDD/F concentrations in flue gas at different sampling points. Results of the flue gas sampling indicate that the PCDD/F concentrations are 1,223 ng-TEQ/Nm^{3}at venture inlet, 1,061 ng-TEQ/Nm^{3}at CY inlet, 444.8 ng-TEQ/Nm^{3}at BF inlet and 145.4 ng-TEQ/Nm^3 at stack. Relevant studies (Mager et al., 2003 and Ruetten, 2001) indicate that basic substances such as CaO can reduce PCDD/F formation during the Waelz process. Hence, the PCDD/F concentration (145.4 ng-TEQ/Nm^3) measured in the Waelz plant investigated with acid substances is significantly higher than that measured at other Waelz plants with basic substances (0.01 ng-TEQ/Nm^3). As indicated in Figure 2, PCDD/F congeners are mostly distributed in solid phase (about 60~65% of the total PCDD/Fs). Figure 3 shows PCDD/F congener distributions in flue gases collected at different sampling points. PCDFs account for about 65~70% of total PCDD/Fs at all sampling points. The major distributor includes 1,2,3,4,6,7,8-HpCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF. If we compare the distributions of PCDD/F congeners in stack gases observed between the Waelz plant investigated in this study and EAF (Chang et al., 2005), the results indicate that the distributions of PCDD/Fs are similar. However, 1,2,3,7,8-PeCDD (based on TEQ) is quite unique and can serve as the indicator for the flue gas emitted from Waelz plant. Figure 4 shows the PCDD/F concentrations of feeding material, dust settling chamber (DSC) ash, CY ash and BF ash in the Waelz plant investigated. PCDD/F concentrations of CY ash and BF ash (0.76~0.97 ng-TEQ/g) of the Waelz plant investigated are lower than the ash samples (1.63~2.94 ng-TEQ/g) collected from MWIs (Chi et al, 2005). However, the PCDD/F concentration of DSC ash (4.17 ng-TEQ/g) is much higher than other ash samples. Fortunately, the DSC ashes will be redischarged into the kiln during the Waelz process and are not discharged into the environment. During the Waelz process, DSC provides sufficient retention time with the operating temperature about 500 ^{0}C. Besides, the chloride content of EAF dust treated is over 5%. With the environment conducive to PCDD/F formation in DSC (temperature window, enough retention time, chloride source and catalysts available), relatively high PCDD/F concentrations are measured in DSC ash and flue gas (Evereart and Baeyens, 2002). Figure 5 shows PCDD/F flows for the Waelz plant investigated. Based on the PCDD/F concentrations measured across APCDs and gas flow rates during the sampling period (about 150 minutes), 109.2 and 107.7 µg-TEQ PCDD/Fs in flue gas are captured by the CY and BF, respectively. On the basis of treating one ton of EAF dust, total PCDD/F discharge is 840.3 µg-TEQ/ton EAF dust, among which 20.3% is discharged with CY ash, 13.0% is discharged with BF ash. About 66.6% of total PCDD/Fs are discharged emitted via stack gas (559.6 µg-TEQ/ ton EAF dust). Hence, the Waelz plant investigated needs to effectively reduce PCDD/F formation at DSC and install better PCDD/F control devices for the perspective of total environmental management.

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Table 1 The condition of flue gas at different sampling points in Waelz plant investigated.

Sampling location	**Venturi inlet**	**Cyclone inlet**	**Bag filter inlet**	**Stack**
O_2 (%)	**18.4**	**19.2**	**17.6**	**18.6**
CO_2 (%)	**1.8**	**2**	**2**	**1.8**
Temperature (^{0}C)	**467**	**215**	**160**	**138**
Particulate matter concentration (mg/Nm^3)	**2,416**	**2,323**	**913.5**	**10.22**

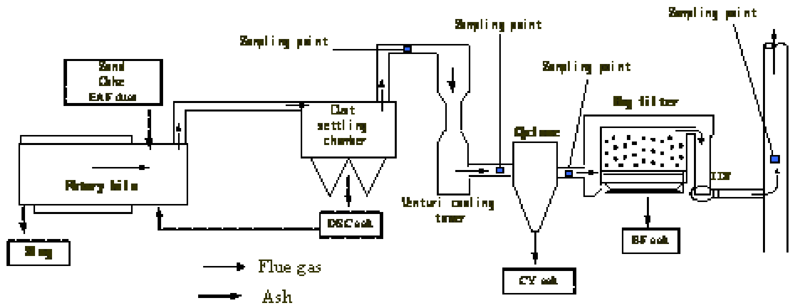

Fig.1 Sampling points in the Waelz plant investigated.

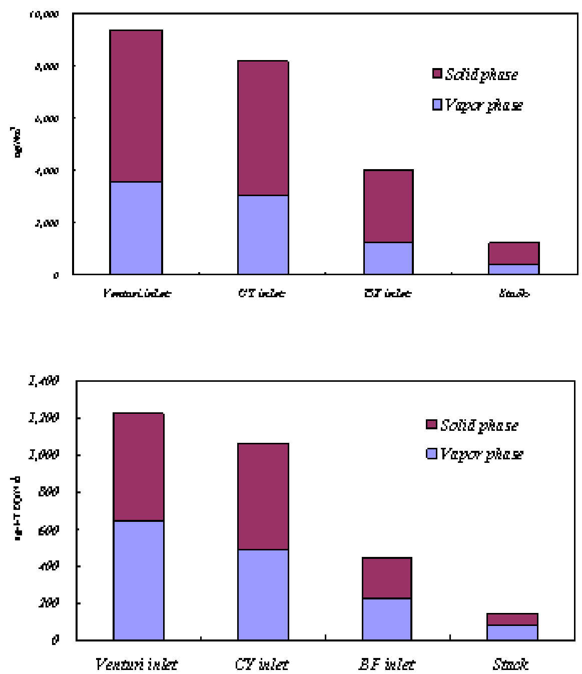

Fig. 2 Variation of PCDD/F concentration in vapor and solid phases at different sampling points in the Waelz plant investigated.

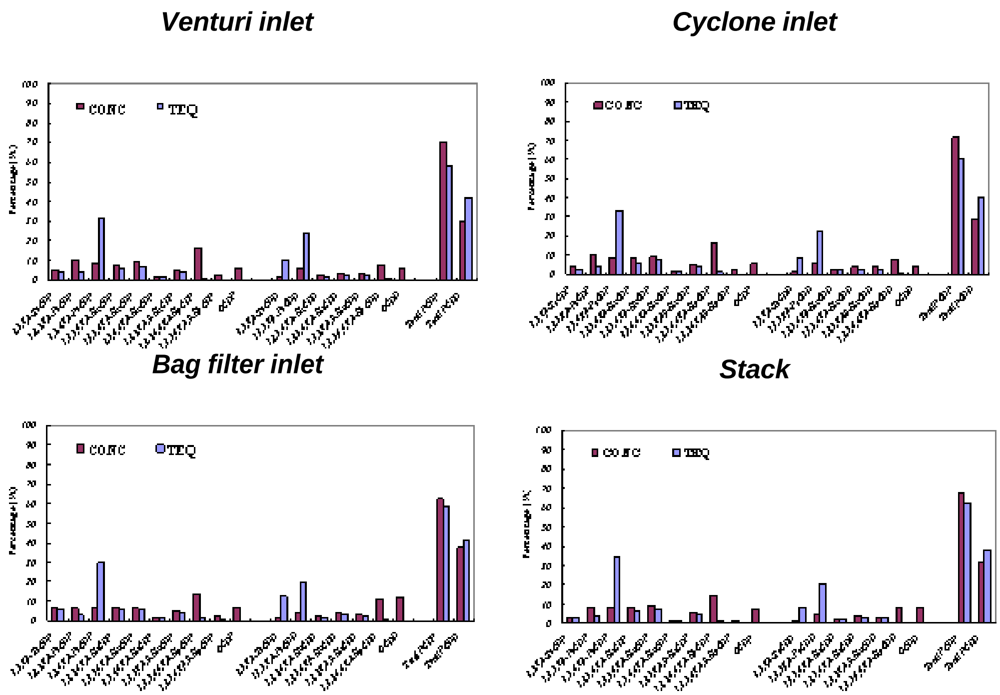

Fig. 3 The characteristics of PCDD/F congener distribution at different sampling points in the Waelz plant investigated.

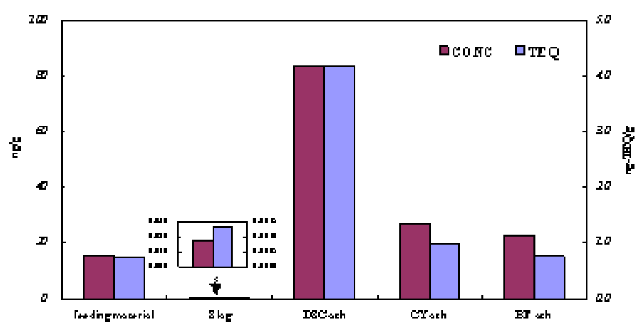

Fig. 4 PCDD/F concentrations in ash samples of the Waelz plant investigated.

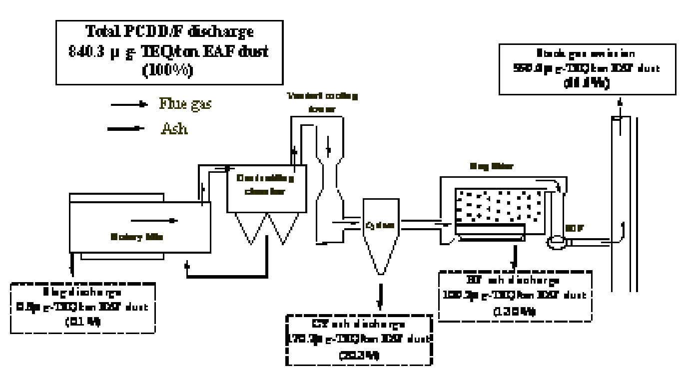

Fig. 5 PCDD/F TEQ flows in the Waelz plant investigated.