REDUCTION OF DIOXIN EMISSIONS FROM COPPER SMELTING PLANT FOR SLUDGE RECYCLING

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Abstract

Secondary non-ferrous smelting is important with saving up to 95 % energy compared with primary smelting, but PCDD/F emission is a serious problem especially for copper smelting plants. Activated carbon injection (ACI) + fabric filter (FF) is considered as one of the best available control technologies for dioxin removal. In this study, flue gas samplings were conducted at different sampling points of a copper smelting plant to evaluate the PCDD/F formation potential and removal efficiency with different copper contents of input material (sludge) and AC injection rates. The results indicate that PCDD/Fs are formed significantly via de novo synthesis and solid-phase PCDD/Fs dominate (over 80%) before FF. The operating temperature in secondary burner (619 ~ 683 ^oC) is not high enough for effective PCDD/F destruction, with the PCDD/F removal efficiency range from 17.6% to 38.5%. Before the retrofit of FF, the particle removal efficiency of FF was between 92.7 % and 95.5 % and the PCDD/Fs emission was higher than 1.0 ng I-TEQ/Nm^3 which is the PCDD/Fs emission standard for this industry set by Taiwan EPA. High PCDD/F formation and low particle removal efficiency are considered as the main causes leading to the relatively high PCDD/F emission. After the retrofit of existing FF, the particle removal efficiency achieved with FF is increased to over 97 %, with PCDD/F concentrations in the stack gas ranging from 0.1 to 0.7 ng I-TEQ/Nm^3.

Introduction

Ferrous and non-ferrous metal wastes can be recovered and refined by secondary smelting process for the sake of saving natural resources and energy. As for non-ferrous metals, the recyclable non-ferrous metals include copper (Cu), zinc (Zn), aluminum (Al) and lead (Pb). Ba et al. (2009) indicated that there are about 2000 secondary copper smelting plants in China, with the annual yield of 2.75 million tons in 2007.[1] Secondary smelting can save up to 95 % of energy consumption compared with primary smelting. Therefore, secondary smelting can produce copper at a much lower cost compared with primary smelting.[2] However, PCDD/Fs are simultaneously formed with thermal process of secondary smelting.[3] Activated carbon injection + fabric filter (ACI + FF) is one of the best available control technologies (BACT) for removing PCDD/Fs from gas streams. CCL (Copper Clad Laminate) is important material for PCB (Printed Circuit Board) process. The CCL process generates waste liquid which contains high concentration of copper ions. The liquid is collected and treated in wastewater processing station. The sludge which contains high concentration of copper is generated and become raw material of secondary copper smelting plants. De novo synthesis is an important reaction in the formation of PCDD/Fs and copper is essential catalyst. Previous studies indicated that the amount of PCDD/F formation increases with increasing copper content.[4,5] By applying AC injection, total amount of PCDD/Fs in fly ash may increase with increasing amount of AC injection.[6] Therefore, copper content in the stream and the rate of AC injected significantly affect the potential of PCDD/F formation. In this study, a secondary copper smelting plant is investigated for the PCDD/F formation and congener distribution with different operating parameters.

Materials and Methods

Sampling site

The process of the secondary copper smelting plant and air pollution control devices (APCDs) equipped are shown in Fig. 1. The copper-containing sludge was fed into the kiln. The flow directions of sludge and gas stream were counter-current. The gas stream passes through secondary burner, dynamic subsiding can (DSC), air cooler tower, water cooler tower, FF and then discharges from stack. The temperature distribution was shown in Fig. 1. Injecting water into DSC helps to remove particles and decrease the temperature. However, the air and water cooler tower which had been installed previously were stopped to operate and the temperature of gas stream decreased about 50 ^{o}C naturally. The particles were collected by FF which was operated at 150 ^{o}C. The temperature of stack was 120 ~ 140 ^{o}C.

PCDD/F emissions with different copper contents and different AC injection rates of this plant were also evaluated. The copper contents of raw sludge were classified into three levels, i.e. low (< 10 %), medium (30 ~ 40 %) and high (> 50 %). As for AC injection, the two injection rates including 3.5 kg/hr and 11.5 kg/hr were tested. Four sampling points were chosen at inlet of secondary burner (Point A), inlet and outlet of DSC (Point B and Point C), and stack (Point D), respectively, for the sampling and analysis of the PCDD/F concentration.

Sample collection and analysis

The flue gas sampling was conducted with the Graseby Anderson Stack Sampling System complying with the USEPA Method 23. Gaseous and solid PCDD/Fs were collected with XAD-2 resin and fiber glass filter, respectively. The internal standard added before Soxhlet extraction and samples were extracted by toluene. The samples were cleaned up with sulfuric acid silica gel column, alumina column and activated carbon column. The recovery standard was added before analysis. Samples were analyzed by HRGC/HRMS (Thermo Trace GC / Thermo DFS) with DB-5MS column (60m × 0.25 mm × 0.25µm, J&W).

Results and Discussions

Raw sludges of three copper contents were processed in this plant. As shown in Fig. 2, PCDD/F concentrations at Point A increase significantly with increasing copper content of raw sludge, especially for those with low and medium copper contents. The total TEQ concentrations measured at Points A to D from low to high copper contents are 63.1, 199 and 246 ng I-TEQ/Nm^3. The pattern is similar to that reported in literatures and 2,3,4,7,8-PeCDF is the major contributor with respect to toxicity equivalent.[1,7]

Fig. 3 presents particle (top) and PCDD/F (bottom) concentrations at 4 sampling points. Both particle and PCDD/F concentrations decrease as gas stream passes from Point A to D. PCDD/F concentrations do not change significantly between Points A and B as the gas stream passes through secondary burner. This was because the operating temperature of secondary burner (650 ^{o}C) was not high enough for the effective destruction of PCDD/Fs. Another reason is the formation of PCDD/F with de novo synthesis. The temperature for de novo synthesis of PCDD/Fs is between 250 and 450 ^{o}C, hence, PCDD/F may be formed as gas streams flow from secondary burner to DSC. PCDD/F removal efficiency achieved with the secondary burner was low(17.6 % ~ 38.5 %) as a result of ineffective destruction and PCDD/F formation via de novo synthesis. PCDD/F formation was not significant after DSC and PCDD/F removal efficiency was increased. The PCDD/F removal efficiencies achieved with DSC and FF were from 58.0 % to 69.1 % and from 89.2 % to 96.1 %, respectively. PCDD/F concentration measured at the stack was from 1.9 to 2.6 ng I-TEQ/Nm^3 with 11.5 kg/hr of AC injection. However, these concentrations were over PCDD/F emission standard in Taiwan (1.0 ng I-TEQ/Nm^3) due to low particle removal efficiency of FF (92.7 % to 95.5 %). Particle removal efficiency achieved with FF can reach 99.9 % with proper design and operation. Solid-phase PCDD/F before FF accounted for 82.9 %, 89.0 % and 94.3 % of total PCDD/Fs with low, medium and high copper-content sludge, respectively.

Fig. 4 indicates the PCDD/F and particle concentrations of FF inlet (Point C) and stack (Point D) after retrofit of FF. The particle concentrations measured at stack were between 5.4 and 10.5 mg/Nm^3 which were significantly lower than the concentrations measured before the retrofit of FF (23.3 ~ 30.7 mg/Nm^3). PCDD/F emission concentrations were significantly lower as a result of lower particle concentrations. The PCDD/F concentrations at stack were between 0.1 and 0.7 ng I-TEQ/Nm^3. The PCDD/F removal efficiencies of FF were increased from 89.2 % to 97.2 % with low copper-containing sludge and high AC injection rate and from 94.7 % to 97.9 % with medium copper-containing sludge and high AC injection rate. So, the retrofit of FF has significantly increased its removal efficiencies for particles and PCDD/Fs.

Conclusion

The levels of copper content in raw sludge significantly affect PCDD/F concentrations in gas streams of a secondary copper smelting plant. As the temperature of gas stream was between 150 ~ 200 ^{o}C, over 80 % of total PCDD/F exist in solid-phase prior to FF and the removal efficiency of FF for particles is important in terms of PCDD/F removal. As FF was retrofitted, the PCDD/F concentration of stack was significantly reduced and could meet the PCDD/F emission standard for this industry in Taiwan (1.0 ng I-TEQ/Nm^3).

Reference

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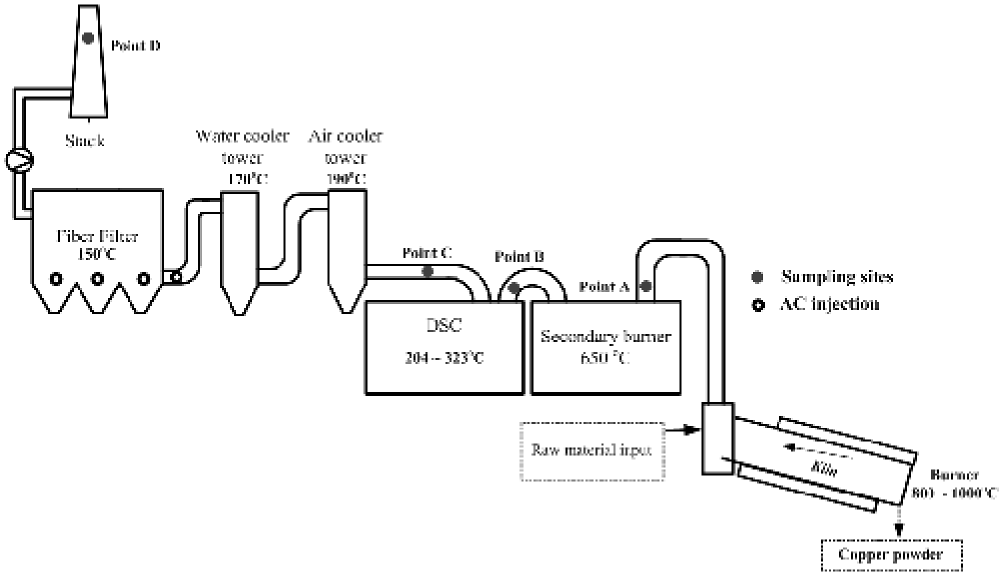

Fig. 1 Schematic diagram of secondary copper smelting process and APCDs.

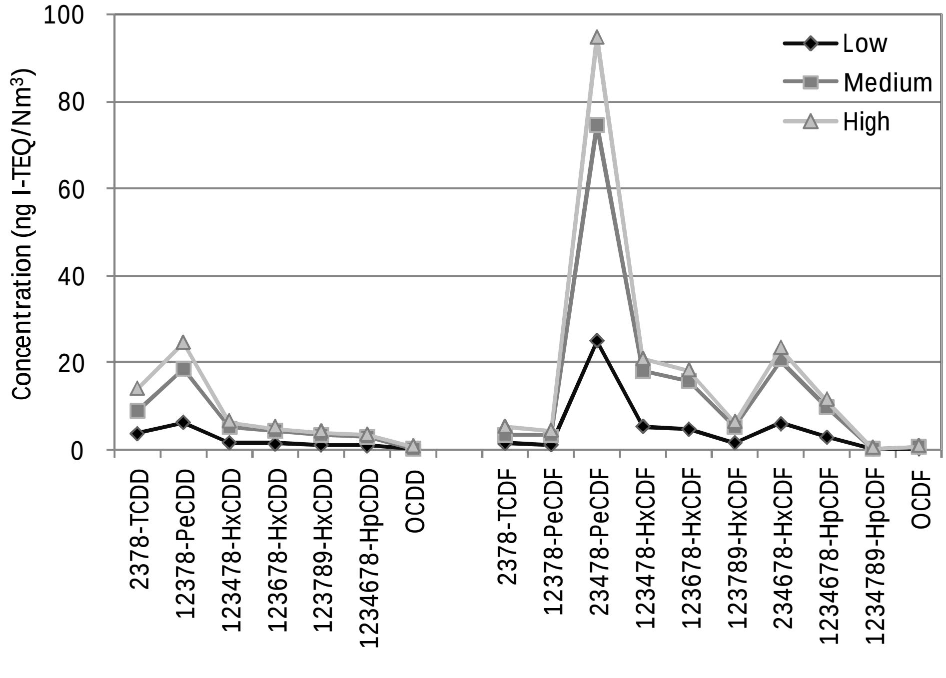

Fig. 2 PCDD/F concentrations with raw sludge of different copper contents before secondary burner (Point A).

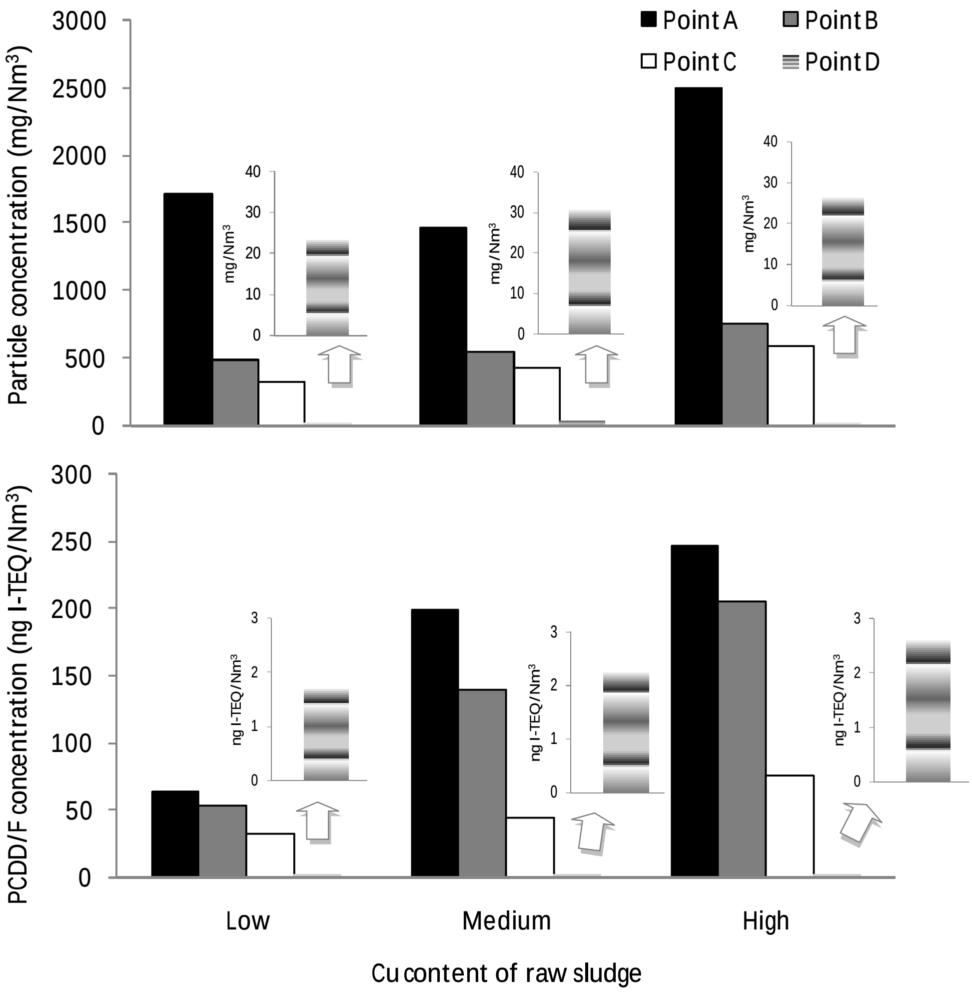

Fig. 3 Concentrations of PCDD/Fs and particles at four sampling points.

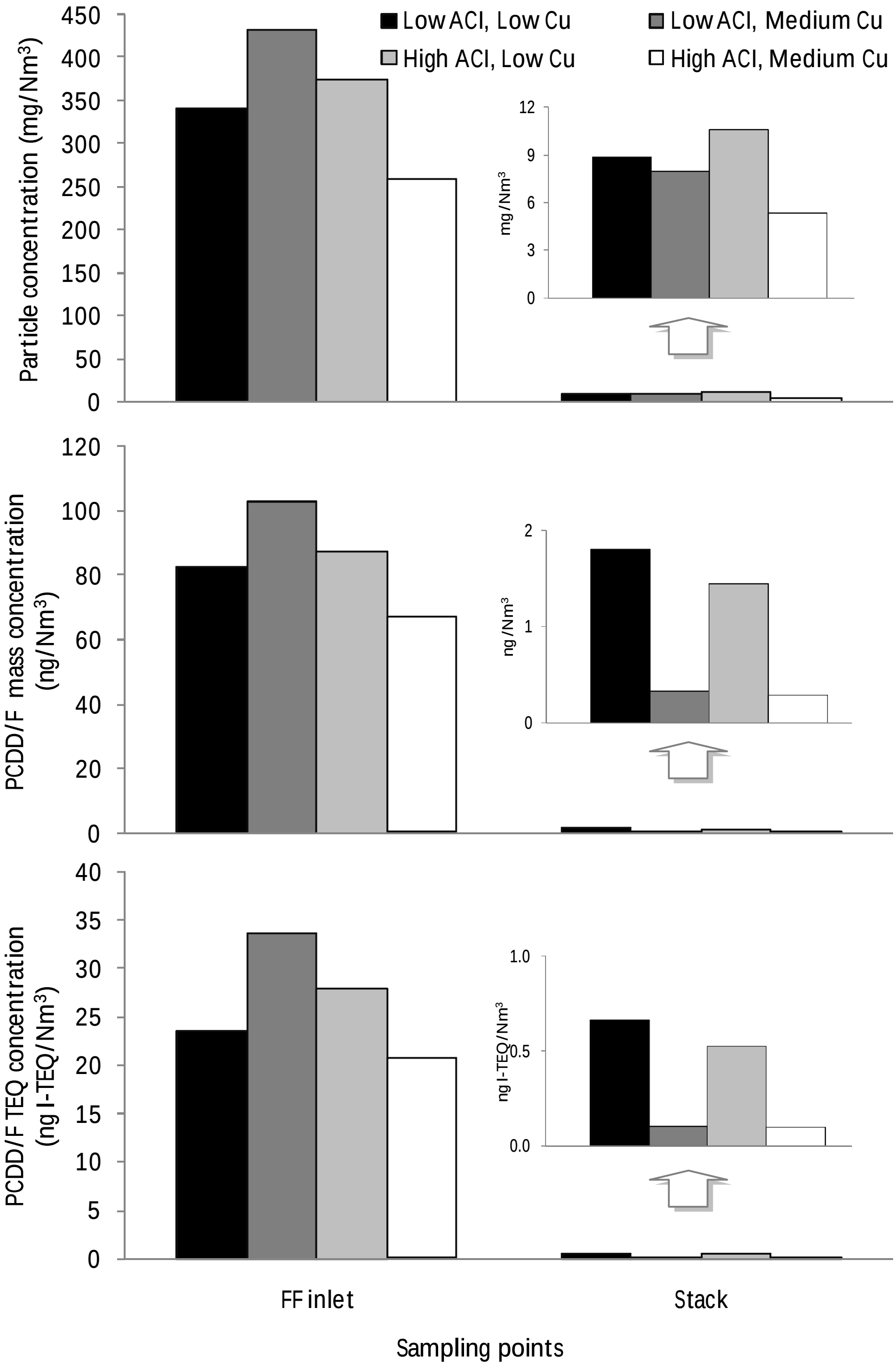

Fig. 4 PCDD/F and particle concentration at FF inlet (Point C) and Stack (Point D) after retrofit of FF.