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Effect of raw materials on emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from the stack flue gases of secondary aluminum smelters

Hsing-Wang Li^{a,b}, Wen-Jhy Lee^{a,b,*}, Kuo-Lin Huang^c, Guo-Ping Chang-Chien^d

^a Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC

^b Sustainable Environment Research Centre, National Cheng Kung University, Tainan 70101, Taiwan, ROC

^c Department of Environmental Engineering and Science, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan, ROC

^d Department of Chemical and Materials Engineering, Cheng Shiu University, Kaohsiung 833, Taiwan, ROC

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Abstract

The present study was undertaken to investigate the effect of raw materials on PCDD/F emission from secondary aluminum smelters (ALS). Four plants each of aluminum ingot smelters (over 50% ingot) and secondary ALS (over 70% waste or recycled aluminum) were selected and the results compared. The secondary ALS yield much higher PCDD/Fs than the aluminum ingot smelters, or 7.94–22.76 ng/Nm³ versus 0.57–2.67 ng/Nm³, due to the large percentage of waste or recycled aluminum used. As for air pollution control devices (APCDs), the wet scrubber system in one of the aluminum ingot smelters exhibits an adverse effect on PCDD/F removal, due to the continuous recycle of the contaminated water through the scrubber system. Another ingot plant equipped with cartridge filter, there is a significant reduction in PCDD/F TEQ (52%). The powdered activated carbon injection at 2 kg/h (110 mg/Nm³) in one ALS reduces 70% of the total PCDD/Fs. The average emission factor of four secondary ALS is much higher than that of aluminum ingot smelters, or 20-fold higher based on either raw materials or product. Consequently, more attention should be paid to the emission reduction of PCDD/Fs from the secondary ALS, including installation of a secondary burner, additional APCDs and the pre-cleaning of raw materials.

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Keywords: Aluminum smelter; PCDD/Fs; TEQ; APCDs

1. Introduction

The polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) exhibit hydrophobic nature and resistance towards metabolism. These chemicals persist in the environment and bioaccumulate in fatty tissues of animals and humans [1]. The impact of PCDD/Fs on the environment in general and health of exposed humans in particular is of great concern. Consequently, a better understanding of the sources and corresponding emission quantity of PCDD/Fs is essential. Based on the PCDD/F release inventory, the major source is combustion [1]. Many studies have been performed about the

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PCDD/F formation in combustion facilities, including a variety of incinerators, and the PCDD/F formation mechanisms are generally known. In general, the PCDD/F formation is governed by the combustion temperature, the type of air pollution control devices (APCDs) and the characteristics of raw materials, among other factors.

Although PCDD/F emission from secondary aluminum smelters (ALS) contributes only about 2.3% of the entire PCDD/F inventory in the USA [2], the information about the PCDD/F released from ALS is generally lacking. Since Taiwan has approximately 196 secondary ALS [3] additional information regarding their PCDD/F emission is needed. Further, the extent of the effect of raw materials on PCDD/F emission from the secondary ALS is lacking. Consequently, this study was undertaken to monitor PCDD/F emission from stack flue gases from two types of ALS plants with completely different raw materials. One type is an aluminum ingot smelter which uses over 50% aluminum ingot as input, and the other is the conventional secondary ALS using most waste or recycled aluminum.

^{*} Corresponding author at: Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC. Tel.: +886 6 275 7575x65831; fax: +886 6 275 2790.

E-mail addresses: wjlee@mail.ncku.edu.tw (W.-J. Lee), huangkl@mail.npust.edu.tw (K.-L. Huang), guoping@csu.edu.tw (G.-P. Chang-Chien).

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Thus, the effect of the impurity of the input for the latter on the PCDD/F emission can be quantified. To the best of our knowledge, there is no PCDD/F emission data from aluminum ingot smelters. Thus, results obtained can provide useful information. In addition, the reduction of PCDD/Fs by different APCDs for aluminum ingot smelters is quantified. The PCDD/Fs from the liquid medium from wet scrubber and fly ash from filter was also monitored.

The resultant PCDD/F concentrations, congener profiles, emission rates, emission factors and total PCDD/F inventory from all secondary ALS in Taiwan should provide background information for decision makers to formulate their control strategies to reduce the overall PCDD/F emissions from secondary ALS.

2. Experimental

2.1. ALS plants and sampling

Stack flue gas samples were collected from four aluminum ingot smelters and four conventional secondary ALS. Each stack gas sampling lasted for 2-3 h, consistent with the batch time of ALS operating processes. Three samples were taken (two samples 1 day and one sample the next day). The basic information of these eight aluminum smelters, e.g., feeding materials, furnace type, product and raw flue gas load, is shown in Table 1. In general, the raw materials of aluminum ingot smelters mainly consist of ingots (over 50%) and other faulty aluminum products or aluminum scraps. On the other hand, the raw materials of secondary ALS are principally waste aluminum materials (over 70%), ingots and Si materials for aluminum recovery. The raw materials of waste or recycled aluminum are collected from secondary aluminum manufacturing processes in domestic plants, and the faulty aluminum products recycled from intrinsic processes. The ingot was imported from China, USA, Australia or Europe, and the silicon was imported from China. The ingot contains over 92-98% of Al, and 2-6% of Si. The silicon contains 99-100% of Si. The faulty, waste or recycled aluminum contains 85-90% of Al, 8-10% of Si, plus other metals and organic compounds which depend on the manufacturing processes.

The flue gas cooling is either via a water or air cooling system. The cyclone, filter and scrubber were the air pollution control devices. The raw flue gas load detected the particular matter (PM: 2–46 mg/Nm³), SO₂ (6.3–35.5 ppm) and NOx (3.3–32.7 ppm). Meanwhile, before the PCDD/F concentration was sampled, the content of O₂ (18.0–20.5%), CO₂ (0.13–2.3%) and CO (<0.2%) was detected to record the actual sampling conditions. Thus, any different PCDD/F emissions may be due to the raw materials used, considering the fact that secondary ALS operated at slightly higher temperatures (800–900 °C) than the aluminum ingot smelters (750 °C).

A total of 29 samples were collected from the flue gas from 8 smelters and 3 samples each after cyclone and before the wet scrubber for plant P1, and after cyclone and before cartridge filter for plant P2 (Table 1). The sampling procedures followed those of the US EPA Modified Method 23 [4]. The PCDD/F content from wastewater of the wet scrubber and fly ash from

Table 1 Basic information for t	the four aluminum ingot s	smelters (P1-P4) and fou	r secondary aluminum sı	nelters (S1–S4)				
	Aluminum ingot smelters				Secondary aluminum sme	lters		
	PI	P2	P3	P4	S1	S2	S3	S4
Feeding materials (kg/h)	268 (faulty aluminum products)	128 (faulty aluminum products)	490 (faulty aluminum products)	850 (faulty aluminum products)	146 (waste aluminum)	335 (recycled materials)	2970 (waste materials)	1900 (recycled materials)
	717 (aluminum scrap) 1097 (ingot)	137 (ingot)	2250 (ingot)	160 (Alloy) 5000 (ingot)	4.6 (S1) 10.4 (ingot)	20 (Si) 47 (ingot)	150 (Si) 470 (ingot)	800 (ingot)
Total feed (kg/h) Furnace type	2080 Reverberatory	265 Reverberatory	2740 Reverberatory	6010 Reverberatory	160 Reverberatory	400 Crucible	3590 Reverberatory	2700 Reverberatory
Air pollution control devices	Cyclone	Cyclone	Baghouse filter	Cyclone	Cyclone	Cyclone	Cyclone	Cyclone
	Wet scrubber	Cartridge filter	Pack-scrubber	Baghouse filter	Baghouse filter	Baghouse filter	Baghouse filter	Baghouse filter
Product (kg/h)	2000 (aluminum liquid)	250 (aluminum liquid)	2500 (aluminum liquid)	5100 (aluminum liquid)	140 (aluminum ingot)	355 (aluminum ingot)	3340 (aluminum ingot)	2600 (aluminum ingot)
Flue gas rate (Nm ³ /h)	19,200	7050	16,570	35,170	24,550	11,060	16,600	19,620
Particular matter (mg/Nm ³)	2	3	46	3-5	30-45	2.2–7.9	38-45	2.8–7.4
NOx (ppm)	9	5	16.8	26-27	4-7	3.3 - 3.7	11.4	15.3–32.7
SO ₂ (ppm)	1	1	26.6	21-33	10-17	7.8–9.3	1.61	$c.c_{E-2}$.0
CO_2 (%)	0.7–0.9	0.1 - 0.2	2.1–2.3	1.8 - 2.1	0.13 - 0.20	0.3 - 0.5	1.1 - 1.3	0.5 - 1.1
O_2 (%)	19.3-19.5	19.9–20.2	18.0-18.3	18.1–18.8	20.3–20.5	19.9–20.3	19.2–19.6	19.1–19.9
CO (%)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

filter was also measured. For the four secondary ALS, all are equipped with cyclones and baghouse filters; the baghouse filters, however, were not replaced (only cleaned) during the study period. To improve the PCDD/F removal, powder activated carbon (PAC, 2 kg/h) was injected to adsorb the gas-phase PCDD/Fs in plant S1. Thus, three additional flue gas samples were taken after the injection of PAC to see the extent of PCDD/F reduction.

2.2. Analysis

Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards prelabeled with isotopes. The stack flue gas samples analysis was performed according to the US EPA Modified Method 23 [4], while the analysis of all fly ash and water samples conformed to the US EPA Method-1613B [5]. Essentially, samples were extracted with toluene for 24 h and this was followed by a series of sample cleanup procedures. The extract was transferred to a vial, and finally further concentrated in a N₂ stream.

Two high-resolution gas chromatographs/high-resolution mass spectrometers (HRGC/HRMS) were used for PCDD/F analysis. The HRGC (Hewlett-Packard 6970 Series gas, CA)

was equipped with a DB-5 fused silica capillary column $(L=60 \text{ m}, \text{ i.d.} = 0.25 \text{ mm}, \text{ film thickness} = 0.25 \mu\text{m})$ (J&W Scientific, CA) with a splitless injection, while the HRMS (Micromass Autospec Ultima, Manchester, UK) had a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring was used with resolving power at 10,000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. The oven temperature program was set according to the following: initially at 150 °C (held for 1 min), then increase by 30 °C/min to 220 °C (held for 12 min), and finally increase by 1.5 °C/min to 310 °C (held for 20 min). Helium was used as the carrier gas. The method detection limits range from 0.002 ng/Nm³ (2,3,7,8-TeCDD) to 0.036 ng/Nm³ (OCDF).

3. Results and discussion

3.1. PCDD/F concentrations in flue gases

The concentration profiles for each PCDD/F congener (7 PCDDs and 10 PCDFs) for 8 aluminum smelters are tabulated in Table 2. The concentrations reported for stack flue gas have

Table 2 Mean PCDD/F concentrations in the stack flue gases for the aluminum ingot, secondary ALS (corrected by the oxygen content)

	Aluminum in	got smelter ^a			Secondary ALS ^a				
	P1 (sample size = 3)	P2 (sample size = 3)	P3 (sample size = 3)	P4 (sample size = 3)	$\overline{S1 \text{ (sample size = 3)}}$	S2 (sample size = 5)	S3 (sample size = 3)	S4 (sample size = 3)	
PCDD/Fs (ng/Nm ³) ^b									
2,3,7,8-TeCDD	0.011	0.009	0.025	0.001	0.039	0.144	0.115	0.144	
1,2,3,7,8-PeCDD	0.025	BD ^c	0.074	0.001	0.147	0.274	0.396	0.295	
1,2,3,4,7,8-HxCDD	0.010	BD ^c	0.042	0.003	0.113	0.144	0.351	0.114	
1,2,3,6,7,8-HxCDD	0.030	0.014	0.099	0.013	0.206	0.274	0.756	0.269	
1,2,3,7,8,9-HxCDD	0.018	0.012	0.081	0.008	0.160	0.167	0.568	0.191	
1,2,3,4,6,7,8-HpCDD	0.116	0.111	0.361	0.146	1.031	0.696	2.424	0.656	
OCDD	0.228	0.242	0.432	0.271	1.690	0.490	2.372	0.513	
Total PCDDs	0.438	0.389	1.114	0.442	3.386	2.189	6.982	2.180	
2,3,7,8-TeCDF	0.084	0.175	0.224	0.006	0.447	1.129	5.199	2.159	
1,2,3,7,8-PeCDF	0.065	0.111	0.144	0.006	0.420	1.084	1.528	0.925	
2,3,4,7,8-PeCDF	0.091	0.133	0.162	0.010	0.655	1.331	1.766	1.499	
1,2,3,4,7,8-HxCDF	0.062	0.080	0.126	0.010	0.432	0.908	1.151	0.433	
1,2,3,6,7,8-HxCDF	0.055	0.085	0.140	0.010	0.452	0.921	0.987	0.369	
1,2,3,7,8,9-HxCDF	BD ^c	BD ^c	0.007	BD ^c	0.040	0.046	0.106	0.019	
2,3,4,6,7,8-HxCDF	0.047	0.105	0.155	0.013	0.523	0.661	1.154	0.331	
1,2,3,4,6,7,8-HpCDF	0.112	0.186	0.307	0.032	0.983	1.278	2.324	0.355	
1,2,3,4,7,8,9-HpCDF	0.019	0.032	0.038	0.006	0.173	0.213	0.221	0.049	
OCDF	0.059	0.118	0.247	0.032	0.426	0.331	1.349	0.236	
Total PCDFs	0.594	1.025	1.550	0.125	4.550	7.902	15.776	6.376	
Total PCDD/Fs (relative standard deviations %)	1.032 (17)	1.413 (17)	2.665 (27)	0.566 (65)	7.936 (17)	10.091 (35)	22.758 (63)	8.556 (46)	
PCDFs/PCDDs ratio	1.356	2.634	1.396	0.282	1.343	3.610	2.260	2.925	
Total PCDDs (ng TEQ/Nm ³)	0.030	0.013	0.0879	0.005	0.173	0.347	0.507	0.355	
Total PCDFs (ng TEQ/Nm ³)	0.075	0.119	0.157	0.010	0.550	1.102	1.846	1.131	
Total PCDD/Fs (ng TEQ/Nm ³)	0.105	0.132	0.245	0.015	0.723	1.449	2.353	1.487	
PCDFs/PCDDs TEQ ratio	2.500	9.154	1.786	1.886	3.179	3.176	3.641	3.186	

^a See Table 1 for APCDs installed in each plant.

^b Nm³ represent volume dry gas, standard conditions was corrected in 1 atm and 273 K.

^c Below detection limit.

been corrected by the oxygen content (18.0-20.5%). The actual sampling concentration multiplied by [(21-11%)/(21-X%)] is the corrected concentration by oxygen content. The 11% is the corrected standard value and the *X* is actual oxygen content in the stack flue gas. The relative standard deviations (from 17% to 65%) for total PCDD/Fs are provided to reflect the sample variations among three to five samples. For aluminum ingot smelter samples, the highest concentration for the PCDD/F congeners is OCDD (0.23–0.43 ng/Nm³). For secondary ALS smelter samples, the highest concentration for the PCDD/F con-

geners is 2,3,7,8-TeCDF (2.16–5.20 ng/Nm³), except for S1 and S2 plants where OCDD (1.69 ng/Nm³) and 2,3,4,7,8-PeCDF (1.33 ng/Nm³), respectively. The distribution of PCDD/F congeners for each smelter plant is different, particularly between aluminum ingot smelters and conventional secondary ALS, apparently due to the difference in raw materials. For example, the second highest concentrations were 1,2,3,4,6,7,8-HpCDD, except for P2, where 1,2,3,4,6,7,8-HpCDF (Fig. 1a–d), whereas for conventional secondary ALS the second highest congeners were 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF,



Fig. 1. Seventeen 2,3,7,8-PCDD/F congener profiles: (a) P1 in stack flue gas (P1, n = 3), (b) P2 in stack flue gas (P2, n = 3), (c) P3 in stack flue gas (P3, n = 3), (d) P4 in stack flue gas (P4, n = 3), (e) S1 in stack flue gas (S1, n = 3), (f) S2 in stack flue gas (S2, n = 5), (g) S3 in stack flue gas (S3, n = 3), and (h) S4 in stack flue gas (S4, n = 3).

Table 3		
Comparison of the mean PCDD/F concentrations in stack flu	e gases from the present study and	others
$DCDD/E_{\pi}(\pi - N_{\pi}^{3})$	TEO(r - TEO(Nr - 3))	ADCD-

	PCDD/Fs (ng/Nm ³)	TEQ (ng TEQ/Nm ³)	APCDs	Reference
P1	1.03	0.11	Cyclone and wet scrubber	This study
P2	1.41	0.13	Cyclone and cartridge filter	This study
P3	2.67	0.25	Baghouse filter and pack-scrubber	This study
P4	0.57	0.015	Cyclone and baghouse filter	This study
S1	7.94	0.72	Cyclone and baghouse filter	This study
S2	10.1	1.45	Cyclone and baghouse filter	This study
S3	22.8	2.35	Cyclone and baghouse filter	This study
S4	8.56	1.49	Cyclone and baghouse filter	This study
Secondary ALS	210	2.97	Baghouse filter	[8]
	99.6	10.6	Baghouse filter	[9]
	28	3.3	Baghouse filter or/and cyclone	[10]
	99.5	9.02	_	[11]
		Up to 21.5	_	[12]
		2-6	-	[13]

1,2,3,4,6,7,8-HpCDD, and 2,3,4,7,8-PeCDF for S1, S2, S3, and S4, respectively (Fig. 1e–h). As for the total PCDD/F concentrations, the four secondary ALS yield much higher amounts than aluminum ingot smelters, or 7.94–22.76 ng/Nm³ versus 0.57–2.67 ng/Nm³ (Table 2), due to a large percentage of waste or recycled aluminum being used in the former.

Note that the PCDFs/PCDDs ratios (1.3-3.6) are all greater than 1, except for P4 (0.282), indicating the de novo mechanisms for the PCDD/F formation. In terms of TEQ, the total PCDD/Fs ranged from 0.72 to 2.35 ng TEQ/Nm³ for secondary ALS and 0.015 to 0.245 ng TEQ/Nm³ for aluminum ingot smelters. Only the PCDD/F emission from S3 exceed the current standard for unclassified stationary PCDD/F emission (2.0 ng TEQ/Nm³ after January 2006) established by the Taiwan Environmental Protection Administration [6], which is certainly higher than the recommended standard proposed by the UN (<0.1 ng TEQ/Nm³) [7].

The mean concentrations of PCDD/Fs for the flue gas as well as those reported by others are summarized in Table 3. The comparisons among different studies must be made with care, since operating conditions such as raw materials, temperatures and APCDs employed are different. Nonetheless, the results from the present study, ranging from 0.015 to 0.25 ng TEQ/Nm³ in the aluminum ingot smelters, are much lower than secondary ALS smelters (0.72–2.35 ng TEQ/Nm³). However, those secondary ALS are still lower than others (3–21.5 ng TEQ/Nm³). The relatively high temperature operated in these smelters along with APCDs used may partially explain the lower PCDD/F emission. For example, the cyclone and filters were connected in series in the aluminum smelter plants and had high removal efficiency of PCDD/F.

3.2. APCD efficiency

As mentioned before, gas samples were taken before the wet scrubber (P1) and cartridge filter (P2) and those of the stack flue gases at the same time to evaluate the efficiencies of these APCDs. The actual PCDD/F mass was used to determine APCD efficiencies (Table 4). Several observations can be made. First, for the wet scrubber system, there is a significantly adverse effect on PCDD/F removal. The mass for all PCDD/Fs except for two (2,3,7,8-TeCDF and 1,2,3,7,8-PeCDF) in fact increased. For example, 2,3,7,8-TeCDD and 1,2,3,6,7,8-HxCDF increased by 300% and 180%, respectively. In the P1 plant, the water (about 40° C) is continuously recirculated through the scrubber system for the removal of HCl and particulate. Unfortunately, the PCDD/F-contaminated water may transfer aqueous PCDD/Fs to the gaseous phase, resulting in increased PCDD/F concentrations in flue gas. This phenomenon has also been reported in the wet scrubber for municipal waste incinerator [14-17] and the removal efficiency of PCDD/Fs ranged from -25% to -5731%[15]. Previous studies described the phenomena as a memory effect, and the wet scrubber composed of plastic material enhanced PCDD/F adsorption/desorption. The adsorbed dioxins are then desorbed slowly and transferred to the outlet gas [15,17].

The PCDD/F mass comparison before and after the wet scrubber clearly indicates the change of the distribution of major congeners. For example, the major congener is 2,3,7,8-TeCDF before the wet scrubber and changes to OCDD after the scrubber (Figs. 1a and 2a). The significantly adverse impact is most for PCDDs, as total PCDDs increased up to 100%. For two PCDF congeners, approximately 77% and 45% reductions were observed for 2,3,7,8-TeCDF and 1,2,3,7,8-PeCDF, respectively. These reductions account for the overall 19% reduction in total PCDF mass. The exact reasons for the reduction of only these two congeners are unclear. However, the aqueous phase contains a high quantity of 2,3,7,8-TeCDF (average 15% of total PCDD/F 0.54 pg/L or 0.059 TEQ pg/L). In short, the wet scrubber in the P1 plant slightly increases both total PCDD/F and PCDD/F TEQ mass.

On the other hand, for the cartridge filter, there is a reduction of 51% and 52% for total PCDD/Fs and total PCDD/Fs TEQ, respectively. The capability of the cartridge filter in removing PCDD/F congeners, however, varies from 4% to 100%. The 100% reductions could be achieved for 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD. In general, the filter performance for PCDDs and PCDFs is the same (47–60%). For comparison with

Table 4	
Mean mass before the APCDs and the stack flue gas, and its reduction efficience	су

Sampling location	Aluminum ingot smelte	n ingot smelter								
	P1			P2						
	Before wet scrubber (sample size = 3)	Stack flue gas (sample size = 3)	Efficiency (%)	Before cartridge filter (sample size = 3)	Stack flue gas (sample size = 3)	Efficiency (%)				
PCDD/Fs (pg)										
2,3,7,8-TeCDD	0.5	1.8	-297	1.1	1.0	13				
1,2,3,7,8-PeCDD	BD ^a	4.3	-100	4.5	BD^{a}	100				
1,2,3,4,7,8-HxCDD	BD ^a	1.7	-100	3.7	BD^{a}	100				
1,2,3,6,7,8-HxCDD	BD ^a	5.0	-100	5.9	1.6	73				
1,2,3,7,8,9-HxCDD	BD ^a	3.2	-100	4.6	1.3	71				
1,2,3,4,6,7,8-HpCDD	9.5	19.6	-107	30.6	12.3	60				
OCDD	26.6	38.2	-44	56.3	26.8	52				
Total PCDDs	36.6	73.8	-102	106.7	43.0	60				
2,3,7,8-TeCDF	61.8	14.3	77	20.3	19.4	4				
1,2,3,7,8-PeCDF	20.2	11.1	45	17.3	12.3	29				
2,3,4,7,8-PeCDF	13.6	15.4	-13	30.1	14.8	51				
1,2,3,4,7,8-HxCDF	5.9	10.4	-76	18.2	8.8	51				
1,2,3,6,7,8-HxCDF	3.3	9.2	-182	19.8	9.4	53				
1,2,3,7,8,9-HxCDF	BD ^a	BD ^a	0	BD ^a	BD^{a}	0				
2,3,4,6,7,8-HxCDF	3.3	7.8	-139	28.2	11.6	59				
1,2,3,4,6,7,8-HpCDF	7.4	18.9	-157	46.9	20.6	56				
1,2,3,4,7,8,9-HpCDF	BD ^a	3.1	-100	7.2	3.5	52				
OCDF	7.9	9.9	-25	25.5	13.1	49				
Total PCDFs	123.4	100.1	19	213.5	113.4	47				
Total PCDD/Fs	160.0	173.9	-9	320.2	156.4	51				
PCDDs TEQ (pg)	0.6	5.2	-786	5.2	1.4	72				
PCDFs TEQ (pg)	15.3	12.6	18	25.1	13.2	48				
Total TEQ (pg)	15.9	17.8	-12	30.3	14.6	52				

^a Below detection limit.

other baghouse filters, the PCDD/F TEQ reduction from this study (52%) is within the same order of magnitude reported by others, or 21% [18] and 84-93% [8,19].

For the P2 plant, fly ash was also collected and analyzed for PCDD/Fs. The mean TEQ value was 0.011 ng TEQ/g, much lower than others, e.g., 5.59 ng TEQ/g for secondary ALS in Taiwan [9] and 0.194 ng TEQ/g in a municipal solid waste incinerator [18]. Since the total flue gas PCDD/F concentrations (both particulate and gaseous phases) are extremely low, its contents in aqueous phase in P1 plant and fly ash in P2 plant are also expected to be low.

In addition, the flue gas sample of the S1 plant was also taken after the PAC injection (2 kg/h or 110 mg/Nm³) to see if there was any PCDD/F reduction in the stack flue gas. The result of total PCDD/Fs TEQ after PAC injection is 0.201 ng/Nm³ (corrected for oxygen content). Indeed, the PAC injection significantly reduces the PCDD/F emission (0.723 ng/Nm³ before PAC injection). The 70% reduction is within the same magnitude of other PAC applications, e.g., 58% total TEQ reduction [20]. The results (not shown) further indicate a better performance for PCDFs, as reported by others [19–21]. Since PAC is for removing the gaseous phase of PCDD/Fs, and the majority of PCDD/Fs is in gaseous phase [22], better PCDF removal by PAC is expected.

3.3. PCDD/F emission rate and factors

The determination of emission factors is necessary to estimate the PCDD/Fs inventory and to assist the regulatory agencies to develop an appropriate control strategy to reduce overall emissions. The emission rates presented in this study were calculated based on the actual PCDD/F emissions (not corrected for oxygen content). The results of both emission rates and corresponding emission factors (based on both feedstock and product) are summarized in Table 5. Since the PCDD/F concentration of the P3 plant is much higher than those of the aluminum ingot smelters (2.67 ng/Nm³ versus 0.57–1.41 ng/Nm³, Table 2), the total PCDD/F emission rate of P3 is expected to be much higher than others, or 1.10 µg TEQ/h versus 0.096–0.335 µg TEQ/h (Table 5). However, the emission factors for the aluminum ingot smelters were between 0.021 and 0.402 µg TEQ/tonne-feedstock), and the average emission factor was 0.237 µg TEQ/tonne-feedstock. As for secondary ALS, the S3 plant exhibits a higher PCDD/F emission concentration (22.76 ng/Nm^3), and its emission rate is higher than others (5.45 µg TEQ/h versus 1.66-4.38 µg TEQ/h. The emission factor of the S1 plant (11.3 µg TEQ/tonne-feedstock) is much higher than others, due to a much lower feeding rate of raw materials.



Fig. 2. Seventeen 2,3,7,8-PCDD/F congener profiles: (a) P1 before APCD (P1, n=3), (b) P2 before APCD (P2, n=3), and (c) S1 with PAC injection in stack flue gas (S1, n=3).

The effect of the type of the raw materials on emission rate is clearly shown in Table 5; the average emission factor of four secondary ALS (4.65 μ g TEQ/tonne-feedstock) is much higher than that of the aluminum ingot smelters (0.237 μ g TEQ/tonne-feedstock), or 20 times higher based on either raw materials or product. This clearly indicates the importance of pre-cleaning of waste aluminum in reducing PCDD/F emission. However, the average emission factor for four alu-

minum ingot smelters (0.237 μ g TEQ/tonne-feedstock) is near the secondary ALS range (0.26 ng TEQ/kg charge material [3]). As for four secondary ALS, the emission factors lie within the range of other data shown in Table 6. Besides, the wide variation of PCDD/F emission factor from the secondary ALS is attributed to different types of feeding material, furnace operation temperature and APCDs. Nonetheless, the emission factors are still higher than the average (0.0939 μ g TEQ/tonne-

Table 5

Mean PCDD/F emission rates and emission factors of stack flues gases for the aluminum ingot smelter and secondary ALS

	Aluminum	n ingot smelter			Secondary ALS			
	P1	P2	P3	P4	S1	S2	\$3	S4
Emission rate								
Total PCDD/Fs (µg/h)	3.26	1.03	11.9	4.89	19.4	11.6	52.7	25.3
Average (µg/h)		5.27			27.3			
Total PCDD/Fs (µg TEQ/h)	0.335	0.0959	1.10	0.128	1.77	1.66	5.45	4.38
Average (µg TEQ/h)		0.415			3.32			
Emission factor (feedstock)								
Total PCDD/Fs (µg/tonne)	1.56	3.89	4.36	0.814	124	28.8	14.7	9.34
Average (µg/tonne)		2.66			44.2			
Total PCDD/Fs (µg TEQ/tonne)	0.161	0.363	0.402	0.021	11.3	4.14	1.52	1.62
Average (µg TEQ/tonne)		0.237			4.65			
Emission factor (product)								
Total PCDD/Fs (µg/tonne)	1.63	4.11	4.79	0.959	141	32.6	15.8	9.73
Average (µg/tonne)		2.87			49.8			
Total-PCDD/Fs (µg TEQ/tonne)	0.167	0.383	0.441	0.025	12.9	4.70	1.63	1.69
Average (µg TEQ/tonne)		0.254			5.23			

 Table 6

 Comparison of emission factors in present study with others

	Total PCDD/Fs TEQ (µg TEQ/tonne- feedstock)	Total PCDD/Fs TEQ (µg TEQ/tonne- product)	Reference
P1	0.161	0.167	This study
P2	0.363	0.383	This study
P3	0.402	0.441	This study
P4	0.021	0.025	This study
S1	11.3	12.9	This study
S2	4.14	4.70	This study
S3	1.52	1.63	This study
S4	1.62	1.69	This study
Secondary ALS	0.01-167	3.22-12.95	[2]
	37	-	[10]
	50.1	-	[11]
	-	0.5–150	[23]

waste) from ten municipal solid waste incinerators in Taiwan [24].

3.4. Annual PCDD/F emissions

The mean emission factors (0.254 and 5.23 µg TEQ/tonneproduct for the aluminum ingot smelters and secondary ALS, respectively), along with the quantity of the aluminum product generated in Taiwan, were used to determine the PCDD/F inventory for secondary aluminum smelters in Taiwan. Out of an annual 229,000 tonnes of aluminum alloys/ingots produced from 267 ALS plants [3,25], it is estimated that 59,500 tonnes (25%) are from aluminum ingot smelters and the remainder from secondary ALS. Consequently, the total annual emissions of PCDD/Fs TEQ from aluminum ingot smelters and secondary ALS would be 0.015 and 0.886 g TEQ/year, respectively, with a total 0.901 g TEQ/year. Again, the effect of the impurities in raw materials on PCDD/F inventory is apparent; PCDD/Fs from secondary ALS were approximately 60 times higher that those of aluminum ingot smelters. Consequently, more attention should be paid to the emission reduction of PCDD/Fs for the secondary ALS, including addition of a secondary burner, installation of additional APCDs and pre-cleaning of raw materials.

4. Conclusions

Four plants each from secondary ALS and aluminum ingot smelters were selected, total PCDD/F emission monitored and the results compared. In all eight plants the ratios of PCDFs/PCDDs are nearly greater than 1. The four secondary ALS yield much higher PCDD/Fs than the aluminum ingot smelters, or 7.94–22.76 ng/Nm³ versus 0.57–2.67 ng/Nm³, due to a large percentage of waste or recycled aluminum used in the former and over 50% ingot used in the latter. Nonetheless, the PCDD/F emission is generally lower as compared to other literature data, probably due to relatively higher temperatures used (750–900 °C). Further, for aluminum ingot smelter samples, the highest concentration for the PCDD/F congeners is OCDD (0.23–0.43 ng/Nm³). For secondary ALS smelter samples, the highest concentration for the PCDD/F congeners is 2,3,7,8-TeCDF (2.16–5.20 ng/Nm³), except for the S1 and S2 plants where OCDD (1.69 ng/Nm³) and 2,3,4,7,8-PeCDF (1.33 ng/Nm³), respectively. The distribution of PCDD/F congeners for each smelter plant is different, particularly between aluminum ingot smelters and conventional secondary ALS, again due to the difference in raw materials.

For APCDs, the wet scrubber system in the P1 plant actually increases the PCDD/F mass, due to the continuous recycling of the contaminated water through the scrubber system. On the other hand, for another ingot P2 plant equipped with a cartridge filter, there is a significant reduction in PCDD/F TEQ (52%). The PAC injection at 2 kg/h (110 mg/Nm³) in the S1 plant reduced 70% of the total PCDD/Fs.

The PCDD/F emission factor is related to either raw materials used or product produced, and the average emission factor of four secondary ALS is much higher than that of aluminum ingot smelters, or approximately 20 times higher based on either raw materials or product. The total PCDD/F emission inventory from about 267 ALS plants is projected to be 0.015 and 0.886 g TEQ/year, respectively, for aluminum ingot smelters and secondary ALS. To further reduce the PCDD/F emission from secondary ALS, the installation of a secondary burner, additional APCDs and pre-cleaning of raw materials should be seriously considered.

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