THE BEHAVIOR OF DIOXIN FORMATION IN A MSWI DURING IMPROVEMENT ENGINEERING

Edward Ma[1], M. S. Hsu[1], P. S. Cheng[1], U. Chou[1], C.N. Chen[2], and Y. C. Ling[1]

[1]Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.
[2]National I-Lan Institute of Technology, I-Lan,Taiwan, R.O.C.

Introduction

This research was aimed to assist a municipal solid waste incineration plant to sample and to analyze the dioxin content in slag and fly ash during dioxin improvement engineering. The major components of the original APCD were using ESP and wet scrubber[1]. However the dioxin emission in stack gas exceeded the regulation permitted level (i.e. 0.1 ng-TEQ/Nm^3). Therefore, a SCR unit was installed after the ESP device. The research results were used to establish the database of dioxin content and characteristic in slag and fly ash, to understand the incineration and operation conditions, to investigate the distribution and movement of dioxins in the incineration process, to evaluate the removal efficiency of newly installed SCR, and to reveal the relationship between dioxin formation and operational parameters.

Methods and Materials

Two samplings were conducted at August and September on 2001, respectively. Four slag samples, and four fly ash samples from the super-heater, waste heat recovery boiler, economizer (EM), and electrostatic precipitator (ESP) were collected at each time. A total of forty samples were collected. One gas sample each was also collected at the entrance and exit of the selective catalytic reactor (SCR). In order to estimate the annual fly ash output, the generation rate at each sampling point was evaluated independently. The analytical procedure referred ROC EPA NIEA A808.70B method and US EPA Method 1613B to analyze the dioxin content in gas and ash samples. All data fulfill the QA/QC requirements. Instrumental analysis was carried out with a HP 5890 series high resolution gas chromatography coupled with a VG Autospec Ultima high resolution mass spectrometer (HRGC/ HRMS). The analysis of PCDD/Fs congener was performed with a DB5-MS capillary column (60 m × 0.25 mm i.d. × 0.25µm film thickness)

Results and Discussion

The analytical results of first (Aug. 6^{th}~7^{th}, 2001) and the second (Sep. 4^{th}~5^{th}) sampling were listed in table 1 and table 2. An average of dioxin content in slag is 4±1 pg-TEQ/g dm. There wasn't significant difference between two sampling results for slag samples that indicated the dioxin level in slag didn't affect by the operational conditions that much. A similar phenomenon was observed at super-heater, 13±8 pg-TEQ/g dm and 15±15 pg-TEQ/g dm, respectively. However, for waste heat recovery boiler (39±18 pg-TEQ/g dm and 68±64 pg-TEQ/g dm), EM (708±143 pg-TEQ/g dm and 1217±692 pg-TEQ/g dm) and ESP (4689±1067 pg-TEQ/g dm and 11106±3062 pg-TEQ/g dm), there exists a significant difference. Obviously, the second sampling is significantly higher than the first one. According to the operating condition records provided by the facility concerned, during the first sampling period, the incinerator was under normal operating status. For the second sampling, it was

Table 1: First analytical result of slag and fly ash samples

date	name	weight (g)	PCDD TEQ conc. (pg TEQ/g dm)	PCDF TEQ conc. (pg TEQ/g dm)	PCDD/PCDF	PCDD+PCDF TEQ conc. (pg TEQ/g dm)
2001/8/6 15:10~18:10	slag	2.00	1.39	4.25	0.33	5.64
2001/8/7 09:15~12:15	slag	2.11	0.98	4.08	0.24	5.06
2001/8/7 12:15~15:15	slag	1.99	0.96	2.41	0.40	3.37
2001/8/7 15:15~18:15	slag	2.08	0.78	2.79	0.28	3.57
2001/8/6 15:10~18:10	super-heater	2.10	1.38	5.84	0.24	7.22
2001/8/7 09:15~12:15	super-heater	2.02	2.8	12.7	0.22	15.5
2001/8/7 12:15~15:15	super-heater	1.99	6.7	18.0	0.37	24.7
2001/8/7 15:15~18:15	super-heater	2.03	2.1	10.4	0.20	12.5
2001/8/6 15:10~18:10	wasteheat recovery boiler	2.02	15.7	47.7	0.33	63.4
2001/8/7 09:15~12:15	wasteheat recovery boiler	1.99	12.8	27.6	0.46	40.4
2001/8/7 12:15~15:15	wasteheat recovery boiler	2.03	10.6	22.5	0.47	33.1
2001/8/7 15:15~18:15	wasteheat recovery boiler	1.99	6.1	14.1	0.43	20.2
2001/8/6 15:10~18:10	economizer	1.99	177	349	0.51	526
2001/8/7 09:15~12:15	economizer	2.03	276	550	0.50	826
2001/8/7 12:15~15:15	economizer	1.99	296	525	0.56	821
2001/8/7 15:15~18:15	economizer	1.97	246	414	0.59	660
2001/8/6 15:10~18:10	ESP	2.02	1360	1826	0.74	3186
2001/8/7 09:15~12:15	ESP	2.02	2263	3243	0.70	5506
2001/8/7 12:15~15:15	ESP	1.99	1794	2879	0.62	4673
2001/8/7 15:15~18:15	ESP	1.99	2292	3098	0.74	5390

Table 2: Second analytical result of slag and fly ash samples

date	name	weight (g)	PCDD TEQ conc. (pg TEQ/g dm)	PCDF TEQ conc. (pg TEQ/g dm)	PCDD/PCDF	PCDD+PCDF TEQ conc. (pg TEQ/g dm)
2001/9/4 09:00~12:00	slag	10.55	0.72	3.39	0.21	4.11
2001/9/4 12:00~15:00	slag	10.73	0.67	3.02	0.22	3.69
2001/9/4 15:00~18:00	slag	10.12	0.54	2.38	0.23	2.92
2001/9/5 09:00~12:00	slag	10.52	1.07	4.38	0.24	5.45
2001/9/4 09:00~12:00	super-heater	5.19	1.07	6.60	0.16	7.67
2001/9/4 12:00~15:00	super-heater	5.15	1.29	9.99	0.13	11.3
2001/9/4 15:00~18:00	super-heater	5.37	0.82	4.06	0.20	4.88
2001/9/5 09:00~12:00	super-heater	5.01	4.95	32.07	0.15	37.0
2001/9/4 09:00~12:00	wasteheat recovery boiler	0.98	10.2	24.7	0.41	34.9
2001/9/4 12:00~15:00	wasteheat recovery boiler	1.00	7.6	18.5	0.41	26.1
2001/9/4 15:00~18:00	wasteheat recovery boiler	1.12	11.6	36.6	0.32	48.2
2001/9/5 09:00~12:00	wasteheat recovery boiler	1.11	50.6	111.2	0.46	162
2001/9/4 09:00~12:00	economizer	0.40	457	794	0.58	1250
2001/9/4 12:00~15:00	economizer	0.41	279	405	0.69	684
2001/9/4 15:00~18:00	economizer	0.40	269	481	0.56	750
2001/9/5 09:00~12:00	economizer	0.58	777	1407	0.55	2184
2001/9/4 09:00~12:00	ESP	0.11	4893	5226	0.94	10118
2001/9/4 12:00~15:00	ESP	0.11	5780	5134	1.13	10915
2001/9/4 15:00~18:00	ESP	0.11	3945	4116	0.96	8061
2001/9/5 09:00~12:00	ESP	0.14	9296	6034	1.54	15330

under a start-up period. At 23:00 Sep. 4th, the incinerator was forced to stop on the following days. During the start-up and stop period, a significant higher emission behavior was observed, this referred to the related literature[2]. When comparing the dioxin level through super-heater to ESP, dioxin concentration increased more than 10 times. Assume there wasn't transfer through gas phase to solid phase of dioxin content, the *de novo* synthesis obvious exists. When observe the normal operating condition against start-up, stop period, ESP had the largest degree of increase, EM had the second. This indicates that under a suitable temperature environment for *de novo* synthesis[3], the operating condition is a very important parameter for dioxin formation.

The dioxin content in fly ash has shown significant relationship with the temperature (Fig 1-1,1-2), which related to *de novo* synthesis after incineration, especially when passing through EM and ESP. The average dioxin contents in the fly ash were 4689, 9698 and 15330 pg-TEQ/ g dm, respectively, on Aug. 6th~7th, Sep. 4th and Sep. 5th. The annual dioxin emission from the fly ash is about 8.02 g-TEQ/ year.

The results also show that the removal efficiency of the SCR is 93% and 98% (Fig 2), respectively. The dioxin emissions in stack gas were still higher than the regulatory level, nevertheless. The high dioxin concentration, i.e., the solid phase, presented in the entrance gas to SCR might be the primary factor.

Acknowledgments

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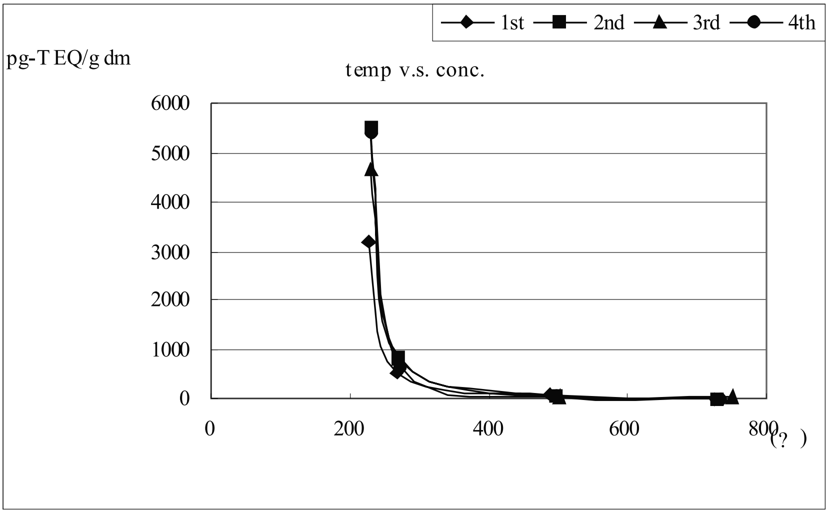

Figure 1-1. The relationship of temp with conc. of the first sampling

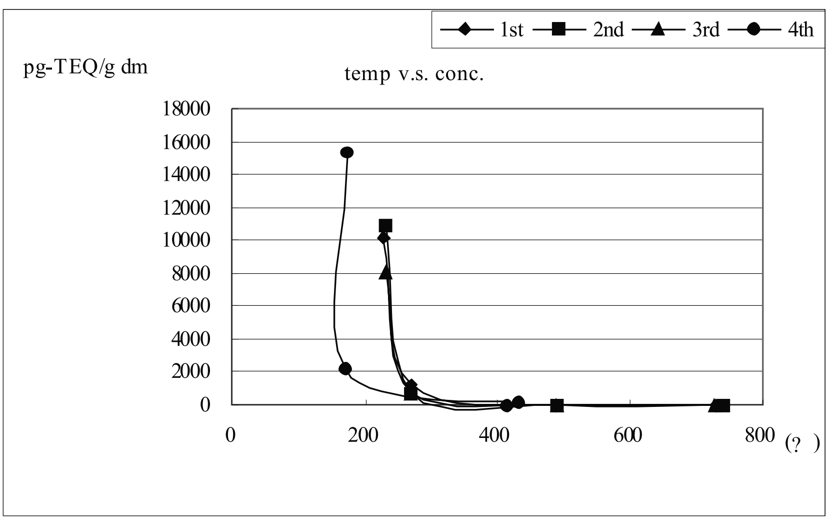

Figure 1-2. The relationship of temp with conc. of the second sampling

1st: super-heater
2nd: waste heat recovery boiler
3rd: economizer (EM)
4th: electrostatic precipitator (ESP)

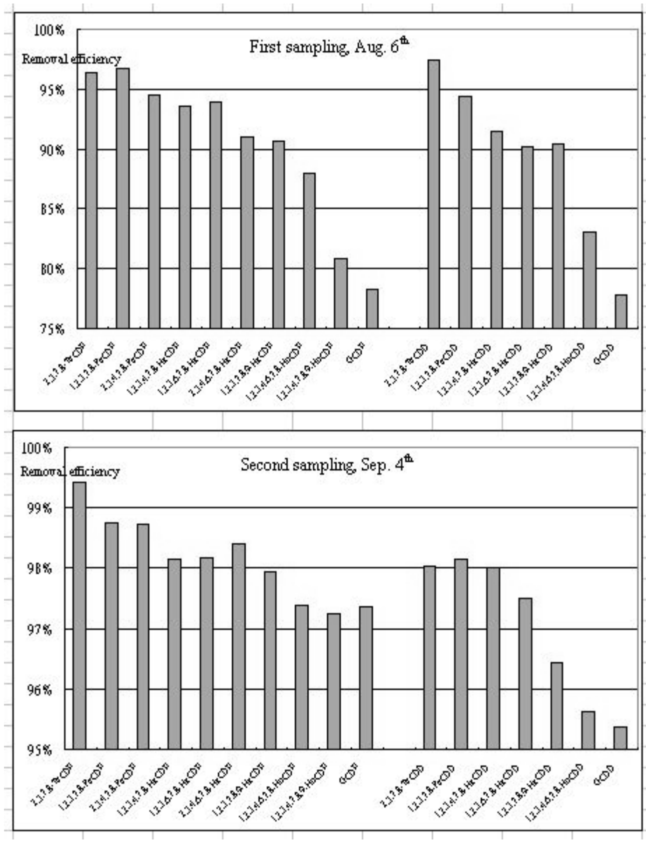

Figure 2. The SCR removal efficiency to each congener

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