THE DEGRADATION WAY OF PCDD/Fs DRUING THERMAL TREATMENT OF FLY ASH SAMPLES FROM MEDICAL WASTE INCINERATOR

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Introduction

MSW and MW incinerator plants is a mainly factitious source of dioxins in some developed cities in China, up to 2010, the capacity of the constructed MSW incinerators was 80,000 tons/day. Thermal treatment is an important way to dispose dioxins, which has been used widely to control Persistent Organic Pollutants (POPs).

Hagenmaier considered that low-temperature treatment had four key factors: (1) Inert atmosphere; (2) temperature is 250~400℃; (3) time is 1h; (4) Emission temperature must under 60℃[1]. Dioxins generate in gas phase, when using low-temperature treatment to heat fly ash. Adrian indicated that municipal solid waste incinerator fly ash was heated to 200℃~400℃ under a simulated flue gas for 4 days, PCDD/PCDF released into the exhaust gases, the maximum emission of PCDD/PCDF occurred at 350℃[2]. At the process of thermal treatment Chen also found PCDD/Fs in gas phase, and the major congener was OCDD, by contract, low chlorinated congeners were the major products in solid phase[3]. Degradation includes three ways. If degree of chlorination reduced, dechlorination may occur; If total mass concentration of PCDD/Fs reduced, decomposition may occur; If PCDD/Fs released to gas phase from fly ash, physical thermal desorption may occur[4-6]. Up to date, the research about using low-temperature thermal treatment to dispose medical waste incinerator fly ash is singularly, and degradation way of PCDD/Fs was not concluded completely, so the aim of this study is to discuss three degradation ways about MW fly ash carefully.

Materials and methods

Two kinds of fly ash (AG and BG) were researched, which came from hazardous waste rotary kiln incineration. AG sampled after fabric filter with activated carbon spray and BG sampled in incinerator pipe before fabric filter, their elemental composition and characteristics were listed in Table 1.

Table 1 The major components and characteristics of fly ash

Item	AG	BG	Item	AG	BG	Item	AG	BG
C(wt%)	10.69	4.80	N(wt%)	0.12	0.39	As(ppm)	1.26	1.71
H(wt%)	1.02	2.10	S(wt%)	0.23	1.16	Al(wt%)	0.08	0.11
O(wt%)	18.95	20.17	Cl(wt%)	6.12	8.35	Ni(ppm)	10.17	8.42
Ca(wt%)	1.38	2.64	Hg(ppm)	36.42	89.56	Cu(wt%)	0.08	0.12
Na(wt%)	10.36	4.53	Fe(wt%)	0.11	0.74	Zn(wt%)	0.42	0.39
K(wt%)	0.46	0.33	Cr(ppm)	ND	ND	Cd(ppm)	12.38	16.57

Installation of thermal treatment was showed as Fig 1, experiments were operated on a small-scale horizontal tube furnace with quartz tube as reactor. For keeping inert atmosphere, Using nitrogen as carrier gas which controlled by gas flow meter. Flue gas gathered by XAD-2 Polymeric resin and toluene. After experiment, thermal treated fly ash was collected to a glass container after cooled, exhaust tube of the reactor and traps were washed out with toluene and acetone, washings were collected. Finally the installation was rinsed out before the next experiment. All samples were kept in sunless and dryness place, waiting for analysis. In this paper,

PCDD/Fs which came from XAD-2, toluene and washings regarded as exhaust gases resultant, PCDD/Fs in treated fly ash regarded as solid phase resultant. The experiment conditions were showed as Table 1.

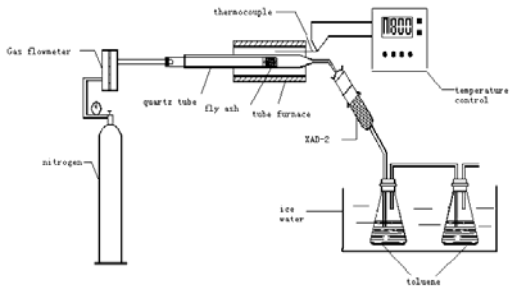

Fig.1 Installation of thermal treatment on fly ash Under nitrogen atmosphere

Table 1 The experiment condition

No	Sample	Time	Temperature	Gas flue	No	Sample	Time	Temperature	Gas flue
AG-1		90min	250℃		BG-1		90min	250℃	
AG-2		45min			BG-2		45min		
AG-3	After	90min	300℃		BG-3	Before	90min	300℃	
AG-4	fabric	45min		1L/min	BG-4	fabric	45min		1L/min
AG-5	filter 1g	90min	350℃		BG-5	filter 1g	90min	350℃	
AG-6		45min			BG-6		45min		
AG-7		90min	400℃		BG-7		90min	400℃	
AG-8		45min			BG-8		45min		

Pretreatment of PCDD/Fs was conducted according to the EPA method 1613 (US EPA, 1994). The analysis was performed by HRGC/HRMS.

Results and discussion

Dechlorination/hydrogenation reactions

Dechlorination of PCDD/Fs can occurred at the process of low temperature thermal treatment under nitrogen atmosphere which has been approved by many researchers[7,8], the degree of chlorination can be used to explore the process of dechlorination and degree of chlorination can be calculate by follows: $Cl_d = \frac{\sum C_j \times n_j}{C} (j = 4,5,\cdots 8)$ (C_j —the concentration of PCDD/Fs congener; n_j —the number of chlorine atoms of PCDD/Fs congener; C —the total concentration of PCDD/Fs).

The degree of chlorination of sample AG and BG was changed by different reaction time which showed as Fig2 and Fig3, the degree of chlorination of PCDDs was higher than PCDFs induced the toxicity of PCDFs was higher than PCDDs, and prolonged reaction time might arose dechlorinate phenomena, which accorded with the total TEQ concentrations became higher.

Dechlorinate trend was also influenced by temperature. When temperature at 250℃, both Sample AG and BG occurred dechlorination, the same result was reported by Peng, he found that heated fly ash under nitrogen atmosphere below 300℃, the concentration of high-chlorinated congeners decreased obviously[9]. At 300℃, AG still present dechlorinate trend, but the degree of chlorination of BG rose. At 350℃, degree of chlorination was

opposite from 300℃ for AG and BG. The results might explain by PCDD/Fs synthesize, because 300~350℃ was the optimal temperature for de novo reaction. In this research, two samples had different physical and chemical properties, it may induced they had different optimal synthesis temperature. Chen found chlorination existed in de novo reaction, under 350℃, gas flue was 300ml/min, reaction time was 30min, O_2/N_2=1/9, high-chlorinated isomers were main products[15], it may explain why chlorination increased at 300℃ or 350℃. Most PCDD/Fs decomposed at 400℃, use degree of chlorination depict dechlorinate trend was not precision[15].

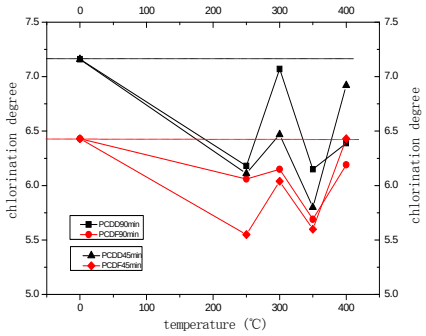

Fig.2 The degree of chlorination of PCDD/Fs in fly ash about Sample BG

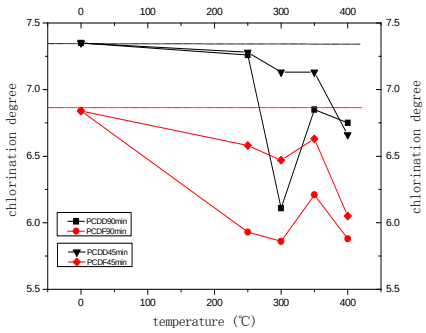

Fig.3 The degree of chlorination of PCDD/Fs in fly ash about Sample AG

Physical desorption reactions

Physical desorption is another way occurred in thermal treatment which made PCDD/Fs transfer from fly ash to exhaust gases. The experiment data was showed as Table2, the first parameter describe how much PCDD/Fs transfer from solid phase to gas phase; the second parameter describe after thermal treatment the distribution of PCDD/Fs in gas phase and solid phase; the third parameter describe I-TEQ of PCDD/Fs transfer condition by comparing gas phase and solid phase. First and third parameter could prove physical desorption exist in thermal treatment, they also showed the relationship between time/temperature and desorption ratio, the desorption ratio of sample AG usually greater than BG, when heating time was 90min desorption ratio was greater than 45min, and with increasing temperature the desorption ratio first increased then decreased, The maximum desorption rate occurred at 350℃, followed by 300℃, Peng found under flowed nitrogen atmosphere, used thermal treatment to decompose dioxins existed in fly ash, At 350℃ the TEQ of PCDD/Fs in gas phase was 25.7 TEQ-pg/g, which was higher than other temperatures[9]. It is worth to notice 350℃ was not only the important temperature for thermal treatment under nitrogen atmosphere, but also for simulated flue gas, Adrian investigated municipal solid waste incinerator fly ash by heating the ash to between 200 and 400℃ under a simulated flue gas for four days reaction time，maximum desorption occurred at 350℃, with the equivalent of nearly eight times the total PCDD/Fs concentration of the original fly ash[3].

Table 2 desorption ratio of dioxins in gas phase after desorption

Temp (℃)	**Time (min)**	$\frac{[PCDD/Fs]_{De}}{[PCDD/Fs]_{Or}}(\%)$		$\frac{[PCDD/Fs]_{De}}{[PCDD/Fs]_{Treated+desorbed}}(\%)$		$\frac{I-TEQ_{Desorbed}}{I-TEQ_{Original}}(\%)$	
		BG	**AG**	**BG**	**AG**	**BG**	**AG**
250℃	90min	0.06	0.23	0.85	0.99	0.10	0.76
	45min	0.04	0.02	0.75	0.75	0.06	0.05

300℃	90min	0.08	0.39	0.36	0.90	0.13	0.75
	45min	0.12	0.11	0.88	0.77	0.09	0.31
350℃	90min	0.14	0.63	0.93	0.65	0.29	3.03
	45min	0.06	0.43	0.70	0.83	0.16	0.75
400℃	90min	0.14	0.22	1.00	0.93	0.19	0.47
	45min	0.04	0	0.83	0.41	0.08	0.01

Destruction reactions

Usually, if the total concentration of PCDD/Fs (include PCDD/Fs in gas phase and treated fly ash) decreased can prove destruction reaction occurred. Weber researched the dechlorinate and destroy of PCDD/Fs, and PCB which came from Fluidized bed incinerator using $Ca(OH)_2$ spray and a stoker incinerator without $Ca(OH)_2$. He found dechlorination and destruction may occur, on both types of fly ash, and were completed at 380℃ within one hour under oxygen deficient conditions in the laboratory[10]. In this paper, the total concentration of PCDD/Fs decreased at different conditions, especially at 250℃ and 400℃, compare with dechlorination, destruction was obviously and was the main reaction. But dechlorination was the main reaction for sample AG at 300℃ and for sample BG at 350℃. Generally speaking, at different conditions, different reaction dominate the reaction process, the result was decided by the competition of various reaction.

Table 3 Total degradation efficiency of dioxin after thermal treatment

		250℃	300℃	350℃	400℃
BG	45min	94.2%	70.7%	92.1%	95.5%
	90min	93.0%	78.2%	85.1%	86.3%
AG	45min	97.0%	85.6%	48.5%	99.4%
	90min	77.1%	59.4%	3.9%	76.7%

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References:

1. Hagenmaier H, Kraft M, Brunner H, Haag R. (1987); *Environ. Sci. Technol*. 21: 1080–84.
2. Chen T. (2006); *Degree thesis*
3. Cunliffe AM, Williams PT. (2007); *Chemosphere*. 66: 1146–52.
4. Misaka Y, Abe T, Takeuchi K, Ohba K, Sawabe K, Shobatake K. (2006); *Chemosphere*. 65: 419–26.
5. Weber R, Sakurai T, Hagenmaier H. (1999); *Applied Catalysis B: Environmental*. 20: 249–56.
6. Lundin L, Marklund S.(2005); *Environ. Sci. Technol*. 39: 3872–77.
7. Stach J, Grabic R. (2000); *Chemosphere.* 41: 1881–87.
8. Song GJ, Kim SH, Seo YC, Kim SC. (2008); *Chemosphere.* 71: 248–57.
9. Peng Z. (2007); *Degree thesis.*
10. Weber R, Nagai K, Nishino J, Shiraishi H, Ishida M, Takasuga T, Konndo K, Hiraoka M. (2002); *Chemosphere*. 46: 1247–53