DECHLORINATION TECHNIQUES OF PCDDS AND PCDFS IN FLY ASH FROM MUNICIPAL REFUSE INCINERATION PLANTS

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Abstrakt

Two real application systems, the continuous heating treatment and solidifcation techniques were newly developed in order to dechlorinate PCDDs and PCDFs in EP fly ash from municipal refuse incineration plants. The former is able to dechlorinate PCDDs and PCDFs mostly at a treating rate of 100 kg/hr EP fly ash. The later is able to solidify EP fly ash as well as to dechlorinate mostly PCDDs and PCDFs. Therefore this method can be contributed to reducing its volume securing and stabilizing it.

Introduktion

Vogg et al. (1986) pointed out the decomposition of PCDDs and PCDFs through the heating treatment of fly ash in the air. We also obtained a promising result which is able to dechlorinate mostly through heating EP fly ash in the sealed stainless steel vessel under the condition ofmore than 500°C (hanai et al. , 1988). To confirm the possibility of practical application the continuous heating treatment system was designed, and tested in the laboratory under the same condition (OK et al. , 1989). On the basis of above preliminary tests, the two real application sytems which are the continuous heating and solidification treatments were newly developed and tested actually in the refuse incineration plants. In this study, the results of this test will be reported.

Experiment

Method 1 ; Continuous heating treatment

This system is shown in Fig.1. The fly ash emitted from the EP was introduced continuously into the screw conveyer, and its resistence time in the screw conveyer was about 15 minutes. This system is able to treat EP fly ash at a rate of 100 kg/hr. Analysis of the chlorinated compounds was carried out at a temperature of 400, 475, 500, 590 and 600°C, respectively.

Method 2 ; Solidification treatment

This sytem consits of a fly ash tank, a solidifying additive container, a mixer, a reactor, as well as heater and controler. The fly ash emitted from the EP was gathered in the fly ash tank, mixed with solidification additive (NaOH-5N) at a ratio of 20g to 5g, held in the reactor for 20 minutes under a reaction pressure of 300kg/cm^2, and then cooled to ambient temperature.

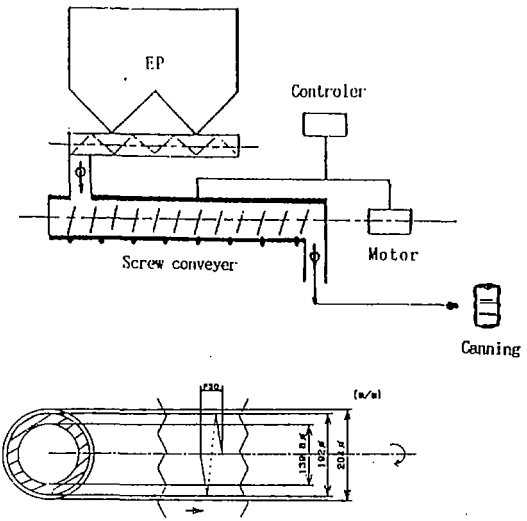

Fig 1. Schematic diagram of continuous heating treatment and a sectional plan of a srew conveyer

Fly ash sample preparation and PCDDs and PCDFs analysis

The EP fly ash in method 1 was sampled into a glass bottel at the inlet and outlet of the screw conveyer with respect to each temerature conditions, and the solidified sample obtained in method 2 was ground into powder. These samples were Soxhlet extracted with a 100ml toluene for 6 hours, concentrated to 1ml, and then analysed by GC/MS/SIM method. JEOL JMS-DX303HF equipped with HP 5890 GC was used for analysis. More details of the sample preparation and analysis method were described in the previous study (Hanai et al., 1985; Hanai et al., 1986; Hanai et. al., 1988)

Resuls and Discussion

Table 1 shows the results of method 1. A total amount of gas which is volatilized from EP fly ash during the test is almost negligible exept for just alittle bit of chlorobenzene (OK et al., 1989). PCdds and PCDFs are dechlorinated mostly above 590°C, in spite of that only very little chlorobenzene remains. As readily seen in Fig. 2, dechlorination occurs in PCDDs, PCDFs and chlorobenzene. In addition, the cleavage reaction in C-C and C-O may also take place. THe results of method 2 are shown in table 2. Considerable dechlorination is observed even at a much lower temperature compared with that of method 1. The chlorinated compounds are dechlorinated mostly at 400°C.

Table 1. Concentration of PCDDs, PCDFs and chlorobenzene by continuous heating treatment (ng/g)

Treatment Max Temp		400℃		475℃		500℃		590℃		600℃	
Compound		in	out	in	out	in	out	in	out	in	out
PCDDs	1CDD	3.45	3.24	10.40	4.31	2.69	19.20	8.90	nd<0.02	1.44	nd<0.02
	2CDD	nd<0.02	0.37	0.07	0.85	0.70	2.18	0.49	nd<0.02	nd<0.02	nd<0.02
	3CDD	nd<0.02	nd<0.02	nd<0.02	nd<0.02	1.39	1.84	nd<0.02	nd<0.02	nd<0.02	nd<0.02
	4CDD	14.30	14.00	20.10	20.70	30.00	30.40	11.00	nd<0.1	13.20	nd<0.1
	5CDD	30.40	25.00	28.70	34.00	51.70	39.40	24.00	nd<0.1	32.00	nd<0.1
	6CDD	42.00	39.00	31.00	31.50	51.90	33.50	37.10	nd<0.1	48.10	nd<0.1
	7CDD	116.00	117.00	80.70	68.70	125.00	72.20	106.00	nd<0.1	147.00	nd<0.1
	8CDD	91.00	88.40	65.50	44.30	86.00	43.50	83.80	nd<0.1	118.00	nd<0.1
	Total	297.00	287.00	226.00	204.00	349.00	242.00	271.00	nd	360.00	nd
PCDFs	1CDF	3.85	3.29	nd<0.02	3.71	6.83	16.60	nd<0.02	nd<0.02	2.21	nd<0.02
	2CDF	16.20	26.00	20.20	32.70	39.40	16.60	15.90	nd<0.02	14.80	nd<0.02
	3CDF	34.40	39.50	33.90	48.10	69.60	67.20	21.80	nd<0.02	30.80	nd<0.02
	4CDF	71.30	79.60	78.70	87.80	134.00	109.00	63.00	nd<0.1	72.80	nd<0.1
	5CDF	220.00	231.00	191.00	188.70	322.00	211.00	168.00	nd<0.1	226.00	nd<0.1
	6CDF	724.00	794.00	539.00	516.00	828.00	612.00	626.00	nd<0.1	709.00	nd<0.1
	7CDF	717.00	689.00	390.00	335.00	520.00	350.00	606.00	nd<0.1	719.00	nd<0.1
	8CDF	84.40	77.70	40.60	36.50	48.40	32.20	60.20	nd<0.1	108.00	nd<0.1
	Total	1870.00	1940.00	1290.00	1250.00	1970.00	1320.00	1460.00	nd	1880.00	nd
Chlorobenzene											
	3CLB	280.00	800.00	290.00	700.00	210.00	363.00	300.00	18.00	240.00	9.20
	4CLB	270.00	870.00	120.00	450.00	399.00	698.00	180.00	6.50	170.00	4.20
	5CLB	310.00	1080.00	210.00	610.00	420.00	597.00	270.00	1.40	440.00	7.50
	6CLB	200.00	600.00	120.00	270.00	164.00	212.00	190.00	6.70	330.00	3.80
	Total	1060.00	3350.00	740.00	2030.00	1190.00	1870.00	940.00	32.60	1180.00	24.70

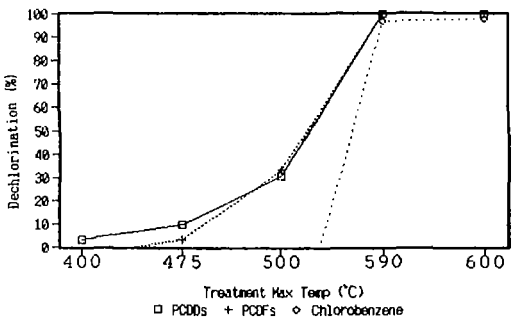

Fig. 2. PCDDs, PCDFs and chlorobenzene dechlorination ratio against temperature (Continuous heating treatment)

Fig. 2. PCDDs, PCDFs and chlorobenzene dechlorination ratio against temperature (Continuous heating treatment)

Table 2. Concentration of PCDDs,PCDFs and chlorobenzene by solidification treatment (ng/g)

Treatment Temp / Compound		the normal Temp	100℃	200℃	300℃	350℃	400℃
PCDDs	1CDD	nd<0.02	nd<0.02	nd<0.02	nd<0.02	32.00	nd<0.02
	2CDD	nd<0.02	nd<0.02	3.00	5.00	nd<0.02	nd<0.02
	3CDD	nd<0.02	nd<0.02	nd<0.02	3.00	nd<0.02	nd<0.02
	4CDD	nd<0.1	nd<0.1	11.00	44.00	nd<0.1	nd<0.1
	5CDD	nd<0.1	nd<0.1	nd<0.1	12.00	nd<0.1	nd<0.1
	6CDD	12.00	17.00	15.00	11.00	nd<0.1	nd<0.1
	7CDD	31.00	42.00	20.00	nd<0.1	nd<0.1	nd<0.1
	8CDD	45.00	65.00	27.00	nd<0.1	nd<0.1	nd<0.1
	Total	88.00	124.00	76.00	85.60	32.00	nd
PCDFs	1CDF	nd<0.02	nd<0.02	nd<0.02	22.00	83.00	nd<0.02
	2CDF	nd<0.02	4.00	3.00	120.00	110.00	nd<0.02
	3CDD	6.00	9.00	10.00	130.00	42.00	nd<0.02
	4CDD	7.00	62.00	44.00	170.00	15.00	nd<0.1
	5CDD	75.00	110.00	92.00	140.00	nd<0.1	nd<0.1
	6CDD	480.00	730.00	390.00	140.00	nd<0.1	nd<0.1
	7CDD	580.00	640.00	250.00	21.00	nd<0.1	nd<0.1
	8CDD	540.00	850.00	30.00	nd<0.1	nd<0.1	nd<0.1
	Total	1690.00	2410.00	819.00	743.00	250.00	nd
Chlorobenzene							
	3CLB	56.00	70.00	70.00	70.00	4.00	nd<0.02
	4CLB	120.00	180.00	110.00	17.00	2.00	nd<0.02
	5CLB	130.00	180.00	32.00	2.00	1.00	nd<0.02
	6CLB	120.00	100.00	10.00	0.40	0.30	nd<0.02
	Total	426.00	530.00	222.00	89.00	7.00	nd

Conclusion

The continuous heating and solidifying systems are shown to be promising methods for dechlorinating PCDDs, PCDFs and chlorobenzene and also to solidify EP fly ash. The fundamental problems in the municipal refuse incineration plants may be solved with the application of these new techniques.

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