

# FORMATION AND SOURCES II

## THE EFFECTS OF ORGANIC- AND INORGANIC-CHLORIDE IN MUNICIPAL SOLID WASTES ON DIOXINS FORMATION AND EMISSION

Noriaki Ishibashi<sup>1</sup>, Yoshinobu Yoshihara<sup>2</sup>, Kazuie Nishiwaki<sup>2</sup>, Shigenobu Okajima<sup>1</sup>, Masakatsu Hiraoka<sup>1</sup>, Haruhisa Shudo<sup>3</sup>

<sup>1</sup> Eco-Technology Research Center, Ritsumeikan University, 1-1-1 Nojihigashi Kusatsu, Shiga 525-8577, Japan

<sup>2</sup> Department of Mechanical Engineering, Ritsumeikan University, 1-1-1 Nojihigashi Kusatsu, Shiga 525-8577, Japan

<sup>3</sup> Global Environment Technology Department, New Energy and Industrial Technology Development Organization (NEDO), 1-1, 3-chome Higashi-Ikebukuro, Toshima-ku, Tokyo, 170-6028, Japan

### Introduction

Formation and emission of dioxins during incineration process of the municipal solid waste have been investigated by using the lab-scale fluidized-bed incinerator. In this study, the effects of organic and inorganic chloride in municipal solid wastes on dioxins formation and emission are examined. In the experiment artificial solid wastes (ASWs) were used to keep the experimental accuracy.

### Experimental Methods and Procedure

Figure 1 shows the schematics of lab-scale experimental incinerator, used in the experiments. The primary combustor, having 74mm in inner diameter and 1100mm in height, was made of quartz. The secondary combustor, having 100mm in inner diameter and 2000mm in height, was made of high-alumina. The temperatures of each combustor were controlled using electric heater and were kept 800°C and 900°C, respectively. The primary and secondary excess air ratios were set to identical 1.0. Feed rate of ASWs was 11g/min. Passing through the gas cooling section, the flue gas was cooled. The cooling section had 83mm in inner diameter and 3000mm in length. The temperature was controlled at 300°C by using water cooler and electric heater. The concentrations of O<sub>2</sub>, CO, NO<sub>x</sub> in the flue gas were continuously monitored (S5). Dioxins and HCl sampling were conducted for 2 hours at the locations S3 and S4, respectively. Table 1 shows experimental procedure. To eliminate the influence of the previous experiment, inner surface of the reactor, combustor and cooling section were cleaned up. The fluidized bed sand was renewed before R1, R2 and R4. In R2 and R4 experiments were carried out for 10 hours. Dioxin sampling was conducted at 4 and 10 hours from starting. In another runs experiments were carried out for 4 hours.

Paper powder (45%), wood powder (20%), flour (15%), PE powder (20%) were the main components used for the base ASW. To keep the Cl content as low as possible, unbleached paper, pine wood, salt free flour and virgin resin PE were chosen as the components. ASW2 and ASW3 had PVC (4%) and NaCl (4%) as Cl sources, respectively. Properties and elementary composition of ASWs are given in Table 2.

# FORMATION AND SOURCES II

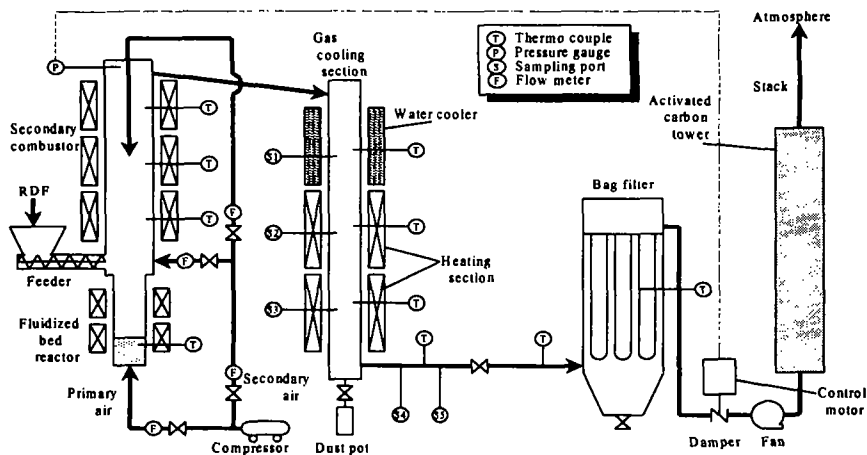


Fig.1 Schematic of lab-scale experimental incinerator

## Results and Discussion

Figure 2 shows the TEQ and total concentrations of dioxins after 4 hours running at R1, R2 and R4. It is noted that ASW1 (Base) emits dioxins. This suggests that the small amount of Cl (0.04wt%) may be a source of dioxins. The result also indicates that PVC has the intense effect in dioxin emission (ASW2) in comparison with NaCl (ASW3). Fig.3 shows the changes in dioxins concentrations with time for R2 and R4. The dioxins concentrations increase with time not only in the PVC case but also in the NaCl case. This seems that some chemical species, influencing for dioxin formations, may accumulate in the fluidized bed sand. To clarify this memory effect on dioxin generation, the sands after 10 hours running for both R2 (ASW2) and R4 (ASW3) were examined by extra 4 hours running with feeding ASW1 (R3 and R5, respectively). The results are shown in Fig.4. In both runs dioxins emission outreaches the level in R1. It seems that the organic-and/or inorganic-chloride may remain in the sand as the residue and these substances will affect on dioxins formation as the Cl source. It seems that organic chloride is accumulated in R2 and inorganic chloride is accumulated in R5. The dioxins concentration in using the sand after R2 decreases about one third in comparison with that in R2 at 10 hours. On the other hand, the sand after R4 shows the almost same level of dioxins concentration as R4 at 10 hours. This suggests that the effect of inorganic residue, such as NaCl, as Cl source in dioxins formation will hold long in comparison with that of organic residue, volatilize easily in the combustion field. To elucidate if inorganic chloride such as NaCl will be the Cl source in dioxin generation, the element fractions of Na and Cl in the sand during R2 and R4 are analyzed. It is obvious that both Na and Cl accumulate in proportion to running time as shown in Fig.5. However, the element ratio of Na to Cl is higher than that of NaCl. This suggests that NaCl reacts with  $\text{SiO}_2$  and/or  $\text{Al}_2\text{O}_3$  to form stable compounds such as  $\text{Na}_2\text{O}_3\text{Si}$  and  $\text{NaAlO}_3$ , and that residual Cl will convert to HCl and volatilized. It is said that HCl is the source of dioxin. The thermodynamic consideration of dioxin formation from HCl will be presented in another paper of this symposium.<sup>1)</sup>

# FORMATION AND SOURCES II

## Acknowledgements

This study was supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## References

- 1) J. Ishizu, Y. Yoshihara, M. Hiraoka, Dioxin 2000 (2000).

Table 1 Experimental procedure

	ASW	Running time[h] <sup>*1</sup>	Fluidized bed sand
Cleaning			
R1	ASW1	4	new
Cleaning			
R2	ASW2	4, 10	new
Cleaning			
R3	ASW1	4	after 10h running in R2
Cleaning			
R4	ASW3	4, 10	new
Cleaning			
R5	ASW1	4	after 10h running in R4
Cleaning			

<sup>\*1</sup>Gas sampling were conducted for last 2hour period of each run.

Table 2 Properties and elementary composition of ASWs

		ASW1	ASW2	ASW3
Moisture	wt% WB	6.1	5.7	6.0
Ash content	wt% DB	5.3	5.0	5.9
Volatile matter	wt% DB	83.7	80.9	80.6
Fixed carbon	wt% DB	11.0	14.1	13.5
C	wt% DB	51.5	51.9	51.7
H	wt% DB	7.7	7.6	7.5
N	wt% DB	0.31	0.30	0.28
T-S	wt% DB	0.02	0.02	0.02
Combustible S	wt% DB	<0.01	<0.01	0.01
T-Cl	wt% DB	0.04	1.64	1.90
Volatile Cl	wt% DB	0.04	1.59	0.64
O	wt% DB	35.1	33.5	32.7
F	mg/kg DB	70	60	70
T-Ca	wt% DB	0.89	0.81	0.76
Na	mg/kg DB	170	160	12940
Cu	mg/kg DB	<1.0	<1.0	<1.0
Fe	mg/kg DB	360	330	340
HHV	cal/g	5500	5560	5370
LHV	cal/g	5090	5150	4960

Fixed carbon = 100 - Ash content - Volatile matter  
 O = 100 - C - H - N - T-S - T-Cl - Ash content  
 WB Wet basis DB Dry basis

# FORMATION AND SOURCES II

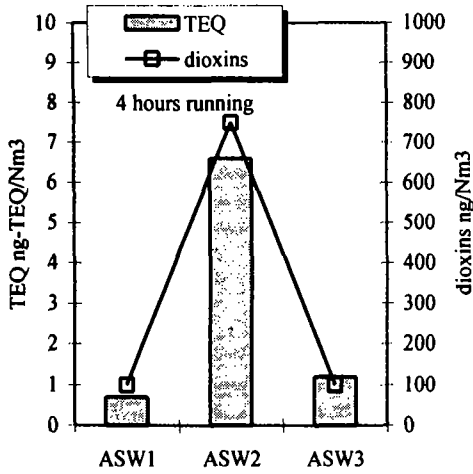


Fig.2 TEQ and total concentrations of dioxins after 4 hours running at R1, R2 and R4

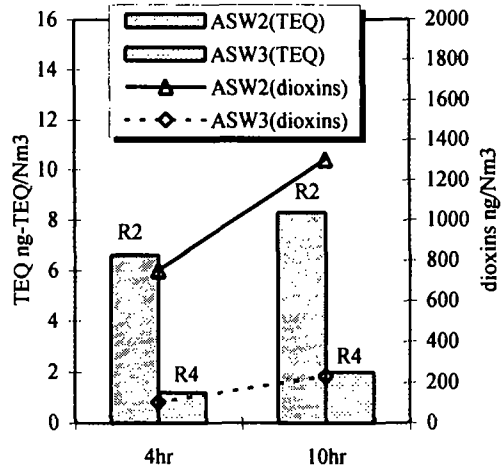


Fig.3 Changes in dioxins concentrations with time at R2 and R4

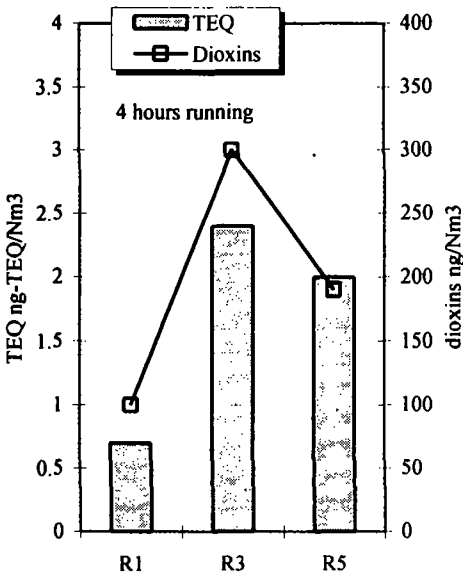


Fig.4 TEQ and total concentrations of dioxins after 4 hours running at R1, R3 and R5

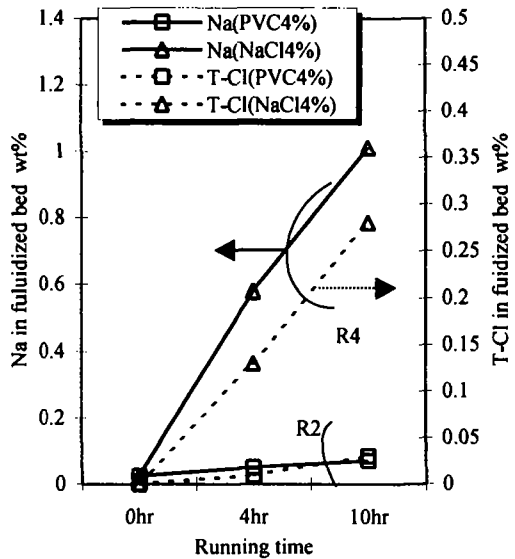


Fig.5 Changes in Na and Cl concentrations during R2 and R4