Formation of Chlorinated Aromatics by Combustion of Solid and Liquid Waste

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1. Introduction

It is very important to identify toxic chemical substances formed by the combustion process during waste disposal in Japan. At present most waste is disposed of by incineration and/or landfill. Regarding the formation of chemical substances during the incineration process, many aspects are still unknown including the mechanism of formation.
Recently, Imagawa et al synthesized some isomers of polychlorinated naphthalenes (PCNs), and identified PCN isomer-specifically[1]. Nakano et al determined PCNs in a water sample using standard mixture of PCN isomers obtained from Imagawa[2]. PCN formation of characteristic isomers in incinerators has been reported by Imagawa et al[3].
In this study, the formation of chlorinated aromatics such as PCNs in waste incinerators treating solid and liquid waste was investigated.

2. Experimental

2.1 Waste disposal process:

The outline of the investigated industrial waste incinerator is shown in Fig.1. In the Solid Waste Incinerator (SWI), industrial wastes including waste plastics are incinerated. In the Liquid Waste Incinerator (LWI), industrial wastes such as chlorinated solvents, waste acids, or waste alkalis are incinerated. In the Solid Waste Incinerator system, supplied industrial water at an Electrostatic Precipitator (EP) is circulated from the EP to a HCl-stripper through a wet scrubber. The circulating water in the process of gas scrubbing seems to function as a trap for collecting high boiling point organic compounds. In addition, amounts of some compounds are collected and accumulated in the circulating water through a desulfurizing-tower. The water circulating through the desulfurizing-tower contains chemical compounds formed in the incinerator and gas scrubbing process. The results allows us to understand the history of substances generated in the past. In the Liquid Waste Incinerator system, the degradation of chlorinated solvents was sufficient and water in the cooling-tower had a low concentration of high boiling point chlorinated compounds. As a result of complete combustion soot was not generated.

2.2 Circulating water in various gas disposal equipments

The circulating water of this incinerator can be divided into three categories: [1] EP to HCl-stripper, [2] desulfurizing-tower, and [3] cooling-tower. [1] and [2] are SWI systems

and [3] is a LWI system.

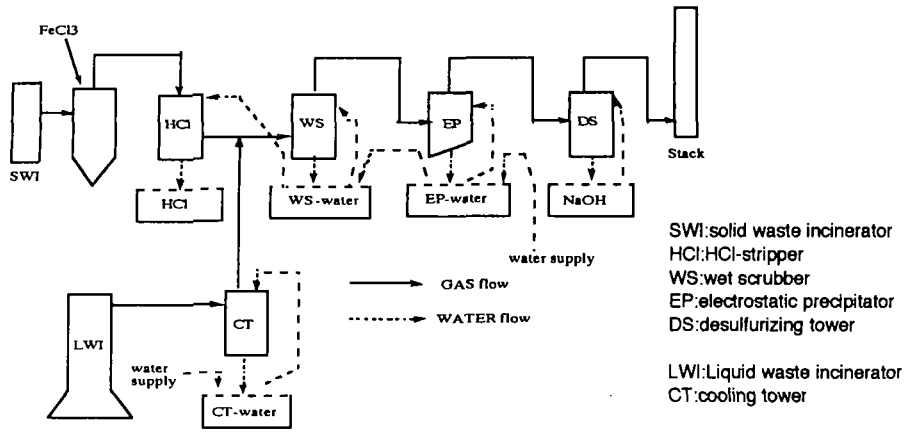


Fig.1 Schematic diagram of an waste incinerator plant

2.3 Collection and extraction of samples

100L of exhaust gas was collected with hexane into an impinger and concentrated before analyzing by GC/MS-SIM. The circulating water was centrifuged into soot (particles) and water. The particles were Soxhlet extracted with acetone and toluene. The water phase was liquid-liquid extracted with dichloromethane. The extract dissolved in n-hexane was washed with sulfuric acid, and further cleaned with SEP-PAK silica.

2.4 Gas chromatography / mass spectrometry (GC / MS)

For library search measurement to detect chlorinated aromatics, the range m/z 35-500 was scanned in 1 sec to obtain full mass spectra using a JEOL DX-303 GC/MS. Polychlorinated benzenes (PCBzs), polychlorinated phenols (PCPs) and PCNs, were analyzed by HRGC/MS-SIM, and were determined for all congeners[2]. For the separation of polychlorophenols, a PTE-5 (id; 0.25mm, length; 30m, thickness; 0.25 μm) was used. For PCNs measurement, ULTRA-2 and WAX-10 were used.

2.5 Calculation of physicochemical parameters

The physicochemical parameters such as enthalpy, dipole moment, electron affinity, ionization potential, polarizabilities, total surface area and volume were calculated using MOPAC for PCNs, PCBzs and PCPs. Keywords used for calculation are AM1, PM3, POLAR, VECTORS, PRECISE, ROT and THERMO. The relationships between calculated enthalpy values and PTRI data [2] were analyzed. HOMO/LUMO graphic images were produced by Macintosh Quadra 840AV using personal CAChe.

(AM1; use the AM1 hamiltonian, PM3; use the MNDO-PM3 hamiltonian, ESP; electrostatic potential calculation, POLAR; calculate first, second and third order polarizabilities, VECTORS; print final eigenvectors, PRECISE; criteria to be increased by 100 times, ROT=n; the symmetry number of the molecule is n, THERMO; perform a thermodynamics calculation.)

3. Results and Discussion

3.1 Chlorinated aromatics

The stack gas samples were analyzed both in the vapor phase and particle phase. The circulating water for HCl-stripper, wet scrubber , cooling tower, electrostatic precipitator and NaOH solution for desulfurizing were analyzed in the water phase and particle phase. PCBzs and PCPs isomer contents were determined and PCNs levels were evaluated for each congener. 2,4,6-Trichlorophenol existed as major component among the trichlorophenol isomers in the circulating water of the desulfurizing tower. This result was considered as ortho-para orientation of halogen / -OH in the electrophilic substitution of phenol. 2,4-DiCP, 2,4,6-TrCP and 2,3,4,6-TeCP were dominant among formed PCP congeners.

The Liquid Waste Incinerator (LWI) acheive complete combustion in its ideal state by proper control of combustion temperature, residence time and oxygen concentration.The combustion control of Solid Waste Incinerator (SWI) for plastics was not as easy as in the LWI. Soot exists in the circulating water of the gas scrubbing equipment due to incomplete combustion. The semi-volatile components are adsorbed on the soot (particles) which is in the circulating water. It showed the characteristic distribution pattern by partition equilibrium from the solid to liquid and to the vapor phase. Organic chlorinated compounds such as PCBzs, PCPs and PCNs, oxides of polycyclic aromatic hydrocarbons (PAH) such as anthraquinone and nitrogen compounds such as quinoline were detected in the circulating water. The concentration levels were 10 μg/ l for PCBzs, and 100 μg/ l for PCPs(Fig.2). Most of the volatile chlorinated hydrocarbon which was discharged from the disposal facility would disperse into the gas as exhaust gas components[4]. On the other hand, only a small amount of the semi-volatile organic compounds which would exist in particles and/or the water phase in the circulating water, would be emitted into the atmosphere as exhaust gas components.

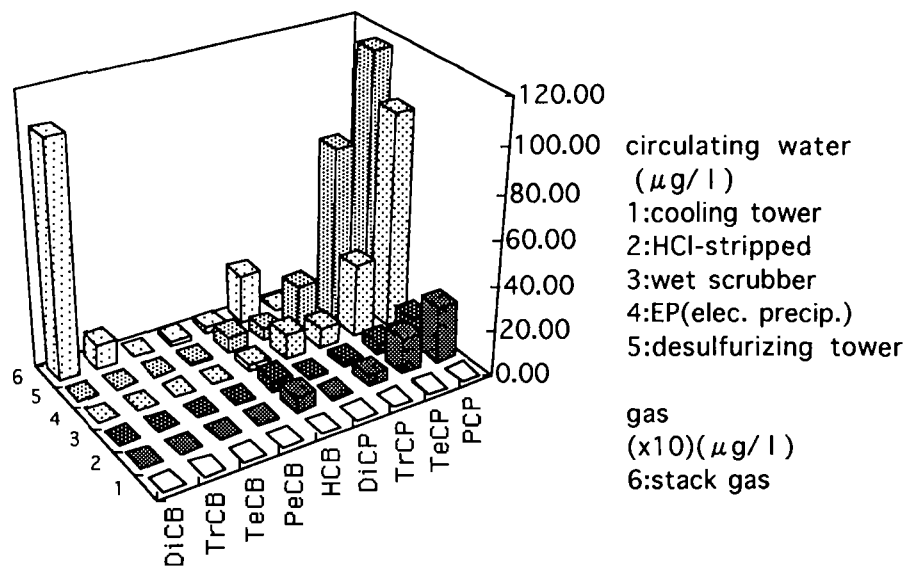


Fig.2 PCBzs and PCPs in the circulating water and stack gas

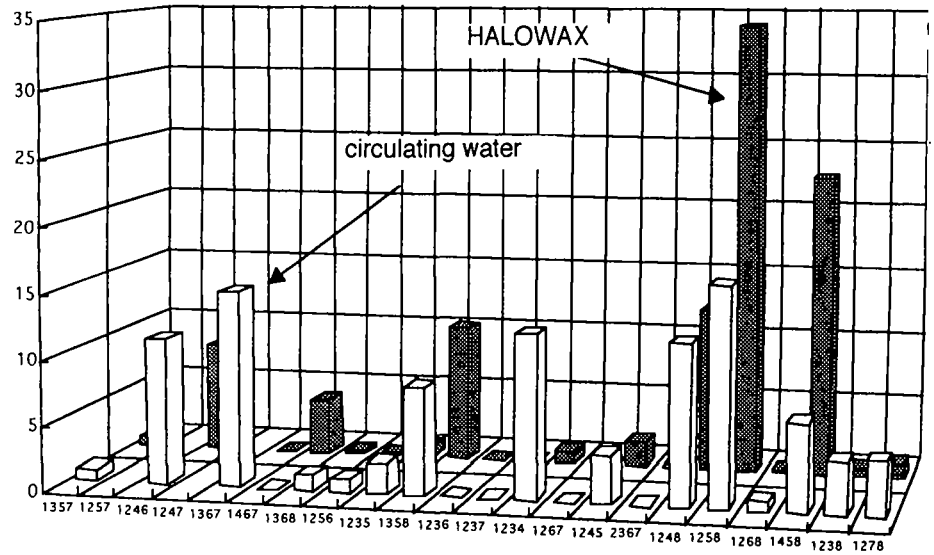


Fig.3 Isomer pattern of TeCN in the particle of the circulating water (desulfurizing tower) and HALOWAX

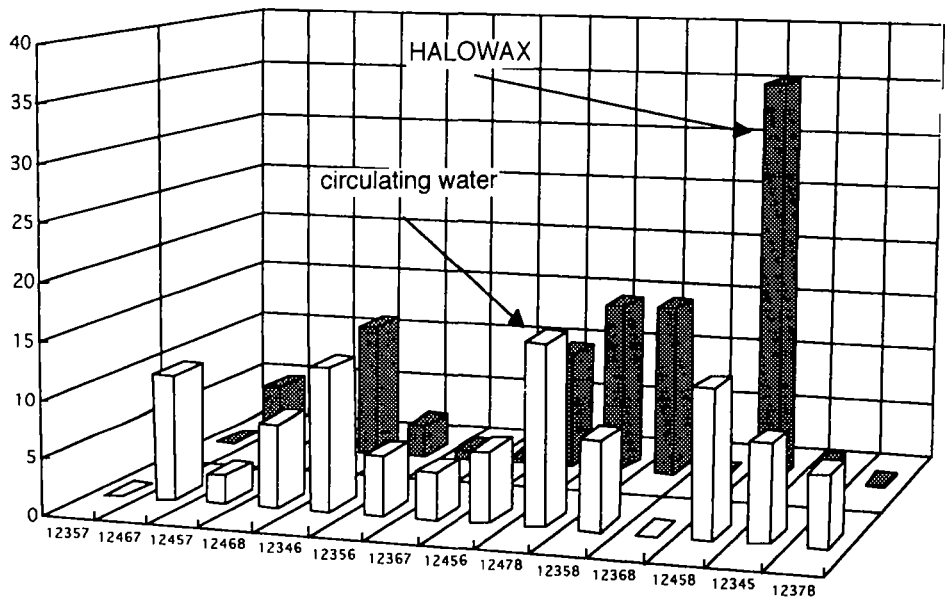


Fig.4 Isomer pattern of PeCN in the particle of the circulating water (desulfurizing tower) and HALOWAX

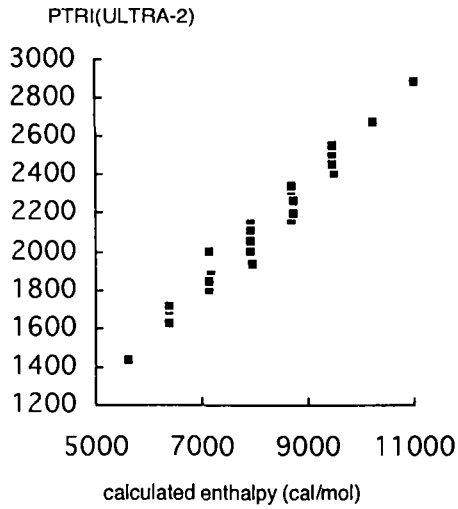
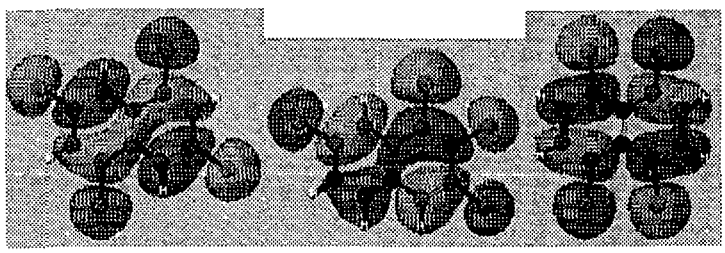
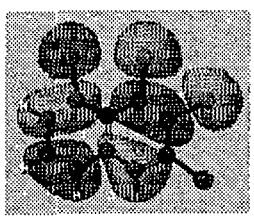
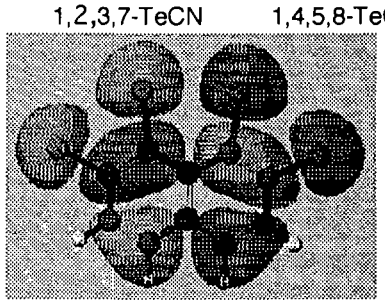


Fig.5 Relationship between calculated enthalpy and PTRI data



1,3,5,7-TeCN 1,2,3,7-TeCN 1,4,5,8-TeCN





1,2,3,8-TeCN 1,2,7,8-TeCN

Isomer	PTRI
1,3,5,7-TeCN	1929
1,2,3,7-TeCN	2035
1,4,5,8-TeCN	2109
1,2,3,8-TeCN	2119
1,2,7,8-TeCN	2135

Fig. 6 Highest Occupied Molecular Orbital(HOMO) of TeCNs

3.2 Isomer distribution of PCNs in the circulating water

In the measurement of combustion products from liquid PCB waste incinerator[5], Tsuji et al reported that the main products were PCPs(PCP > PCBz > PCB > PCDD/PCDF). Scrubbers that include cooler and caustic scrubber play a very important role in eliminating PCDD/PCDF and PCP in the combustion system. However, no data for PCN were available. Recently, 1,2,3,4,6,7- and 1,2,3,5,6,7-HeCN in human adipose tissue was reported[6].
In the circulating water of desulfurizing tower, PCNs isomer distribution was analyzed. In HALOWAX, 1,4-, 1,4,5-, 1,4,6-, 1,2,5,8-, 1,4,5,8-, 1,2,4,8-, 1,3,5,8-, 1,2,4,5,8-, 1,2,4,7,8-, 1,2,3,5,8-, 1,2,4,6,8-, 1,2,4,5,6- congeners were dominating, and 1,2,6,7-TeCN, 1,2,3,6,7- and 1,2,3,6,8-PeCN were not contained. However, 1,2,8-, 1,4,5-, 1,2,5,8-, 1,2,4,8-, 1,2,4,6-, 1,3,6,7-, 1,2,3,4-, 1,2,4,7,8-, 1,2,4,5,8-, 1,2,3,4,6-, 1,2,4,6,7- congeners dominated in the circulating water(Fig.3, Fig.4). This result is demonstrated by a trend for initially formed products to revert to more stable isomers at high temperatures. The alpha-chlorine in the naphthalene is sterically hindered by the chlorine in the peri- position. At high temperature, the unhindered beta- isomer is the more stable of the two compounds.
Hoffman et al[7] reported that the yield ratio of 1- and 2-chlorinated naphthalene were 1:16 in the chlorination of aromatics on fly-ash with HCl. Chlorination in the 2- position of naphthalene may be the more dominating process at high temperatures.

3.3 Estimation of retention time

The enthalpy of the chlorinated aromatics were calculated by MOPAC[8]. The relationship between the PTRI data and the enthalpies of the chlorinated aromatics are given in Fig.5. Highest Occupied Molecular Orbital (HOMO) of TeCNs are given in Fig. 6. Retention time of 1,3,5,7-TeCN is shortest, and 1,2,7,8-TeCN is longest among 22 tetra isomers. To estimate the retention time of chlorinated aromatics such as PCNs, we will try to analyze the physicochemical parameters with the symmetry of Huckel HOMO for PCNs.

4. Acknowledgments
We thank Dr. Imagawa for providing us with a standard mixture of PCN isomers.

5. References

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