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Leachability of Dioxins from Mixture of Fly Ash and Bottom Ash

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1. INTRODUCTION

Since more than 70% of the municipal solid waste (MSW) have been incinerated in Japan, Japanese MSW landfill sites mainly are filled with inert materials of incombustibles and incineration residues, such as bottom ashes and fly ashes. Dioxins are known as the highly hydrophobic substances and dioxins in those materials theologically cannot be dissolved in water media. Thus most dioxins have usually been observed in a suspended solid fraction of leachates released from MSW landfill sites [1]. However, it has been reported that some MSW landfill sites and industrial waste sites containing incineration residues emitted certain amounts of dioxins in a liquid fraction, in some cases with a high concentration more than the environmental standard (1 pg-TEQ/L) [1]. So it is important to clarify the potential of dioxin release from incineration residues. It has been reported that several organic substances [2, 3, 4, 5, 6, 7, 8] coexisting in natural and discharged water could affect the dioxins' solubility to water. The bottom ash usually contains certain amounts of dissolved organic substances affecting on the leachability of dioxins, so it has possibility that those organic substances could enhance the leachability of dioxins from fly ashes to leachate matrixes. In this study, we attempt to estimate the effects of a bottom ash on the leachability of dioxins from a fly ash by the leaching test of the mixtures of bottom ashes and a fly ash..

2. METHODS

2.1 Leaching Test

Three ash samples were collected from two municipal solid waste (MSW) incinerators. They are a bottom ash (MB) and a fly ash (MF) sample from one incinerator, and a fly ash (FF) sample from another incinerator. The sample FF, MB and two mixtures of the fly ash and bottom ash at ratio of 1:4 by weight, sample MF+MB and FF+MB, were subjected to the leaching test. Dioxins contents of these samples are showed in **Fig. 1**. The content of dioxins in the sample FF (6,620,000 pg/g) much more than any other samples.

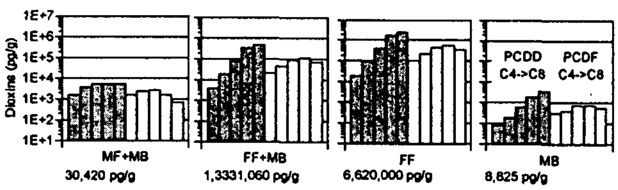

Fig.1 Congener distributions of PCDDs and PCDFs in ash samples

The leaching test was basically conducted according to the Japanese standard method for industrial waste inspection [9]; Distilled water (more

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than 500 mL) was added to solid samples at 10 times by weight as much as the solid samples in glass vessels. They were shoken for 6 hr at room temperature (ca. 20℃). During shaking, pH of the liquid phase was maintained at 4, 7 or 11 by the automatic titration (ATR-9002, Dainippon-Seiki) of 1N/5N HNO_3 and NaOH. Then leachates for the chemical analysis were obtained by the vacuum filtration through the 1μm glass fiber filter.

2.2 Chemical Analysis

The pH, electric conductance (EC), DOC, BOD, Cl, Ca, Pb, Cd, and Fe in leachates were measured by conventional methods according to JIS K0102 12.1, 13, 22.1, 21, 35.1, 50.3, 54.3, 55.3, and 57.4, respectively. Methanol, ethanol and iso-butanol were determined by the GC-FID method. Major volatile fatty acids (VFAs, C_1-C_6) were separated by the HPLC and determined by the EC detector.

Dioxins and other hydrophobic organic substances in 5 L leachate samples (acidificated to pH 3 by HCl) were extracted with 1 L of dichloromethane and concentrated by a rotary evaporator. Concentrated extracts were prepared by the stepwise clean-up procedure using a silica gel and a alumina column, and dioxins (including Cl_4-Cl_8 of PCDD and PCDF) in samples were determined by the HRGC-HRMS method. These procedures were performed according to the Japanese standard method for the waste management [10].

3. RESULTS AND DISCUSSION

3.1 Matrix of Leachate

Cl conc.s in leachates from samples of MF+MB and FF+MB were similar (1,800-2,300 mg/L) in spite of pH. Ca conc. in the leachate from the sample of MB at pH 4 was the highest (9,400 mg/L) and then Ca conc.s in leachates from samples of MF+MB and FF+MB at pH 4 was higher (12,000 and 8, 000 mg/L, respectively) than those at the other pH settings. Metals (especially Pb) were also tended to leach out at low pH (**Fig.2**).

The DOC was leached out at higher concentration from the sample of MB than the others and its

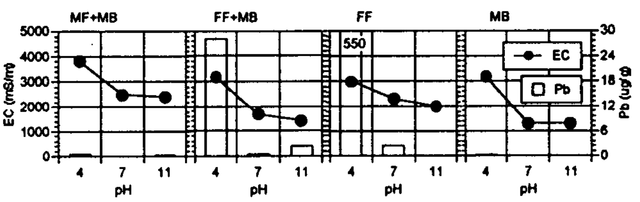

Fig.2 Matrix of leachate (EC and Pb)

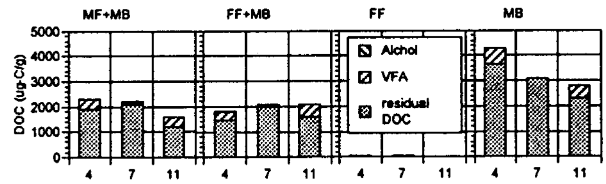

Fig 3 Matrix of leachate (DOC, Alchols and VFAs)

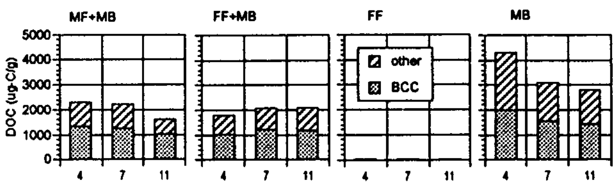

Fig.4 Matrix of leachate (DOC and BCC)

highest concentration was 390 mg-C/L at pH 4. However, these pH dependencies were unclear for mixtures of the fly ash and the bottom ash (**Fig.3**). The sample FF released the less DOC as 3 mg-C/L. DOC in leachates except that of FF contained 0.02-25 % of VFAs and less than 0.01 % of alcohols. Concentrations of VFAs in leachates tended to be higher at low and high pH and to be lower at neutral.

Fig. 4 shows biochemical carbon consumption (BCC) contents in the DOC. The BCC was estimated as C in carbon dioxide which all BOD could be transformed to. The difference between the DOC and the BCC (bio-available carbon) should be expected as the refractory portion in a DOC. However there were no apparent tendencies between those and pH for mixtures of the fly ash and the bottom ash.

3.2 Leachability of Dioxins

The range of dioxins concentration in leachates of the leaching test was 6.9-59 pg/L or 0.0066-0.26 pg-TEQ/L (as I-TEF) (**Fig. 5**). These concentrations are at lower level than those observed in landfills [1]. The highest leaching, of 0.66 pg/g-ash (0.0012 pg-TEQ/g-ash) was observed in leachate from the sample of FF+MB at pH 11.

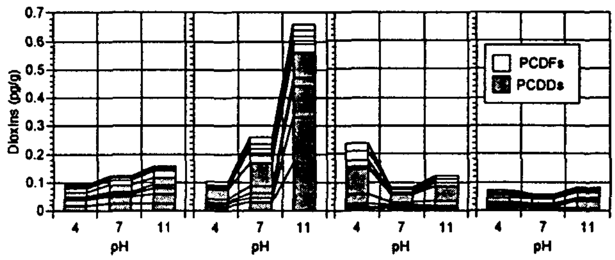

Fig.5 Dioxins in leachates

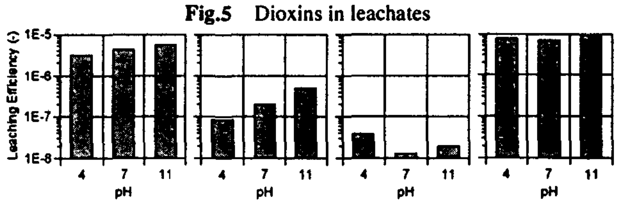

Fig 6 Leaching efficiency of dioxins

The mixtures of the fly and the bottom ash at pH 7 and 11 were more leached the dioxins than the fly ash of FF, which had the highest dioxins content (**Fig.1**). Moreover, dioxins concentrations in leachates tended to increase with pH. In respect of the leaching rate, which is defined as a ratio of the content in liquid to solid, the fly ash solely had rates of the order of 10^{-8} while mixtures of the fly ash and the bottom ash had rates of the order of 10^{-8}-10^{-6} (**Fig. 6**). **Fig. 7** shows the distributions of PCDDs and PCDFs congener concentrations in leachates. For mixtures of the fly ash and the bottom ash, especially for the sample of FF+MB, PCDDs congeners of the lower chlorine number were remarkably increased in leachate at pH 11.

Several components in the matrix of water, such as phospholipid [2], humic substances [3, 4, 5], surfactants [6, 7, 8] and solvents [6], have been reported as factors affected the leachablity of dioxins and other hydrophobic chemicals to water. The ion strength would be also expected to affect the leachability of hydrophobic chemicals and other components in water. Especially, a similar study by Kim and Lee [4] showed that dioxins in leachates from fly ashes increased by coexistence of dissolved humic matters. With results in only this study, it is difficult to verify the effects of substances leached from bottom ashes, such as humic matters, on the leachability of dioxins from fly ashes. However, it is remarkable that the DOC concentrations in leachates from the bottom ashes were higher than those of the fly ash, then it remains a possibility that DOC could consist of some

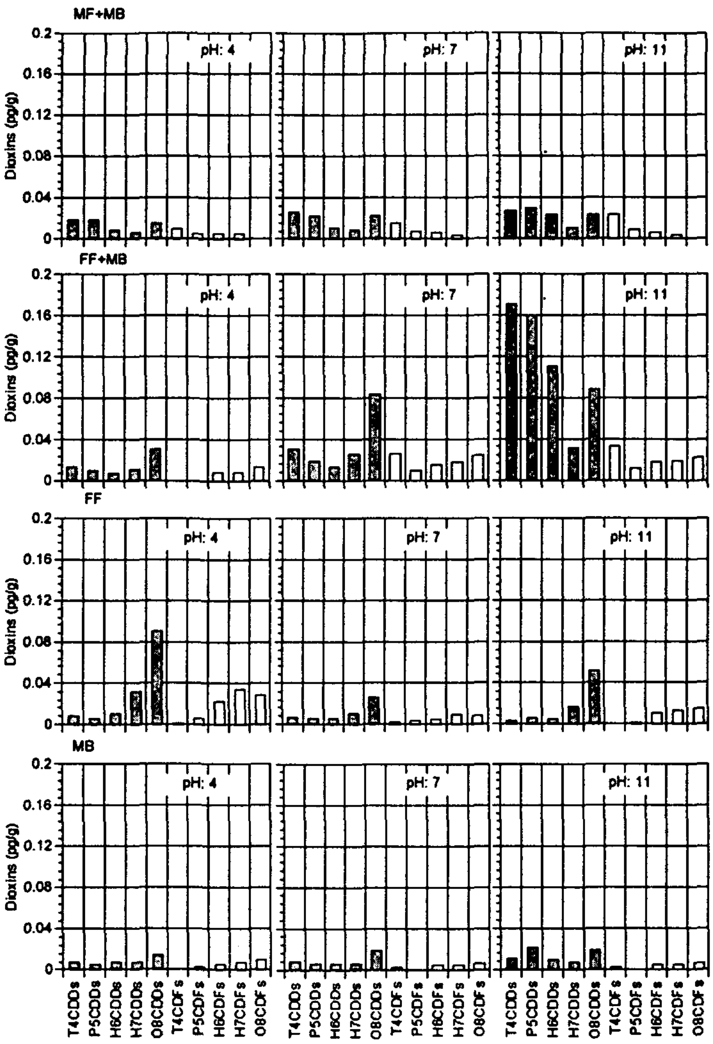

Fig 7 Congener distributions of dioxins in leachates

organic substances having surface-activity or co-solvency and its complex behavior in water matrix could relate to the high leachability of dioxins.

4. CONCLUSION

We investigated the leachability of dioxins and other substances by mixting the bottom ash and fly ash using the leaching test procedure with constant pH control. Higher DOC was released to leachates from the bottom ashes than the fly ash. It is notable that The mixtures of the fly and the bottom ash at pH 7 and 11 were more leached the dioxins than the fly ash of FF, which had the highest dioxins content. Moreover, dioxins concentrations in leachates tended to increase with increasing pH. There is a possibility that some organic substances having the surface-activity or the co-solvency, which DOC consists of and which are originated from the bottom ash, could enhance the leachability of dioxins containing in the fly ash at high level.

ACKNOWLEDGEMENT

Major component of this study was conducted at the research committee organized by Waste Study Foundation and was supported by the Science Study Fund of the Ministry of Health and Warfare. We thanks to all committee's members for their comment sand discussions.

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