

## PRELIMINARY STUDIES FOR REDUCTION OF DIOXINS FROM POLLUTED WASTE AND ENVIRONMENTAL SAMPLES BY HOT WATER

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### Introduction

Clearing and remediation of the environment heavily contaminated by dioxins and the other contaminants is the most serious subject for residents and governments of all countries. In Japan, a polluter or a local government has been obligated to removal and/or remediation, of soil polluted by dioxins over the standards since enforcement of Law Concerning Special Measures against Dioxins (Law No.105 of 1999). Moreover, treatment of contaminated waste and environmental media such as sediment is also an important problem to form the material cycles and sustainable society.

Though various techniques of decomposition and reduction of dioxins have been reported<sup>1-3</sup>, only a few could be applied on the actual spot by reasons on operation, removal efficiency, energy consumption and economies.

The aim of this study is making a proposal concerning the practical method for reduction of dioxins from contaminated waste and environmental media. In this study, a method using hot water was examined due to a unique property of water, which dissolves organic matter better at higher temperature<sup>4</sup>, and is friendly to the environment. This is the report of preliminary studies on reduction of dioxins from flyash and soil samples by hot water.

### Materials and Methods

Samples: Soil and flyash, which were the certified reference materials (NIES-CRM, #21 and #19), were given to experiments.

Water: Distilled and ion-exchanged water by a Milli-Q (Waters) was used.

Apparatus: An apparatus (JASCO, Japan) was modified for our experiments. The apparatus is illustrated in figure 1. It is consisted two pumps, an oven that can be controlled from room temperature to 450°C and a cell, which is containing sample and has a capacity of 50mL.

Experimental methods & conditions: About 50mL of sample was packed into a cell made of Hastelloy, then experiments were carried out under several conditions listed in table 1. The flow speed of water through the cell is set at 2.0 mL/min. After water was passed through the sample, it was sequentially extracted with acetone.

An extract collected in a bottle for each period was transferred into a separation funnel and added <sup>13</sup>C-labeled compounds. Collected water solution was shaken with toluene for 10 minutes and

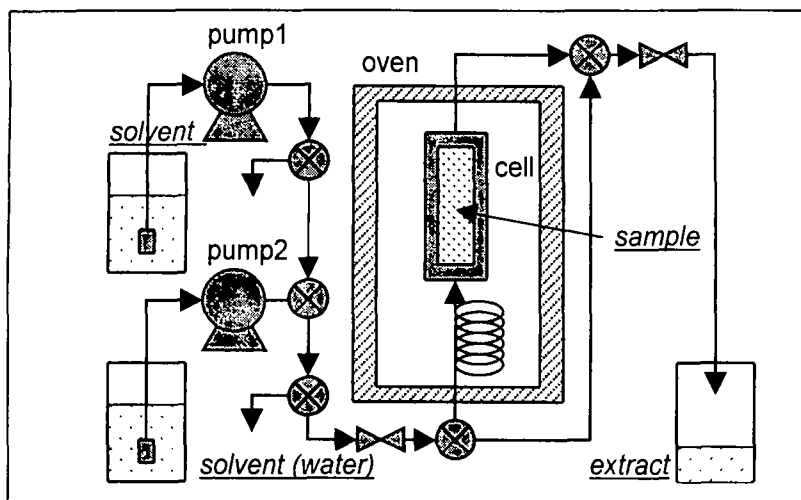


Figure 1 Illustration of the apparatus used for experiments

Table 1 Conditions (temperature, pressure and driving time) of reduction experiments

	solvent		
	Water		acetone
Driving time (minutes)	0-120	120-240	100 minutes
Experiment 0	room temp, 0kgf (LLW1)	room temp, 0kgf (LLW2)	100°C, 100kgf (LLR)
Experiment 1	350°C, 250kgf, 0-180 mins (HHW1)		100°C, 100kgf (HHR)
Experiment 2	350°C, 0kgf (HLW1)	350°C, 0kgf (HLW2)	100°C, 100kgf (HLR)

extracted further twice with toluene. On the other hand, acetone solution was concentrated and added water before shaking extraction. Extract was dehydrated by anhydrous sodium sulfate and concentrated to re-dissolve to hexane.

The solution was purified with sulfuric acid shaking and silica gel and activated carbon column chromatography. The GC/MS analysis was performed on a JMS-700 high performance double focusing mass spectrometer (JEOL, Japan) coupled to a HP 6890 gas chromatograph (Agilent, US).

### Results and Discussion

Reduction of dioxins, transferring to water and change of the composition of compounds were investigated by passing hot water through solid samples containing dioxins without additives. As a result, it was confirmed that hot water could effectively reduce dioxin concentrations in a solid sample such as soil and flyash. The reduced rates from the sample were 99.3%, 98.7% and 91.4% of PCDDs, PCDFs and planer PCBs, respectively, at 350°C, 0 kgf, soil (experiment 2), while few

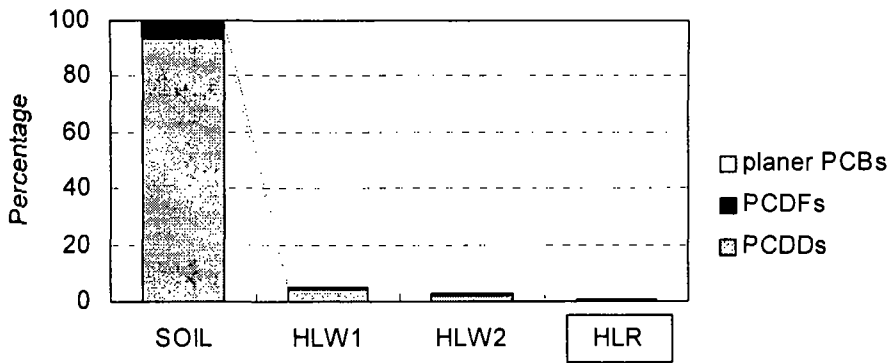


Figure 2 Residual (in soil) and transferred (to water) levels of dioxins (PCDDs, PCDFs and planer PCBs) in experiment 2.

SOIL: original soil, HLW1 and HLW2: water, HLR: residue

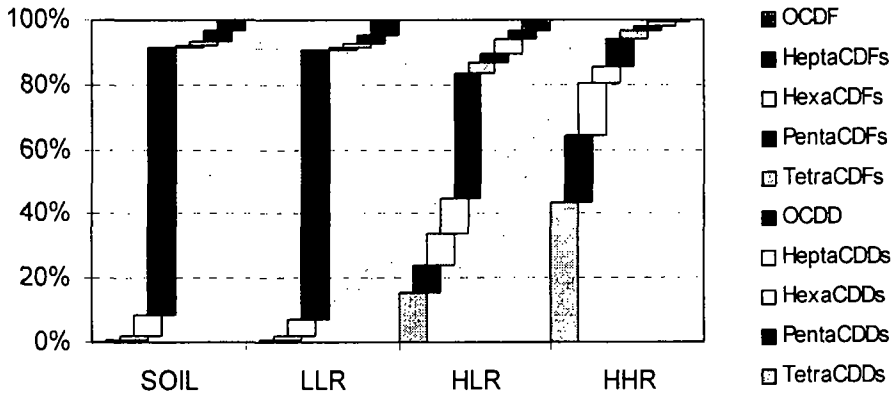


Figure 3 Compositions of dioxin homologues in the samples

SOIL: original soil, LLR, HLR and HHR: residues treated with water at room temp., 0kgf; 350°C, 0kgf; and 350°C, 250kgf; respectively

dioxins decreased at room temperature, 0 kgf, soil (experiment 0). It means that water heating is necessary to reduce of dioxins in soil. And dioxins were also detected in extracted water. The ratios of the compounds in water to in soil were calculated 6.5%, 16.5% and 79% of PCDDs, PCDFs and planer PCBs, respectively. However the sum of amounts of dioxins in soil and water was not equal to the original one (in figure 2). It means to get poor recovery in this method as against the report by Bavel *et.al.*<sup>5</sup>. Though it is suggested that the gap has been decomposed, some additional treatment of the water after extraction should be required to achieve perfect cleanup of media.

Difference of homologues composition was observed in the soil samples as shown in figure 3 and 4. The composition in the soil treated at room temperature, 0kgf (LLR) was not similar to the soils treated with hot water (HLR&HHR), but similar to original soil (SOIL). It was considered that

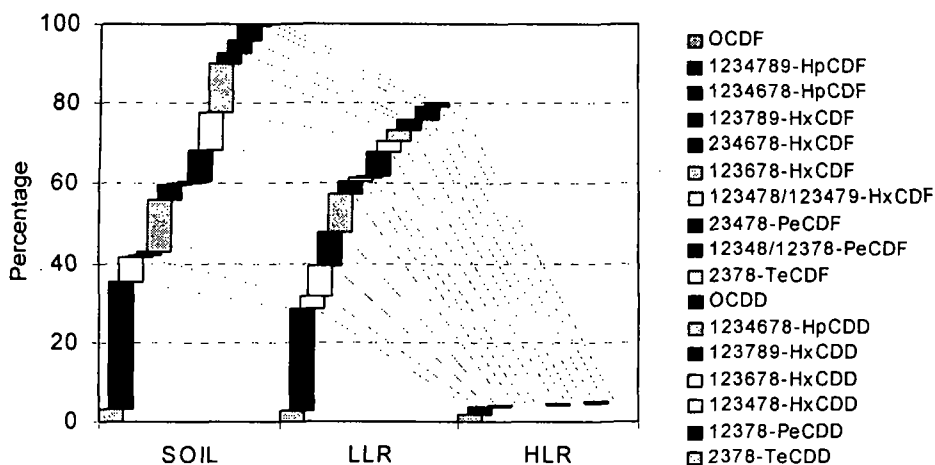


Figure 4 TEQs of dioxin (PCDD and PCDF) isomers in the samples SOIL: original soil, LLR and HLR: residues treated with water at room temp., 0kgf; and 350°C, 0kgf, respectively

dechlorination might be caused by hot water due to the proportion inclining fewer chlorines substituted homologues. In addition, it was suggested that high pressure might promote the reaction according to comparison between the compositions in HLR and in HHR.

TEQ levels also decreased by hot water treatment as shown in figure 4. However the TEQ level of 2,3,7,8-tetraCDD hardly decreased while the other isomers' ones were reduced in effective, especially more chlorinated ones. It is considered that the profile has been made as the result of dechlorination reaction as well as the homologue compositions. Therefore, it may be supposed that 2,3,7,8-tetraCDD does not decrease until chlorine would be removed from the sample further. Because the homologues substituted more than four chlorines can become 2,3,7,8-tetraCDD by dechlorination. Anyway, some improvement, e.g. to extend the running time or to increase efficiency, is needed for complete reduction of dioxins.

Some characteristics of reduction of dioxins in a solid sample were understood on this preliminary study. For applying this method to contaminated media as a practical use, however, it is necessary to study the mechanisms of decomposition of dioxins during treatment, the effects on the other chemicals or conditions and optimization of the cost.

## References

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