

CLEANUP OF DIOXINS-CONTAMINATED SEDIMENT BY INDIRECT HEATING TREATMENT

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Abstract

Sediment contaminated with polychlorinated biphenyls (PCBs)-originated polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) was treated by an indirect heating method using a bench scale reactor (BSR) and a pilot plant (PP) to investigate the effects of their operational conditions on removal of PCDD/Fs. In indirect heating treatment (IHT) using BSR at 450°C under 10% O₂/N₂, PCDD/Fs were sufficiently removed; however, the exhaust gas contained a significant amount of PCDFs which was twenty seven times higher than that in the sediment sample prior to IHT, thereby confirming the occurrence of unintended PCDFs formation from precursors such as PCBs. In the treatment using PP under the same temperature condition, the elevation of PCDFs in exhaust gas was moderated by 12%. Furthermore, increase of the PP treatment temperature to 650°C resulted in apparent PCDFs degradation. The obtained results clearly indicate that treatment temperature is a critical parameter for IHT to remedy sediment contaminated with PCBs-originated PCDD/Fs with avoidance of unintended PCDFs formation.

Introduction

Soil highly contaminated with dioxins has been found in the vicinity of industrial and municipal solid waste incineration facilities, as well as dioxins-contaminated sediment in harbors and canals. Indirect heating treatment (IHT) has attracted growing interest as a remediation technology, where contaminated soil is cleaned up by desorption and/or degradation of dioxins. Many pilot plant scale experiments have been carried out to confirm the feasibility of cleaning up dioxins-contaminated soil¹; however, only limited information is available for IHT of dioxins-contaminated sediment. Since matrices of sediment including precursors of dioxins are generally more abundant and complex than those of soil, this study investigated the effects of IHT operational conditions on removal of PCDD/Fs using BSR and PP.

Materials and Methods

Figure 1 shows the schematic diagram of BSR, where a sediment sample is treated in a quartz tube reactor (2.0 l) at 450°C for 5 min at 10% O₂/N₂-flow of 1 l/min. After IHT, PCDD/Fs remaining in the sample and those

collected from the quartz tube reactor and the cold/XAD resin/toluene traps were analyzed. By summing up PCDD/Fs in the reactor and traps, the amount of PCDD/Fs in exhaust gas was calculated.

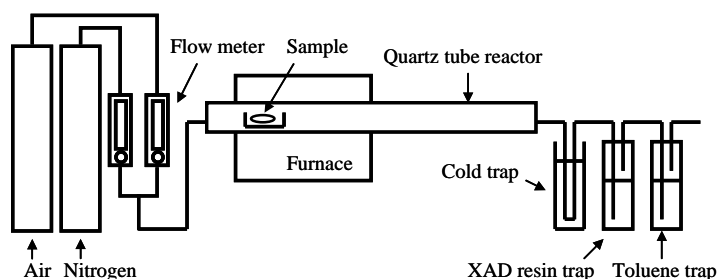


Fig. 1 Schematic diagram of the bench scale reactor (BSR).

In IHT using PP (Figure 2), the sediment sample was treated in the two-stage indirect heating drums in which air flowed at 3 m³N/h. Treatment temperature was 450°C or 650°C, while the residence time of the sample in each indirect heating drums was 20 min. In order to determine the amount of PCDD/Fs in the exhaust gas, exhaust gas was sampled between a dust collector operated at 500°C and burner.

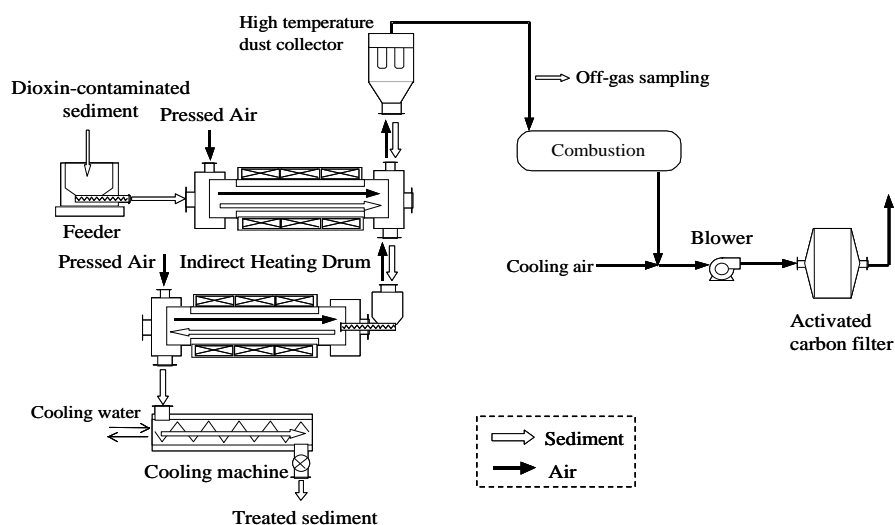


Fig. 2 Schematic diagram of the pilot plant (PP).

Real sediment samples contaminated with PCBs-originated PCDD/Fs were taken from Tagonoura Bay, Japan. The initial concentrations of PCDD/Fs in the samples used for BSR and PP were 97 pg-TEQ/g and 290 pg-TEQ/g, respectively.

Results and Discussion

Tables 1 and 2 summarize normalized balance of PCDD/Fs on the TEQ basis in IHT of the sediment using BSR and PP, respectively. Their homologue patterns are shown in Figs. 3 and 4 where PCDD/Fs concentration is expressed as amounts of PCDD/Fs per a gram of dry sediment. As shown in Table 1, PCDD/Fs were sufficiently removed by IHT using BSR at 450°C under 10% O₂/N₂; however, the exhaust gas contained a significant amount of PCDFs which was twenty seven times higher than that in the sediment sample prior to IHT. The homologues of PCDFs increased by the IHT were TeCDFs, PeCFDs, and HxCDFs (Fig. 3), thereby confirming the occurrence of unintended PCDF formation. Similar results were reported Koizumi et al. who performed IHT of the PCBs-originated PCDD/Fs contaminated sediment (120 pg-TEQ/g, 1.6 µg-PCBs/g) taken from Shourenjigawa River, Japan at 400°C under 7%O₂/N₂². Surprisingly, the elevation of PCDFs in exhaust gas was moderated in the treatment using PP, though the same temperature condition was applied (Table 2, Fig. 4). Furthermore, increase of the PP treatment temperature to 650°C resulted in apparent PCDFs degradation, thereby indicating that treatment temperature is a critical parameter for IHT to remedy sediment contaminated with PCDD/Fs with avoidance of unintended PCDFs formation.

Table 1 TEQ-based balance of PCDD/Fs in IHT using BSR. TEQs of PCDD/PCDFs before treatment (450°C) were normalized as 100%.

	Before		After	
	Sediment [%]	Sediment [%]	Sediment [%]	Exhaust gas [%]
PCDDs	100	0		70
PCDFs	100	18		2700

Table 2 TEQ-based balance of PCDD/Fs in IHT using PP. TEQs of PCDD/PCDFs before treatment were normalized as 100%.

Temp. [°C]	PCDD/Fs	Before		After	
		Sediment [%]	Sediment [%]	Sediment [%]	Exhaust gas [%]
450	PCDDs	100	1.6		8.2
	PCDFs	100	34		330
650	PCDDs	100	0.38		0.072
	PCDFs	100	6.9		8.4

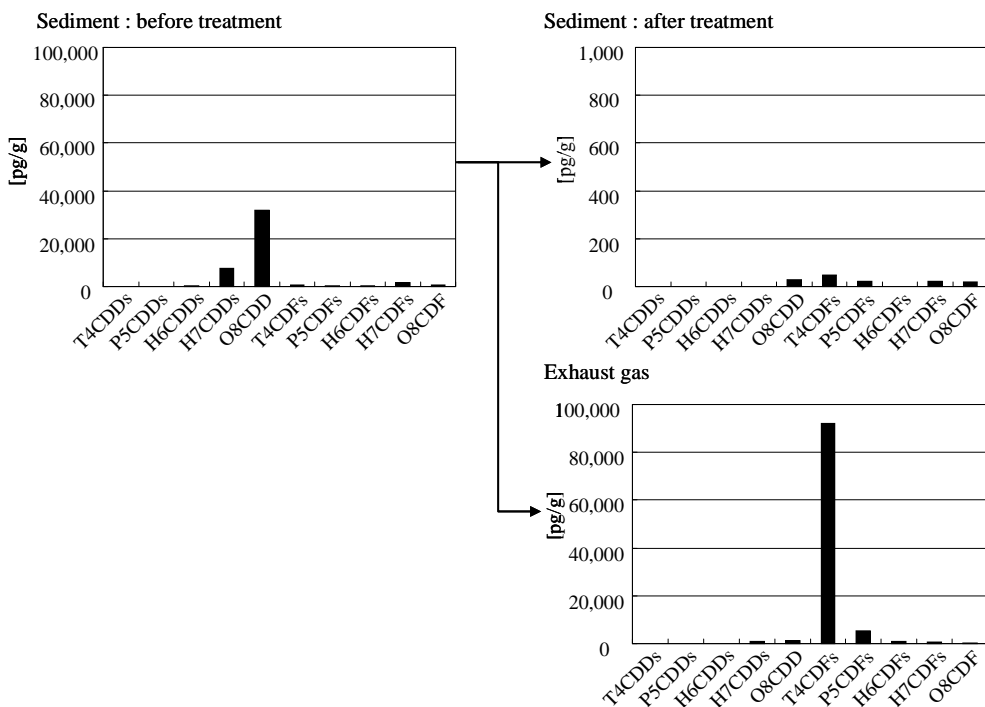


Fig. 3 Homologue patterns of PCDD/Fs before and after IHT at 450°C using BSR.

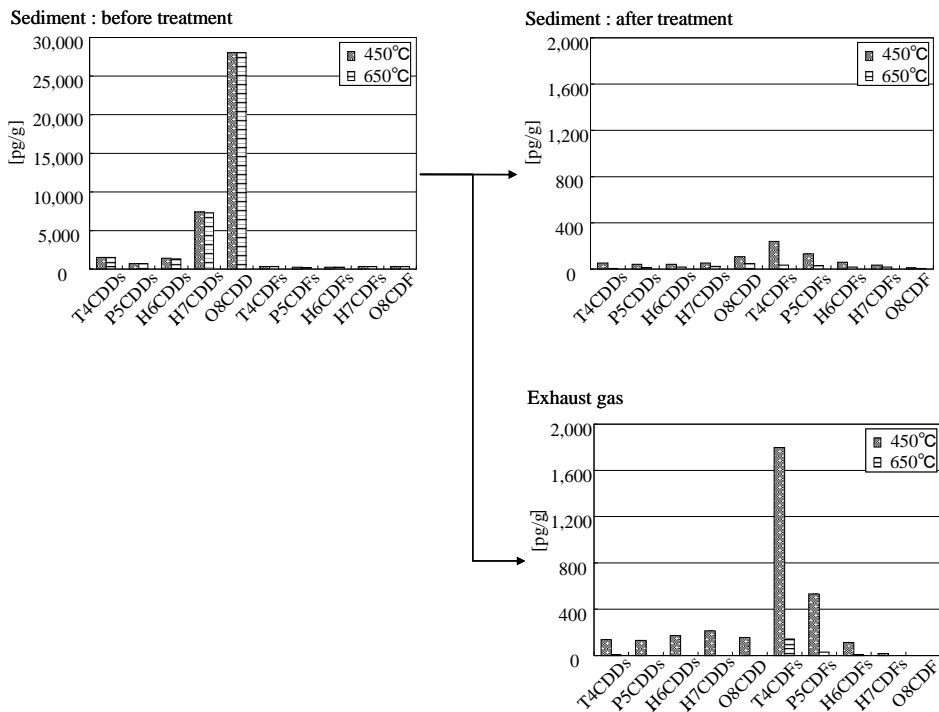


Fig. 4 Homologue patterns of PCDD/Fs before and after IHT at the indicated temperature using PP.

Since the sediment sample treated by the IHT using BSR contained 8.7 $\mu\text{g/g}$ of PCBs which was much higher than that of unintentionally formed PCDFs (Fig. 3), PCBs might be the major precursor of PCDFs unintentionally formed by the IHT. Weber³ has reported the possible pathways of PCDD/Fs formation in thermal decomposition processes of persistent organic pollutants; i) PCDD/Fs formation within the high temperature zone. ii) emission of precursors from high temperature processes and subsequent PCDDs/PCDFs formation in the cooling zone. iii) PCDD/Fs formation via degradation of incomplete thermal decomposition products such as PAHs in the cooling zone (*de novo* synthesis). Although the pathways of PCDD/Fs formation in the IHT using BSR are still unknown, the second hypothesis may be plausible due to the existence of cooling zone at the outlet of quartz tube reactor (Fig. 1). Since most of PCDFs were found in the exhaust gas (Table 1), it was surmised that PCBs desorbed at 450°C flowed in the quartz tube reactor to reach its cooling zone at which PCBs were transformed to PCDFs. By contrast, such cooling zone did not exist in the indirect heating drums (Fig. 2). This seems to be a reason why the elevation of PCDFs in exhaust gas was moderated in the IHT using PP.

References

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