Influence of Seawater in the Process of Heat Treating Sediments Contaminated with PCDDs/DFs

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Introduction

Due to industrial activities, a variety of chemicals are discharged on a large scale into the environment. In Japan, persistent organochlorine compounds (in particular, dioxins and its related compounds), derived from industrial wastewater and chemical herbicides sprayed on paddy and other crops, have accumulated in the sediments of rivers, ports and harbors.[1,2] In order to reduce the contamination in sediments, the Japanese government set-up an environmental standard in July 2002, which requires the reduction of dioxins in sediments to a level less than 150 pg-TEQ/g. Since this demands appropriate remedial technology, our research group has conducted studies on the methodologies of lowering dioxins in sediments by heat-treatment in air or low oxygen atmosphere. Furthermore, we compared the behavior of chlorine and sulfur, in the sediment added with artificial seawater and fresh water.

Material and Methods

Fig. 1 shows the schematic diagram of our experimental equipment. The cylindrical tube reactor, fabricated using quartz was rotated by an electric motor at a speed of 2 rpm. An air and nitrogen feed-line was connected to one end of the tube. Further, a supply line was attached to the top of the tube to supply steam from a water heater. At the other end, exhaust gases from the tube are forced to pass in sequence through three absorption containers (one containing water and the other two containing toluene) in order to prevent the gases from escaping from the system.

Three samples—samples 1, 2, and 3—were used in the experiment. Sample 1 was obtained from dioxin-contaminated sediments from a fresh water area. Sample 2 was prepared by adding 4% artificial seawater to sample 1, and sample 3 by adding 8% artificial sea water to sample 1. Total concentration of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in sample 1 was 8,700,000 pg/g (7,100 pg-TEQ/g).

A tube with 15 g of sample was heated at a rate of 10 °C/min while being rotated. Two operating conditions were employed in the experiment: In condition 1 air and steam were supplied to the tube continuously once the heating commenced. Condition 2 was similar to condition 1 with the exception that nitrogen was used in place of air. Chlorineof PCDDs/DFs was substituted by hydrogen at the low oxygen atmosphere heating, as a result of which the toxic chemicals were converted to non-toxic compounds. The oxygen concentration in the gas mixture of condition 1 was approximately 2%. The tube was heated to designated temperatures (450℃,550℃,650℃), and the system was maintained under this condition for 20 min. Subsequently, the top cover of the heater was opened to circulate air around the outer surface of the tube for cooling the sample in the tube rapidly; this was done in order to ensure that no dioxin was produced again[3].

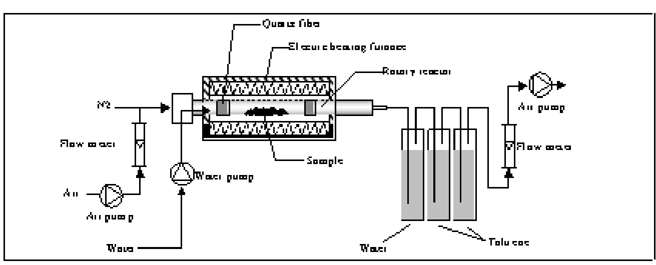

Fig 1: Schematic diagram of the experimental equipment

Results and discussion

(1) Behavior of PCDDs/DFs

Table 1 lists the PCDDs/DFs concentrations remaining in the sediment samples that were heat treated under the experimental conditions as described above. The results proved that the heat treatment reduce PCDDs/DFs in the sediment at all the experimental conditions. Further, the experiments suggest that higher the temperature, lesser are the residual PCDDs/DFs in the sediments. A comparison of the residual PCDDs/DFs concentrations in sample 1 that were heat -treated under conditions 1 and 2 indicates that the sample obtained from a fresh water area (i.e., sample without the effect of sea water) carries less PCDDs/DFs when treated in the non-oxygen atmosphere (condition 2) than in the 2% oxygen atmosphere (condition 1) (Fig.2). It was also found that, as a result of the heat-treatment of Samples 1, 2, and 3 under Condition 2, the PCDDs/DFs levels remaining in sample 1 (fresh water sample) was the lowest, indicating a highest removal rate among all the samples under our experimental conditions (Fig. 3). Further, there was hardly any difference between samples 2 and 3.

(2) Behavior of Chlorine and Sulfur

Fig. 4 shows the relationship between the residual ratio of the total chlorine in the sediment and temperature, calculated on the basis of the experiments conducted on sample 3 under conditions 1 2. It shows that, under both the conditions, a higher heating temperature accelerates chlorine elimination from the sediment resulting in the gasification of more than 30% chlorine at 650 °C.

Apart from chlorine, residual ratio of sulfur in the sediment was also studied. The result suggests that a higher heating temperature accelerates gasification of sulfur as well. The ratio was approximately 70% indicating a higher gasification ratio of sulfur than that of chlorine.

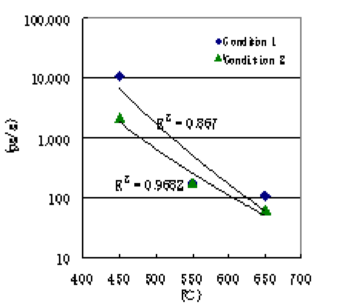

Fig. 2 : Relationship between PCDDs/DFs concentrations in heat-treated sediment 1(Sample 1) and temperature.

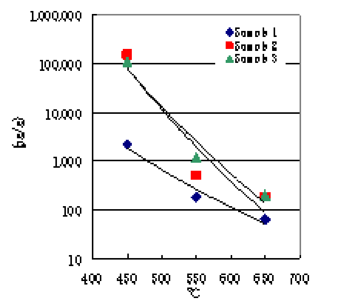

Fig. 3 : Relationship between PCDDs/DFs concentrations in heat-treated sediment (Sample 1 - Sample 3) which was heated under the nitrogen atmosphere (condition 2) and temperature.

Table 1. PCDD/DF concentrations in sediment, which was

heated in each condition

	Sample	Temperature (℃)	Condition	PCDDs/DFs Conc. (pg/g)
Run 1	1	450	1	11,000
Run 2	1	550	1	180
Run 3	1	650	1	110
Run 4	1	450	2	2,200
Run 5	1	550	2	180
Run 6	1	650	2	63
Run 7	2	450	1	4,800
Run 8	2	550	1	240
Run 9	2	650	1	80
Run 10	2	450	2	150,000
Run 11	2	550	2	500
Run 12	2	650	2	180
Run 13	3	450	1	3,200
Run 14	3	550	1	2,800
Run 15	3	650	1	680
Run 16	3	450	2	110,000
Run 17	3	550	2	1,200
Run 18	3	650	2	200

Condition 1: Air and steam were supplied to the tube (O_2: 2%)

Condition 2: Nitrogen and steam were supplied to the tube

The above mentioned results suggest that exhaust gas treatment is required not only for removal of PCDDs/DFs but also for chlorine and sulfur when PCDDs/DFs -contaminated sediments are heat-treated. Although the secondary combustion process of exhaust gases is popular in the conventional heat -treatment system, there is concern that HCl and SO_x are produced during the combustion of materials containing chlorine and sulfur compounds. Further, such acid gases would corrode the exhaust duct of the heat -treatment system, resulting in operation failure. While the acid gases generated in the secondary combustion process have to be neutralized, the neutralization process could produce a large amount of wastewater and wastes. In order to control and minimize the production of such wastes, it is important to keep the oxygen concentration and the treatment temperature as low as possible in the heating chamber. On the other hand, the low -temperature heat-treatment may result in a less efficient elimination of PCDDs/DFs. So, laboratory assessment has to be implemented to find out the optimum operating conditions for PCDDs/DFs removal and chlorine/sulfur gasification.

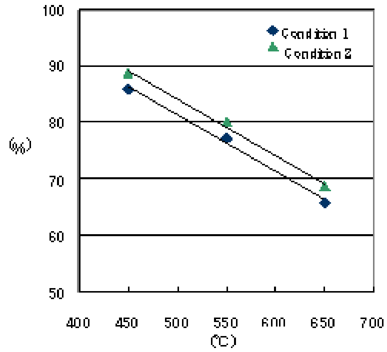

Fig. 4 : The relationship between residual ratio of chlorine in heat-treated sediment and heating temperature

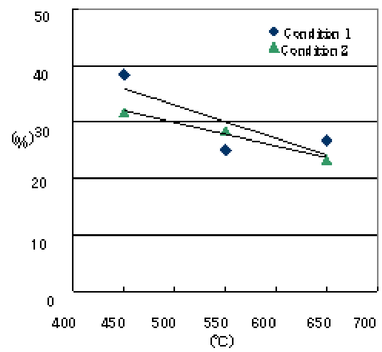

Fig. 5 : The relationship between residual ratio of sulfur in heat-treated sediment and heating temperature

The summary of the results is as follows:

w A higher heating temperature accelerates the PCDDs/DFs removal ratio when contaminated sediments are heat-treated.

w Removal ratio of PCDDs/DFs from contaminated sediments from a fresh water area by heat -treatment in a non -oxygen atmosphere was higher than that in an oxygen atmosphere.

w The PCDDs/DFs removal ratio of the fresh water sample was higher than that of other samples when heat -treated in a non -oxygen atmosphere, suggesting that seawater affects such thermal reactions.

w A higher heating temperature tends to accelerate the chlorine/sulfur gasification of the sample.

w Sulfur is desorbed from sediments more easily than chlorine by heat-treatment, eliminating approximately 70% of sulfur to the exhaust gas.

w Not only PCDDs/DFs but also chlorine and sulfur should be to be taken into consideration during treatment of exhaust gases produced during heat treatment.

References

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