

REMOVAL OF DIOXINS IN FLY ASH BY VACUUM HEAT TREATMENT II. TEMPERATURE DEPENDENCE AND THE OUTCOME OF OCDD

Tsuyoshi Abe², Kazuhiko Takeuchi¹, Youhei Misaka¹, Hiroyuki Hattori, Masashi Itoh³, Kazuo Ohba³, Masatoshi Watanabe³, Tatsumi Imura¹, Kyoichi Sawabe¹, and Kosuke Shobatake¹

¹Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

²Visiting researcher from Research and Development Division, Houei Shokai Co. Ltd, Teraike 66, Tsutsumi-cho, Toyota, 473-0962, Japan

³Dioxin Analysis Research Center, Nagoya City Environmental Science Research Institute, Shimoshidami, Moriyama-ku, Nagoya, 463-0003, Japan

Introduction

Many a technique has been developed for removing dioxins from fly ash and residues obtained from refuse incineration plants and contaminated soils. Simply heating the fly ash in the oxygen deficient atmosphere is known to reduce concentrations of dioxins¹. It was expected that, since heating of fly ash in vacuum would enable dioxins to be pumped out from the ash in the closed system and collected into a small volume, this technique would be safe for the workers at remediation plants and the people living near it. Therefore previously we studied the temperature dependence of dioxin concentrations in the fly ash heated in vacuum in the temperature range from 450 to 800 K². We have found that, by heating in vacuum at temperatures above 650 K for four hours, 99.98 % of dioxins in TEQ are removed from fly ash. However, since essentially no dioxins were detected in the liquid N₂ trap, we concluded that dioxins were chemically converted mainly via dechlorination/hydrogenation (DCH) reactions inside the fly ash.

The questions we now want to answer are 1) if dioxins on the fly ash surfaces really don't evaporate into vacuum and 2) if the DCH reactions are the only processes that dioxin molecules undergo in the fly ash. In the present study a known amount of octachloro-dibenzo-p-dioxin (OCDD) was added to a fly ash sample from which dioxins were removed by heating in vacuum and then the OCDD-containing fly ash was heated in vacuum. The amounts of 0- to 8-chlorinated PCDD's and PCDF's in the fly ash as well as in the liq. N₂ cooled trap were analyzed. In conclusion 1) after the heat treatment in vacuum for 4 hours at a sample temperature $T_s=650$ K 99.9 % of the dioxins in TEQ is removed, 2) the dioxins which were originally adsorbed on the fly ash surfaces can evaporate; at $T_s = 650$ K about 30 % of the OCDD is found in a liq. N₂ cooled trap, 3) at $T_s = 650$ K about 4 % of dibenzodioxin (DD) skeleton is converted into dibenzofuran (DF) skeleton, and 4) the total amount of dioxins and dibenzofurans decreases by vacuum heat-treatment and thus the DCH reaction is not the only reaction channels. The difference between the evaporation behaviors for the two experiments is invoked to interpret the difference between the states of the presence of dioxin molecules in the two fly ash samples; adsorbed on the ash surfaces and occluded in the ash particles.

Methods and Materials

First, the fly ash from a municipal refuse incineration plant of the City of Nagoya, which is hereafter called the "original fly ash" was heated at 750 °C in vacuum for four hours and dioxin-free fly ash was obtained. 5.00 ml toluene solution containing 55.0 µg of OCDD was added to 10.0 g of

REMEDIATION TECHNOLOGIES

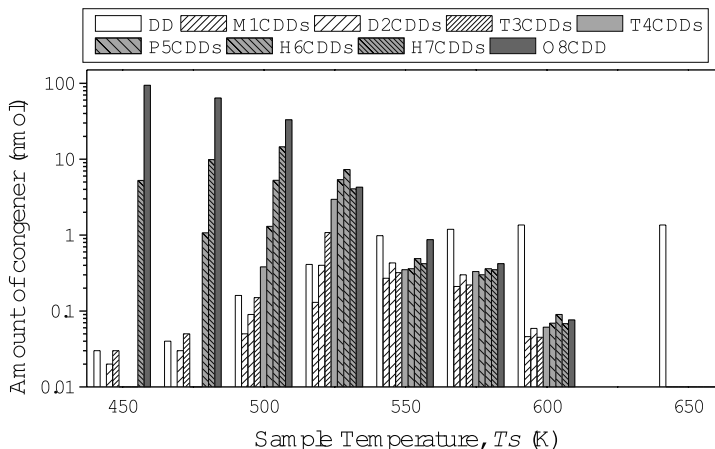


Figure 1. Amounts of PCDD congeners as well DD which remained in the fly ash obtained after heating the OCDD added sample in vacuum at sample temperatures T_s of 450, 475, 500, 525, 550, 575, 600, and 650 K. The OCDD added sample contained 120 nmol of OCDD

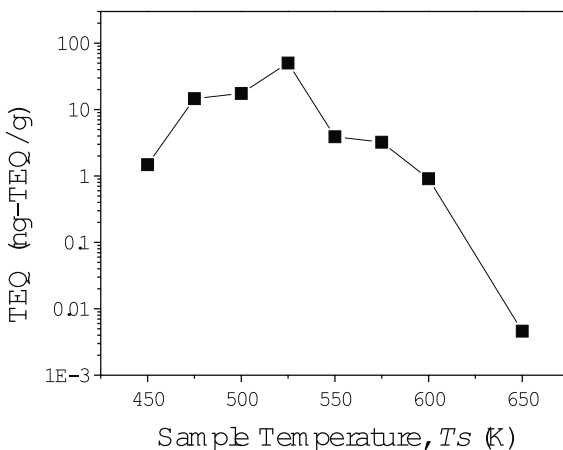


Figure 2. Toxicity level (ng-TEQ/g) of the vacuum-heat treated fly ash vs. T_s .

dioxin-free fly ash packed in a Pyrex tubing. After toluene was slowly evaporated from the ash sample kept at 20 °C, the tubing was wrapped with layers of Al foils and inserted in a Cu tubing wound with two sheath heaters around it. Then the fly sample was pumped at 120 °C for one hour to remove remaining toluene. Then the temperature was raised to the preset temperature, T_s at a heating rate of about 2 K/min, while being pumped by a 50 l/s turbomolecular pump through a Pyrex tubing (10 mm in diameter and ca 25 cm long) followed by a liquid nitrogen cooled trap. The sample temperatures were monitored using two thermocouples. After the pumping experiment is over, the glass tubing was fused just above the joint of the sample container. The dioxin contents in the heat-treated fly ash samples and in the liq. N₂ trap were analyzed by the authors at the Dioxin Analysis Research Center for octa-

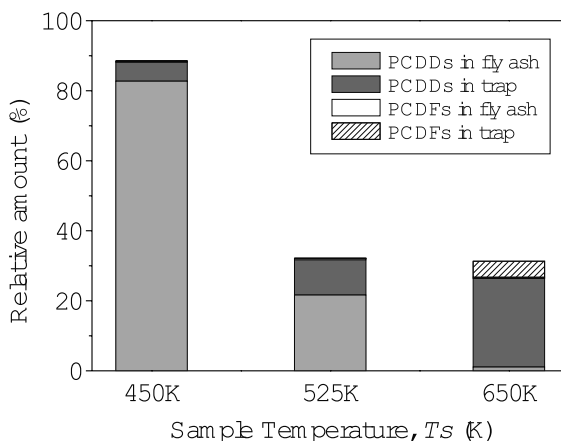


Figure 3. Amounts of PCDD and PCDF homologues found in fly ash and the liq. N_2 trap relative to the original

tetrachloro-DD's and DF's and by Shimadzu Techno-Research Inc. for trichloro- to monochloro-DD's and DF's as well as non-chlorinated DD (DD) and DF(DF).

Results and Discussion

The untreated sample of 10.0 g fly ash which hereafter we call "OCDD added sample" contains 55.0 μg (120 nmol) of OCDD, i.e. 5.5 ng TEQ. Fig.1 summarizes the amounts of PCDD's as well as DD which remain in the fly ash sample treated at temperatures of $T_s = 450, 475, 500, 525, 550, 575, 600,$ and 650 K. After heating in vacuum at $T_s = 650$ K for 4 hours, the TEQ level goes down to 0.1 % of that for the OCDD added sample. It is clearly seen that the fractions of less chlorinated PCDD congeners increase as T_s is raised. The results also indicate that DCH reactions proceed during the heat-treatment of the sample. It is rather surprising that the amount of DD levels off above $T_s = 525$ K.

Fig. 2 shows the temperature variation of TEQ (ng TEQ/g) of the fly ash treated at sample temperature, T_s for 4 hours. At $T_s = 500$ K the toxicity level in TEQ exhibits the maximum (50.2 ng TEQ/g) which is 91 times that of the OCDD added sample.

Previously we reported that the vacuum heat-treated fly ash from the municipal incineration plant exhibits a higher TEQ level than that of the original fly ash for $T_s = 475\text{-}500\text{K}$. The present results also corroborate the fact that, as the DCH reactions proceed, the amounts of PCDD's with higher TEF's increase and the TEQ level becomes much higher than that of the original sample with 120 nmol of OCDD.

Dioxins in liq. N_2 -cooled trap and outcomes of dioxins after the heat treatment

As is already described in Introduction, when the original fly ash sample was heated in vacuum, essentially no dioxins were detected in the liquid N_2 -cooled trap², and thus we have concluded that dioxins do not evaporate into vacuum but they undergo mostly DCH reactions in fly ash or on the surface². Therefore, before the present experiment was started we thought that no dioxins would evaporate into vacuum and thus dioxins were analyzed for the traps for only three runs carried out at $T_s = 450, 525$ and 650 K. Fig. 3 summarizes the relative amounts of PCDD and PCDF homologues which are found in the fly ash as well as in the trap normalized to the original OCDD (120 nmol) added for three treatment temperatures. From this result one can see that 1) some portion of the DD homologues

REMEDIATION TECHNOLOGIES

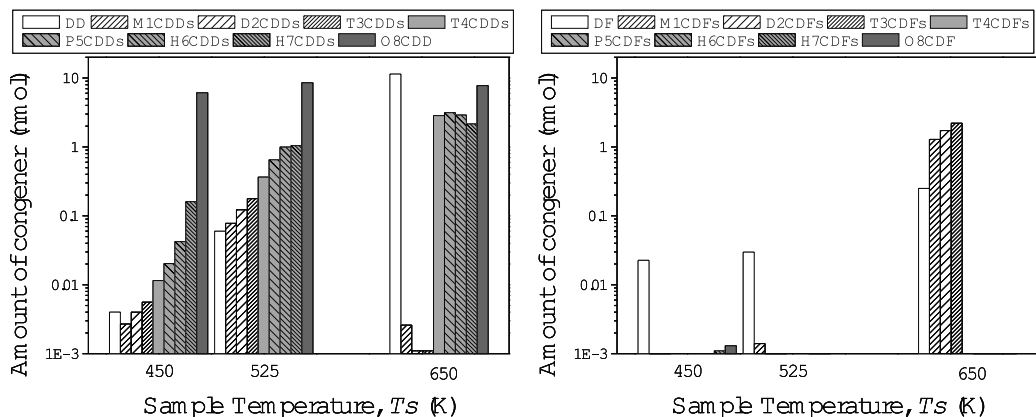


Figure 4. Amounts of polychlorinated DD(left) and DF(right) congeners trapped in the liq. N_2 cooled trap after vacuum heat-treatment for 4 hours at $T_s = 450, 525,$ and 650 K.

is converted into other molecules than PCDD and PCDF homologues, that is, at $T_s = 525$ and 650 K more than two thirds of dioxins are converted. As T_s is raised, the mole fraction of dioxins which are converted into other molecules than dioxins tend to increase, 2) dioxin molecules evaporate into vacuum and trapped in the cold trap even at $T_s = 450$ K, 3) at $T_s = 650$ about 30% of the original amount is found in the trap, and 4) about four per cent of the OCDD skeletons is converted into PCDF homologues. From the analyses of congeners in the trap, OCDD has been found to be the major congener for $T_s = 450$ K. Therefore even at $T_s = 450$ K about 6% of the added OCDD would evaporate into gaseous phase and be trapped in the cold trap. As T_s is increased the fractions of the less chlorinated PCDD congeners tend to increase, since DCH reactions form less chlorinated congeners. Fig. 4 also shows that four percents of original OCDD skeletons appear as tri-, di- and monochloro-DF's, which indicate conversion of DD skeleton can occur at high temperatures.

Conclusions that have been reached from the previous² and the present studies, seem to be contradictory, since from the previous study it was concluded that dioxin molecules do not evaporate into vacuum during the heat treatment of the original fly ash whose toxicity level was found to be about 5 ng TEQ/g. One possible way to get away with the present contradiction is *to invoke a difference in the state of presence of dioxin molecules in fly ash samples between the two experiments*; i.e. in the present experiment the OCDD molecules were originally on the fly ash surface and can be evaporated into vacuum, whereas in the original fly ash samples dioxin molecules may be present mostly in an occluded state inside the fly ash particles and had low probability of being evaporated into vacuum. Another possible reason is that since, in the OCDD added experiment, the amount of OCDD added was about 20 times that of dioxins in the original fly ash and thus the number of the active sites remaining on the ash surfaces is less for the former than the latter, the probability of the PCDD/DF congeners being evaporated is higher for the former. More experiments should be carried out to confirm what is really happening.

References

1. Hagenmaier H., Kraft M., Brunner H., and Haag R., (1987), *Environ. Sci. Technol.*, 21, 1080.
2. Shobatake K., Yamanaka K., Takeuchi, Seki T., Imura T., Abe T., and Sawabe K., (2001), *Organohalogen Compounds*, 54, 230.