REMOVAL OF DIOXINS FROM FLY ASH BY VACUUM HEAT TREATMENT I. TEMPERATURE DEPENDENCE

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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 dioxins[1]. By vacuum heating of fly ash one can expect to remove dioxins in the closed environment and thus this technique is expected to be safe for the workers at remediation plants and the people living near it. Here we present the results of the study on the temperature dependence of dioxin concentrations in the fly ash heated under vacuum as well as on the formation of dioxins in the vacuum-treated fly ash heated in flowing air. We show that heating fly ash under vacuum is very effective in removing dioxins.

Methods and Materials.
Two types of experiments were carried out. One is the heat treatment of fly ash under vacuum. Fly ash used was collected with a bag filter at a municipal refuse incinerator of the City of Nagoya. About 15 g of fly ash was packed in a Pyrex tubing, which is 15 cm long and 20 mm in outer diameter and closed at the bottom end, wrapped with layers of Al foils and wound with two sheath heaters around it. In order to remove water the fly ash was heated at 120°C for two hours and then pumped through a Pyrex tubing (10 mm in diameter and ca 25 cm long) through a liquid nitrogen cooled trap using a 50 l/s turbomolecular pump backed by a rotary pump. The baking temperatures were monitored with three thermocouples. After the pumping experiment is over, the glass tubing was fused just above the joint of the sample container.
In the second type of experiment the vacuum heat-treated fly ash, from which dioxins were almost completely removed, was treated in flowing air at 300°C to see how much dioxins are regenerated. The elemental analyses of metals contained in fly ash were carried out using ICP-AES. The main elements (in units of mg/g) are Ca (233), Si (73), Al (48), K (30), Na (26), Mg (14.4), Ti (6.7), Fe (6.2), Zn (6.0), P (4.3), Pb (1.1), and Cu (0.71). The concentrations of all of tetrachloro- or higher chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) and PCB's in fly ash as well as in the trap were analyzed by Japan Food Research Laboratories (JFRL), Inc.

Results and Discussion
The untreated sample which hereafter we call "original fly ash" contains 4.70±0.26 ng TEQ/g, 163±16ng/g of PCDDs and 96±4 ng/g of PCDFs. Fig.1 shows the TEQ's as a function of treatment temperature, T_s. One can obviously see that the toxicity levels of dioxins remaining in fly ash samples treated at 650, 717, and 800 K are less than 0.02 % of that for the original fly ash. Thus we conclude that dioxins are removed after vacuum treatment over 650 K for four hours.

Fig. 1 also shows that, at T_s around 475 K the toxicity level becomes higher than that for the original fly ash, despite of the fact total amount of PCDD/PCDFs decreases. The raw data show that the amounts of dioxins with high TEF's, e.g., 2,3,7,8-tetraCDD (T_4CDD) and 1,2,3,7,8-pentaCDD (P_5CDD), are much higher than those for original fly ash. In fact the mole fractions of less chlorinated homologues increase as the treatment temperature is raised and thus the TEQ level
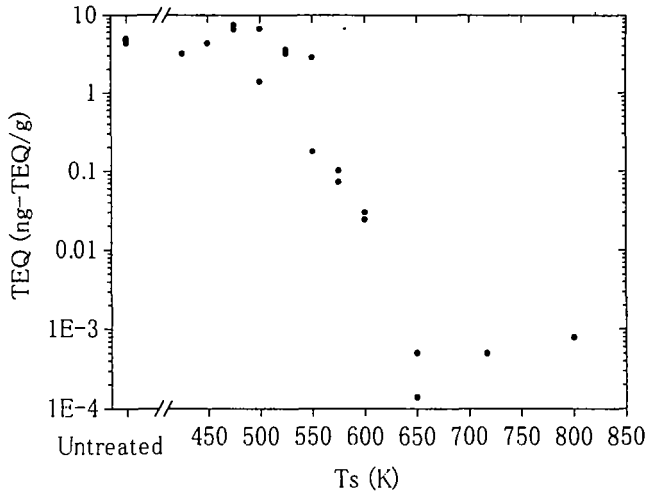

Fig.1 The total amount of dioxins(ng-TEQ/g) remaining in the fly ash treated at a treatment temperature,Ts

increases in a certain range of T_s, indicating that the dechlorination/hydrogenation reactions (DHR's) proceed as the treatment temperature is raised. Fig. 2 depicts the mole fractions of the homologues with the same number of chlorine atoms for PCDDs and PCDFs. Although raw data are not shown here, it is noted that, whereas the absolute amounts of dioxins and total TEQ's vary quite a lot from sample to sample at the same treatment temperature as is shown in Fig. 1, the relative ratios of the homologues do not vary very much. It is thus concluded that the main chemical processes are dechlorination/hydrogenation reactions as suggested by Hagenmaier et al.[1]

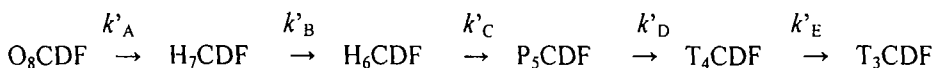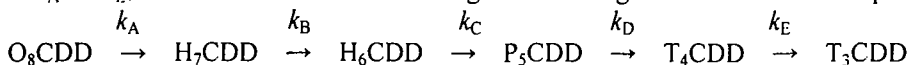Fig. 2 Mole fractions of the homologues with the same number of chlorine atoms for PCDDs and
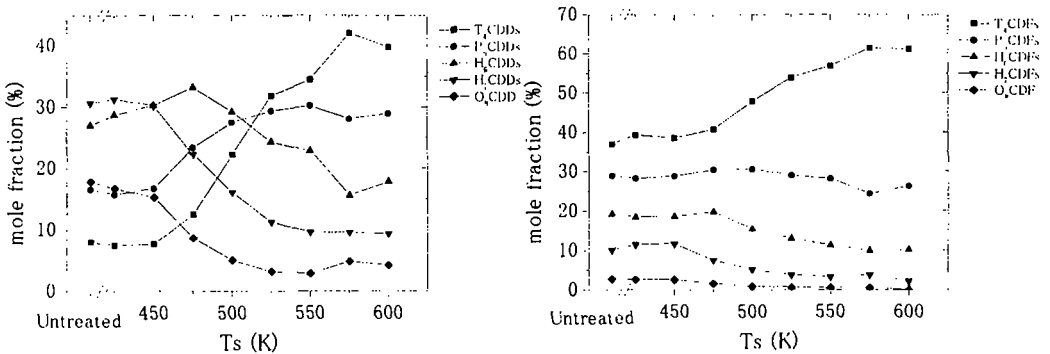
PCDFs vs. treatment temperature, T_s.

Concentrations of Dioxins in the Cooled Trap It is also noted that no PCDDs nor PCDFs with more than four chlorine atoms were detected in a liquid nitrogen cooled trap as well as in the

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Pyrex tube leading to the trap for the vacuum-treated samples at 500 and 650 K, which suggests that DHR's proceed and more importantly PCDDs and PCDFs do not evaporate into vacuum. When fly ash is heated in the flowing air, some portions of dioxins formed are detected in a cooled trap. The difference between the degrees in evaporation rates for the present treatment and the flowing air treatment might be due to the facts that either 1) dioxins evaporated into gas phase are more effectively transported in flowing air or 2) vacuum-treated "dry" fly ash surfaces exhibit higher desorption energies for dioxin molecules than those exposed to flowing air.

Dechlorination/Hydrogenation Rates for PCDD and PCDF Homologues   The DHR rates, k_A to k_E and k'_A to k'_E, have been determined assuming the following consecutive reactions proceed:

$$O_8CDD \xrightarrow{k_A} H_7CDD \xrightarrow{k_B} H_6CDD \xrightarrow{k_C} P_5CDD \xrightarrow{k_D} T_4CDD \xrightarrow{k_E} T_3CDD$$

$$O_8CDF \xrightarrow{k'_A} H_7CDF \xrightarrow{k'_B} H_6CDF \xrightarrow{k'_C} P_5CDF \xrightarrow{k'_D} T_4CDF \xrightarrow{k'_E} T_3CDF$$

Since we did not obtain the concentration for each isomer, the reaction rates for each isomer were assumed to be the same for the homologue. Solving the differential equations for the consecutive reactions, the reaction rates were determined for each treatment temperature and each homologue. From the Arrhenius plots shown in Fig. 3 the rate parameters for these reactions were determined. In determining the Arrhenius parameters the rate data at low treatment temperatures, 425 and 450K, were not adopted since the concentrations of the homologues are close to those for the original fly ash.
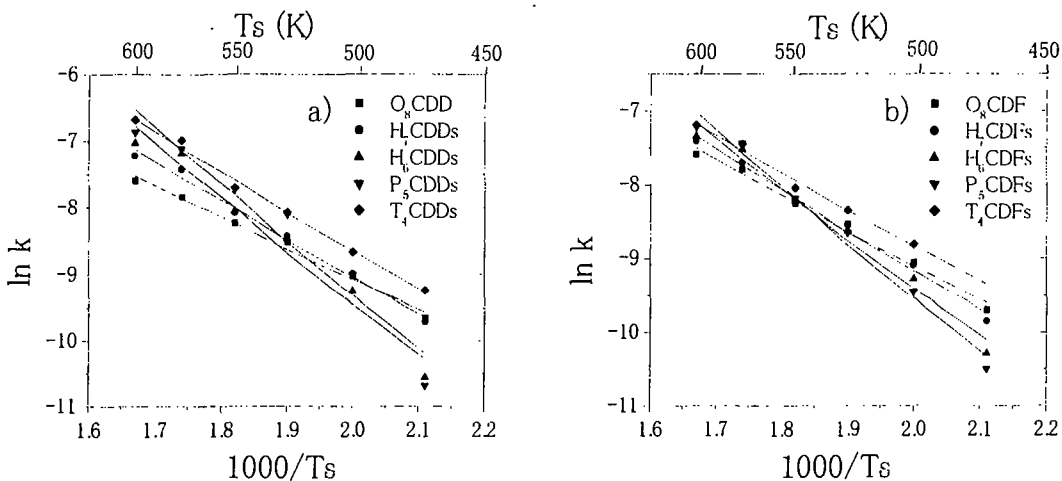

Fig. 3 Arrhenius plots for the DHR's, i.e. ln k vs. $1/T_s$. a) Rates for PCDD's and b) PCDFs.

The activation energies thus determined for PCDDs, i.e. k_A to k_E, are 45, 65, 62, 44, and 35 kJ/mol, respectively, and those for PCDFs, i.e. k'_A to k'_E are 37, 58, 51, 41, and 35 kJ/mol, respectively. The activation energies for the PCDFs are somewhat smaller than those for PCDDs. Although they vary from homologue to homologue, the activation energies are rather comparable to the heat of evaporation of H_2O (45 kJ/mol at 0°C) and are about two to three times smaller than the heat of

evaporation of 2,3,7,8-T$_4$CDD (125 kJ/mol), which might suggest that these activation energies correspond to heats of migration of dioxins on fly ash surfaces combined with the activation energies for DHR's.

Heat Treatment of the Vacuum-treated Fly Ash in Flowing Air   The fly ash that had been vacuum-treated at 800 K for four hours and contains very small amounts of dioxins was treated in flowing air as well as moist air at 300°C for four hours. The results are summarized in Table 1. Note that 1) PCDD and PCDF homologues with smaller numbers of chlorine atoms are dominantly formed in the regeneration reactions and 2) the total amount of PCDFs is about 30 times larger than that ᴏr PCDDs, i.e. 14 vs. 0.47 ng/g for dry flowing air experiment and 19 vs. 0.66 for wet flowing air experiment. Similar congener distributions have been also observed by Stieglitz et al.[3] and Weber and Hagenmaier[4], which suggests that dioxins are regenerated from the fused organic residues on fly ash.

Table.1 Amounts of PCDDs and PCDFs in the fly ash treated at 800K and treated fly ash at 300°C in dry and humid air along with their TEQ's.

Homologue	after treatment at 800K(p mol/g)	Retreated in dry air (p mol/g)	Retreated in humid air (p mol/g)
T$_4$ CDDs	0.015	0.60	1.03
(2,3,7,8-T$_4$CDD)	(N.D.)	(0.06)	(0.11)
P$_5$ CDDs	N.D.	0.38	0.54
H$_6$ CDDs	N.D.	0.14	0.18
H$_7$ CDDs	0.158	0.09	0.06
O$_8$ CDD	0.031	0.11	0.08
T$_4$ CDFs	N.D.	26.7	39.7
P$_5$ CDFs	N.D.	12.0	15.7
H$_6$ CDFs	N.D.	3.43	3.40
H$_7$ CDFs	0.001	0.70	0.43
O$_8$ CDF	0.087	0.07	0.03
TEQ (ng/g)	0.0008	0.31	0.41

References
1. Hagenmaier H., Kraft M., Brunner H., and Haag R., (1987), *Environ. Sci. Technol*, **21**, 1080.
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4. Weber R. and Hagenmaier H., (1999), *Chemosphere*, **38**, 529.