

## DECHLORINATION/HYDROGENATION REACTIONS OF DIOXINS IN ACTIVATED CARBON HEATED UNDER VACUUM

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### *Introduction*

There are presently many emission control and remediation techniques for removing dioxins in fly ash from municipal waste incinerators and contaminated soils. Simply heating fly ash in the oxygen deficient atmosphere is known to reduce concentrations of dioxins<sup>1</sup>. We have been developing a technique for removing dioxins in fly ash or contaminated soils by heating under vacuum<sup>2-4</sup>, since it is carried out in a closed system and thus this procedure is safe for the people working at the plant and/or living near them. We have found that 99.98% of dioxins in TEQ are removed from fly ash by the vacuum heat treatment above 650 K for 4 hours<sup>2</sup>. Furthermore, we have found dechlorination/hydrogenation (DCH) reactions as well as destruction reactions of dioxins proceed by heating fly ash which originally contain octachlorodibenzo-*p*-dioxins (OCDD) under vacuum<sup>3</sup>. And it has been demonstrated that dioxins in contaminated soils are pyrolyzed under vacuum at temperatures above 650 K<sup>4</sup>.

In the present paper we report the study on the outcome of heating OCDD in activated carbon under vacuum at temperatures ranging from 550 to 900 K for the purpose of finding conditions to pump out OCDD from activated carbon. Before the experiment we expected that dioxins could be pumped out by heating under vacuum, since activated carbon contains very small amount of Cu and Fe whose compounds are known to catalyze DCH reactions. From the obtained results, however, we have found that DCH reactions also occur in the activated carbon under vacuum.

### *Methods and Materials*

Toluene (5.00 ml) / n-hexane (about 15-20 ml) mixed solution of OCDD was added to high-purity activated carbon powder (DARCO® G-60, 100 mesh) (5.00 or 10.00 g) in a Pyrex container in the concentration ratio of 275 ng (598 pmol) of OCDD per one gram of activated carbon. After the solvent mixture was evaporated at low temperatures by lyophilization, the container was wrapped with layers of Al foils and inserted in a Cu tubing wound with a sheath heater around it. The sample was evacuated at 120°C for two hours in order to remove the remaining solvents. Then the dry activated carbon was heated to the preset temperature under vacuum at a heating rate of 2 K/min and then the sample temperature  $T_s$  was kept for four hours. The Pyrex container was pumped through a Pyrex tubing followed by a liquid N<sub>2</sub> trap using a 50 l/s turbomolecular pump backed by a rotary pump. After heating was over, the container was cooled to room temperature under vacuum and the tubing connecting the container to the liquid N<sub>2</sub> trap was fused. The concentrations of tetra- to octa-chlorinated DD/DFs and coplanar PCBs in the activated carbon powder as well as in the liquid N<sub>2</sub> trap were analyzed using GC/MS. The elemental analysis of activated carbon was carried out using ICP-AES, as shown in Table 1. The contents of Cu and Fe whose compounds are known to catalyze DCH reactions are low. ESR spectra were measured

using a JEOL JES-RE1X for powder samples containing each approximately 0.02 g activated carbon which was exposed to the air and then evacuated in a quartz tube to determine the

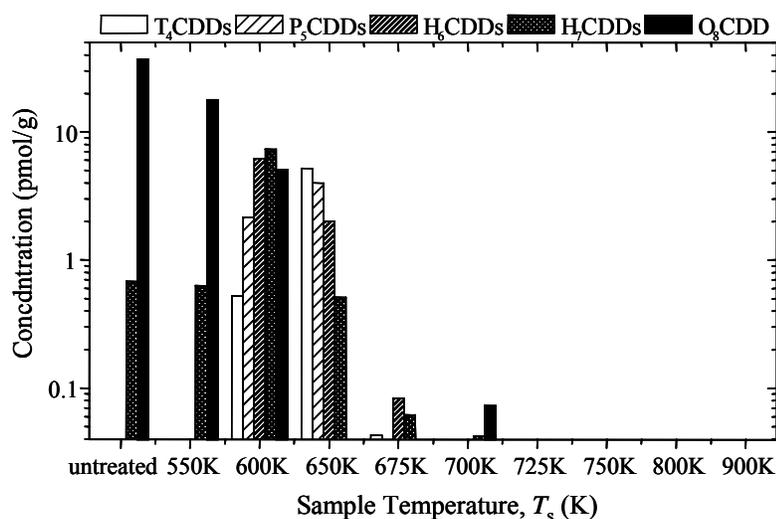
**Table 1. Concentration of the elements contained in activated carbon powder determined using ICP-AES**

Element	Concentration (mg/g)	Element	Concentration (mg/g)	Element	Concentration (mg/g)
Si	15.8	Na	0.71	Mn	0.0474
K	5	Fe	0.649	Ba	0.0474
Ca	1.04	P	0.33	Sr	0.0192
Al	0.831	Ti	0.21	Cu	0.017
Mg	0.753	Pb	0.18		

concentration of the doublet radicals present.

### Results and Discussion

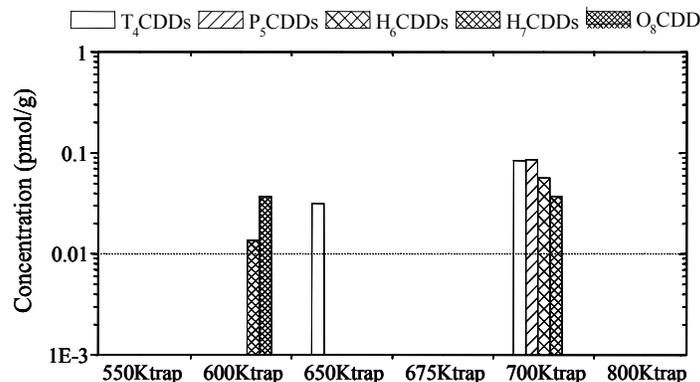
Figure 1 summarizes the concentrations of PCDD homologues that remained in activated carbon as a function of sample temperature as well as those of untreated sample. Note that 598 pmol of OCDD/(g activated carbon) was added. We have found that (1) once OCDD solution is added to activated carbon and solvents are evaporated, only 37 pmol/g of OCDD (i.e., 6.2 % of the added OCDD) was detected, (2) for  $T_s \geq 725$  K no PCDDs were detected in the activated carbon, (3) the activated carbon treated at  $T_s = 550$  K mostly contains OCDD, (4) whereas those heated at  $T_s = 600$  and 650 K contain more PCDDs that are less chlorinated than OCDD, and (5) as the sample temperature is increased, the fractions of less chlorinated PCDDs increases; i.e. (6) *DCH reactions proceed by treating OCDD in the activated carbon under vacuum*.



**Figure 1: Concentrations of dioxins which remained in activated carbon treated in vacuum for four hours at  $T_s = 550, 600, 650, 675, 700, 725, 750, 800,$  and 900 K.**

Figure 2 shows the concentrations of PCDD homologues collected in a liquid nitrogen cooled trap after the heat treatment at  $T_s = 550, 600, 650, 675, 700,$  and 800 K. Only approximately 0.01 mole % of the added OCDD, which is comparable to the detection limit of the PCDD homologue,

was detected at  $T_s = 600$  and  $650$  K, and 0.04 mole % was detected at  $700$  K; i.e. hardly no dioxin molecules desorb into the vapor phase from the activated carbon. Figure 3 also shows the levels of

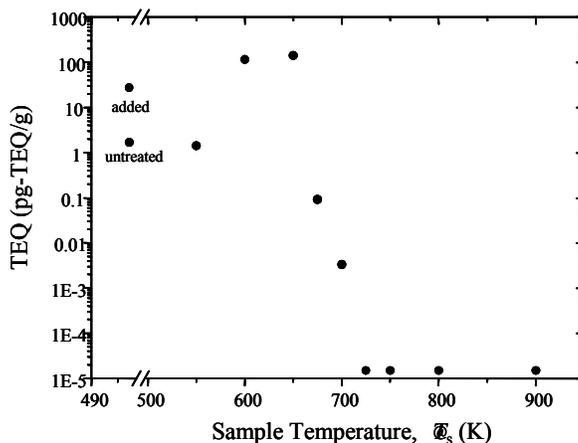


**Figure 2: Concentrations of dioxins in liquid nitrogen cooled trap after the heat treatment at  $T_s = 550, 600, 650, 675, 700,$  and  $800$  K.**

approximate detection limits at  $0.01$  pmol/g.

Figure 3 shows the toxicity levels (in pg-TEQ/g) of activated carbon samples as a function of  $T_s$ . The toxicity level is found to increase as  $T_s$  is increased from  $550$  K to  $650$  K and is peaked at  $650$  K at a value of  $142$  pg-TEQ/g, which is 5.2 times higher than that of the added OCDD ( $27.5$  pg-TEQ/g). Above  $725$  K, however, the toxicity levels were found to be below the detection limit.

From these results the following questions arise: (1) Why are the relative amounts of dioxins that remain in the activated carbon powder and in the liquid  $N_2$  trap so low? (2) Are OCDD molecules, added to activated carbon powder in n-hexane/toluene solution and then followed by evaporating the solvents under vacuum, present in a completely different environment from those adsorbed from the vapor phase? In order to find possible answers to the first question, the concentrations of doublet radicals in activated carbon were measured using electron spin resonance spectroscopy (ESR) as a function of  $T_s$ . The results in Table 2 show that the concentration of organic radicals in the activated carbon increases as  $T_s$  is increased and they are about 400 times higher than that of OCDD added ( $3.60 \times 10^{14}$  molecules/g). Although the origin of the radical formation is not clarified, we may be able to conclude that a large number of reactive sites are present in activated carbon. Therefore the possible answers to the first question are (a) PCDDs readily react with radicals present in activated carbon even at room temperature, and (b) at elevated temperatures activated carbon catalyzes the DCH reactions because of the presence of metallic elements such as Cu ( $0.017$  mg/g) and Fe ( $0.649$  mg/g). We have reported that, heating OCDD under vacuum for 4 h at  $T_s = 650$  K in the fly ash that contained at least ten times more



**Figure 3: Toxicity level of activated carbon vs. sample temperature  $T_s$ .**

metallic elements, e.g. Cu (0.706 mg/g) and Fe (6.17 mg/g), the added OCDD was almost completely converted to non-toxic, less chlorinated PCDD/DFs<sup>3</sup>.

As to the second question mentioned above, we give a few comments. After activated carbon powder was immersed in OCDD solution and then the solvents were evaporated, would OCDD molecules be imbedded between the layers of condensed aromatic rings of activated carbon or are they adsorbed on the activated carbon particles? Similarly to well-known graphite intercalation

**Table 2. Concentrations of doublet radicals in activated carbon (ESR measurements)**

sample name	original	untreated	550 K	600 K	750 K
concentration of doublet radicals (g <sup>-1</sup> )	1.58E+17	1.24E+17	2.08E+17	2.34E+17	3.04E+17

compounds, OCDD molecules may be imbedded and thus hardly be evaporated into the vapor phase. If gaseous OCDD molecules are adsorbed on the particle surfaces of activated carbon, they may be desorbed more readily than the case as was carried out in the present experiment. We plan to carry out experiments to find if the state of existence of the dioxin molecules in activated carbon makes any difference in their physical and chemical behaviors.

### Conclusions

The activated carbon powder (high purity carbon, 100 mesh) to which OCDD was added in mixed toluene/n-hexane solution was heated under vacuum at  $T_s$ 's ranging from  $T_s = 550$  to 900 K, after evaporating the solvents. Dioxins that remained in the activated carbon and trapped in the liquid N<sub>2</sub> trap were analyzed using GC/MS. We have found that (1) only 6.2 mole % of the OCDD added was recovered from the activated carbon even when it was not heated under vacuum, (2) even at  $T_s = 700$  K, the highest of the three temperatures at which dioxins were detected in the trap, only 0.04% of dioxins were captured in the liquid N<sub>2</sub> cooled trap, and only 0.01 mole % was detected in the trap for both  $T_s = 600$  and 650 K, (3) at sample temperatures of  $T_s \geq 600$  K less chlorinated PCDDs than OCDD were detected, which means that dechlorination/hydrogenation reactions proceed, (4) the toxicity level of activated carbon was peaked at  $T_s = 650$  K and was essentially zero above 725 K, and (5) the concentrations of doublet radicals present in activated carbon were found to be more than 400 times higher than that of the added OCDD. We conclude that activated carbon also works to deactivate dioxins when heated above 725 K for 4 h under vacuum, although its reactivity is lower than that of fly ash from municipal incineration plants.<sup>2</sup>

### References

1. Hagenmaier, H., Kraft, M., Brunner, H., and Haag, R.; (1987) *Environmental Science & Technology*, 21, 1080.
2. Shobatake, K., Yamanaka, K., Takeuchi, K., Seki, T., Imura, T., Abe, T., and Sawabe, K.; (2001) *Organohalogen Compounds*, 54, 230.
3. Abe, T., Takeuchi, K., Misaka, Y., Hattori, H., Itoh, M., Ohba, K., Watanabe, M., Imura, T., Sawabe, K., and Shobatake, K.; (2002) *Organohalogen Compounds*, 58, 149.
4. Abe, T., Mizuno, H., Noguchi, K.; (2001) *Organohalogen Compounds*, 54, 157.