

## The change in the chemical form of copper in fly ash in a suitable temperature region for de novo synthesis

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### Introduction

Copper chloride as an important catalyst generates many polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/DFs) and related compounds in heat experiments involving model fly ash<sup>1-4</sup>. We investigated the chemical forms of copper in actual fly ash before heating experiments and discuss the relationship that we discovered between the copper species  $\text{Cu}(\text{OH})_2$ ,  $\text{CuO}$ , and  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3 \cdot \text{H}_2\text{O}$  and the formation of chlorinated aromatics in actual fly ash using X-ray absorption near-edge spectroscopy (XANES)<sup>5</sup>. Other results using model fly ash differ from ours<sup>1-4</sup>. The thermal stabilities of these compounds are not high, so these compounds might not exist in fly ash in the temperature region suitable for *de novo* synthesis. Therefore, we conducted *in situ* XANES experiments using actual fly ash and two models of fly ash to understand the behavior of copper in fly ash in the temperature region suitable for *de novo* synthesis.

### Materials and Methods

Actual fly ash was sampled from a bag filter with no lime and no activated carbon injection in a stoker-type municipal solid-waste incinerator (MSWI). The measured copper, chlorine, and total organic carbon levels were 2600 mg/kg, 14%, and 1.5%, respectively. The detailed measurement procedures are presented elsewhere<sup>6</sup>. We prepared two kinds of model fly ash: a mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , activated carbon (AC), and boron nitride (BN); and a mixture of  $\text{CuO}$ , KCl, AC, and BN. Each model fly ash contained 1.8% Cu, 2.0% Cl, 5.0% AC, and almost all the remainder was BN. After grinding the fly ash using a mortar for 10 minutes, 200 mg was pressed into disks 13 mm in diameter.

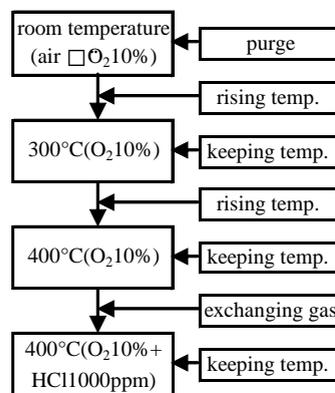
The direct speciation of copper in fly ash was examined using XANES with an *in situ* cell, as shown in Fig. 1. XANES was performed using beamline BL01B1 in



Fig.1 In situ cell

SPring-8, a synchrotron radiation facility in Japan<sup>7</sup>, while a disk of fly ash was heated in the *in situ* cell. The heating procedure and atmospheric conditions are shown in Fig. 2. The spectra were collected in fluorescence mode using a 19-element Ge solid-state detector for actual fly ash disks and in transmission mode using an ionization chamber for model fly ash with an Si(111) monochromator. The data were analyzed using REX 2000 ver.2.3.3 (Rigaku co. Ltd.). A pattern-fitting analysis of the XANES spectra was conducted, which assumed that the unknown spectra were linear combinations of reference spectra in our library (Cu, Cu<sub>2</sub>O, CuCl, CuO, CuCl<sub>2</sub>·2H<sub>2</sub>O, CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>·H<sub>2</sub>O, CuS, Cu(OH)<sub>2</sub>, CuSO<sub>4</sub>, CuFeO<sub>4</sub>, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub>). The Cu K edge XANES spectra of twelve of the reference materials are shown in Fig. 3. The residual value (R) calculated using Eq. (1) was used to evaluate the fit of the model predictions to the experimental data.

$$R: \text{residual value } R = \frac{\sum (XANES_{\text{Measured}} - XANES_{\text{Calculated}})^2}{\sum (XANES_{\text{Measured}})^2} \times 100 \quad (1)$$

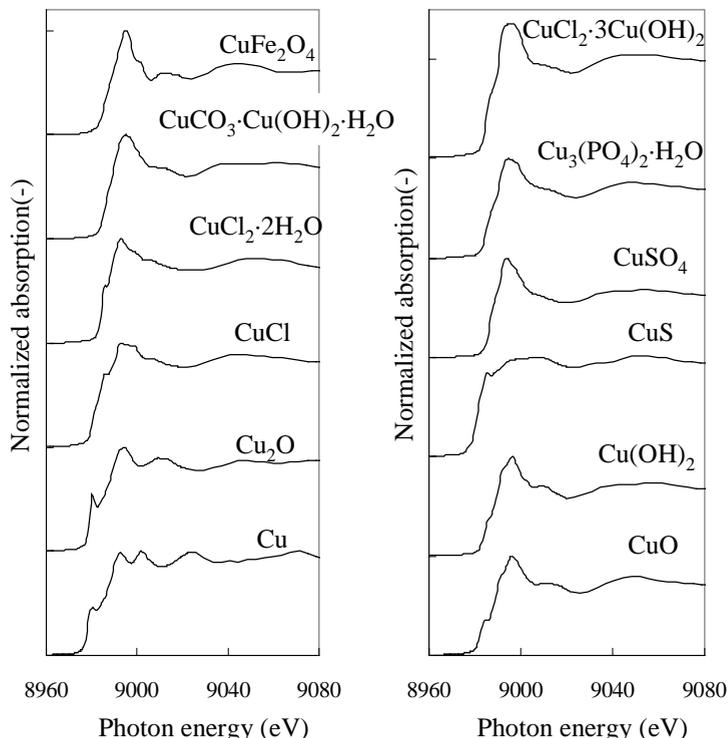


**Fig.2 Heating procedure in *in situ* XAFS experiment**

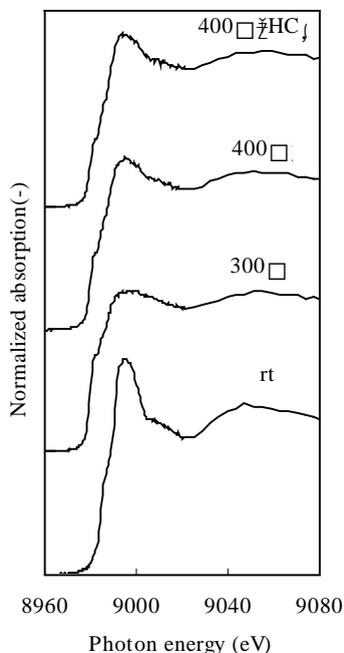
## Results and Discussion

### The change in the chemical form of copper in actual fly ash

The change in the chemical form of copper in actual fly ash with heating is shown in Fig. 4 and Table 1. At room temperature, the XANES spectra indicated that the copper compounds consisted of 75% CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub>, 14% CuCl, and 11% Cu(OH)<sub>2</sub>. CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> is a copper chloride hydroxide mineral that resembles CuCl<sub>2</sub>·CuO in structure, and is thought to be a vital catalyst in the chlorination of ethylene<sup>8</sup>. CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> is dehydrated to form CuCl<sub>2</sub>·CuO when the temperature reaches ca. 270°C<sup>9</sup>.



**Fig.3 The Cu K edge XANES spectra of twelve of the reference materials**



**Fig.4 The Cu K edge XANES spectra in actual fly ash with heating**

XANES showed that the chemical form of copper in fly ash depended on the temperature, and that cupric compounds at room temperature were transformed into cuprous compounds or elemental copper by heating.

To confirm the temperature at which the reaction starts, the same fly ash was heated from room temperature to 200°C. CuCl, Cu, and Cu<sub>2</sub>O were found instead of cupric compounds at 200°C. When the temperature was increased to 300°C, the ratios of these copper compounds were the same as at 200°C. Therefore, the reduction of cupric compounds began at below 200°C, which suggests that fly ash can form dioxins or other chlorinated compounds at temperatures below 200°C, although the rates of the gasification and chlorination reactions of carbon are so slow that little dioxin is generated.

When the atmosphere contained 1000 ppm HCl, the ratio of CuCl increased and that of Cu<sub>2</sub>O decreased. Although HCl did not influence the chlorination of copper in fly ash at 400°C, it might contribute to the chlorination of copper at 300°C.

#### The change in the chemical form of copper in model fly ash

Using the model fly ash, XANES spectra were measured at room temperature, 300°C, and 400°C, and at intermediate temperatures as the temperature increased. Note that the temperature at the beginning of these intermediate XANES spectra differs from that at the end, because it took 6.5 minutes to complete a measurement in the XANES region.

**Table1 The change in the chemical form of copper in actual fly ash with heating**

actual fly ash A; O <sub>2</sub> 10%; rt □ 300°C □ 400°C □ 400°C+HCl							
	Cu	Cu <sub>2</sub> O	CuO	CuCl	CuOH <sub>2</sub>	CuCl <sub>2</sub> ·3Cu(OH) <sub>2</sub>	R
rt				14	11	75	0.014
300°C	29	26		44			0.041
400°C	20	19		61			0.019
400°C+HCl	21	14	16	49			0.017

We detected CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> in the actual fly ash.

When the fly ash was heated to 300°C, the chemical forms of copper changed dramatically to 45% CuCl, 29% Cu, and 26% Cu<sub>2</sub>O. We could not recognize CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> in the heated fly ash. Heating fly ash to 300°C transformed the cupric compounds in the fly ash into cuprous compounds or elemental copper. This indicates that the atmosphere in fly ash is very reductive. When the temperature of the fly ash increased to 400°C, the ratio of CuCl increased to 61% of the total Cu and the ratios of Cu and Cu<sub>2</sub>O decreased to 20% each. Then, the atmosphere was changed from 10% O<sub>2</sub> (90% N<sub>2</sub>) gas to 10% O<sub>2</sub> + HCl 1000 ppm (balance N<sub>2</sub>) to observe the effect

of chlorination by HCl at 400°C. The ratios of CuCl and Cu<sub>2</sub>O decreased to 49 and 14% of the total Cu, respectively, and CuO appeared. Oxidation of Cu<sup>+</sup> compounds to CuO occurred rather than the chlorination of copper in fly ash by HCl. *In situ*

**Fly ash model A (CuCl<sub>2</sub>·2H<sub>2</sub>O+AC+BN)**

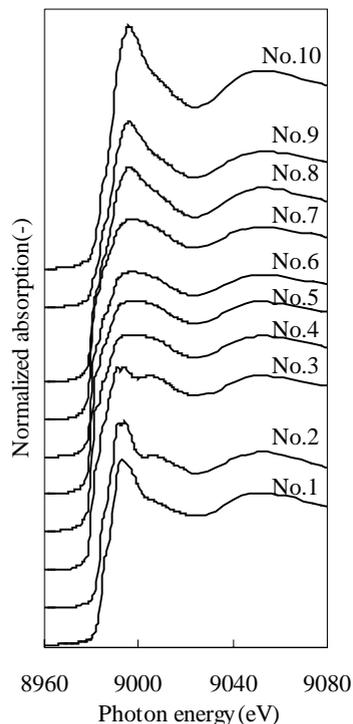
The change in the chemical form of copper in fly ash model A on heating is shown in Fig. 5 and Table 2. At room temperature, the copper compounds consisted of 77% CuCl<sub>2</sub>·2H<sub>2</sub>O and 23% CuO. Therefore, some of the CuCl<sub>2</sub>·2H<sub>2</sub>O changed into CuO while we were grinding and pressing the model fly ash into a disk. During the first temperature increase, the CuO disappeared, while CuCl and Cu<sub>2</sub>O appeared, and the ratio of CuCl<sub>2</sub>·2H<sub>2</sub>O did not change. Therefore, the CuO at room temperature is very unstable. In the second temperature increase, no CuCl<sub>2</sub>·2H<sub>2</sub>O was observed and CuCl was the predominant species, with 22% Cu<sub>2</sub>O and 15% Cu. This means that the CuCl<sub>2</sub>·2H<sub>2</sub>O in this model fly ash is strongly reduced at low temperatures. This change in the chemical form of copper in fly ash model A agrees with that in actual fly ash.

Although there was some variation, at temperatures below 300°C CuCl made up 60% of the total Cu, while Cu<sub>2</sub>O and Cu contributed 20% each. Therefore, copper compounds with a low valence, such as CuCl, play an important role in the formation of PCDDs/DFs, polychlorinated biphenyls (PCBs), and chlorinated benzenes (CBzs) in fly ash at temperatures near 300°C.

As the temperature increased to 400°C, the ratio of CuCl remained at about 60%, while the ratios of Cu<sub>2</sub>O and Cu decreased and CuO appeared. At a constant temperature of 400°C, the ratio of CuCl decreased to 5.2%, whereas the ratio of CuO increased to 60% and was the main component. Note that although the starting material CuCl<sub>2</sub>·2H<sub>2</sub>O was not observed in the intermediate temperature region, it reappeared at 400°C.

We measured XANES spectra of this model fly ash

after cooling the *in situ* cell from 400°C to room temperature and dismantling the cell. Low-valence copper compounds vanished from the model fly ash, and CuCl<sub>2</sub>·2H<sub>2</sub>O and CuO accounted for 28 and 72% of the



**Fig.5 The Cu K edge XANES spectra in fly ash model A on heating**

**Table2 The change in the chemical form of copper in fly ash model A on heating**

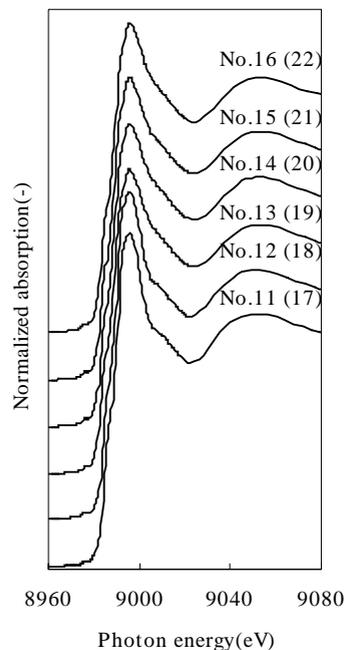
No.	step	starting temp.	Cu <sub>2</sub> O	CuCl <sub>2</sub> ·2H <sub>2</sub> O	CuCl	Cu	CuO	R
1	rt	35		77			23	0.011
2	rt □ 300°C 1st loop	41	11	78	11			0.023
3	rt □ 300°C 2nd loop	170	22		63	15		0.044
4	rt □ 300°C 3rd loop	306	26		54	20		0.053
5	rt □ 300°C 4th loop	298	24		54	22		0.053
6	300°C	298	20		58	22		0.045
7	300°C □ 400°C 1st loop	313	21		60	18		0.049
8	300°C □ 400°C 2nd loop	390	11		58	15	16	0.024
9	400°C	391		23	5.2	11	60	0.018
10	400°C □ rt(cooling)	-		28			73	0.027

total Cu, respectively.

In these measurements, low residual values (R) were obtained at room temperature and at 400°C, which meant that the spectra fits were adequate, although the residual values at 300°C were relatively high. Therefore, at 300°C, the model fly ash might contain unknown compounds that were not included in the references used. Alternatively, the very fast redox reaction in the model fly ash might distort the spectra at 300°C. We exposed the *in situ* cell for model fly ash A to air for 34 hr after measuring the final state of copper in the model fly ash in this experiment. We wanted to confirm whether the chemical form of copper remains in the final state at the end of the experiment or returns to the original forms before heating (*i.e.*, 77%  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 23%  $\text{CuO}$ ). We also wanted to check whether the same changes in chemical form occur on reheating at 300°C.

Cu K edge XANES spectra from this experiment are shown in Fig. 6 and Table 3. The spectrum after exposure to air for 34 hr differed from that measured immediately after the experiment and closely resembled the spectrum of  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ . If the only copper compounds in fly ash model A were  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuO}$ , the ratio of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CuO}$  was the same as in the final state of the initial experiment. However, the residual factor increased from 0.027 to 0.054. In other words, the chemical form of copper changed slightly on exposure to air for 34 hr. Consequently, we performed spectral fits with and without  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ . As the temperature increased to 300°C, the ratio of  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$  decreased remarkably to 10%.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuO}$  accounted for 30 and 60% of the total Cu, respectively, when considering the presence of  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ . The distribution did not change at 300°C.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuO}$  accounted for 30-34 and 66-71% of the total Cu in the spectra fit without  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ , respectively. In both

cases, the chemical form of copper did not change dramatically compared with the final state in our experiment. When pure  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was used as the starting material, it was strongly reduced to  $\text{Cu}_2\text{O}$  and Cu at around 300°C. By contrast, no low-valence copper compounds were observed on reheating



**Fig.6 TheCu K edge XANES spectra in fly ash model A on reheating**

**Table3 The change in the chemical form of copper in fly ash model A on reheating**

No.	step	starting temp.	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{CuO}$	$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$	R
11	rt	35		14	86	0.021
12	rt□300°C 1st loop	41		18	82	0.015
13	rt□300°C 2nd loop	170	30	61	9.1	0.021
14	rt□300°C 3rd loop	306	29	63	9.1	0.022
15	rt□300°C 4th loop	298	29	61	10	0.023
16	300°C	298	26	62	12	0.025
17	rt	35		29	71	0.054
18	rt□300°C 1st loop	41		33	67	0.047
19	rt□300°C 2nd loop	170	34	66		0.022
20	rt□300°C 3rd loop	306	33	67		0.023
21	rt□300°C 4th loop	298	33	67		0.023
22	300°C	298	31	69		0.026

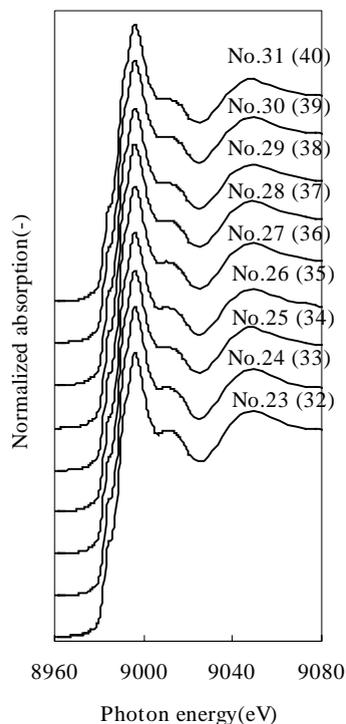
the model fly ash after the experiment. The same change in chemical form did not recur on reheating at 300°C. This occurred because the change in the composition of the model fly ash on heating at 400°C prevents the redox reaction of copper compounds from taking place.

#### Fly ash model B (CuO+AC+KCl+BN)

Cu K edge XANES spectra of fly ash model B are shown in Fig. 7 and Table 4. Spectra fits were also performed with and without  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ . At room temperature, the copper compounds were 95% CuO, 4%  $\text{Cu}_2\text{O}$ , and 1%  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . Although a small portion of CuO changed into  $\text{Cu}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  while we were grinding and pressing the model fly ash into a disk, CuO was more stable than  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . Assuming that  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$  was absent, the ratio of CuO decreased slightly from 95 to 88%, while the ratio of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  increased from 1 to 7% as the temperature rose from room temperature to 400°C. The ratio of CuO in the spectra fit with  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$  was just slightly lower than that without  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ , but showed the same tendency to decline. The ratio of  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$  rose from 7 to 11% with temperature. This indicates that the amount of CuO does not vary markedly in model fly ash in the temperature region suitable for *de novo* synthesis.

**Table 4** The change in the chemical form of copper in fly ash model B on heating

No.	step	starting temp.	$\text{Cu}_2\text{O}$	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	CuO	$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$	R
23	rt	35	3.1	1.2	96		0.009
24	rt □ 300°C 1st loop	41	0.7	3.0	96		0.008
25	rt □ 300°C 2nd loop	170	4.6	4.9	90		0.008
26	rt □ 300°C 3rd loop	306	5.0	4.9	90		0.008
27	rt □ 300°C 4th loop	298	3.3	5.8	91		0.005
28	300°C	300	3.8	5.4	91		0.007
29	300°C □ 400°C 1st loop	313	4.7	6.3	89		0.009
30	300°C □ 400°C 2nd loop	390	6.1	5.9	88		0.010
31	400°C	390	4.8	6.6	89		0.008
32	rt	35	4.2		89	6.9	0.008
33	rt □ 300°C 1st loop	41	2.5		89	9.0	0.006
34	rt □ 300°C 2nd loop	170	6.8		84	9.3	0.007
35	rt □ 300°C 3rd loop	306	7.1		84	9.0	0.007
36	rt □ 300°C 4th loop	298	5.7		85	9.7	0.005
37	300°C	300	6.0		85	9.3	0.007
38	300°C □ 400°C 1st loop	313	7.2		82	11	0.008
39	300°C □ 400°C 2nd loop	390	8.5		81	10	0.009
40	400°C	390	7.4		82	11	0.008



**Fig. 7** The Cu K edge XANES spectra in fly ash model B on heating

Previously, we indicated that CuO,  $\text{Cu}(\text{OH})_2$ , and  $\text{Cu}(\text{OH})_2 \cdot \text{CuO}_3 \cdot \text{H}_2\text{O}$  were more important than CuCl and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  for *de novo* synthesis in MSWI fly ash. By contrast, the present results suggest that CuCl and

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  play a vital role in the formation of chlorinated aromatics. This discrepancy appears to result from newly considering  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ , which resembles  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$  in shape, in the XANES spectrum. Moreover, the results suggest that it might be difficult to predict the chemical forms that will be seen in fly ash during heating from those present before heating.

### Acknowledgements

The synchrotron radiation experiments were performed at the SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No.2002B0370-NX-np & 2003B0215-Nxa-np). We greatly thanks the financial support by a Grand-in-Aid for Waste treatment Research from Ministry of the Environment, Japan (Proposal No.K1514).

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