CHANGE IN CHEMICAL FORM OF COPPER IN FLY ASH AT TEMPERATURES SUITABLE FOR DIOXIN FORMATION

Understanding the mechanisms involved in the formation of dioxins in fly ash is necessary in the control of dioxin emission. Dioxins are secondarily formed in a post-combustion zone, which is considered to occur primarily on and in fly ash, as first described by Stiegltiz and Vogg [1]. According to many studies, copper compounds are regarded as influential catalysts that generate large amounts of dioxins in heat experiments involving model fly ash. Nevertheless, only limited information on the chemical forms of copper or their changes in real fly ash is available in the literature. Previously, we investigated the chemical forms of copper in eight types of real fly ash before heating experiments using XANES [2]. However, to understand the exact formation mechanism, it is necessary to study the reaction that takes place with Cu compounds during the heating of fly ash. Here, we conducted *in situ* XANES experiments using real fly ash.

Real fly ash was sampled from a bag filter in a normal 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 direct speciation of copper in fly ash was examined using XANES with an *in situ* cell (see Fig. 1) at beamline **BL01B1**. The heating procedure and atmospheric conditions are shown in Fig. 2. The spectra were collected in a fluorescence mode using a 19-element Ge solid-state detector with a Si(111) monochromator. Species have also been distinguished using the linear combination fit (LCF) technique, in which the spectra of known reference species are fitted to the spectrum of an unknown sample.

Fig. 1. XANES experiment using *in situ* cell.

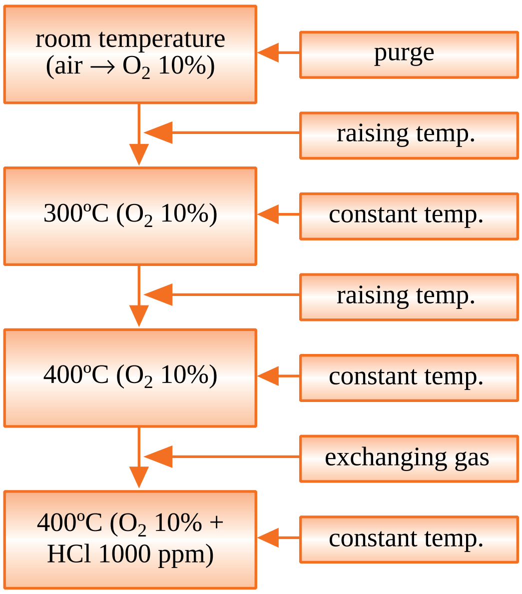

Fig. 2. Heating procedure of *in situ* XANES experiment.

The change in the chemical form of copper in real fly ash during heating is shown in Fig. 3. At room temperature, the XANES spectra indicated that the copper compounds consisted of 75% $CuCl_2{\cdot}3Cu(OH)_2$, 14% CuCl, and 11% $Cu(OH)_2$. $CuCl_2{\cdot}3Cu(OH)_2$ is one of the species present as a catalyst in the chlorination of ethylene [3] and as the main species in real fly ash [2]. In the second temperature increase, the shape of the XANES spectra dramatically changed and the edge position of the spectra shifted to a low energy. Hence, it was found that the reduction of cupric compounds begins below 200°C. When the fly ash was heated to 300°C, the chemical forms of copper dramatically changed to 45% CuCl, 29% Cu, and 26% Cu_2O. We did not recognize $CuCl_2{\cdot}3Cu(OH)_2$ in the heated fly ash. Heating the fly ash to 300°C transformed the cupric compounds in the fly ash into cuprous compounds or elemental copper. This indicates that the atmosphere surrounding the 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, while the ratios of Cu and Cu_2O decreased to 20%. The atmosphere was then changed from 10% O_2 (90% N2) gas to 10%O_2 + HCl 1000 ppm (balance of N_2) to observe the effect of chlorination by HCl at 400°C. The ratios of CuCl and Cu_2O decreased to 49 and 14% of the total Cu, respectively, and CuO appeared. Oxidation of Cu^+ compounds to CuO occurred rather than the chlorination of copper in fly ash by HCl. *In situ* XANES showed that the chemical form of copper in the fly ash depends on the temperature, and that cupric compounds at room temperature are transformed into cuprous compounds or elemental copper by heating. The trend observed in the XANES spectra of an oxychlorination catalyst is similar to those obtained by us [3]. Thus, we can conclude that oxychlorination occurs in real MSWI fly ash. Some researchers have suggested that oxychlorination occurs in real fly ash [4], although until now, only limited evidence of this is available. However, in this study, we found stronger evidence for this in our *in situ* XANES experiment. Since it is thought that the state of copper in fly ash depends on the temperature, fly ash composition, and surrounding environment, research on its effects on the chemical forms of copper is required. Furthermore, the correspondence between the amount of dioxin generated and the change in the chemical form of copper should also be investigated.

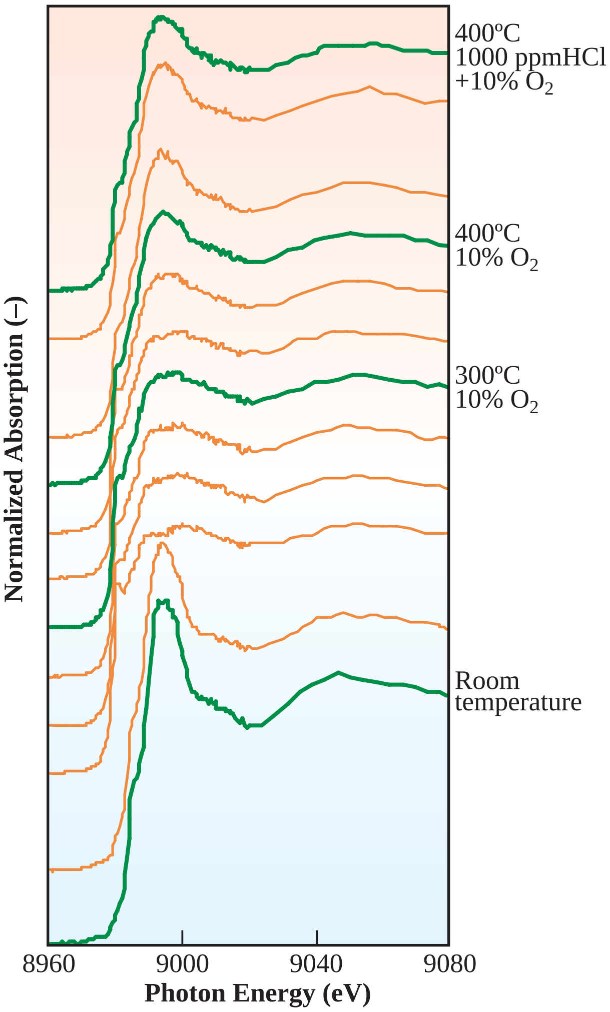

Fig. 3. Change in the chemical form of copper in real fly ash during heating.

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References

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