Chemical Structure of Copper in Incineration Dry Scrubber and Bag Filter Ashes

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Abstract. Speciation of copper in waste incineration fly ashes (dry scrubber (DS) and bag filter (BF)) has been studied by X-ray absorption near edge structural (XANES) spectroscopy in the present work. Copper species such as metallic Cu, CuO, Cu(OH)₂, and a small amount of CuCO₃ in the fly ashes could be distinguished by semi-quantitative analysis of the edge spectra. Interestingly, nano CuO (37%) were found in the BF fly ash, that might account for its relatively high leachability of copper.

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INTRODUCTION

Incineration of municipal solid wastes (MSW) has been widely practiced in Taiwan for many years. Toxic metal-containing ashes especially the electrostatic precipitator or bag house fly ashes are frequently discharged from the incineration process [1]. Because of the excess leachable toxic metals, fly ashes have been considered as hazardous wastes, which required chemical stabilization or solidification prior to the final land fill treatments. The toxicity characteristics leaching procedure (TCLP) is generally used in regulation of threshold concentrations of leachable toxic metals in environmental solids [2]. However, the TCLP data can only provide the level of pollutant concentrations with little chemical structural information.

XANES with a single-ion probe can interrogate an element in a complicated matrix. Furthermore, the X-ray absorption by an ion is almost directly proportional to concentration. Therefore, XANES can provide chemical compositions of select elements in the environmental solids [3]. By XANES and EXAFS (extended X-ray absorption fine structural) spectroscopies, we found that copper species involved in the catalytic decomposition of NO [4] and oxidation of chlorophenols in supercritical water [5]. These molecular scale data turned but to be very useful in revealing speciation of copper in the catalysis processes.

Copper may be carcinogenic and has been suspected causing breast and brain cancers [6]. Copper may catalyze formation of dioxins at 473-973 K [7]. It is, therefore, of great importance and interest to study speciation of copper especially in the semi-dry scrubber (DS) and the downstream bag filter (BF) units where dioxins tend to yield in the incineration process.

EXPERIMENTAL

Fly ash samples were obtained from DS and BF units in a MSW incineration plant in Taiwan. The incinerator was operated at 1073-1173 K. Representative fly ashes were sampled for XANES spectroscopic studies. The TCLP experiments were carried out according to the Taiwan EPA method. Generally, ash samples were leached in an acetic acid solution (pH = 2.85) at 298 K for 18 hours. Concentrations of total and leachable copper were determined by inductively coupled plasma emission spectrometry (Jobin Yvon, Model JY32/38).

The XANES spectra of the ashes were collected at 298 K on the Wiggler beamline at the Taiwan National Synchrotron Radiation Research Center (NSRRC). The electron storage ring provided energy of 1.5 GeV (current of 80-200 mA). X-ray absorption spectra
were recorded with a fluorescence detector (Lytle detector). The photon energy was calibrated against the adsorption edge of copper foil at an energy of 8979.3 eV. Fitting of the data to model structures was performed using FEFFIT from UWXAFS 3.0 in combination with FEFF 8.0. Semi-quantitative analyses of the edge spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample.

RESULTS AND DISCUSSION

In Table 1, concentrations of total copper in the DS and BF ashes are 1000-2000 mg/kg. The copper content in the BF ash is relatively low, nevertheless, its copper leachability was greater than that in the DS ash by 48 times approximately.

In order to further understand speciation of copper in the ashes, their XANES spectra were determined. XANES can be utilized as a valence probe, although the underlying details of this spectroscopy are still not well understood. Principal component (factor) analysis was used in the data treatment to optimize the quantitative extraction of relative concentrations [8]. The useful information is the valence state of copper by comparing the chemical shift of the absorption edge energy. We have estimated the energy of the absorption threshold for copper model compounds (such as CuO) by the maximum of the derivative at the edge (inflection point). Cu(II) or Cu(I) can be identified from the chemical shift in the absorption spectra edge.

The pre-edge XANES spectra of the ashes are shown in Fig. 1, which exhibits a very weak 1s-to-3d transition (8975-8980 eV) (forbidden by the selection rule in the case of perfect octahedral symmetry). A shoulder at 8984-8988 eV and an intense feature at 8995-9002 eV can be attributed to the 1s-to-4p\(_{\alpha,\beta}\) transitions, respectively that also indicated the existence of Cu(II). However, the feature at 8981-8984 eV, which is due to the dipole-allowed 1s-to-4p transition of Cu(I), was not found in the DS and BF ashes. Metallic copper (8999-9001 eV) was not observed in the ashes (Fig. 1).

| TABLE 1. Leachable concentrations of copper in the dry scrubber (DS) and bag filter (BF) ashes. |
|-------------------------------------------------|-----------------|-----------------|
| Total copper conc. (mg/kg)               | 1960            | 1190            |
| Leachable copper conc. (mg/L)            | 0.05            | 1.41            |
| Leachability (%)                         | 0.05            | 2.40            |

In order to make the XANES features more distinct, their first derivatives were also calculated (Fig. 1). The Cu(II) species observed at 8983.7 eV possessed a square planer symmetry, while an octahedral symmetry (at 8987.8 eV) for Cu(II) could also be resolved. As expected, metallic Cu (Cu(0)) (8979.3, 8999 eV) and Cu(I) (8981.7 eV) were absence in the DS and BF ashes.

A semi-quantitative compositional analysis of the ashes was also conducted with a least square fitting of the XANES spectra using a linear combination of spectra of model compounds acquired under the same experimental condition. XANES spectra of model compounds such as CuCl\(_2\), Cu\(_2\)O, Cu(OH)\(_2\), CuO, CuS, CuCO\(_3\), CuSO\(_4\), CuCl, and Cu foil were also measured on the Wiggler beamline. We fitted the near-edge 3d-to-4p mixing features from the experimental absorption edge. A calibration curve could, therefore, be obtained [9]. The XANES spectra were mathematically expressed with a set of linearly-combined XANES fit vectors, using the absorption data in the energy range of 8960-9020 eV. The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species. On the average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fit results. We found that Cu(OH)\(_2\) and CuO were the main copper species in the ashes. A small amount of CuCO\(_3\) was also found.

In addition, about 37% of nano CuO was found in the BF ash. About 0.05% and 2.4% of copper were leached from the DS and BF fly ashes, respectively. The relatively high leachability of copper in the BF ash might be due to its high content of nano CuO. Copper in a form with low solubility product such as Cu(OH)\(_2\) and CuO has a low leachable copper in the TCLP tests.
CONCLUSIONS

Cu(II) was the main copper species in the fly ashes. Cu(OH)$_2$, CuO and a small amount of CuCO$_3$ were found in the fly ashes by a semi-quantitative analysis of the edge spectra. The relatively high leachability of copper from the BF fly ash might be due to its high fraction of nano CuO. This work illustrates the usefulness of XANES for tracking the leachable copper species in the incineration fly ash scrubbing process.

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REFERENCES