EXAFS study of copper in waste incineration fly ashes

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Copper species such as $CuCO_3$, $Cu(OH)_2$, CuS and CuO were found in the bag house and EP (electrostatic precipitator) fly ashes of waste incineration processes by X-ray absorption near edge structural (XANES) spectroscopy. A small amount of Cu(I) and metallic Cu was found in the bag house fly ash. The averaged Cu-O bond distance in the fly ashes determined by EXAFS (extended X-ray absorption fine structural) was 1.96 Å with coordination numbers of 2.4-3.9. However, the Cu-(O)-Cu (2nd shell) bond distance of the fly ashes in the incineration process was decreased by 0.19-0.21 Å if compared to that of the CuO standard. The coordination numbers of the 2nd shell contribution to the bag house fly ash were not very significant.

Keywords: EXAFS; XANES; Fly ash; Copper.

1. Introduction

Fly ashes of municipal solid waste incineration processes generally contain toxic heavy metals such as Zn, Pb, Cu, Cr, As or Cd (Bosshard et al., 1996). Copper being of great important elements for many living systems may potentially be very toxic, for instance, copper may be carcinogenic and is suspected cause breast and brain cancers (Warren and Dudas, 1988; Willemin et al., 1995). Effectiveless of a landfill processing is determined frequently by the conventional TCLP (toxicity characteristics leaching procedure) method that generally used in regulation of threshold concentrations of leachable metals in environmental solids (Francis and White, 1987; Yoshida et al., 1993; Yucel et al., 1994). However, the TCLP data can only provide the level of pollutant concentrations with little chemically structural information.

Basic understanding at a molecular-scale is of increasing importance and interest in the management of environmental contaminants. EXAFS can provide structural information including the coordination number, bond distance, and oxidation state (Yu et al., 1990; Oday et al., 1994; Mosselmans et al., 1995; Foster et al., 1998). By EXAFS, we found that copper oxides involved in the catalytic decomposition of NO (Huang and Wang, 1999) and oxidation of chlorophenols in supercritical water (Lin and Wang, 1999). These molecular scale data were very useful in revealing the structure of catalysts in the catalysis process.

Speciation of toxic elements in a complex matrix can be determined by EXAFS, that also facilitates the development of an effective method for disposal of hazardous wastes (Manceau et al., 1996; Oday et al., 1998). Copper oxides may catalyze the formation of PCDD/DFs in incineration processes (Chang and Chung, 1998). Thus the main objective of this work was to investigate the speciation of copper in the complex fly ashes by EXAFS.

2. Experimental

Fly ash samples were sampled from bag house and EP units of two typical municipal solid waste incineration plants. The secondary combustion chambers of the incinerators are frequently operated at 1073-1173 K. Major particle size of the fly ashes were <0.15 mm. In general, bag house possessed a small particle size fly ash than the EP. TCLP concentrations of copper from these fly ashes were 6-12 mg/L.

EXAFS spectra of the fly ashes were measured at 298 K on the Wiggler BL17C beamline in the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring operated at an energy of 1.5 GeV (ring current = 80-200 mA). The energy resolution ($\Delta E/E$) of the beamline was about 1.9×10^{-4}. X-ray absorption spectra were recorded using a fluorescence detector (Lytle detector) and the photon energy was calibrated against the adsorption edge of Cu foil at an energy of 8979.2 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter.

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 7.0 programs (Stern et al., 1995). The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum post-edge intensity. The isolated EXAFS was normalized to the edge jump and converted to wavenumber scale. The Fourier transform was performed on k^3-weighted EXAFS oscillations in the range of 3.5-10.0 $Å^{-1}$.

3. Result and discussion

XANES spectra of the fly ashes are shown in Figure 1. The pre-edge XANES spectra of the fly ashes exhibit a very week 1s-to-3d transition (8975-8980 eV), which is forbidden by the selection rule in the case of perfect octahedral symmetry (Grunet et al., 1994; Yamashita et al., 1996). A shoulder at 8984-8988 eV and an intense feature at 8995-9002 eV were attributed to the 1s-to-$4p_z$ and 1s-to-$4p_{x,y}$ transitions, respectively that also indicated the existence of Cu(II). Since fly ashes were formed in the excess oxygen and high-temperature (>1073 K) combustion conditions, copper is frequently in high oxidation states. Note that copper oxide (surface energy (ΔG_s) = -31.9 Kcal/mole)) tends to aggregate on the surfaces of fly ashes. Interestingly, the pre-edge features at 8981-8984 eV that is due to the dipole-allowed 1s-to-4p transition of Cu(I) and metallic copper (8999-9001 eV) was found only in the bag house fly ash. In order to make the XANES features more distinct, the first derivatives of the XANES spectra are also shown in Figure 1. Cu(I) (8981.7 eV) was able to be distinguished. Cu(II) observed at 8983.7 eV possessed a square planer symmetry. An octahedral symmetry (8987.8 eV) for Cu(II) could also be resolved.

Semi-quantitative compositional analysis with a least square fitting of the samples was also conducted. We fitted the near-edge 3d-4p mixing features from the experimental absorption edge. A calibration curve could, therefore, be obtained (Ressler et al., 2000). The XANES spectra were mathematically expressed with a set of linear-combined XANES fit vectors, using the absorption data in the energy range of 8960-9020 eV (see Figure 1). The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species. XANES spectra of standard samples such as $CuCl_2$, Cu_2O, $Cu(OH)_2$, CuO, CuS, $CuCO_3$, $CuSO_4$, CuCl, and Cu foil were also measured on the Wiggler beamline. Relative contents in the fly ashes with over 90% reliability in the fitting process are also shown in Table 1. We found that CuS, $CuCO_3$, $Cu(OH)_2$, and CuO were the main species of copper in the fly ashes. It seems that a high amount of low solubility product such as $Cu(OH)_2$ or CuO might lead to a low leachable copper in the TCLP tests.

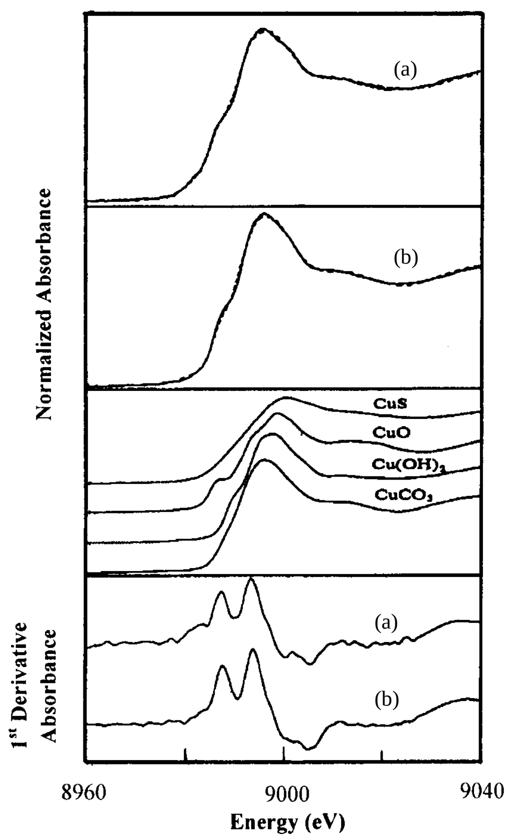

Figure 1
XANES spectra and the first derivatives of (a) bag house and (b) EP fly ashes. Insets are experimental (—) and least-squares fits (···) for the XANES spectra of the fly ashes.

Table 1
Copper species in fly ashes studied by XANES.

Species	Composition (%)	
	Bag house fly ash	EP fly ash
$CuCO_3$	30.4	26.0
$Cu(OH)_2$	25.8	38.4
CuO	18.2	18.4
CuS	25.6	17.2

The Fourier-transformed EXAFS spectra of copper in the fly ashes are shown in Figure 2. All data were given without any corrections for phase shifts. Quantitative analysis of the spectra can identify bond distance and coordination number for the copper atoms at 0-6 Å. Fine structural parameters of copper in fly ashes are also shown in Table 2. The Cu-O bond distance (1st shell) was 1.96 Å with coordination numbers (CN) of 2.4-3.9 in the fly ashes. The Cu-(O)-Cu (2nd shell) bond distances were 2.72 and 2.70 Å (CN of 0.7 and 1.2) for bag house and EP fly ashes, respectively. The Cu-(O)-Cu bond distances of the fly ashes decreased by 0.19-0.21 Å if compared to that of the CuO (Table 2). The coordination numbers of the 2nd shell contribution to the bag house fly ash were not very significant.

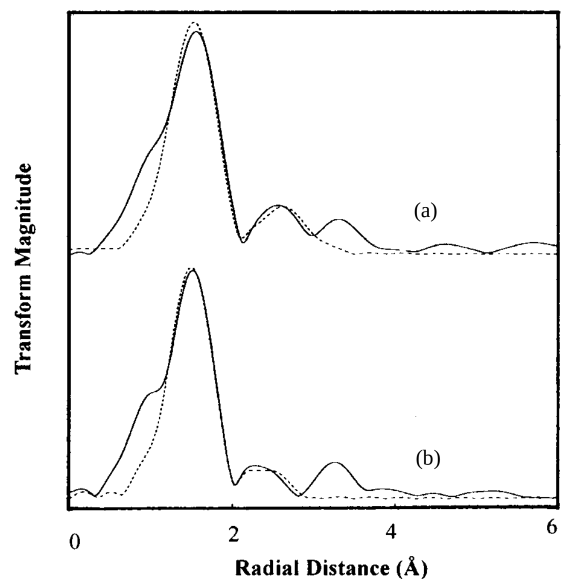

Figure 2
Fourier transformed Cu K edge EXAFS spectra of (a) bag house and (b) EP fly ashes.

Table 2
Fine chemical structural parameters of the fly ashes and the CuO standard sample.

Fly ashes	Shells	Bond Distance (Å)	Coordination Number
Bag	Cu-O	1.96	2.4
house	Cu-(O)-Cu	2.72	0.7
EP	Cu-O	1.96	3.9
	Cu-(O)-Cu	2.70	1.2
CuO	Cu-O	1.95	2.1
Standard	Cu-(O)-Cu	2.91	1.1

σ : Debye-Waller factor

4. Conclusions

By XANES, we found that copper in the fly ashes was consisted of $CuCO_3$, CuS, $Cu(OH)_2$ and CuO. A small amount of Cu(I) and metallic Cu was also observed in the bag house fly ash. The averaged Cu-O bond distance of fly ashes determined by EXAFS was 1.96 Å with coordination number 2.4-3.9. However, the Cu-(O)-Cu (2nd shell) bond distances of the fly ashes in the incineration process was decreased by 0.19-0.21 Å if compared to that of the normal CuO. The coordination numbers of the 2nd shell contribution to the bag house fly ash were not very significant. This work is also an example of the usefulness of EXAFS for revealing the speciation of copper in the very complex fly ashes.

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References

Bosshard, P. P., Bachofen, R. & Brandl, H. (1996). *Environ. Sci. Technol.* **30**, 3066-3070.

Chang, M. B. & Chung, Y. T. (1998). *Chemosphere* **36**, 1959-1968.

Foster, A. L., Brown, G. E. J. & Parks, G. A. (1998). *Environ. Sci. Technol*. **32**, 1444-1452.

Francis, C. W. & White, G. H. (1987). *Journal WPCF* **59**, 979-986.

Grunet, W., Hayes N. W., Joyner, R. W., Shpiro, E. S., Siddiqui, M. R. H. & Baeva, G. N. (1994). *J. Phys. Chem*. **98**, 10832-10846.

Huang, Y.-J. & Wang, H. P. (1999). *J. Phys. Chem*. **103**, 6514-6516.

Lin, K. S. & Wang, H. P. (1999). *Applied Catalysis B-Environmental* **22**, 261-267.

Manceau, A., Boisset, M-C, Sarret, G., Hazemann, J.-L., Mench, M., Cambier, P. & Prost, R. (1996). *Environ. Sci. Technol*. **30**, 1540-1552.

Mosselmans, J. F. W., Charnock, J. M., Garner, C. D., Pattrick, R. A. D. & Vaughan, D. J.(1995). *Physica B* **208/209**, 609-610.

Oday, P. A., Brown, G. E. J., Parks, G. A. (1994). *J. Colloid Interface Sci*. **165**, 269-289.

Oday, P. A., Carroll, S. A., Waychunas, G. A. (1998). *Environ. Sci. Technol*. **32**, 943-955.

Ressler, T., Wong, J., Roos, J. & Smith, I. L. (2000). *Environ. Sci. Technol*. **34**, 950-958.

Stern, E. A., Newville, M., Ravel, B., Yacoby, Y. & Haskel, D. (1995). *Physica B* **209**, 117-120.

Warren, C. J. & Dudas, M. J. (1988). *The Science of The Total Environment* **76**, 229-246.

Willemin, J. A., Nesbitt, C. C., Dewey, G. R., Sandell, J. F. & Sutter, L. L. (1995). *J. Air & Waste Manage. Assoc.* **45**, 871-876.

Yamashita, H., Matsuoka, M., Tsuji, K., Shioya, Y., Anpo, M. & Che, M. (1996). *J. Phys. Chem*. **100**, 397-402.

Yoshida, D., Ikeda, Y. & Nakazawa, S. (1993). *J. Neurooncol*. **16**, 109-115.

Yu, Y. H., Tyliszczak, T. & Hitchcock, A. P. (1990). *J. Phys. Chem. Solids* **51**, 445-451.

Yucel, I., Arpaci, F., Ozet, A., Doner, B., Karayilanoglu, T., Sayar, A. & Berk, O. (1994). *Biol. Trace Elem. Res.* **40**, 31-38.

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