



Speciation of copper in the incineration fly ash of a municipal solid waste

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Abstract

The speciation of copper and zinc in the incineration fly ash of a municipal solid waste in Taiwan was investigated in the present work. By the least-squares fitted X-ray absorption near edge structural (XANES) spectroscopy, we found that CuCO_3 , Cu(OH)_2 , and CuO (fractions of 0.09, 0.39 and 0.51, respectively) were the main copper species in the fly ash. Quantitative analysis of the extended X-ray absorption fine structural (EXAFS) spectra indicated that the bond distance of Cu–O in the fly ash was 1.96 Å with a coordination number (CN) of 3.9 in the first shell of copper. In the second shell, the bond distance and CN of Cu–(O)–Cu were 2.91 Å and 2.7, respectively. In addition, speciation of Zn was also examined in the same X-ray absorption energy (8780–9970 eV). The bond distance of Zn–O and Zn–O–Zn were 1.97 and 2.94 Å, respectively. However, the Zn–O–Cu structure was not found because of the physically unreasonable σ^2 (Debye–Waller factor) values in the EXAFS data fitting process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: EXAFS; XANES; Fly ash; Copper; Zinc

1. Introduction

Fly ashes discharged from municipal solid waste (MSW) incineration processes generally contain a considerable amount of toxic metals [1]. Copper and zinc, being elements of great importance for many living systems, may potentially be very toxic, for instance, Cu(II) exerts adverse effects even at concentrations slightly higher than its physiological range [2]. Copper has also been suspected to be carcinogenic and may cause breast and brain cancers [3,4].

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The US Toxicity Characteristics Leaching Procedure (TCLP) generally sets threshold concentrations of leachable toxic metals in environmental solids [5]. However, the TCLP can only provide the data in concentrations of toxic elements with little chemical structure information. It is also not clear as to what specific reactions take place during the chemical extraction of the operationally defined phase during the TCLP experiments.

The main scientific issues concerning the chemical forms or speciation of contaminants have to do with their molecular-scale properties. Basic understanding at this scale is essential in the management of environmental contaminants. Commonly employed speciation methods (such as X-ray diffraction (XRD)) can potentially avoid such limitations, however, these methods have often not been sensitive enough to detect the molecular structure of toxic elements in the complex environmental solids. Generally, structural analyses must be conducted under conditions that may alter chemical species distributions or modify the sample, thus, excluding other potential artifacts which may confuse data interpretation [6].

X-ray absorption spectroscopy can be used in characterization of valence and local structure ($<10 \text{ \AA}$) of elements in a complex solid matrix [7,8]. Local structural information including the coordination number (CN), bond distance, and oxidation state can be determined by extended X-ray absorption fine structural (EXAFS) spectroscopy [9–13]. EXAFS and X-ray absorption near edge structural (XANES), in fact offer molecular structure data of toxic elements in a very complex matrix that may help the development of effective methods for disposal of hazardous wastes [14,15]. By EXAFS, we found that copper oxides involved in the catalytic decomposition of NO and the oxidation of chlorophenols in supercritical water [16,17]. These molecular-scale data were very useful in revealing the structure of the active species in the catalysis processes.

It has been recognized that copper oxides in fly ashes may catalyze the formation of PCDD/DFs in the incineration processes [18]. Because of the dilute nature of toxic metals in the fly ash, the literature lacks molecular scale studies of these metals. Thus, the main objective of the present work was to investigate the speciation of copper embedded in the complex matrices of a fly ash by EXAFS and XANES spectroscopies. In addition, since the X-ray absorption energy of zinc was in the energy range of copper (8781–9970 eV), EXAFS spectra of zinc in the fly ash were also studied.

2. Experimental

The fly ash sample was obtained from bag houses at an MSW incineration process (300 TPD) in Taiwan. The TCLP tests of the fly ash were conducted using the US EPA standard method [19]. Concentrations of leachable toxic elements in the fly ash were determined by ICP–AES (Jobin Yvon Model JY32/38). Structures of fly ashes were studied by XRD spectroscopy (Rigaku Model D/MAX III–V) with Cu $K\alpha$ radiation. Samples were scanned from 10 to 60° (2θ) at a scan rate of 4° min^{-1} .

The EXAFS spectra of the fly ash were collected at 298 K on the Wiggler beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring operated at an energy level of 1.5 GeV (ring current = 80–200 mA). A Si(111) double-crystal monochromator was used with an energy resolution ($\Delta E/E$) of about 1.9×10^{-4} (eV/eV). The X-ray absorption spectra were recorded by a fluorescence detector (Lytle). Photon

energy was calibrated against the absorption 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 isolated EXAFS data were normalized to the edge jump and converted to the wave number scale. Fitting of the data to model structures was performed using FEFFIT from UWXAFS 3.0 in combination with FEFF 8.0. The Fourier transform was performed on k^3 -weighted EXAFS oscillations in the range of 2.5–9.2 and 2.7–8.5 Å⁻¹ for copper and zinc, respectively. Variables in the fits included the CN, radial distance (R) and the Debye–Waller-type disorder factor (σ^2) for each shell and the scale factor (S^2) were applied to all shells. CN and R values were derived by non-linear least-squares fitting with S^2 fixed to 0.8 and E_0 fixed to the best fit for the first shell [20]. An over 90% reliability of the EXAFS data fitting for Cu was obtained. Generally, empirical fits of model compounds have an error of ± 0.01 Å in radius and of $\pm 10\%$ in CN for the first shell atoms, and of ± 0.02 Å and $\pm 25\%$ for the second shell atoms. Detailed EXAFS data analysis procedures are described in the literatures [20–22].

The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectrum with a pre-edge baseline subtraction and normalization to the maximum post-edge intensity. 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. XANES spectra of standard copper compounds such as Cu(OH)₂, CuO, CuCO₃, and Cu foil were also measured on the Wiggler beamline. To convert XANES fit percentages into the more commonly used weight-percentages, a series of synthetic binary mixtures of CuO, CuCO₃ and Cu(OH)₂ and a plot of weight-percent of CuCO₃ (model compound) versus the obtained XANES fit percentage were determined. It was found that the XANES fitting percentages almost directly correspond to weight-percentages. On the average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fitting results.

3. Results and discussion

Table 1 shows concentrations of total and leachable copper and zinc in the incineration fly ash. The fly ash sampled from the bag houses in the MSW incineration process had a low leachability (<0.5%) of toxic metals. Nevertheless, the leachable copper and zinc in

Table 1
Concentrations of total and leachable toxic metals in the fly ash

Element	TCLP concentration (mg/l)	Total concentration (mg/kg)	Leachability ^a (%)
Cu	0.659	890	1.5
Zn	6.410	5600	2.3
Ni	0.123	510	0.48
Cd	0.078	340	0.46

^a Leachability = (1000 g/1000 ml)(100 ml (leachate vol.)/5 g (fly ash)) (Cu concentration (leachable))/(total Cu concentration).

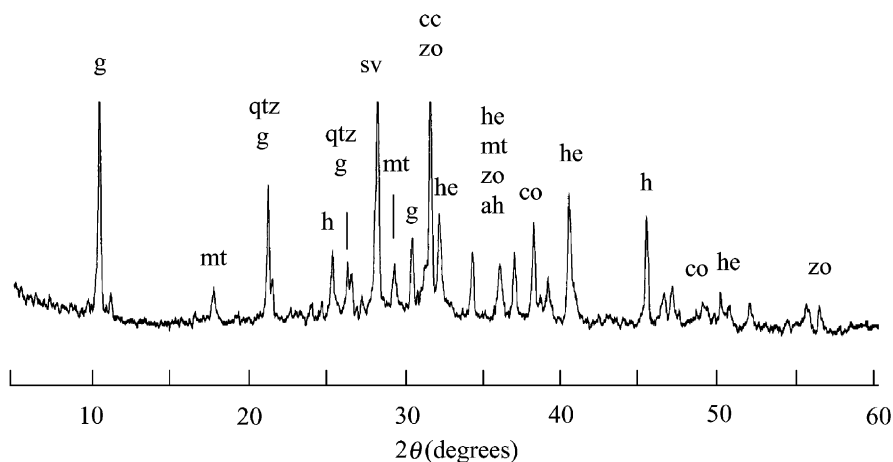


Fig. 1. XRD pattern of the fly ash. Abbreviations: cc: calcite (CaCO_3); g: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); h: halite (NaCl); he: hematite (Fe_2O_3); mt: magnetite (Fe_3O_4); qtz: quartz (SiO_2); sv: sylvite (KCl); ah: anhydrite (CaSO_4); zo: zinc oxide (ZnO); co: copper oxide (CuO).

the fly ash were noticeable. The leachabilities of zinc and copper in the fly ash were about 2.3 and 1.5%, respectively. Generally, due to a large negative surface free energy of ZnO and CuO, zinc and copper may be enriched on the surfaces of fly ashes. Since, contents of S and Cl were $<0.1\%$ in the fuels and MSW, copper and zinc oxides were expected to be predominant in the particulate stream of the incineration process.

Fig. 1 shows that hematite, magnetite, halite, sylvite, quartz, calcite, and gypsum were the major species in the fly ash. We also found that CuO and ZnO were the main copper and zinc species, respectively, in the fly ash. However, the chemical structure of copper and zinc in fly ash could not be revealed in detail by XRD simply due to the very complex matrix of the fly ash.

In order to more thoroughly examine the speciation of copper in the fly ash, XANES and EXAFS spectra of the fly ash were also studied. Fig. 2 shows the X-ray absorption spectrum of copper in the fly ash. Since, the X-ray absorption energy of zinc was in the absorption energy range of copper (8780–9970 eV), XANES and EXAFS spectra of zinc in the fly ash were also determined.

The pre-edge XANES spectrum (Fig. 3) of the fly ash exhibited a very weak 1s-to-3d transition at 8975–8980 eV, which is forbidden by the selection rule in the case of perfect octahedral Cu(II) symmetry [23]. A shoulder at 8984–8988 eV and an intense band 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). The pre-edge band at 8981–8984 eV that was due to the dipole-allowed 1s-to-4p transition of Cu(I) was not found in the fly ash. However, a weak band at 8999–9001 eV was also observed, that suggested a very small amount of Cu(0) present in the fly ash. In the high-temperature combustion conditions, high oxidation state oxides would be predominant in the fly ash. A shoulder at 9669 eV observed in Fig. 2 was attributed to the 1s-to-3d transition that indicated the existence of Zn(II).

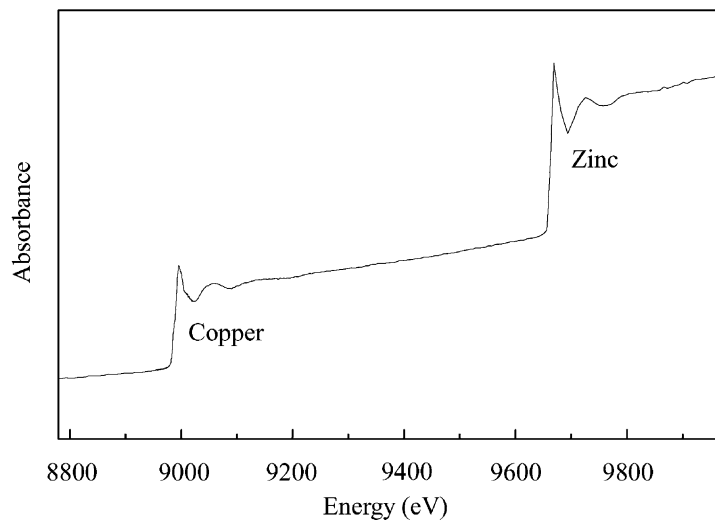


Fig. 2. X-ray absorption spectrum of copper and zinc in the fly ash.

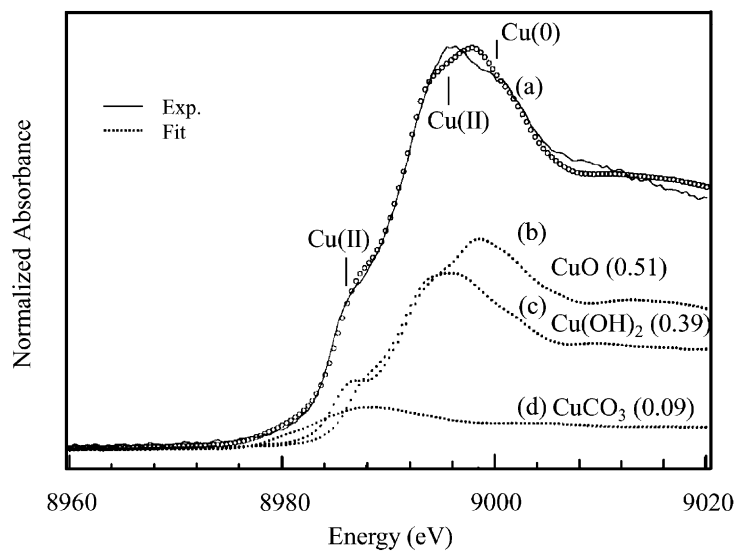


Fig. 3. Experimental data (solid line) and the least-squares fits (circles) for the XANES spectra of copper in (a) the fly ash and selected model compounds including (b) CuO, (c) Cu(OH)₂ and (d) CuCO₃. Dotted lines underlying the fly ash XANES spectrum denote fractional contributions of the three principal components making up the fitted spectra (CuCO₃ (0.09), Cu(OH)₂ (0.39), and CuO (0.51)).

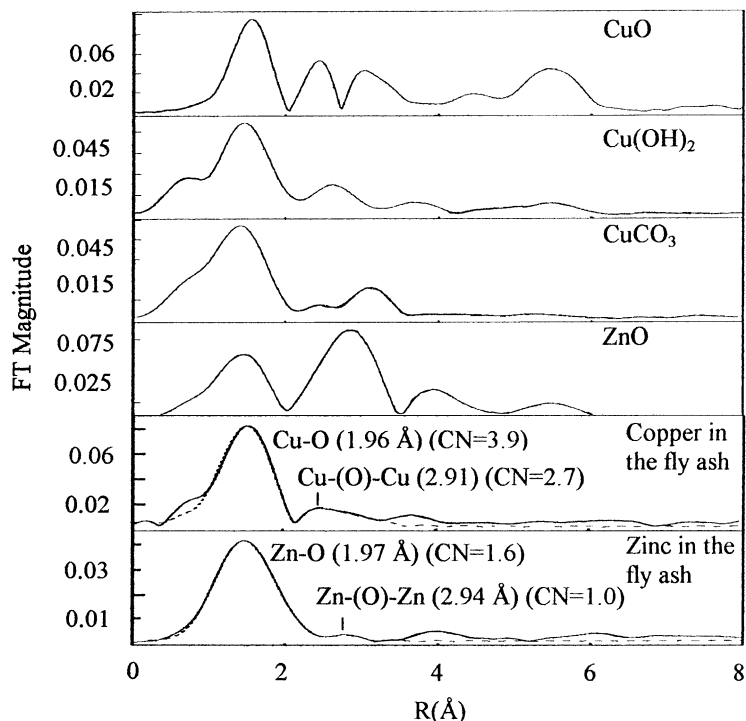


Fig. 4. Fourier-transformed EXAFS spectra of model compounds (CuO , $\text{Cu}(\text{OH})_2$, CuCO_3 , and ZnO), and copper and zinc in the fly ash. Dotted and solid lines denote the best fitting and experimental data, respectively.

XANES can also be utilized as a valence probe, although the underlying details of its spectra are still not well understood. We fitted the near-edge 3d-to-4p mixing features from the experimental absorption edges of 0–5% CuO/SiO_2 , $\text{Cu}(\text{OH})_2/\text{SiO}_2$, and $\text{CuCO}_3/\text{SiO}_2$. A calibration curve could, therefore, be obtained. The XANES spectrum was mathematically expressed in terms of 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. We found that fractions of the main copper species such as CuCO_3 , $\text{Cu}(\text{OH})_2$, and CuO in the fly ash were 0.09, 0.39, and 0.51, respectively (results of linear least-squares fits are shown in Fig. 3).

Quantitative analysis of the EXAFS spectra can reveal the speciation of copper in the complex fly ash. Fig. 4 shows the Fourier-transformed EXAFS spectra of copper in the fly ash. In all EXAFS data analyses, the Debye–Waller factors ($\Delta\sigma^2$) were <0.019 . The bond distance of Cu–O in the fly ash was 1.96 Å with a CN of 3.9 in the copper first shell. In the second shell, the bond distance of Cu–(O)–Cu was 2.91 Å. We also found that bond distances of Zn–O and Zn–(O)–Zn were 1.97 and 2.94 Å, respectively. Low CNs for Zn in the first and second shells were also observed. However, the Zn–O–Cu structure was not found because of the physically unreasonable σ^2 values in the EXAFS data fitting process.

4. Conclusions

The least-squares fitted XANES spectra of the fly ash showed that CuCO_3 , $\text{Cu}(\text{OH})_2$, and CuO with fractions of 0.09, 0.39, and 0.51, respectively, were the main copper species in the fly ash. Fourier-transformed EXAFS spectra of copper in the fly ash showed that the bond distance of Cu-O was 1.96 Å with a CN of 3.9 in the first shell of copper. In the second shell, the bond distance of Cu-(O)-Cu was 2.91 Å. We also found that bond distances of Zn-O and Zn-(O)-Zn in the fly ash were 1.97 and 2.94 Å, respectively. However, the Zn-O-Cu structure was not found by EXAFS in the present study. This work exemplifies the utilization of EXAFS for simultaneously revealing the speciation of copper and zinc in the very complex fly ash in the X-ray absorption measurements.

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