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Journal of Hazardous Materials B138 (2006) 539–542

Journal of Hazardous Materials

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Tracking of copper species in incineration fly ashes

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Received 31 March 2006; received in revised form 25 May 2006; accepted 26 May 2006
Available online 3 June 2006

Abstract

Speciation of copper in the incineration waste heat boiler (HB) and the down stream electrostatic precipitator (EP) fly ashes during the flue gas cooling down (1123 → 473 K) has been studied by X-ray absorption near edge structural (XANES) spectroscopy in the present work. Copper species such as $Cu(OH)_2$ (59–67%), $CuCl_2$ (5–12%), CuO (24–26%), and a small amount of CuS (3–4%) in fly ashes were determined by semi-quantitative analyses of the XANES spectra. In the toxicity characteristics leaching procedure (TCLP) tests, about 83 and 20% of copper were leached from the EP and HB fly ashes, respectively. The relatively high leachability of copper for the EP fly ash might be due to the fact that $CuCl_2$ was enriched on the surfaces as observed by X-ray photoelectron spectroscopy (XPS). On the contrary, $CuCl_2$ was mainly encapsulated in the HB fly ashes.

Keywords: XANES; Fly ash; Copper; XPS; TCLP

1. Introduction

Fly ashes discharged from the waste heat boiler/economizers (HB), electrostatic precipitators (EP) or bag house filters in the municipal solid waste (MSW) incineration processes frequently contain toxic metals such as Cr, Cu, Ni, Zn, Cd, Hg or Pb and are considered as hazardous wastes [1]. Copper, being of great important elements for many living systems, may potentially be very toxic; for instance, Cu^{2+} exerts adverse efforts even at concentrations slightly higher than its physiological range [2]. Copper may be carcinogenic and has been suspected causing breast and brain cancers [3,4].

The toxicity characteristics leaching procedure (TCLP) is generally used in regulation of threshold concentrations of leachable toxic metals in the environmental solids [5]. However, the TCLP data can only provide the levels of pollutant concentrations with little chemical structure information. Nevertheless, it is not clear what specific reactions take place during the chemical extraction of operationally defined phases. A basic understanding of contaminants at molecular scale is essential in the management of environmental pollution.

X-ray absorption near edge structural (XANES) spectroscopy can be used in characterization of oxidation state of an atom and the symmetry and bonding of its local environment in a complex environmental solid [6,7]. XANES is a single-ion probe that can interrogate selective elements in a complex matrix. X-ray absorbance of an ion is almost directly proportional to its concentration. By XANES and EXAFS (extended X-ray absorption fine structural) spectroscopies, we found that copper oxide clusters involved in the catalytic decomposition of NO [8] and catalytic oxidation of 2-Chlorophenol in confined channels of ZSM-48 [9]. These molecular scale data are very useful in revealing speciation of copper in the catalysis processes.

Copper-containing particulates in the flue gas stream may play an important role in catalytic formation of dioxins at 473–973 K in the waste incineration processes [1,10–12]. Dickson and co-workers have found that $CuCl_2$ in the flue gas have a close relationship with the formation of dioxins [13]. In a MSW (municipal solid waste) incineration process, a relatively high dioxin emission was found as the waste heat boiler (HB) and electric precipitator (EP) units were operated at 1123 → 523 K and 473 K, respectively. It is of great importance and interest in revealing speciation of copper that may involve in catalytic

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doi:10.1016/j.jhazmat.2006.05.087

formation of dioxins during incineration flue gas cooling down. Thus the main objective of this work was to study speciation of copper in the HB and EP fly ashes by XANES. Surface compositions of copper on the fly ashes were also investigated by X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

In the incineration process, generally, municipal solid wastes are fed to the combustor. The hot gas is cooled down rapidly in the waste heater boiler. In the down stream of the waste heat boiler, particulates in the flue gas are separated by an EP. The acid gases are then treated with a scrubber. Fly ashes (HB and EP) were collected from the waste heat boiler and electrostatic precipitator operated at 1123–523 and 473 K, respectively in a MSW incineration plant in Taiwan. Generally, the combustion chamber of the incinerator was operated at 1123–1223 K. The TCLP experiments of the fly ash samples were carried out with the Taiwan EPA method (code NIEA R201.10T). Briefly, the fly ashes were extracted with an acetic acid solution (pH 2.85) in a zero-volume extractor at 298 K for 18 h. Concentrations of total and leachable copper in the fly ashes were determined by inductively coupled plasma emission spectrometry (JOBIN YVON, Model JY32/38). Chemical structures of the fly ashes were determined by X-ray diffraction spectroscopy (RIGAKU Model D/MAX III–V) with a Cu Kα radiation (5–60° (2θ) at a scan rate of 4°/min). Concentrations of Cu and Cl on surfaces of the fly ashes were determined by XPS (VG ESCA 210 system).

The XANES spectra of the fly ash samples 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). A Si(1 1 1) double-crystal monochromator was used for selection of energy with an energy resolution ($\Delta E/E$) of 1.9×10^{-4} (eV/eV). The X-ray absorption spectra were recorded with a fluorescence detector (Lytle detector) and the photon energy was calibrated against the adsorption edge of Cu foil at an energy of 8979.3 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. 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. Fitting of the data to model compounds was performed using FEFFIT from UWXAFS 3.0 in combination with FEFF 8.0.

3. Results and discussion

Table 1 shows the concentrations of total and leachable copper in the HB and EP fly ashes. The leachability of copper in the HB fly ash was less than that in the EP fly ash by 6.6 times. It should be noted that the HB fly ash contained more finer particles (<140 mesh) (than the EP fly ash). It seems that the HB fly ash which was formed at high temperatures (~1123 K) and experienced a rapid cooling process (1123 → 473 K) that might stabilize copper therein.

Table 1
Particle size distribution and leachable copper concentrations of the waste heat boiler (HB) and electrostatic precipitator (EP) fly ashes

	HB	EP
Particle size distribution (%)		
>80 mesh	47.0	55.7
80–140 mesh	27.2	26.7
140–200 mesh	14.8	10.6
<200 mesh	11.0	7.0
TCLP		
Total copper (mg/kg)	2120	1250
Leachable copper (mg/L)	0.94	6.24
Leachability (%)	0.89	10.0

Note that the TCLP test provides only the leachable concentration of copper in fly ashes. XRD was, therefore, used to determine chemical structures of major components and copper species in the fly ashes. In Fig. 1, the XRD patterns show that hematite (Fe_2O_3), halite (NaCl), sylvite (KCl), quartz (SiO_2) and magnetite (Fe_3O_4), were the major crystalline species in the HB and EP fly ashes. Copper species such as $Cu(OH)_2$, $CuCl_2$, and CuO were barely observed simply due to the fact of the relatively low concentration of copper as well as the complex matrix of the fly ashes.

In Fig. 2, the pre-edge XANES spectra of the fly ashes exhibited a very weak 1s-to-3d transition (8975–8980 eV), which is forbidden by the selection rule in the case of perfect octahedral symmetry [14]. A shoulder at 8984–8988 eV and an intense feature at 8995–9002 eV may be attributed to the 1s-to-4p_z and 1s-to-4$p_{x,y}$ transitions, respectively that also indicate the existence of Cu(II).

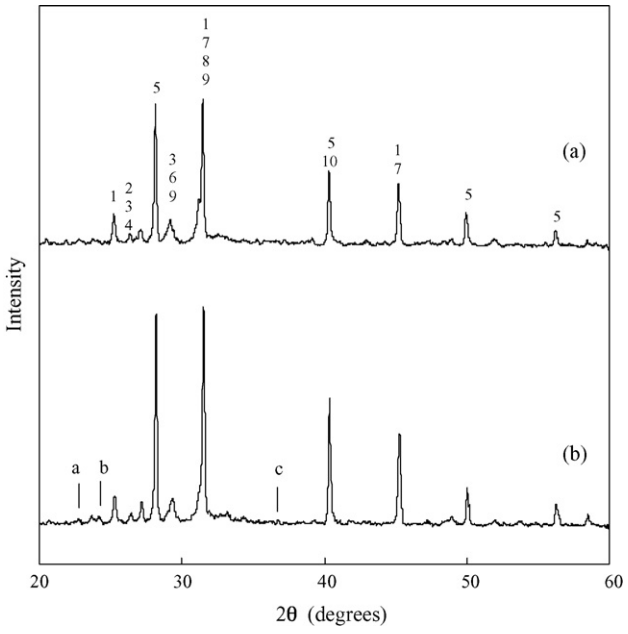

Fig. 1. XRD Patterns of: (a) waste heat boiler (HB) and (b) electrostatic precipitator (EP) fly ashes (1: NaCl; 2: SiO_2; 3: $Ca_2Al_2SiO_7$; 4: $Ca_2Al_2Si_2O_8$; 5: KCl; 6: Fe_3O_4; 7: $SiCl_2$; 8: $CaSO_4$; 9: $CaCl_2$; 10: Fe_2O_3; a: $Cu(OH)_2$; b: $CuCl_2$; c: CuO).

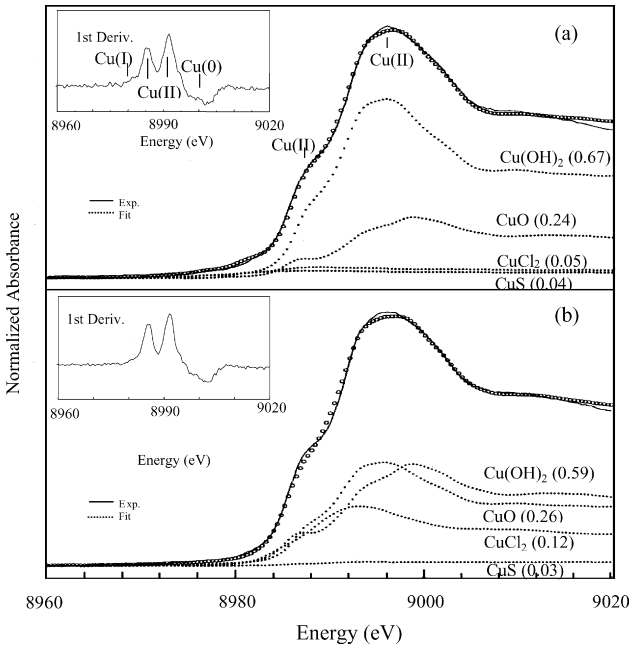

Fig. 2. XANES and component fitted and the first derivatives (shown in the upper corner) of: (a) waste heat boiler (HB) and (b) electrostatic precipitator (EP) fly ashes.

In order to make the XANES features more distinct, their first derivatives are also shown in the upper corner of Fig. 2. The Cu(II) species at 8983.7 eV has a square planer symmetry. In addition, an octahedral symmetry at 8987.8 eV for Cu(II) can also be resolved. Since fly ashes are formed in the high-temperature combustion in the presence of excess air, copper in the fly ash is frequently in high oxidation states. Metallic Cu (Cu(0)) (9001 eV) and Cu(I) (8981.7 eV) were observed in neither the HB nor EP fly ashes.

A semi-quantitative compositional analysis of the fly ashes was also conducted with a least square fitting of the XANES spectrum using a linear combination of reference spectra acquired under the same experimental condition. XANES spectra of model compounds such as $CuCl_2$, $Cu(OH)_2$, CuO, CuS, Cu_2O and Cu foil were also measured on the Wiggler beamline. The XANES spectra were mathematically expressed with a set of lineary-combined XANES fit vectors, using the absorption data in the energy range of 8960–9020 eV. The height and area of the near-edge features in the copper spectrum were quantitatively proportional to the amount of copper species. 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 was found.

Fig. 2 shows that $Cu(OH)_2$, CuO and $CuCl_2$ were the main copper species in the fly ashes. A small amount of CuS was also found in the fly ashes. Since $Cu(OH)_2$, CuO, or CuS has extremely low solubility products, the leachable copper species might be mainly contributed by $CuCl_2$. Although the HB fly ash has relatively finer particle sizes (Table 1) if compared with its downstream EP fly ash, about 83% of $CuCl_2$ were leached from the EP fly ash while <20% of $CuCl_2$ were leachable in the HB fly ash. At the incineration temperatures (1123–1273 K), $CuCl_2$ (mp = 903 K) was in the gaseous phase while $Cu(OH)_2$, CuO and CuS were in the solid phase. During the incineration flue gas cooling down in the waste heat boiler, temperatures of the HB fly ash were fast dropped from 1123 to 473 K and $CuCl_2$ might be mainly encapsulated in the fly ash. In the down stream electrostatic precipitator, at $T < 473$ K, most $CuCl_2$ was, therefore, condensed on the fly ash. $CuCl_2$ with a low surface free energy might be predominant on the surfaces of the EP fly ash, that might account for its high leachability of copper during TCLP.

Table 2
XPS data for Cu and Cl on the surfaces of the waste heat boiler (HB) and electrostatic precipitator (EP) fly ashes

	HB		EP	
	Cu 2p3	Cl 2p	Cu 2p3	Cl 2p
Binding energy (eV)	934.00	199.20	932.96	199.07
Normalized band area	123	5580	211	9400

Table 2 shows relative concentrations of Cu and Cl on the surface of the fly ashes. It is clear that copper was enriched on the surfaces of the EP fly ash. On the contrary, the concentration of Cu on the surfaces of the HB fly ash was relatively low, and that might account for the less leachability if compared with that of the EP fly ash.

4. Conclusions

Mainly $CuCl_2$, $Cu(OH)_2$ and CuO with a small amount of CuS were found in the fly ashes by a semi-quantitative analysis of the edge spectra. The XANES and XPS observations suggested that $CuCl_2$ was enriched on surfaces of the EP fly ash, that might account for its high leachability of copper. Nevertheless, during the fast cooling down (1123 → 523 K) of the flue gas, $CuCl_2$ might be mainly encapsulated in the HB fly ash. This work illustrates the usefulness of XANES for tracking of copper species in the fly ashes during cooling down from 1123 to 473 K.

Acknowledgements

The financial supports of the Taiwan National Science Council and Bureau of Energy are gratefully acknowledged. We also thank Prof. Y.W. Yang and Dr. Jyh-Fu Lee of the Taiwan NSRRC for their XANES experimental assistance.

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