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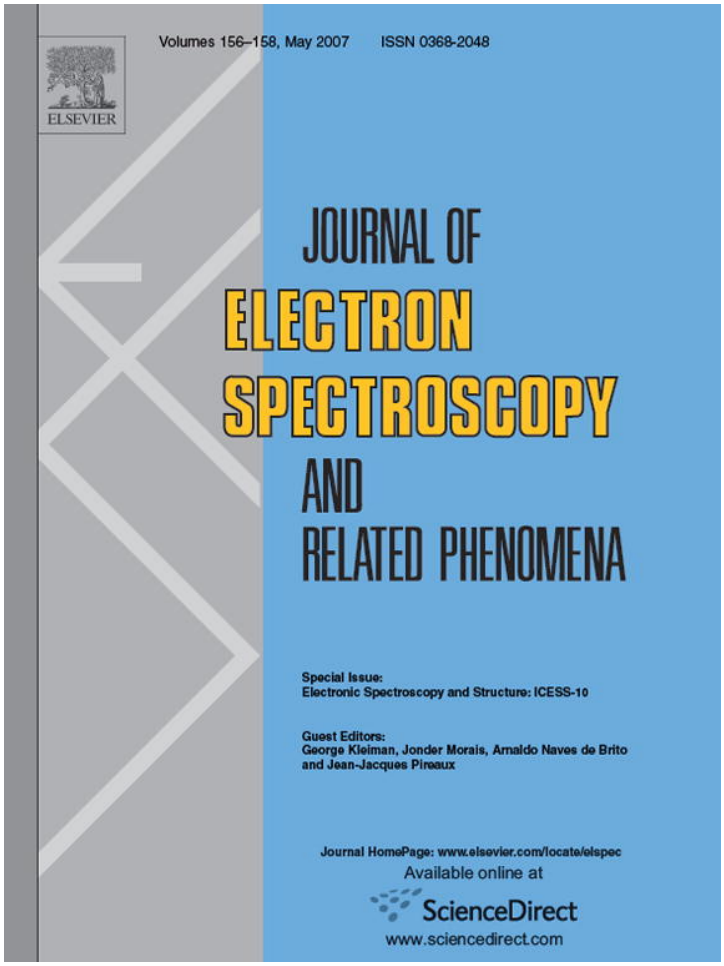

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Speciation of copper in plasma-melted slag

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Abstract

Speciation of copper in the laboratory waste incineration ashes and plasma-melted slag has been studied by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXFAS) spectroscopies. The component-fitted XANES spectra show that main copper species in the bottom and fly ashes are CuO (9–45%), $Cu(OH)_2$ (25–40%) and nanosize CuO (30–35%). During the plasma melting process at 1773 K, about 97% of Cu_2S in the slag is observed possibly due to sulfurization and self-reduction of CuO at high temperatures. By EXAFS, we also found that copper in the bottom and fly ashes possessed Cu─O bond distances of 1.97 and 1.99 Å with coordination numbers (CNs) of 2.1 and 2.3, respectively. In the slag, the bond distance of Cu–S is 2.3 Å with a CN of 3.8.
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Keywords: Fly ash; Plasma-melted slag; XANES; EXAFS

1. Introduction

About 2 × 10 tonnes/year of ashes were discharged from the waste incineration processes in Taiwan [1]. The ashes are considered as hazardous wastes because leaching concentrations of toxic elements are frequently exceeding the limits [2,3]. Thermal plasma melting of hazardous wastes has attracted world-wide interest simply due to the reduction of the waste volume as well as yields of the extremely high chemical stability of slags [4]. In a high current plasma melting reactor, a very intense radiation and heating power can be transferred into wastes. Organic species can be atomized while inorganic compounds may be vitrified (formed slags as cooling down) in the plasma melting processes [5,6]. Toxicity characteristic leaching procedure (TCLP) concentrations of plasma melting slags are generally much lower than the Taiwan Environmental Protection Agency (EPA) limits.

Speciation information such as the oxidation state and the coordination geometry of select elements in the environmental solids can be determined by X-ray absorption near edge structure (XANES) spectroscopy. Extended X-ray absorption fine structure (EXAFS) spectroscopy can also identify elements with a different environment, degree of aggregation or location. By EXAFS spectroscopy, we found that copper oxide clusters (in ZSM-5 or ZSM-48) are involved in the catalytic decomposition of NO and oxidation of chlorophenols in supercritical water [7,8]. Speciation of nanosize CuO in the waste heat boiler fly ash was also observed by XANES spectroscopy [9]. It is worthwhile to note that copper species in fly ashes may catalyze the formation of dioxins in the incineration processes [10]. The basic understanding at the molecular scale is of great importance and interest in the management of toxic elements in the fly ashes. Thus, the main objective of the present work was to investigate speciation of copper in the bottom and fly ashes and plasma-melted slag by EXAFS and XANES spectroscopies.

2. Experimental

The bottom and fly ashes were collected from the laboratory waste incineration plant in the Environmental Resource Management Research Center (ERMRC) of National Cheng Kung University in Tainan, Taiwan. Bottom and fly (1:1) ashes were melted in the plasma melting (plasma torch power = 350 W) system at 1773 K for 4 h.

XANES and EXAFS spectra of the slag and ashes were determined on the Wiggler BL17C beamline at the National

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Synchrotron Radiation Research Center (NSRRC). The electron storage ring was operated at an energy of 1.5 GeV. A Si(1 1 1) double-crystal monochromator was used for the selection of energy. Energy resolution ($E/\Delta E$) of the beamline was about 1.9×10^{-4}. The data were collected at 298 K for all samples using fluorescence detection in the region of the copper K edge (8979 eV) after calibration of the photon energy by characteristic pre-edge peaks in the absorption spectrum of a copper foil.

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 7.0 programs [11]. The isolated EXAFS data have been normalized to the edge jump, converted to the wavenumber scale, and Fourier transformed using k^3-weighted oscillations in the range of 3.0–12 Å^{-1}. The absorption edge has been 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. Principal component (factor) analysis was used in the data treatment to optimize the quantitative extraction of relative concentrations of copper species. 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 copper compounds such as $CuCl_2$, Cu_2O, $Cu(OH)_2$, CuO, Cu_2S, $CuCO_3$, CuS, and Cu foil were also measured on the Wiggler beamline. On average, an uncertainty limit of 5% was found corresponding to an error of ca. 2.0% in the fitting results.

3. Results and discussion

In order to understand the structural changes of copper in the bottom and fly ashes during plasma melting, XANES spectra of copper were determined. The least-square fitted XANES spectra of copper in the slag and ashes are shown in Fig. 1. The pre-edge XANES spectra of copper in the slag and bottom and fly ashes exhibit a very weak absorbance feature for the 1s-to-3d transition (8975–8980 eV) which is forbidden by the selection rule in the case of perfect octahedral symmetry. In Fig. 1(a and b), a shoulder at 8984–8988 eV and an intense feature at 8995–9002 eV can be attributed to the 1s-to-4p transition that indicates the existence of the Cu(II) species. The pre-edge band at 8981–8984 eV may be due to the dipole-allowed 1s-to-4p transition of Cu(I) (see Fig. 1(b and c)).

The least-square fitted XANES spectra of copper in the bottom and fly ashes are also shown in Fig. 1(a and b). The main copper species in the bottom and fly ashes were CuO and $Cu(OH)_2$, respectively. About 30–35% of nanosize CuO were also found. However, in the plasma-melted slag, about 97% of Cu_2S is observed. Cu_2S may be formed via sulfurization and self-reduction at 1773 K.

EXAFS spectra of copper in the slag and bottom and fly ashes were recorded and analyzed in the k range of 3.0–12.0 Å^{-1}. The best fitted structural parameters of copper species in the slag and ashes are shown in Table 1. The Cu–O bond distances in bottom and fly ashes are 1.97 and 1.99 Å with a coordination numbers (CNs) of 2.1 and 2.3, respectively. In the plasma melting process at 1773 K, Cu_2S was formed. The Cu–S bond distance and CN are 2.30 Å and 3.8, respectively.

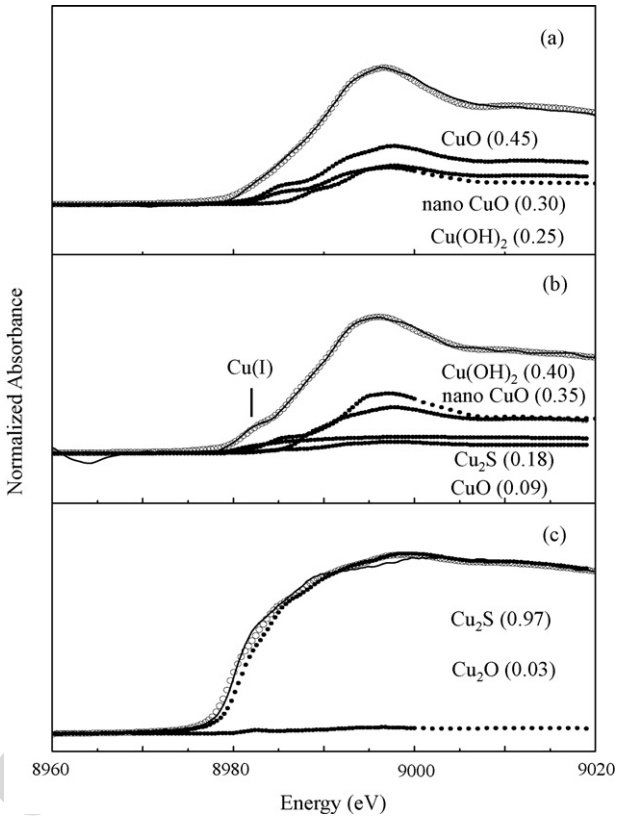

Fig. 1. XANES spectra of copper in the (a) bottom and (b) fly ashes and (c) plasma-melted slag. Solid lines and circles represent experimental data and the least-square fits, respectively.

Table 1
Structural parameters of copper in the bottom and fly ashes and slag studied by EXAFS

	Shell	Bond distance (Å)	Coordination number	σ^2 (Å)
Model compounds				
CuO	Cu–O	1.96	3.8	0.003
Nano CuO	Cu–O	1.95	3.3	0.003
$Cu(OH)_2$	Cu–O	1.97	3.1	0.003
Cu_2S	Cu–S	2.27	3.8	0.014
Bottom ash	Cu–O	1.97	2.1	0.001
Fly ash	Cu–O	1.99	2.3	0.004
Slag	Cu–S	2.30	3.8	0.013

σ^2: Debye–Waller factor.

4. Conclusions

It was found by least-square fitted XANES spectroscopy that the main copper species in bottom and fly ashes are CuO and $Cu(OH)_2$. About 30–35% of nanosize CuO was also observed. Due to sulfurization and self-reduction of copper at 1773 K, about 97% of Cu_2S was formed in the plasma-melted slag. The EXAFS data indicate that the bottom and fly ashes have Cu–O bond distances of 1.97 and 1.99 Å with CNs of 2.1 and 2.3, respectively. Treatments of the bottom and fly ashes in the plasma melting process at 1773 K led to formation of Cu_2S with a Cu–S bond distance of 2.30 Å and a CN of 3.8.

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