

X-ray absorption spectroscopy study of a copper-containing material after thermal treatment

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Abstract

Thermal immobilization of copper contaminant in a copper-containing solid material collected from local copper smelting and foundry area is investigated in the present work. X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) are employed for copper speciation. XAS results indicate that cupric hydroxide is the major copper species in the solid material dried at 105 °C. After being subjected to a 500 °C thermal process, cupric hydroxide still remains as the main copper species, but some Cu(II) is chemically reduced to Cu(I). More cupric hydroxide is progressively converted to Cu(I) as the sample was heated at 1100 °C than that heated at 500 °C. The sample heated at 500 °C is in its original powder form. However, thermal treatment at 1100 °C transforms the powder into a hardened granule-like form that is much bigger in size and difficult to be ground into powders. The sample is sintered with the sparingly soluble cuprous oxide and elemental copper being encapsulated inside. Toxicity characteristic leaching procedure (TCLP) results depict that amount of copper leached from the sample (containing 133,000 mg copper kg⁻¹) heated at 1100 °C for 2 h is considerably minor, being 367 mg copper kg⁻¹.

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1. Introduction

Waggoner et al. reported that copper contamination could cause many adverse effects, such as hepatic cirrhosis, anemia, abnormal behaviour of the nervous system, vascular sclerosis, and others to human health [1]. Copper is extensively used in various industries and it may be mobile in the environment. If not properly treated, copper-containing waste can pose great harm to the environment and human through the food chain. Previous studies indicate that a major portion of heavy metals can be effectively stabilized in some inorganic sorbents including aluminosilicates and silica through a heating process at 200–1300 °C [2–7]. The sintered or/and melted materials, depending on their composition, can be recycled as component resources for the manufacture of brick, porcelain, firebrick, and ceramics. The thermal immobilization of heavy metals can be achieved via two mechanisms: (i) encapsulation of the heavy

metals, and (ii) formation of less soluble species of the heavy metals.

Thermal encapsulation process based on a melting process in a pilot plant was reported to be effective in immobilizing heavy metals in Superfund site samples, as tested in a Superfund Innovative Technology Evaluation program by US Environmental Protection Agency (USEPA) [2]. The melting process can result in minimal leaching of heavy metals in acidic environment [2], as tested by the toxicity characteristic leaching procedure (TCLP) formulated by USEPA [8]. However, no information on heavy metal speciation was reported in previous study [2].

Thermal immobilization of copper in copper-doped silica and kaolinite is feasible. A previous study shows that, as inferred from the simulation of a sample XANES spectrum with a set of copper reference compounds, most of the artificially doped cupric nitrate was transformed into cupric hydroxide due to hydroxylation at room temperature [7]. After heating, the cupric oxide became the major copper species in samples; quantification of copper species is successful due to the intrinsic simplicity of the silica matrix used. Hsiao et al. investigated copper species distribution in various incinerator fly ashes and also found the

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presence of cupric hydroxide [9,10]. The copper content in the high-temperature derived fly ashes used previously is less than 0.1 wt.%.

The objective of this study is to determine: (i) fraction of copper leached from heated samples, and (ii) copper species transformation in a real-world copper-containing solid material after thermal treatment up to 1100 °C. The real-world sample matrix in the present study is much more complicated than the previously studied model compound matrixes where the matrix sintering activity was minimal at ≤ 900 °C [7]. The real-world sample contains 13.6 wt.% copper, being much higher than the copper content in fly ashes, so it is very hazardous and imposes quite a challenge on immobilization technologies.

2. Experimental

The Cu-containing solid material that mainly consists of residues resulting from local copper smelting and foundry sectors was sampled from an illegal dump in Taiwan. As expressed in weight percentage of metal oxides and loss upon ignition (LOI), the solid material contains 50.6% silica oxide, 5.1% ferric oxide, 2.5% aluminum oxide, 2.0% sodium oxide, 16.6% cupric oxide, and 27.9% LOI (including 13.4% sulphur in light yellow powder). The solid material was dried in an oven at 105 °C for 3 days, ground and sieved to less than 297 μm in size. The pre-treated solid material was digested with a combined acid (i.e., 9 mL concentrated nitric acid + 1 mL concentrated hydrochloric acid + 1 mL hydrogen peroxide + 3 mL hydrofluoric acid) in a microwave oven and its copper content was determined to be 133,000 mg copper kg^{-1} using a flame atomic absorbency spectrometer (FAAS). Thermal treatment of the sample is outlined as follows. The pre-treated solid material (in powder form) was introduced to a crucible, covered, and heated under stagnant air in an electric furnace at 500 and 1100 °C for 2 h. The crucible used in present study is made of ceramic material that is free of copper. The sample was observed to stick to crucible surface after the treatment at 1100 °C so that care was taken to avoid scratching off the stuck part of the sample for further analyses. The furnace was pre-heated to a preset temperature before the samples were placed in. After various thermal treatments, the samples were discharged, cooled, and stored for analyses using: (i) XRD with Cu $K\alpha$ radiation under 40 kV and 30 mA at a scanning rate of 0.05°/s, and (ii) Cu K-edge XAS. Furthermore, TCLP experiment was carried out on the heated samples to examine the extent of copper immobilization after the heating process. The concentration of copper in the leached liquids was determined with FAAS and it was mathematically converted to copper leaching from the heated samples in the unit of “mg of copper (kg of heated sample) $^{-1}$ ”.

Copper stock solution of 1000 mg Cu L^{-1} was diluted to six different concentrations to prepare the calibration curve for determining copper concentrations in the liquids collected during the TCLP experiments. Each calibration curve covers six different cupric ion concentrations ranging from 0.00 to 8.00 mg Cu L^{-1} . The correlation coefficient (r^2) for the calibration curve was set to be greater than 0.995 in the present study. Copper concentration in a quality control standard was

routinely measured to examine the validity of the calibration curve. Acceptable copper recovery of the quality control standard was set to be within the range of 80–120%. If the copper recovery was outside this range, another acceptable calibration curve was constructed. The method detection limit was determined to be 0.36 mg Cu (kg of sample) $^{-1}$.

Cu K-edge (at 8979 eV) XAS spectra were recorded on the wiggler beam line (BL-17C) at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. During the XAS experiments, the facility was configured by storage ring energy of 1.5 GeV, beam current of 120–200 mA, span of the monochromatic photon energy of 4–15 keV, and energy resolution of 1.9×10^{-4} . All spectra were recorded in transmission mode at room temperature. The reference compounds used were cupric hydroxide, cupric oxide, cuprous oxide, and elemental copper. WinXAS 2.0 software [11] was used for XAS data reduction.

3. Results and discussion

The copper concentrations in the TCLP extracts from the solid material heated at 105, 500, and 1100 °C are determined to be 9615, 1852, and 367 mg copper (kg of sample) $^{-1}$. The copper leached by TCLP experiment only represents 7.2 wt.% of the total copper content in the 105 °C sample; most copper species remain insoluble in the sample. The extent of copper leaching is progressively reduced with increasing thermal treatment temperature.

Fig. 1 presents the XRD patterns from the samples heated at 105 and 500 °C. The 105 °C sample exhibits well-recognized diffraction peaks associated with quartz, cristobalite, Si_2O_5 , $\text{Cu}(\text{OH})_2$, and FeS (mackinawite). In contrast, the 500 °C sample shows some weak diffraction peaks from elemental copper. These XRD results suggest that copper compounds in both samples are largely amorphous. The XRD peak intensities from quartz decrease significantly after the treatment at 500 °C, indicating a decrease in the crystallinity of quartz. The cristobalite phase observed in the 105 °C sample no longer exists after the treatment at 500 °C, implying a change into amorphous phase. It is worth noting that the sample heated at 1100 °C was too hardened to be ground to fine powder in size small enough for XRD measurement.

Fig. 2 displays the normalized XANES spectra of copper reference compounds (left column) and their first derivative curves (right column). There appear obvious differences among the XANES spectra of the reference compounds, as well as among their derivative curves, except between those of cupric hydroxide and cupric sulphate. The energy of each peak of the derivative curves was also shown in Fig. 2. The characteristic shoulder in the XANES spectra of reference compounds appear at relatively different photon energies, consistent with the observation in previous studies [9,12]. Thus it would be appropriate for the present study to compare the sample XANES spectra and their derivative curves with those of reference compounds.

Fig. 3 presents the normalized XANES spectra (left column) and their first derivative curves (right column) for the heated solid materials. Both the XANES spectrum of the 105 °C sample and its derivative curve (top compartment of Fig. 3) bear more

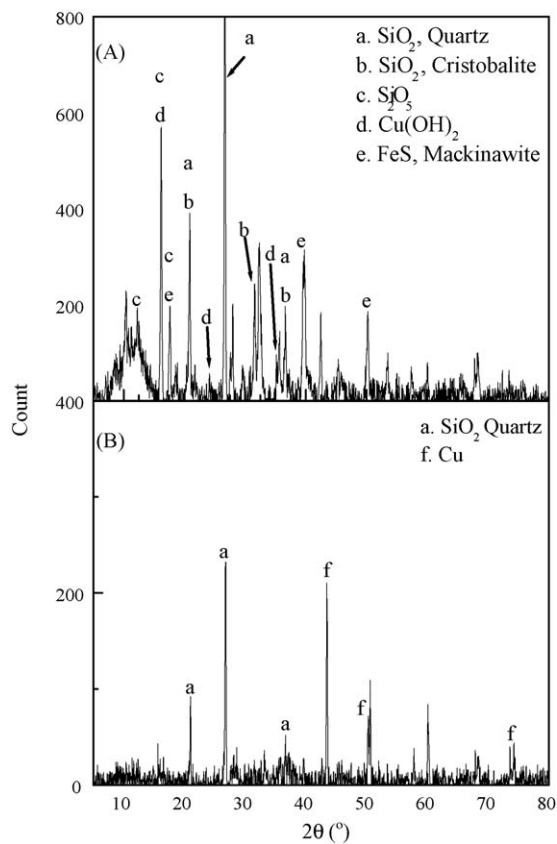


Fig. 1. XRD patterns of the solid materials heated at: (A) 105 and (B) 500 °C.

resemblance to those of cupric hydroxide than to those of cupric sulphate. It is well recognized that cupric sulphate is highly water-soluble and it would be easily ionized into cupric and sulphate ions under natural rainfall in the dump site [13]. The cupric ion was then hydroxylated to form cupric hydroxide with sparing solubility. Accordingly, we suggest that copper species in this sample is mainly in the form of cupric hydroxide due to the hydroxylation reaction of cupric ion. Previous studies also revealed that copper ions readily form cupric hydroxide through hydroxylation reaction at room temperature [7,9].

For the 500 °C sample, although the XANES spectrum (middle left panel of Fig. 3) still carries obvious cupric hydroxide characteristics, its white line intensity is lower than that of cupric hydroxide. Both the peak position and the relative peak ratio in the derivative curve (middle right of Fig. 3) are similar to that of cupric hydroxide reference, but the absolute peak intensities are relatively less than those of cupric hydroxide. Furthermore there appears an additional tiny peak at 8.981 keV in the derivative curve of the 500 °C sample. This additional peak may be attributed to the existence of small amount of cuprous oxide. Although the XRD patterns (see Fig. 1) indicate the formation of Cu(0) after the treatment at 500 °C, the XANES spectrum does not show clear evidence for Cu(0). This fact suggests that Cu(0) in the 500 °C sample represents such a small portion of total copper that its contribution to XANES spectrum is negligible, but of high crystallinity to be detectable by XRD method.

For the sample heated at 1100 °C, the XANES spectrum (bottom left of Fig. 3) shows less cupric hydroxide characteristics

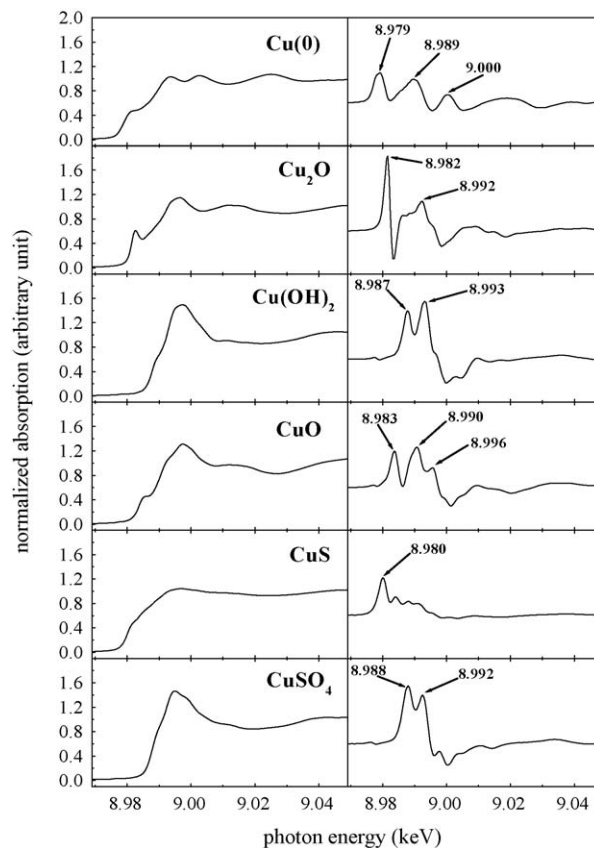


Fig. 2. Normalized XANES spectra (left column) and their first derivative curves (right column) of reference copper compounds: cupric hydroxide, cupric oxide, cuprous oxide, and elemental copper.

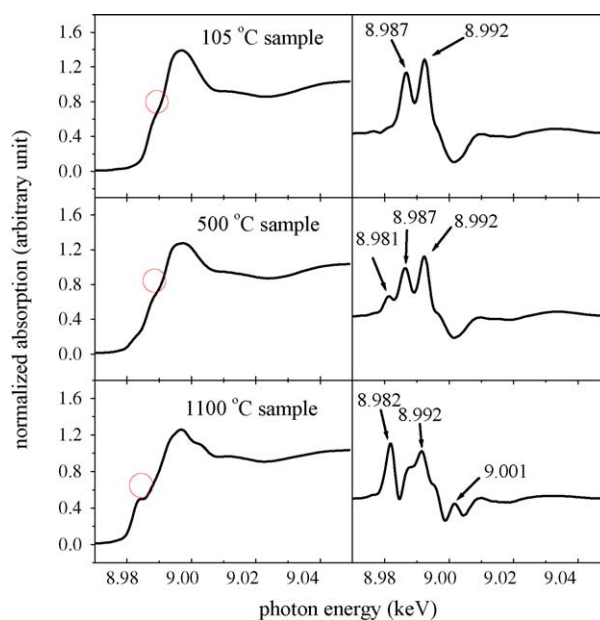


Fig. 3. Normalized XANES spectra (left column) and their first derivative curves (right column) of heated solid materials.

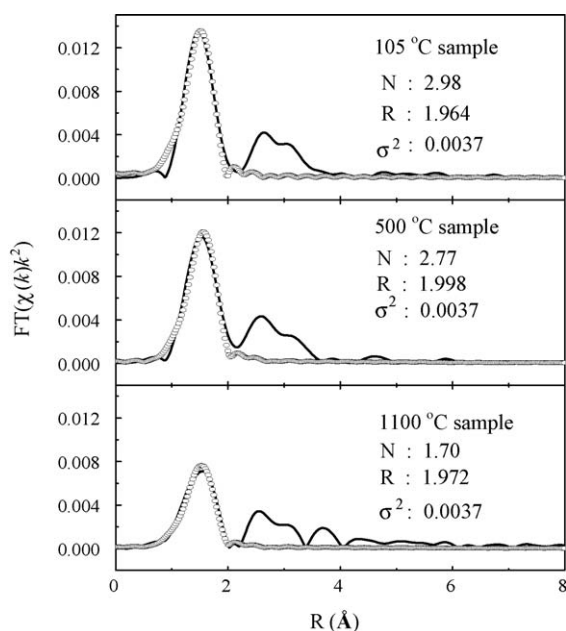


Fig. 4. Fourier transformed EXAFS spectra (solid line) and fitted results (open circle) of heated solid materials.

than the 105 and 500 °C samples. It has a distinct shoulder characteristic of cuprous oxide in the 8.983–8.985 keV region. The derivative curve (bottom right of Fig. 3), compared with that of reference compounds (in Fig. 2), also indicates that cuprous oxide is the major copper species in the 1100 °C sample.

Fig. 4 presents the Fourier transformed EXAFS functions along with the computer-fitted results, whereby the first-shell structural parameters including coordination number (N), interatomic distance (R), and Debye-Waller factor (σ^2) are derived. The numerical values are listed in each panel of Fig. 4. Cupric oxide crystallographic data is used to construct the structural model for calculating the backscattering amplitude and phase shift functions, and the Debye-Waller factor is fixed as 0.0037 during the fitting process. The residuals (in percent) associated with the EXAFS fittings are 5.75, 9.52, and 8.77 for the 105, 500, and 1100 °C samples, respectively; and the corresponding value is 6.08 for the cupric oxide reference. Fig. 4 shows that N -values of the 105 and 500 °C samples are almost the same (2.98 versus 2.77), whilst N decreases to 1.70 for the 1100 °C sample. The considerable decrease in N -value for the 1100 °C sample is suggested to result from the chemical dissolution of copper compounds into the sample minerals through lattice diffusion [7]. In a previous study, it was also observed that a weaker spectral intensity of the Fourier transformed EXAFS resulted from a copper containing kaolin heated at 900 °C, as compared with that at 500 °C [7]. R -values (i.e., 1.964, 1.998, and 1.972 Å) for all three samples can be considered as being equivalent to each other within the uncertainty level in EXAFS technique, given the matrix complexity of the solid sample and the relatively higher residuals derived from the EXAFS fitting for the 500 and 1100 °C samples than that from cupric oxide reference. It is noted that, in samples having much simpler matrix than what studied in this study, the uncertainty in R -value derived from EXAFS fitting is approximately $\pm 1\%$ [14]. Two- and three-

shell fittings were also attempted in the present study but never succeeded. The poor resolution of higher coordination shells beyond the first shell prevents the EXAFS data from detailed analysis.

4. Conclusion

The copper contaminant in the real-world solid material dried at 105 °C is mainly in the form of cupric hydroxide, as revealed by the XANES spectrum. The cupric hydroxide characteristics in the XANES spectrum for the sample heated at 500 °C becomes less clear, as compared with that of the 105 °C sample. In addition, the XANES spectrum of the 500 °C sample indicates the presence of Cu(I) species. Formation of Cu(I) species becomes much more pronounced in the 1100 °C sample, implying that more chemical reduction of Cu(II) occurs at higher temperature. After thermal treatment at 1100 °C for 2 h, Cu(II) was chemically reduced to sparingly soluble cuprous oxide and elemental copper, which was then encapsulated inside sample matrix due to sintering/melting reaction, and hence copper leaching from the thermally treated sample was greatly diminished. We suggest that to effectively immobilize copper, the thermal treatment temperature needs to be high enough to decompose CuO and/or Cu(OH)₂ into Cu(I) and Cu(0) and to effectively incur considerable matrix sintering/melting.

The structural results indicate that copper compounds chemically dissolve into the sample minerals through lattice diffusion during the heating process at 1100 °C, whilst the lattice diffusion does not occur when the samples are heated at 105 and 500 °C. The first-shell interatomic distances of the samples heated at 105, 500, and 1100 °C are considered equivalent.

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