Copper and Zinc Forms in Bottom Ash from Solid Waste Incineration

Combustion of industrial and municipal solid waste for energy recovery is common in many countries around the world. The combustion generates millions of tons of bottom ash (BA) each year only within the European Union. Fresh BA is highly reactive but after treatment (sorting and weathering) it can be used for construction purposes.

However, there are concerns that metals like Cu and Zn may leach from BA to the surrounding environment, causing problems. Total content of metals in the BA is a poor predictor of the potentially leached concentrations. Instead, metal leaching depends heavily on which metal forms that are present. For example; Cu and Zn ions in soluble minerals or adsorbed to particle surfaces will be more prone to leaching than Cu and Zn fixed in poorly soluble mineral matrices and metallic forms. Immobilization or release of metal ions is also coupled to other properties of the ash, especially pH (a higher pH usually gives lower metal concentrations in leachates).

Although speciation of metals is a key factor to understand and predict metal leaching, speciation of Cu and Zn in BA is not well known. We studied Cu and Zn speciation in six metal separated and weathered ("carbonized") BA from different waste to energy plants with a combination of methods: x-ray absorption spectroscopy, x-ray diffraction, leaching/extraction tests at different pH values, and geochemical modelling of the pH-dependent leaching tests. Five of the BA were from grate boiler incinerators (named/called G-A etc.) and one from fluidized bed incinerator (called FB-D). The aims were to identify main species of Cu and Zn in the ashes and to see if speciation varied between the different ashes.

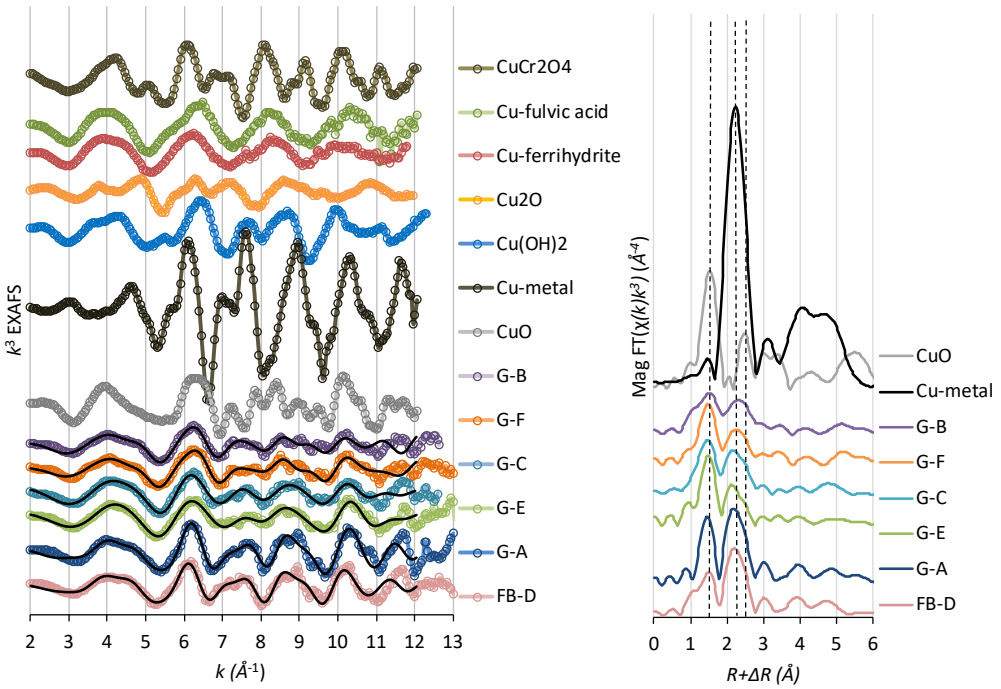

Figure 1. (a) k^3-weighted Cu-EXAFS spectra of standards and bottom ashes, black solid lines are fits (only ashes); (b) Fourier transforms of k^3-weighted Cu-EXAFS spectra. The first dashed vertical line marks a Cu-O distance in CuO, the second and third dashed lines mark Cu···Cu distances in Cu-metal and CuO, respectively (FT is not phase corrected).

Using extended x-ray absorption fine structure (EXAFS) spectroscopy we identified two main Cu species present in all ash samples: Cu(II) oxide and metallic Cu. This is illustrated in the Fourier transform of EXAFS spectra where the peaks of the ash samples matches the peaks of Cu(II) oxide (CuO) and metallic Cu (Figure 1 b). The content of metallic Cu could be quantified to range between 10 and 40% of total Cu in the ashes. Geochemical modelling revealed that concentrations in leachates may be determined by Cu(II) oxide, since the ion activities matched the solubility product of CuII) oxide in leachates.

For Zn, EXAFS indicated that the main species were Zn(II) oxide and willemite (Zn_2SiO_4), which was also in line with results from geochemical modelling where ion activities in leachates matched the solubility product of willemite. Comparing spectra from samples exposed to leaching at pH 6.5 and 8.5, it was obvious that some mineral dissolves in this pH range, illustrated by the disappearance of the peak representing the Zn···Zn distance at ~3.2 Å in the Fourier transform at pH 6.5 (Figure 2b). It may be that it is willemite that dissolves between pH 6.5 and 8.5.

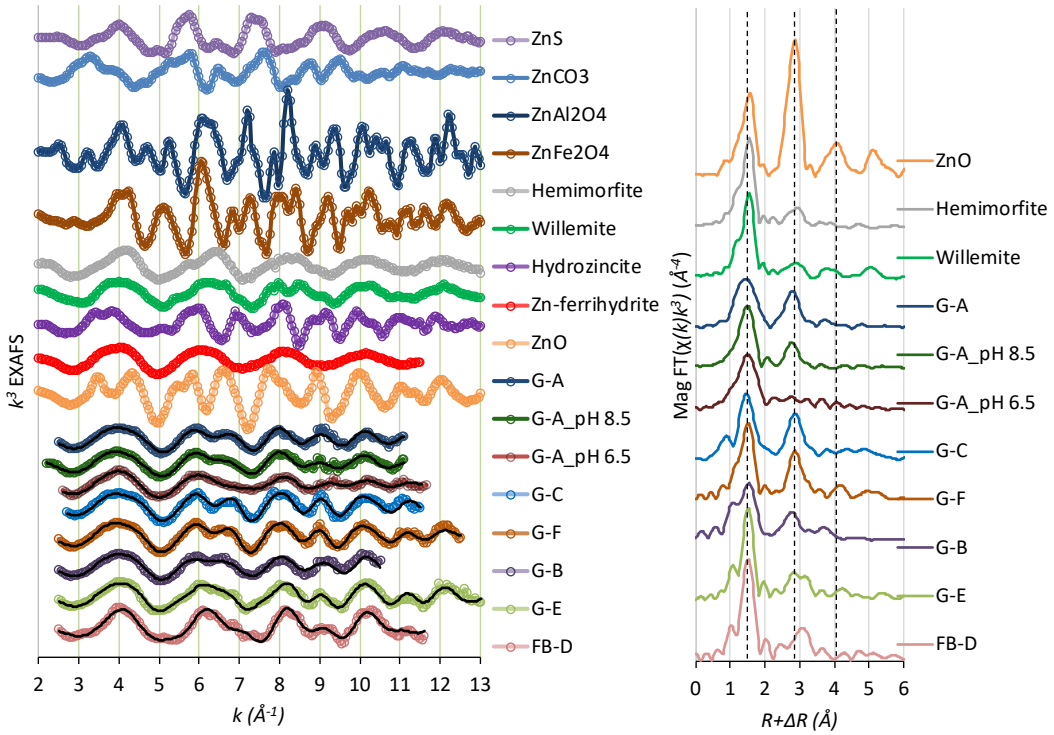

Figure 2. Results from EXAFS measurements: (a) k^3-weighted Zn-EXAFS spectra of standards and bottom ashes, black solid lines are fits (only ashes); (b) Fourier transforms of k^3-weighted Zn-EXAFS spectra. The first dashed vertical line marks a Zn-O distance at ~2.0 Å. The second and third lines are Zn···Zu distances at ~3.2 and ~4.6 Å (the FT is not phase corrected).

Our findings have implications for classification and risk assessment of metal separated and weathered BA. In EU, legislation classification of e.g. ecotoxicity (HP14, hazardous property 14) can be based on presence of specific compounds (species of e.g. Cu) in the BA. If the speciation of a "hazardous" metal is not known, assessment is based on

worst case assumptions which may lead to very conservative assessment. The increased knowledge about the actual speciation reduces the uncertainties in classification.
We also show that leaching of Cu and Zn from the BA is governed by dissolution of minerals, probably Cu(II) oxide (tenorite) and Zn_2SiO_4 (willemite). As these minerals are stable above neutral pH, they will limit leaching providing pH does not drop drastically (which is unlikely due to the large buffering capacity of BA). Consequently, leaching of Cu and Zn is predictive and can be assessed against set criteria and timeframes.

Speciation was similar in the different BA, especially the grate boiler BA, and we expect the results to be representative for metal separated and weathered bottom ashes from large-scale grate boiler incineration of municipal and industrial solid waste.

Primary Citation

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