Transformation of Cu (nanoparticles) during sewage sludge incineration studied by bulk- and micro-XAS

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Engineered nanoparticles (NP) are well retained during wastewater treatment (WWT) and accumulate in the sewage sludge. In Switzerland sewage sludge is mostly digested and incinerated preferably in mono-combustion facilities for volume reduction and energy recovery. The resulting ash is landfilled for potential phosphate recovery in the future. Previous studies suggested that CuO-NP transform into Cu-sulfides during the WWT and in environments with comparable redox conditions (Donner et al., 2011; Gogos et al., 2017; Ma et al., 2014) but did not address further Cu transformation during sludge incineration.
We spiked CuO-NP or dissolved Cu to digested sewage sludge and reacted the sludge under mesophilic, anaerobic conditions for 24 h. Sludge aliquots were collected and freeze dried for solid-phase analysis. The remaining sludge was dried at 105 °C overnight and incinerated in a pilot- bubbling bed type fluidized bed incinerator. To determine the speciation of Cu in the spiked sludges and ashes, the homogenized sludge and ash samples were prepared as 7-mm diameter pellets for bulk EXAFS analysis at the SuperXAS beamline at the Swiss Light Source (SLS, Paul Scherrer Institute, Villigen). To assess the distribution and speciation of Cu at the micrometer-scale, the undisturbed samples were embedded in resin and cut into thin sections (30 µm) on Si-wafers. These sections were investigated at the microXAS beamline at the SLS. One 500×500 μm^2 area was mapped by X-ray fluorescence (XRF) with a 3×3 μm^2 spatial resolution at an incident photon energy of 18 keV to assess the spatial distribution of Cu and other elements (Fe, Ce, etc.). On the same area, 7 XRF maps were recorded at incident photon energies around the Cu K-edge to obtain spatially-resolved information on Cu speciation.
Linear combination fit (LCF) analysis of the bulk-EXAFS spectra indicated complete sulfidation of Cu spiked in dissolved form to digested sludge after 24 h reaction time, whereas a minor fraction (8%) of the spiked CuO-NP were still present in the digested CuO-NP-spiked sludge (Fig. 1). LCF analysis of the ash samples indicated that incineration lead to a significant change in Cu speciation which was independent of the initially spiked form of Cu. The respective EXAFS spectra were described as a combination of about 33% amorphous CuS, 33% tenorite (CuO), 17% copper sulphate ($CuSO_4$) and 17% cupro spinel ($CuFe_2O_4$) (Fig. 1). A preliminary analysis of the spatially-resolved measurements revealed an uneven distribution of individual Cu species in the sludge and ash samples. Whether CuO-NP spiked to digested sludge and the corresponding ashes

resulted in distinct distribution patterns in terms of Cu concentration or bonding environment is currently under investigation.

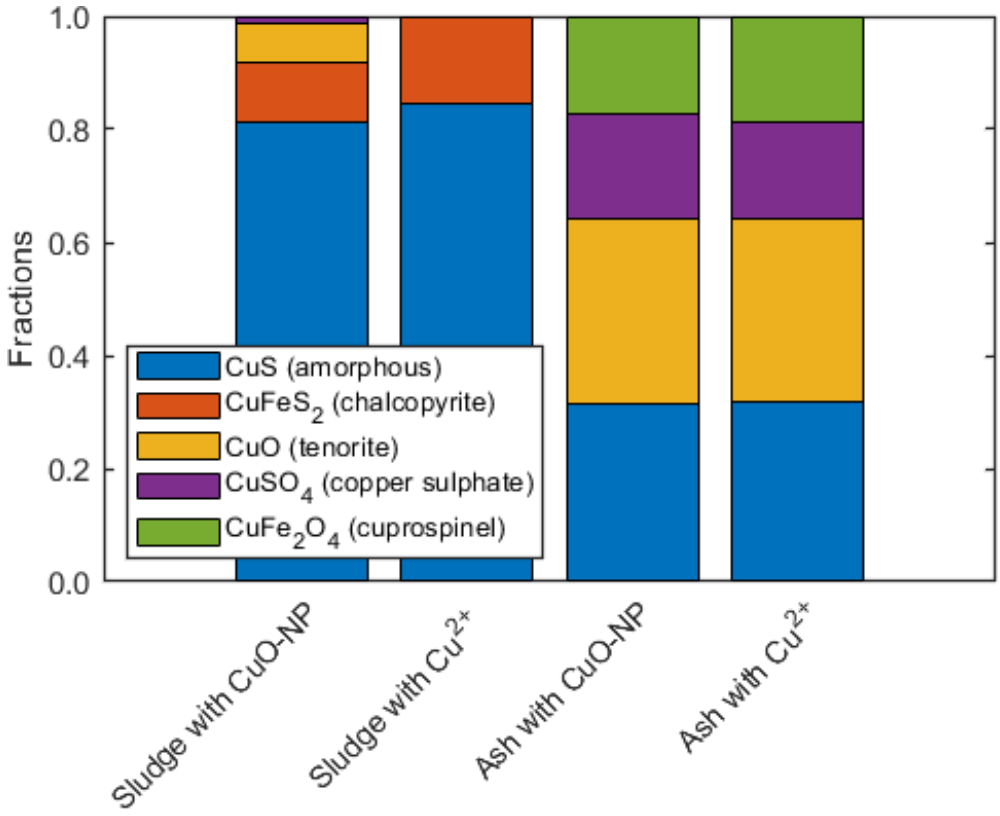

Figure 1. Results of LCF to sludge and ash samples. Digested sludge was spiked with either CuO-NP or dissolved Cu, reacted for 24 h and incinerated in a pilot reactor.

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