

Summary

Mineralogical and geochemical characteristics of metallurgical wastes from the Cu-Co smelters situated in the Zambian Copperbelt have been investigated. A number of instrumental analytical methods (XRD, SEM/EDS, EPMA, TEM/EDS) has been used to identify primary and secondary phases in smelter slags and dusts. A set of leaching experiments (CEN/TS 14997 pH-static test, EN 12457 batch test) in combination with geochemical modelling has been performed, with the emphasis on the leaching behaviour of potential contaminants and their release as a function of the pH. The effect of sample preparation on metal leachability from slag was also evaluated, considering the grain size reduction required by the standardised leaching protocols. Environmental and health risk assessments of the dust samples have been performed.

It was shown that the main carriers of metals in the studied slags were Cu sulphides (bornite, digenite, chalcocite), Co sulphides (cobaltpentlandite), Co-bearing intermetallic phases and alloys. Copper and cobalt were detected in major silicates and spinels, substituting for Fe or Mg in their structures, and in glass. The presence of secondary metal-bearing phases observed on the slag surfaces indicated the reactivity of the slags on contact with water/atmosphere. It was reported that in justified cases, high-resolution methods (such as FIB-TEM) need to be employed to verify the element speciation in solid waste materials. Dust from slag crushers (herein *slag dust*), dust from electrostatic precipitator (herein *ESP dust*) and dust from water filters (herein *fly ash*) were also studied. Different solid speciation of metals was observed for the dusts. Minor to trace Cu sulphides of various compositions (Cu(Fe,Co)S) were detected in all the studied dust samples.

The leaching behaviour of the slag and dust was strongly pH-dependent. For the slag, the highest concentrations of Cu, Co and Zn were released at pH 4–5. Based on the PHREEQC calculations, several Cu- and Co-bearing carbonates, hydroxides, oxides or sulphates were suggested to attenuate the metal release under near-neutral conditions. Various slag sample pretreatment (crushing, sieving, cleaning) has resulted in significant differences in contaminant leachability. Greater release of Cu, Co and Zn was reported for samples with a higher portion of fine dust particles. Extensive contaminant leaching was observed for the *ESP dust*, even at the natural pH (~ 4.3) of the dust suspension. About 30–40% of the total Cu, Co and Zn were released at pH 3. Primary chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was readily dissolved and secondary Cu sulphates precipitated. The leaching of metals from the *fly ash* was mainly attributed to the dissolution of minor metallic phases and partial dissolution of silicates and/or glass. The ORCHESTRA model suggested CoO and ZnO to control the solubility of Co and Zn, respectively. Sorption on hydrous ferric oxides was assumed to effectively attenuate the release of Pb and Cu from the *fly ash*. Near-equilibrium conditions were achieved in the *fly ash*–water system during the standard testing time of 48 h as only slight changes in leachability were observed after 168 h.

The pH-dependent reactivity of slags and dusts showed high risk of contamination for acidic soils in the Zambian Copperbelt smelting area, particularly during the rainy season. Furthermore, high gastric bioaccessibility of Co, Cu, Pb, Zn and As reported for the smelter dusts indicated severe health risks for local populations in this mining and smelting region.