

Chemical and mineralogical investigation of smelting slags from the Copperbelt district, Zambia

M. VÍTKOVÁ^{1*}, V. ETTLER¹, O. ŠEBEK²,
M. MIHALJEVIČ¹ AND B. KŘÍBEK³

¹Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic
(*correspondence: vitkova3@natur.cuni.cz, m.vitkova@seznam.cz)

²Laboratories of the Geological Institutes, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic

³Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

Several types of slags originating from processing of Cu and Co-rich ores in the smelting areas of the Copperbelt (Zambia) were studied. Bulk chemical analyses were combined with mineralogical investigation using XRD, SEM/EDS and EPMA. Generally, the slags are composed of silicate matrix, oxides, glass and sulphide/metallic inclusions and contain high amounts of contaminants [1, 2]. Thus, through weathering and interaction with water in dumps and tailing ponds these metallurgical wastes represent potential environmental risk [3, 4]. The slags are enriched with Cu (3-350 g/kg), Co (0.5-24 g/kg) and As (600-3650 mg/kg). Based on XRD analysis, calcium pyroxenes of approximate composition $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ corresponding to diopside-hedenbergite series were determined as the main phases of the studied material. Detailed chemical and mineralogical investigations revealed possible substitutions of metals in the pyroxene structure (Cu and Co substitute for Fe). Various forms of Fe- and Cr- spinels with relatively high content of Co (1-5 wt.% CoO) were observed. The presence of the olivine-group phases was also detected. In particular, glassy slag samples with 50-70 wt.% SiO_2 contain trace levels of Ti, Cu and Co. The presence of cuprite (Cu_2O) as an important Cu-bearing phase was locally determined in the silicate matrix of the slags. Metallic inclusions are mostly composed of Cu or Cu-Fe sulphides, Co-Fe sulphides, native Cu or various intermetallic phases (Co-Fe, Co-As-Fe). The characterisation of primary phases in the slags represents the first step of their environmental assessment.

[1] Ettler *et al.* (2001), *Can. Mineral.* **39** 873-888. [2] Ettler *et al.* (2009), *Appl. Geochem.* **24** 1-15. [3] Kříbek *et al.* (2006), *MS Czech Geol. Surv.* 160-162. [4] Ganne *et al.* (2006), *Sci. Total Environ.* **356** 69-85.

Lithologic, hydrologic and biogeochemical influences on spatio-temporal variability of As and Hg concentrations in groundwater

D. VLASSOPOULOS^{1*}, B. BESSINGER¹, V. ILLERA²
AND P.A. O'DAY²

¹S.S. Papadopoulos & Associates, Portland OR 97204 USA
(*correspondence: dimitri@sspa.edu)

²University of California, Merced, CA 95340 USA

Soil geochemical characterization at a major construction project site near Seattle, Washington, resulted in 3-D delineation of a body of As-enriched soils (up to 600 mg/kg), whose extent coincides with the limits of a water-saturated peat deposit up to 5 m thick. Vertical profiles show As increasing with depth, indicating accumulation from groundwater flowing through the peat. Absence of current or past As point sources in the area implies an ambient and/or natural background source. Sequential extraction, SEM, XRD, and XAS data indicate that peat soils contain abundant framboidal pyrite and As occurs in a form with orpiment-like (As_2S_3) coordination, implicating sulfate-reducing bacteria in the accumulation of As. Alluvial organic-poor soils in the surrounding areas do not contain sulfides, and are lower in As (<50 mg/kg), which is associated mainly with iron oxides. In contrast, groundwater within peat deposits is generally low in As (mostly As(III)), while elevated As (mixed III/V) and PO_4 concentrations are often observed in alluvial groundwater, within anaerobic groundwater plumes downgradient of peat.

As and Hg levels (up to 60 and 0.03 $\mu\text{g/L}$, respectively) in area groundwater display large variability both spatially and temporally. Elevated As is generally associated with moderately to strongly (Fe(III), As(V), and/or SO_4) reducing conditions, linked to microbial oxidation of peat organic matter and limited by the supply of oxygenated recharge water. Dissolved As and PO_4 are strongly correlated with dissolved Fe, indicating release of these ions during reductive dissolution of iron oxides. Spatially localized redox excursions to very low Eh during drier periods results in release of adsorbed As, while aerobic conditions during wetter periods stabilize iron oxides which adsorb As from solution. In contrast, the mobility of Hg appears to depend more on complexing with dissolved organic matter, which is generated from peat during enhanced recharge events.

Geochemical modeling demonstrates that the observed As and Hg levels in groundwater are readily explained by assuming that only a small fraction (i.e. <1%) of the natural soil content of these elements is available to participate in spatially and seasonally variable biogeochemical processes.