Geochemistry of fly ash-brine co-disposal systems: Solubility controls on trace elements

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Fly ash is a waste material generated from coal combustion in power stations. Fly ash, which contains major and trace elements such as Ca, Mg, Na, K, SO_4, Cl, As, Se, Zn, Cd, Pb, Cu and Mo among others, are produced in significant quantities in South African power utilities. Apart from the generation of fly ash, a hyper-saline wastewater known as brine is also generated in significant quantity during coal combustion processes. Brine contains major elements such as Na, Cl, Ca, SO_4, K, Mg in large quantities, and trace elements such as Fe, Mn, Cr, V, Ti, P, Si, and Al (1). There is need to safely dispose these waste materials due to the possible release of contaminants to the surrounding soils and groundwater. Due to the ability of fly ash to effectively adsorb species in wastewaters (2), the co-disposal of fly ash and brine is expected to result in precipitation of salts, which may result in effluents with reduced TDS. It is expedient to understand the geochemistry of the fly ash-brine co-disposal systems. The study aims at understanding the solubility controlling the release or removal of trace species in the fly ash ash-brine systems. Fly ash and brine were reacted in a batch reaction test at different reaction times varying from 5 minutes to 24 hours. The filtrates from the batch reaction tests were analyzed for trace elements using ICP-MS. The results of the tests revealed the removal of some species such as As, Cu, Pb and Zn from the brine solution. PHREEQC geochemical modeling predicted that the saturation indices (SI) for some mineral phases such as Cupricferrite ($CuFe_2O_4$) and $Ba_3\ (AsO_4)_2$, were oversaturated while Pb $(OH)_2$ and Zn $(OH)_2$ were almost at equilibrium.

[1] Turek (2004) *Desalination* **162**, 355–359. [2] Erol *et al.* (2005) *Energy Conversion & Management* **46**, 1319–1331.

Selective chemical extraction of heavy metals and arsenic in soils contaminated by mining activity (Northern Portugal): Biogeochemical implications

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A chemical sequential extraction of heavy metals (Fe, Mn, Cu, Zn, Pb, Cd, Sn, W, Bi, Ni, Cr, Mo, Co) and As in tailings and soils samples around a five W/Sn mines (Northern Portugal) was realized using a 7-steps fractionation procedure [1]: (1) water-soluble; (2) exchangeable; (3) bound to Fe oxyhydroxides (easily reducible); (4) bound to Fe oxides (moderately reducible); (5) bound to organic matter and secondary Cu-sulfides; (6) bound to primary sulfides; (7) residual. The extracted element contents were measured by ICP-MS. Samples were also analysed for pH, electrical conductivity and organic matter.

The results allowed us to notice that: 1) The pH was the main factor for controlling the geochemical distribution of the studied elements. The tailing and soil samples were very acid, with an average pH of approximately 4, 37. Some metal cations (Mn, Cd, Cu, Zn, Pb, Co, Cr, Ni) behave in a similar way, revealed important enrichments in the most bioavailable fractions (water-soluble and exchangeable fractions). In contrast, oxyanions as Mo and As show low mobility through adsorption to Fe (III) oxyhydroxides dissolved in the two reducible fractions. These results reflect the pH dependent adsorption on the clay minerals, Fe and Mn oxyhydroxides and the co-precipitation with these secondary minerals; 2) Residual fraction was the most important fraction for Sn, Mn, Cr and Zn. These results suggest that in these soils these elements are in a detrital, non available form; 3) Scavenging of mobilized elements (mainly Fe, Mn, Cu, Zn, Cd, Pb, W, Bi, Mo, Cr, Ni, Co and As) in secondary mineral phases and sulfides could be considered a temporary mechanism of metal retention. These metal fractions are susceptible of being set free depending on some changes of environmental conditions.

[1] Dold & Fontboté (2001) ‘Element cycling & secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, & mineral processing.’ *J. Geochem. Explor.* **74**, 3–55.