KindisP modelisation of the chemical stability of Zn-bearing phases in pyrometallurgical slags

M. Vanaecker[1]*, P. Vieillard[2], A. Courtin-Nomade[1] and H. Bril[1]

[1]University of Limoges, FST, 123, avenue A.Thomas, 87060 Limoges cedex, France
(*correspondence: maxime.vanaecker@unilim.fr)
[2]University of Poitiers, FST, CNRS UMR6532, 40 Av du Recteur Pineau, 86022 Poitiers, France

Materials collected from three Zn-industrial former sites contain various Zn-phases such as analogues to zincite (ZnO), franklinite ($ZnFe_2O_4$), hardystonite ($ZnCa_2Si_2O_7$), willemite (Zn_2SiO_4), petedunnite ($CaZnSi_2O_6$) and wurtzite (ZnS). These phases were formed during high temperature processes and are metastable under ambient conditions. They were affected by weathering and Zn neoformed phases are mainly hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$), smisthonite ($ZnCO_3$) and goslarite ($ZnSO_4.7H_2O$).

Hemimorphite is typically developed on willemite, goslarite on zincite and smithsonite on zincite and hardystonite.

However, formation of secondary products widely depends on *in situ* chemical factors (pCO_2, pO_2, Eh, pH) and activities of associated ions (SO_4^-, Ca^{++}…). Formation of Zn-carbonates and Zn-sulfates are then limited by calcite and gypsum precipitation.

Observations and models developed by KindisP, for which the database was updated with estimated free Gibbs enthalpies values, permit to describe this competition, to precise the fields of stability of primary and secondary phases as well as the role of external fluids. Dissolution of primary phases is most effective in acidic conditions, favored by sulfides dissolution. Neoformation is highly dependent to the released elements.

In order to validate kinetics models, 1 year leaching experiments were carried out on polished sections in adjusted pH solutions (water, lime and citric acid). Materials are unstable in acidic conditions and equilibrium is reached with a pH increase.

Under weathering conditions, sulfides react first due to oxidizing conditions. Dissolution of melilites and willemite is underlined by an important release of Ca, Zn and silica, necessary to the precipitation of sulfates, carbonates and hemimorphite.

Modeling carbon and chlorine stable isotope fractionation to assess and quantify degradation of chlorinated ethenes in groundwater

B.M. van Breukelen*

Faculty of Earth and Life Sciences, VU University Amsterdam, 1081 HV, Amsterdam, the Netherlands
(*correspondence: boris.van.breukelen@falw.vu.nl)

Degradation of chlorinated ethenes primarily occurs via reductive dechlorination in the anoxic core of pollution plumes, while lower chlorinated ethenes may additionally become oxidized at the more oxidized fringes of plumes. Assessing the occurrence of oxidation processes is complicated as reaction products (Cl- and CO_2) are usually already present in high background concentrations in groundwater. Compound-specific stable isotope analysis (CSIA) provides essential information as it enables to quantify the extent of degradation of an organic pollutant based on its observed change in isotopic ratio away from source zones. Furthermore, two-dimensional carbon and chlorine isotope analysis may enable discrimination among these two main degradation processes resulting in reliable degradation estimates if degradation is being shared over two competing pathways [1].

Carbon isotope fractionation during sequential reductive dechlorination of perchloroethene to ethene was simulated before [2]. This model has been integrated in a 3-D reactive transport model [3] to enable simulation of competing core- and fringe processes within pollution plumes, and extended to include chlorine isotope fractionation. Interpretation and simulation of chlorine isotope fractionation is different and less straightforward than carbon isotope fractionation because of (i) the high natural abundance of the heavy Cl-37 isotope resulting in various relevant isotopologues of each higher chlorinated ethene, and (ii) the removal of one chlorine atom during each sequential degradation step. First simulation results showed that chlorine isotope ratio patterns were strikingly different from carbon isotope patterns.

The model is being applied to simulate lab and field observations, while results of scenario modeling give insight in the spatial carbon and chlorine isotope ratio distributions of chlorinated ethenes that can be expected to occur at typical contaminated sites.

[1] Van Breukelen (2007) *Environ. Sci. Techol.* **41**, 4004-4010. [2] Van Breukelen *et al.* (2005) *Environ. Sci. Techol.* **39**, 4189-4197. [3] Van Breukelen & Prommer *Environ. Sci. Techol.* **42**, 2457-2463.