Experimental study of slag stability under different geochemical conditions

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Slags from iron metallurgy are considered as important material used in many field of industry and civil-engineering. Slag is composed of high-temeperature phases that might be very reactive for a long time. They may contain harmful elements (e.g., Ni, Cu, Pb, Zn, Cr, As, Sb) that can be released into the environment during alteration or leaching. The aim of the study was to determine mineralogy and mobilization of potentially harmful elements in various experimentally simulated geochemical conditions.

Blast furnace and stealmaking slags after different ageing periods were investigated. Experimental study that simulated long term alterations were made using Soxhlet aparatus in the following solutions: destiled water, H_2O +NaCl, $H_2O+CaSO_4.2H_2O$ and in humic acid alkali solution. Chemical and mineral composition of slag samples after experiments were studied using with XRD, SEM-EDS, ICP-MS, and ICP-ES analyses.

The blast furnace slag is composed mainly of calcium silicates (melilites - akermanite and gehlenite, rankinite, pseudowollastonite). Small amounts of sulphur (>3 wt. %) is dispersed within calcium silicates. Samples of stealmaking slag consist of calcium ferrites (srebrodolskite, brownmillerite), larnite, but also other Ca-Fe-Mg-Mn oxides and silicates.

After experiments presence of main phases have not been changed, but differences in XRD peaks intensities may suggest that some of the slag components were partly modified New phases like merwinite, calcium magnesium iron silicates, or hydrated calcium silicates (bicchulite or xonotlite) were formed.

Mobilization of harmful elements during four series of experiment is not very advanced. The most mobile elements in blast furnace slags during experiments are: Ni, Pb, As, Se, Cd, Tl, Ba, Se and in stealmaking slags: Fe, Ni, Cr, Co, Sc, Se, Sb and As. The mobility of those elements is not very high, but it is important to take into consideration the fact that the laboratory conditions are different than in nature where slags are reactive under the influence of natural long-term processes.

Apatite from calcium carbonates: A pseudomorphic replacement reaction

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The replacement of calcium carbonate by apatite at temperatures of 100-200°C results in perfect pseudomorphs of their initial structures [1]. Micro-scale observations reveal that single inorganic aragonite crystals can be replaced by a polycrystalline apatite that has no clear orientation and no apparent structural relationship with the parent crystal. However, the hexagonally twinned aragonite can be pseudomorphed by apatite crystals at an advancing reaction front initiating at the crystal faces and proceeding towards the core, always retaining the hexagonal crystallographic form, via a dissolution re-precipitation process [2]. Under the same conditions, biogenic aragonite (such as cuttlebone) is replaced by an apatite that does not form the typical hexagonal crystals and also contains β-TCP, a second calcium phosphate phase, indicating that the presense of an organic component can alter the precipitating mineral in different ways. The solubility differences between parent calcium carbonate and product apatite could be considered as the driving force for this reaction, but many parameters affect the overall process. The starting material, the presense of organics, the composition of the interfacial fluid, temperature and pressure are all components of a complex geochemical puzzle that includes replacement processes and their resulting pattern formations.

Raman spectroscopy, scanning electron microscopy and X-ray powder diffraction techniques have been employed in order to study the replacement of aragonite by apatite.

[1] Kasioptas A. *et al*. (2008) *Mineralogical Magazine* **72**, Issue 1, 77-80. [2] Putnis A. & Putnis C.V. (2007) *Journal of Solid State Chemistry*, **180**, 1738-1786.