

## **μXAS investigation of the source and behaviour of vanadium leaching in the BOF steel slag-water system.**

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Steel slags are a by-product of steel manufacture produced in large quantities worldwide. Whilst some slags are recycled (e.g. as construction aggregate) much is still dumped in open air slag heaps. Steel slag is generally composed of Ca, Al, Mg and Fe oxides and silicates and is often significantly enriched in toxic trace metals. Rainwater interacting with CaO and Ca-silicate phases in steel slags produces a high pH leachate (pH 12). In recent years concerns have been raised over the potential for mobilisation of trace metals such as V and Cr into leachate during weathering processes. This study presents data concerning speciation of V in steel slags during aerobic and anaerobic leaching, and; reports findings from a combined field and laboratory investigation of the fate and behaviour of V in leachates during aerobic neutralisation.

BOF slag samples were collected from the Yarborough Landfill, Scunthorpe, UK and leached in DIW under aerobic and anaerobic conditions for 6 months. SEM/EDX identified 4 principal mineral phases in unweathered slag comprising a CaO-rich phase, a Ca-silicate phase, a brownmillerite-like phase and a wustite-like phase. V was hosted primarily within the Ca-silicate and brownmillerite phases. μXANES analysis showed V to be predominantly present as V(V) within Ca-silicate and as V(IV) within brownmillerite. Following weathering a 20-50μm thick 'rind' was visible with similar composition in aerobic and anaerobic systems. This region was depleted in V(V) and contained neoformed C-S-H. Little alteration of the brownmillerite phase was evident hence weathered regions were enriched in V(IV) compared to the unweathered sample. Results show that V is leached preferentially from Ca-silicates as V(V) due to dissolution of these phases. Supersaturation with respect to  $\text{Ca}_3(\text{VO}_4)_2$  then controls the final aqueous V concentrations in anaerobic leachates. Removal of  $\text{Ca}^{2+}$  by reaction with atmospheric  $\text{CO}_2$  forms calcite under aerobic conditions, which in turn leads to higher aqueous vanadate concentrations due to the lower  $\text{Ca}^{2+}$  concentrations. Release of V is environmentally significant, however, precipitation of C-S-H may have an armouring effect reducing the long term potential for V release by protecting the interior portion of slag blocks.

At sites where steel slag leachates enter surface drainage, in gassing of atmospheric  $\text{CO}_2$  produces large volumes of secondary carbonate precipitation and neutralises the alkalinity present. The concentration of trace metals (e.g. V and Al) are also reduced during this process. This study Field investigation showed that aqueous vanadium concentrations are reduced downstream of the point where leachate enters surface streams concurrent with significant reductions of water pH and Ca concentrations. In laboratory experiments only modest removal (<20%) of V occurred in neutralisation experiments where calcite or kaolinite clay were the only sorption surface present. However, when iron oxide (goethite) was present the degree of removal increased substantially (>50% removal). XANES analysis of the V speciation in solids recovered after neutralisation revealed only V(V) was present, most likely in surface sorption bonding environments. EXAFS analysis on selected samples revealed that V formed strong inner sphere complexes with goethite surfaces during neutralisation, accounting for the increased degree of V removal observed. These results showed that pH dependant sorption processes ultimately control the behaviour of V in surface waters affected by steel slag leachates and that interaction of V with iron oxides can be expected to limit V mobility in affected environments.

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