

## Trace element distribution in an extremely basic environment in mine tailings

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Element distribution in a 10 years old low-sulphide and high-carbonate tailings profile covered with a 50cm thick fly ash layer have been investigated. The dissolution of fly ash created an extremely basic environment (pH >11) in the underlying tailings. This resulted in a depletion zone where weathering of Ca-, Fe-, Mg- and Mn-silicates was extensive. Only quartz and K-, Na-, Ca-feldspars covered with CaCO<sub>3</sub> remained. The depletion zone was 47cm thick, which indicates a very high weathering rate due to the presence of hydrated hydroxyl ions. Chromium and Ni were accumulated in the depletion zone, while Cd and Cu showed a relatively unchanged content. These elements were added from the ash layer. Chromium and Ni were not identified by scanning electron microscope, but found in the residual phase by sequential extraction, indicating insoluble phases. Elements such as Fe, Pb and S were depleted in the upper part of the tailings, but accumulated together with Cd and Cu, 20cm below the depletion zone, where the pH decreased to circum-neutral. Detailed determination of secondary phases present in the accumulation zone is in progress and the result will be presented. The ash layer was hardened due to pozzolanic properties which reduced the oxygen diffusion which was confirmed by oxygen analysis. Alkaline materials are often used in remediation of contaminated areas, but should be carefully used to avoid leaching of metals. Accumulated elements can be remobilized by changes in the chemical environment when for example the weathering front moves downward and/or the lime content is exhausted.

## Development of *in situ* measurements of REE in deep groundwater using Diffusive Gradient in Thin Film

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The Äspö Hard Rock Laboratory (HRL), SE Sweden, is an underground facility where the Swedish concept for storage of nuclear fuel waste is tested under natural repository conditions [1]. This laboratory also offers an environment for researchers interested in conducting experiments as well as testing equipment *in situ* at the deep granitoid subsurface.

An ongoing activity at the Äspö HRL is monitoring of hydrogeochemistry where several borehole are characterized and sampled every year since two decades. The program includes the rare earth elements (REE), which generally however occur in concentrations below detection limit with the utilizes conventional sampling and analytical techniques.

In order to develop a monitoring-technique with which the REEs can be detected above the detection limit, a principle with passive samplers, DGT (Diffusive Gradient in Thin-Film) [2], has been tested. The DGT technique makes it possible to determine labile trace elements, such as REE, by allowing the metals in solution to accumulating to binding agents over a defined period of time.

To obtain as little disturbance as possible and maintain the pressure and the reduced state in the bedrock fractures a special designed container was constructed. The container can hold three DGT's and are constructed in stainless steel to maintain a high pressure of 50 bar and the inside is made of PEEK polymer material to minimize the risk of contamination.

The sampling was performed in three boreholes at depths of -144 m, -280 m and -450 m at three different locations in the Äspö HRL tunnel. Different deployment times were tested (1-4 weeks) and the results are compared with spot sample measurements (<0.45 µm). Overall, the technique works well and the results show that DGT can be used to monitor low-levels of REE (and other trace metals) in reduced groundwater in deep-lying bedrock fractures.

[1] SKB (2012) Annual Report 2011. SKB TR-12-03 [2] Zhang *et al* (1995) *Anal. Chem.* **67**, 3391-3400