

4.64.P11**Exploring the diffusive interaction between Opalinus Clay and concrete using reactive transport modelling**

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The diffusive interaction between concrete and host rock of a repository for nuclear wastes will take place over time-scales much greater than what can be investigated with experiments. Reactive transport modelling is a powerful tool in exploring such systems: Boundary conditions that are not known a priori, e.g. the reaction products, can be varied and thereby their importance for the overall outcome of the modelling be studied.

Our work is based on earlier modelling and experiments under advective-diffusive transport conditions [1] that used drill cores of Opalinus Clay, which is a potential host rock in Switzerland, and simplified cement pore solution. Because the latter is not a constant over long time-scales, the present model includes simplified concrete consisting of aggregate, portlandite, CSH, ettringite, hydrogarnet and hydrotalcite.

In the Opalinus Clay and on a time-scale of 50 000 years, the modelling predicts a zone of less than 23 cm where pH increases from initially 7.2 to values larger than 9. The altered zone is characterised by consumption of primary dolomite, kaolinite, quartz as well as illite in some scenarios, and the formation of zeolites, hydrotalcite, sepiolite as well as in some cases neoformation of illite.

The degradation of the concrete mainly consists of consumption of portlandite and transformation of the CSH towards lower Ca/Si-ratios. Most primary concrete constituents are consumed within thousands of years, except the aggregate. First results suggest that on time scales of ten thousands of years, concrete degradation is mainly driven by internal degradation processes, i.e., reactions between aggregate and pore fluid.

The mineral reactions result in zones of elevated and of reduced porosity. Precipitation of zeolites in the Opalinus Clay is an important sink of mass, which is mainly derived from the concrete. If zeolite formation is excluded, mass is transferred from the Opalinus Clay to the concrete where CSH phases precipitate. On a 50 000 years time-scale and if porosity is set constant for the transport calculations, the zones with important porosity variations in concrete and Opalinus Clay are less than 30 cm thick. Model runs accounting for the feedback of mineral reactions on transport predict clogging of porosity within tens to hundreds of years.

References

[1] Adler M. (2001), PhD thesis, University of Bern

4.64.P12**Rare earth elements in natural calcite**J.T. CHRISTENSEN¹, S.L.S. STIPP¹, J.A. BAKER² AND
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Rare earth elements (REE) are a useful proxy for the behaviour of actinides in the environment, because the REE behave in the same fashion as the actinides. One issue of particular interest is how REE can be used as proxies for the actinides when making risk assessment modelling for radioactive waste repositories. Given that calcite is present in nearly all geological settings either as a primary mineral, or as fillings in fractures or pore spaces, and is also one of the main secondary phases precipitated when concrete breaks down, we have studied the REE in 70 natural calcite samples. The calcite samples were taken from a broad range of geological environments including igneous (carbonatite, pegmatite), metamorphic (skarn, marble), sedimentary (limestone) and hydrothermal settings. REE abundances were determined by isotope dilution analysis using a multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

Some systematic trends characterise total REE concentrations and distributions. For example, limestone is notably enriched in the light REE and depleted in the heavy REE and has a negative Eu-anomaly and, in some cases, negative Ce-anomalies. Hydrothermal precipitated calcite exhibits less light REE enrichment and flatter middle REE and heavy REE patterns. The maximum concentrations of REE confined with the calcite mineral are interesting. Absolute amounts range from a minimum of Lu which is below the detection limit to a maximum of 272 ppm for Ce. If all REE are added together on a molar basis, the maximum total REE concentration for any calcite is $4 \cdot 10^{-3}$ mol/kg which is a carbonatite sample from Greenland. Assuming the actinides behave similarly to the lanthanides, a calcite precipitating in a fracture after accidental escape of radioactive waste from a facility should incorporate significant quantities of actinides.

Calcite synthesised from Eu-containing solutions showed up to $6 \cdot 10^{-3}$ moles Eu per kg calcite. By comparison with the REE abundances in natural calcite, it seems that REE uptake by natural calcite is limited by the amount available in solution, and not by the ability of Eu to be incorporated in the mineral structure.