Green rust interaction with cerium

S. NEDEL*, K.DIDERIKSEN, B.C. CHRISTIANSEN,
N. BOVET AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark
(*correspondence: sorin@nano.ku.dk)

Repositories are currently being planned in several countries for long-term storage of spent fuel rods and other radioactive waste (for example U, Pu, Am, Np). Reactive barriers will be constructed to prevent radionuclide release to the environment and reactive transport modelling is being refined to assess mobility in the event of leakage. However, current models do not consider the potential of contaminant uptake by members of the green rust (GR) family of minerals. GR is a redox active compound with high surface area, that forms where iron concentrations are high such as with Fe(0) corrosion. To improve understanding of the behaviour of actinides, researchers often use lanthanides as analogues. The aim of this work was to investigate the interaction of $GR_{Na,SO4}$ with Ce(III), as an example of an *f*-group element that has an oxidised counterpart. The results contribute to fundamental understanding about the interaction of tri- and tetra-valent actinides with crystalline Fe-(oxyhydr)oxides.

$GR_{Na,SO4}$ was synthesised by two methods: recrystallisation of ferrihydrite in an Fe(II) bearing solution and oxidation of an Fe(II) solution. pH was maintained at 7 by addition of NaOH and cerium was added as Ce(III) (10^{-4} M $CeCl_3$). It was labelled with a radioactive tracer (^{141}Ce) to make it possible to measure very small concentrations. From precipitation experiments, we could detect no uptake of Ce, within analytical uncertainty (~1%), for at least 48 hours when $GR_{Na,SO4}$ was the only detectable phase. With decreased Fe(II)/Fe(III) in the solutions, Fe-(oxyhydr)oxides formed in addition to $GR_{Na,SO4}$. Goethite and magnetite effectively scavenged Ce(III) and X-ray photoelectron spectroscopy showed Ce was adsorbed. During formation of $GR_{Na,SO4}$ by air addition, Ce(III) was oxidised to Ce(IV) and removed from solution. Dissolved Ce oxidised without $GR_{Na,SO4}$ but removal rate increased when $GR_{Na,SO4}$ was present, suggesting that it catalyses the reaction.

Considering the behaviour of Ce(III) as an analogue for trivalent actinides, these results show that the extent of An(III) adsorption to green rust would be rather low, but in an oxidising environment, $GR_{Na,SO4}$ can first affect oxidation rates (as shown with Ce), then the Fe(III) phases resulting from its oxidation can contribute even more to the removal of radionuclides.

Lead isotopes in groundwater as indicator of water-rock interaction (Masheshwaram catchment, Andhra Pradesh, India)

PH. NÉGREL[1], R. MILLOT[1], S. ROY[1], C. GUERROT[1]
AND H. PAUWELS[2]

[1]BRGM, Metrology Monitoring Analysis Department, Orléans, France (p.negrel@brgm.fr, r.millot@brgm.fr, s.roy@brgm.fr, c.guerrot@brgm.fr)
[2]BRGM, Water Department, Orléans, France (h.pauwels@brgm.fr)

The present study deals with chemical weathering in a small (50 km^2) endoreic granitic watershed in India (Masheshwaram, Andhra Pradesh). Its main focus is on granitic parent rock composition, water chemistry and isotope tracing, through the determination of lead isotopes in groundwater by MC-ICPMS Neptune using an improved new procedure.

In the framework of this project, more than 60 samples were collected and analysed for lead content and Pb-isotopes. The aim of this study is to determine the lead isotopic signature in groundwater from a granite matrix. This will help i) to trace and fingerprint the processes of water-rock interaction in a semi-arid context, and ii) to incorporate isotopic- and chemical-tracing data and constraints into methods for evaluating groundwater circulation.

Lead concentrations span over one or two orders of magnitude (0.1 to 22.2 $\mu g. L^{-1}$), Pb-isotopes fluctuate largely as exemplified by the $^{206}Pb/^{204}Pb$ ratio (17.01 to 25.35). Lead in the groundwaters is mainly from natural origin and using the Pb-isotopes, we traced and fingerprinted the processes of water-rock interaction using the separate minerals. We defined the role of accessory phases in the control of the Pb-isotopes ratios through a weathering model and evidenced the role of the main mineral from the granite in a second step of weathering.

We evidenced large variations in lead contents and Pb-isotopes ratios with depth. Such stratification being never reported for isotopic ratios of heavy metals that can be used for the identification of flowpaths and mixing process.