 ROBL-CRG	Experiment title: Competitive sorption investigations of Am(III) and Y(III) sorption on corundum	Experiment number: 20-01-769
Beamline: BM 20	Date of experiment: from: 26.02.2016 to: 01.03.2016	Date of report: July 2017
Shifts: 12	Local contact(s): André Rossberg	<i>Received at ROBL:</i>
Names and affiliations of applicants (* indicates experimentalists): Sinikka Virtanen Laboratory of Radiochemistry University of Helsinki, Finland Nina Huittinen Institute of Resource Ecology Helmholtz-Zentrum Dresden-Rossendorf		

Report:

In this study, we have investigated the potential competitive influence of Y^{3+} on the uptake of trivalent lanthanides and actinides on corundum in combined batch sorption (Eu^{3+}), TRLFS (Cm^{3+}), and EXAFS (Am^{3+}) investigations.

The batch sorption experiments show that the uptake of Eu^{3+} on the mineral surface decreases with increasing Y^{3+} concentration, pointing toward competition between the trivalent elements. The same results are obtained in TRLFS investigations where Cm^{3+} remains in solution at much higher pH values in the presence of Y^{3+} than in the absence of it. In addition, the speciation of the actinide changes in the alkaline region when Y^{3+} is present, as deduced from the pronounced red-shift of the luminescence emission spectra. In order to explain the speciation change observed in the laser spectroscopic investigations, EXAFS studies were conducted for Am^{3+} in the presence and absence of Y^{3+} . By varying the Am and Y concentrations in the corundum samples a total metal ion

concentration between 6×10^{-6} M and 2.2×10^{-4} M was achieved. The fitted EXAFS data clearly show that the overall coordination number of Am^{3+} decreases from approximately 9 to 8 with increasing metal ion loading, leading to a contraction of the Am-O distance (Fig. 1, top). For the Am-Al scattering shell the CN is seen to decrease from approximately 3 to 2, while the distance to the surface gets slightly longer (Fig. 1, bottom).

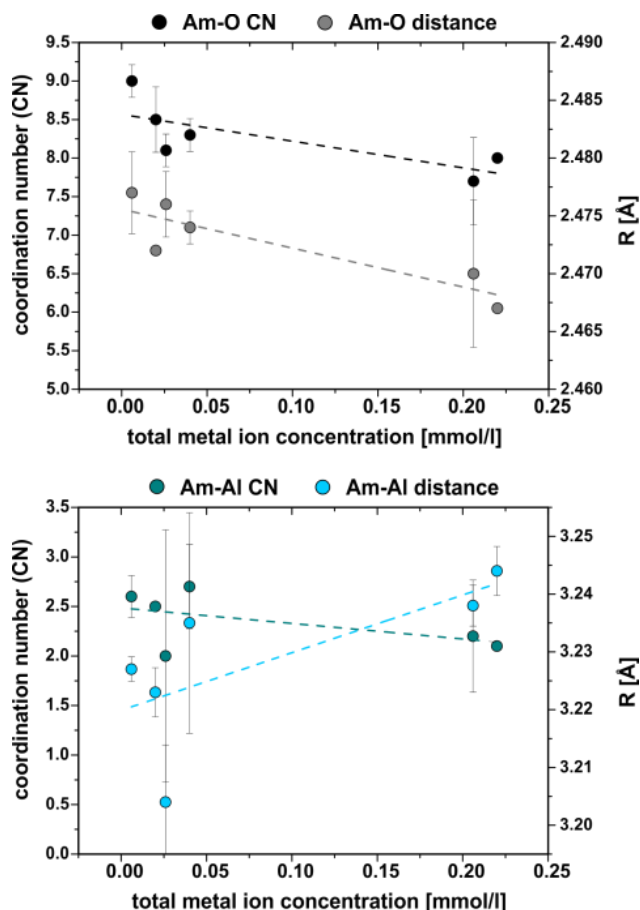


Fig. 1: Obtained coordination numbers (CN) and distances (R) for Am-O (top) and Am-Al (bottom) scattering shells in the EXAFS investigations on Am^{3+} uptake by corundum in the presence and absence of Y^{3+} .

Based on the changes in the CNs and recorded luminescence lifetimes in the Cm^{3+} TRLFS investigations, the attachment of the actinides on the corundum surface could be assigned. The luminescence lifetimes indicate the presence of 5 H_2O molecules in the first coordination sphere of the actinide ion over the whole investigated pH- and metal-ion concentration range. Thus, for an overall coordination number of 9 at lower metal ion loadings, tetradentate coordination to the surface must occur on a site connected to three aluminum atoms. With increasing metal ion concentration the overall CN decreases to 8, implying that a complex with tridentate coordination to the surface

becomes prevailing.

Our results have clearly shown that the presence of cations with similar chemistries will influence the uptake properties of one another on solid surfaces. In addition, a speciation change may be accompanied by the presence of competing ions on the mineral surface if the overall concentration is high enough.