

Stainless steel corrosion and actinide uptake by corrosion products under anoxic and high saline conditions

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INTRODUCTION

Many countries consider the disposal of high-level nuclear waste (HLW) in a deep geological repository (DGR) as a prime solution for the safe management of this waste. Containers containing vitrified HLW are typically made of stainless steel, which is known to be prone to localized corrosion. For this reason, these containers are usually proposed to be emplaced in thick walled overpacks that should corrode first before the porewater can reach the inner stainless steel container.

Depending on the country, the HLW repository could be hosted in salt rock. In the unexpected case of solution access to the emplacement caverns during the long-term evolution of the repository, metallic containers will be exposed to highly saline brines. The nature of the formed corrosion products depends on the composition of the steel and of the solution. Dedicated experiments under conditions expected to be representative of HLW disposal in salt rock with relevant canister materials are thus required in order to identify the nature of the corrosion products.

The contact of the porewater with the waste matrix following canister failure will result in the mobilization of radionuclides (RNs), such as the long-lived and radiotoxic actinides. It may be anticipated that reducing conditions will prevail in the repository near-field as a consequence of e.g., hydrogen evolution during metallic corrosion. Under these conditions, actinides can be expected to occur in lower oxidation states, *i.e.*, Am(III), Pu(III), Pu(IV) [1]. Fortunately, secondary phases formed during metallic corrosion can act as a sink and represent the first barrier able to retain these RNs in the repository near-field.

Within this work, the corrosion of the inner stainless steel container material under anoxic, highly saline and elevated temperature conditions was investigated with emphasis on the forming corrosion phases. In the second part, the uptake of trivalent actinide ions under anoxic and highly saline conditions by secondary phases identified in corrosion experiments was investigated.

DESCRIPTION OF THE WORK

Corrosion experiments were performed in closed vessels under anoxic and highly saline conditions at 90°C [2]. Polished stainless steel coupons were suspended in 5 mol/L

NaCl or 3.4 mol/L MgCl₂ at their natural pH. At the end of the experiments (up to 294 days), vessels were cooled down to room temperature, pH and E_h were measured *in situ* and the ultracentrifuged contacting brines were analyzed by (HR-)ICP-MS. A combination of microscopic and spectroscopic techniques was applied to analyze the corroded coupons and to identify the nature of the formed corrosion products.

Uptake experiments were performed with Eu(III) or Am(III) and well-characterized corrosion products (Fe₃O₄, NiFe₂O₄, Cr₂O₃) under anoxic, high saline and room temperature conditions [3,4]. Distribution coefficients (K_D in L/kg) were obtained from batch sorption experiments, and complexation constants were obtained from fits to the experimental data using available structural information. Corrections due to high salt contents are described in [3].

RESULTS

In all corrosion experiments, pH_m and E_h hardly changed with the exposure time and the nature of the salt had no significant effect [2]. The overall corrosion rates were low and the amounts of dissolved metal ions remained low, in agreement with the formation of only sparingly soluble corrosion products. Surface analytics revealed the formation of a passivation layer mostly made of Cr(III) (hydr)oxides. Under the applied geochemical conditions, no localized surface attack could be detected.

The coupon corroded in concentrated NaCl solution was embedded in resin and cross-cut for further analyses using synchrotron-based techniques (X-Ray Fluorescence XRF), X-Ray Diffraction (XRD), X-ray Absorption Near-Edge Structure (XANES)) with a small beam footprint (μXRF, μXRD, μXANES). Element distribution maps revealed the presence of a very thin (<1 μm) layer of corrosion products, with regions enriched either in Cr or in Fe and Ni. X-ray diffractograms identified the presence of spinel type compounds (Fe₃O₄, NiFe₂O₄) and Cr₂O₃. These findings were corroborated by recording μXANES at the Cr, Fe and Ni K-edges. The presence of further compounds such as layered double hydroxides as well as NiO and Ni(OH)₂ was also evidenced. Overall, results point at the formation of a corrosion layer having a duplex structure, with an inner-layer mostly of chromium (hydr)oxides and an outer-layer made of Fe- and Ni-based spinel compounds admixed with nickel (hydr)oxides.

In batch sorption experiments ($m/V = 0.5$ g/L, exposed surface area 6.55 m²/L), Eu(III) showed a high affinity for magnetite at $pH_m > 6.4$ with > 99 % sorption ($\log K_D > 4.9$) and no ionic strength effect up to 6.6 m NaCl at $[Eu(III)] = 6 \times 10^{-10}$ m [3]. Lower $\log K_D$ values and a small ionic strength were observed at $[Eu(III)] = 1.2 \times 10^{-5}$ m for the same m/V . X-ray absorption spectroscopy at the Am L₃-edge confirmed the insignificant effect of ionic strength on the pH_m dependent sorption to magnetite. Using results from potentiometric titration of the solid phase, from batch sorption experiments and from spectroscopic measurements, a charge distribution multi-site triple layer surface complexation model was developed to account for all experimental findings, including a surface coordination of the metal ion via a tridentate binding mode [3].

Uptake experiments ($m/V = 0.08$ g/L, exposed surface area 6.60 m²/L) further showed that at $pH_m > 6.1$ the Eu(III) affinity for NiFe₂O₄ ($\log K_D > 4.7$) is comparable to that for Fe₃O₄, with no significant effect of ionic strength either, at $[Eu(III)] = 6 \times 10^{-10}$ m [4]. Solid phase titration suggests that the point of zero charge for NiFe₂O₄ is slightly higher (8.3) compared to Fe₃O₄ (6.4). Overall, sorption data may suggest that the exposed octahedral Ni(II) has higher affinity for Eu(III) than octahedral Fe(II). At the macroscopic scale the higher affinity of Ni(II) compared to Fe(II) is compensated by a higher point of zero charge for NiFe₂O₄, resulting in comparable Eu(III) uptake behavior for Fe₃O₄ and NiFe₂O₄.

For an exposed surface area comparable to that of Fe₃O₄ and NiFe₂O₄ (6.55 m²/L), the Eu(III) uptake by Cr₂O₃ is comparable to that for both spinel compounds at $[Eu(III)] = 6 \times 10^{-10}$ m, reaching $\log K_D > 4.2$ at $pH_m > 6.3$ [4]. Even for this substrate only a minor ionic strength effect was observed under given chemical conditions. When the exposed surface area was reduced to ~ 1.15 m²/L, the Eu(III) uptake showed a typical pH_m dependence, reaching > 98 % sorption at $pH_m > 7.0$, without significant effect of the ionic strength.

For NiFe₂O₄ and Cr₂O₃ no accurate surface complexation model could be developed due to the absence of structural information. However, batch sorption data showed a high Eu(III) affinity for all investigated mineral surfaces and at all investigated ionic strengths. It may thus be concluded that the formation of these identified corrosion products represents an efficient sink for trivalent actinides in the near-field of a repository hosted in salt rock.

REFERENCES

1. Schramke J.A. et al., Plutonium oxidation states in the Waste Isolation Pilot Plant repository. *Applied Geochem.* 116, 104561 (2020).
2. Finck N. et al., Corrosion of austenitic stainless steel at 90°C under highly saline and anoxic conditions: A

microspectroscopic study. *Corrosion Sci.*, submitted manuscript.

3. Morelovà N. et al., Sorption of americium / europium onto magnetite under saline conditions: Batch experiments, surface complexation modelling and X-ray absorption spectroscopy study. *J. Colloids Interface Sci.*, **561**, 708-718 (2020).

4. Finck N., Corrosion and sorption processes at steel surfaces at elevated temperature and pressures under anaerobic saline conditions. Project final report, part B, KIT-INE. INE Scientific Working Documents 3, KIT, Germany, 2021. DOI: 10.5445/IR/1000130282. URL: <http://www.ine.kit.edu/53.php>

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