

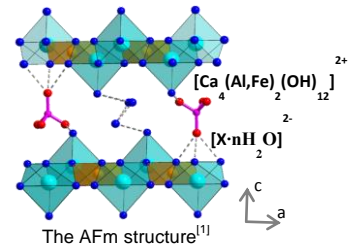
Iodine uptake by AFm phases

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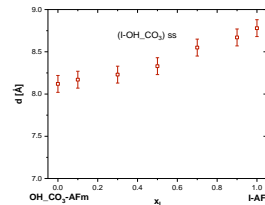
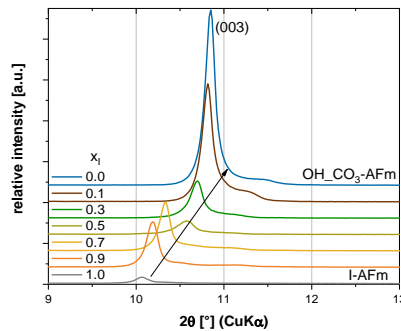
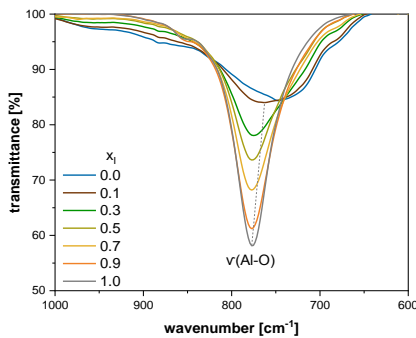
Introduction

Under the alkaline and reducing conditions expected in cement-based low and intermediate level radioactive waste (L/ILW) repositories the thermodynamically stable aqueous species of the dose-determining radionuclide iodine-129 is iodide (I⁻). A good candidate for the immobilization of the hazardous I⁻ anions are AFm phases due to their interlayer anion exchange capacity. The ability of AFm phases to bind I⁻ was investigated in two sets of experiments: (1) solid solution experiments between the iodine AFm end member (I-AFm) and the common AFm phases hemicarbonate (OH₂CO₃-AFm), monocarbonate (CO₃-AFm) and hydroxy-AFm (OH-AFm); (2) I⁻ sorption experiments on OH₂CO₃-AFm, monosulfate (SO₄-AFm) and sulfide-AFm (HS-AFm).



Results

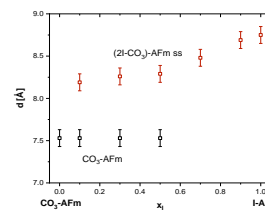
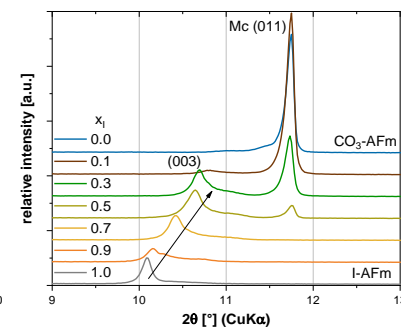
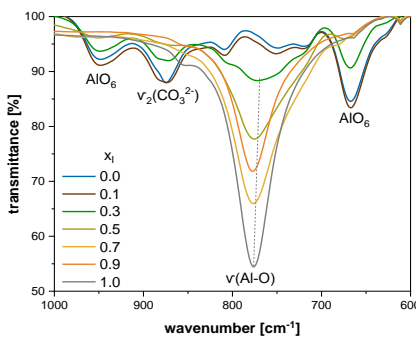
Solid solution formation. Continuous solid solution vs. incomplete solid solution with miscibility gap: FTIR and XRD analyses showing the evolution of the Al-O absorption band and the interlayer distance in the (I-OH₂CO₃)-AFm and the (I-CO₃)-AFm solid solution series with changing total iodide mole fraction ($x_I = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1.0).



(I-OH₂CO₃)-AFm solid solution series

FTIR spectra (left): Al-O absorption band is gradually weakened and shifts from ~775 cm⁻¹ ($x_I = 1.0$) to ~745 cm⁻¹ ($x_I = 0.0$) as Al environment changes

XRD (right): Gradual peak shift of the basal reflexion and the interlayer distance towards lower d-values with progressive substitution of iodide (x_I) in the interlayer
=> continuous solid solution



(I-CO₃)-AFm solid solution series

FTIR spectra (left): additional absorption bands appear at composition $x_I = 0.5$ indicating the presence of a second phase

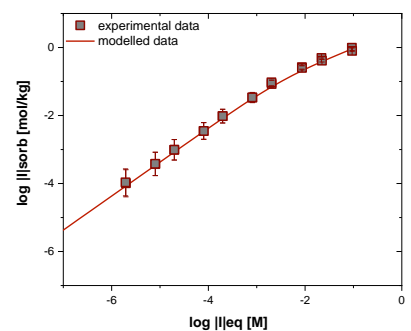
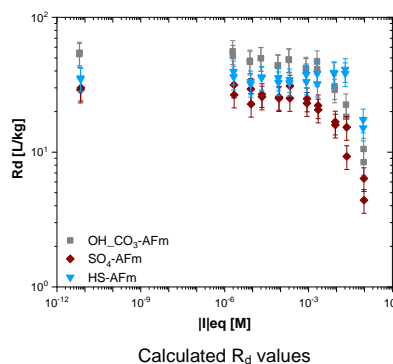
XRD (right): at compositions $0.5 \leq CO_3/(2I+CO_3)$ two phases coexist – a mixed (I-CO₃)-AFm phase and CO₃-AFm, marking the limits of the solid solution
=> incomplete solid solution with miscibility gap

Sorption experiments. The partitioning of the radionuclide ¹²⁵I between solid and liquid phase measured and expressed in terms of the distribution coefficient R_d [L·kg⁻¹]

- Mean calculated R_d values at low loadings:
OH₂CO₃-AFm: 48 ± 10 L·kg⁻¹
SO₄-AFm: 27 ± 5 L·kg⁻¹
HS-AFm: 35 ± 7 L·kg⁻¹

Sorption isotherms modelled with the thermodynamic modelling program GEMS^[2]

- Use of solubility products (log K) for the AFm end members determined in the solid solution experiments



I⁻ sorption isotherm on OH₂CO₃-AFm: experimental data and modelled with GEMS^[2]

Conclusions

- Intercalation of I⁻ in the AFm interlayer where anion exchange leads to the formation of solid solutions
- Solid solution formation favored by end members with similar crystal symmetry

- Sorption of I⁻ is dependent on the type of the interlayer anion: stronger sorption by AFm phases with a singly charged anion in the interlayer (HS-AFm) than by AFm with divalent ions (SO₄-AFm)