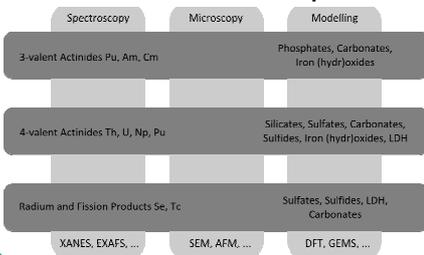


Incorporation and stability of Se doted iron minerals

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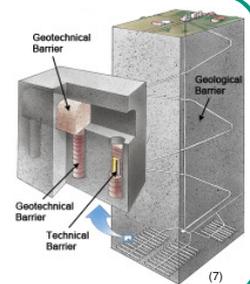
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The ImmoRad concept



The radionuclide ^{79}Se plays an important role for disposal sites of high-level nuclear waste (HLW). Due to its long lifetime and high mobility, the behavior of selenium to migrate into the biosphere is of great interest. In aqueous solutions the geochemical properties of Se strongly depends on its speciation. Under oxidizing conditions, Se exists as selenate (Se^{6+}) or selenite (Se^{4+}), which have a high mobility. In contrast, under reducing conditions, Se is sparingly soluble as elemental selenium (Se^0) and selenide (Se^{2-}).

The BMBF project "ImmoRad" focuses on the interaction of long-lived radionuclides with minerals that occur in the host rock or barrier materials of deep geological HLW-disposal sites. The subproject at the IMG examines the interaction of Se with synthesized iron sulfide and iron oxide phases with regard to the behavior of the radionuclide ^{79}Se . This research will be divided into two PhD theses.

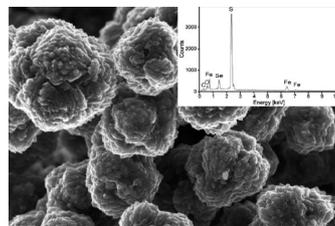


Work package 1:

Se interaction with iron sulfides

State of the art

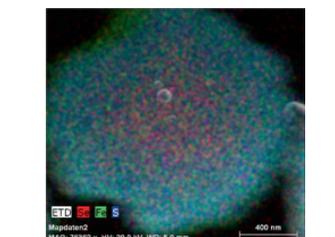
- Se is incorporated in high concentrations in many sulfides^(2,3,4,5)
 - Pyrite is the most widespread sulfide in the Earth's crust⁽⁶⁾ with up to 5 wt.% in HLW-concerning geological formations⁽⁷⁾
 - Natural pyrite can incorporate Se between 8 and 760 ppm⁽⁸⁾
- Experimental studies document structural incorporation of selenium into synthesized pyrite:



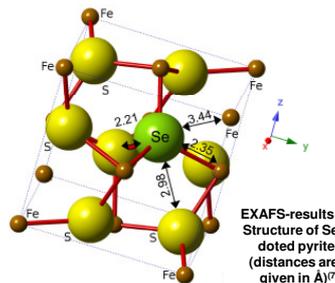
SEM image of selenide-doted pyrite and its EDX spectra, spheroidal particles⁽⁹⁾

- Structural incorporation during fast precipitation in batch experiments (argon atmosphere, aqueous Se concentrations 10^{-3} – 10^{-6} mol/l, pH 3.5–7, Eh -200–100 mV)⁽⁹⁾:

- XRD and SEM showed, that the Se^{2-} uptake was up to 98.6 %.
- FIB and ED-XRF demonstrated an inhomogeneous Se distribution with a high accumulation in the center of the pyrite grains.
- Also the XAFS investigations indicated using initially dissolved Se^{2-} , that S was substituted by Se and led to a slightly distorted pyrite structure.
- Coating experiments on grounded natural pyrite to simulate pyrite crystal growth in a mixed-flow reactor (MFR) (continuous mixing of three separate solutions of Fe, S and Se)⁽¹⁰⁾:
- XRD and SEM showed, that the Se^{2-} uptake was up to 99.5 %.
- XAFS investigations showed an incorporation of Se^0 without further lattice bonding by changing the valence state of initial Se^{2-} or Se^{4+} .



EDX/FIB: Mapping of the Se content within a pyrite. High Se concentration in the center of the grain.⁽⁹⁾



Research goals of the PhD

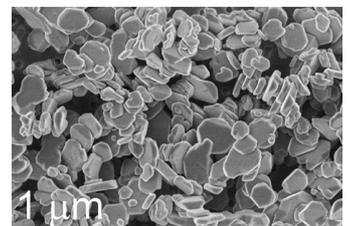
- Investigations of stability under oxidized conditions and at different pH-conditions on synthesized Se doted pyrite
- Thermodynamic modeling of stability of synthesized Se doted pyrite
- Comparison of synthesized and natural pyrites with synthesized Se doted pyrite

Work package 2:

Se interaction with iron oxides

State of the art

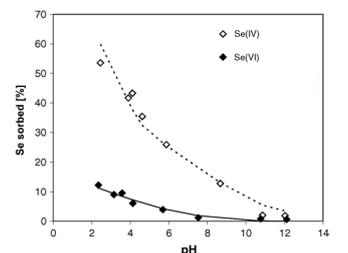
Iron oxides are ubiquitous in nature and are furthermore corrosion products of zerovalent iron⁽¹²⁾. Therefore, they are most likely produced in the near-field of nuclear waste repository during the corrosion of steel canisters⁽¹³⁾. Because of their surface hydroxyl groups, iron oxides in contact with aqueous solutions are able to remove charged dissolved species such as selenate or selenite.



SEM image of plate-like hematite particles⁽¹¹⁾

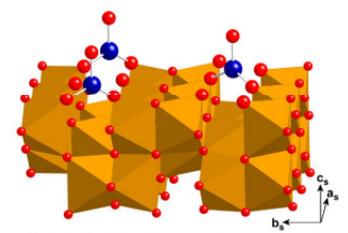
Previous sorption studies of Se oxyanions on iron oxide minerals have shown that:

- Large amounts of Se can be removed from solution⁽¹⁴⁾
- The sorption mechanism of Se can mainly be attributed to adsorption processes (inner- and outer-sphere complexes)⁽¹⁵⁾
- Ferrous-bearing minerals can cause a Se reduction and precipitation^(16,17,18)
- Sorption behavior of Se is affected by several parameters, including pH-value, redox potential and ionic strength of the solution, the concentration and speciation of Se as well as the nature, structure and morphology of the iron oxide minerals^(12,14,15,19,20)



Sorption of selenate resp. selenite (2×10^{-5} M Se) on 0,1 g magnetite as a function of pH⁽²¹⁾

For this reason, the immobilization of Se by sorption processes depends on the stability of the sorption mechanisms against leaching processes as well as on the thermodynamic stability of the iron oxides. However, little is known about a possible incorporation of Se within the crystal structure of iron oxides or about the sorption behavior during the formation and growth of iron oxide minerals.



Model of Se(IV) surface complexes on hematite (Selenite complex shown as planar complex)⁽²²⁾

Research goals of the PhD

- Quantitative investigation of Se sorption and characterization of the mechanisms
- Thermodynamic modeling and experimental investigation of the influence of Se sorption by various hydrochemical parameters

Analytical methods

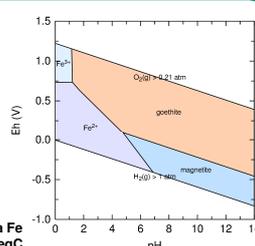
Mineral synthesis and Se sorption/incorporation

- Mineral phases: XRD
- Microscopic analyses: SEM/EDX, TEM/EDX
- Chemical composition & distribution: ED-XRF, FIB/EDX
- Valence state & binding structure: XPS, XANES, EXAFS
- Solution analyses: HR-ICP-MS, ICP-OES
- Specific surface area analyses: BET

Thermodynamic modeling

- PhreeQC
- GEMS

Pourbaix diagram for a Fe solution modeled with PhreeQC



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