Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.19818

REDUCTIVE IMMOBILIZATION OF ^{99}Tc(VII) BY PYRITE AND MARCASITE

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^{99}Tc is a fission product with a long half-life of 2.14×10^5 years. Its migration and bioavailability strongly depend on its oxidation state and speciation in aqueous solution. Under oxidizing conditions, Tc mainly exists as pertechnetate, $Tc^{VII}O_4^-$, a highly water-soluble anion with negligible sorption to most minerals. Under reducing conditions, Tc^{IV} prevails, whose main species, $TcO_2\ xH_2O$, is a polymer of low solubility. As the presence of reductants like Fe^{2+} in the near-field of a nuclear waste repository is expected due to canister corrosion, several studies consider $^{99}Tc^{VII}$ reductive immobilization by minerals containing reductant moieties, such as magnetite ($Fe^{II}Fe_2^{III}O_4$) or mackinawite (FeS) [1]

Pyrite (cubic FeS_2) is a redox sensitive sulfide mineral that has been identified as a good sorbent for Tc^{VII} from soil and groundwater [2]. Under repository conditions, both pyrite and marcasite (orthorhombic FeS_2) are expected to form by corrosion processes and microbial interaction [3]. Moreover, both iron sulfides are also accessory minerals in granitic and argillaceous rocks. Therefore, reliable data on $^{99}Tc^{VII}$ retention by both minerals and their mixtures is relevant for the safe disposal of nuclear waste.

We have studied the Tc retention by pure pyrite and by a mixture of marcasite and pyrite (60:40) at pH 6 and pH 10 using a combination of batch experiments and spectroscopy (Raman microscopy, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy). [4, 5]. We confirm the $^{99}Tc^{VII}$ reduction and subsequent $^{99}Tc^{IV}$ retention on the mineral surfaces and shed new light on different retention mechanisms for pyrite and marcasite at pH 10.

We acknowledge funding from the German Federal Ministry of Economic Affairs and Energy (BMWi) for VESPA II project (02E11607B) and from the German Federal Ministry of Education and Research (BMBF) for the NukSiFutur TecRad young investigator group (02NUK072).

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