
Redox Chemistry of UO_2 under Repository Relevant Conditions in the Presence of Zircaloy and Waste Canister

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ABSTRACT:

This project aims to gain a fundamental understanding of how the redox chemistry of UO_2 in contact with cladding and waste container material determines the matrix corrosion of spent nuclear fuel (SNF) in a deep geological repository (DGR). Currently, there is no clear understanding which processes control the redox state in the waste package in case of technical barrier failure. By providing a macroscopic and microscopic understanding of UO_2 redox chemistry in a DGR the proposed project will advance the current state of the art for waste isolation in a generic deep geological environment and thus support the DOE mission of investigating and evaluating the safety of a DGR. In case of a technical barrier failure in a DGR, the waste form and the waste container would interact with the groundwater. In the presence of groundwater, this complex system consisting of the waste form, i.e. SNF, the cladding and canister material will not be in equilibrium. Material degradation due to corrosion will take place. As a result, solid corrosion phases will form and deposit at the surfaces of SNF, and at the cladding and waste container interfaces. This newly formed assembly of solid phases will supply the system with a set of competing redox pairs (e.g., $\text{UO}_2/\text{U}_3\text{O}_8$, $\text{Fe}/\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$). The redox potential formed within the failed canister will depend on the buffer capacity of each of these pairs, and kinetic restrictions, which are still poorly understood. At the same time, this redox potential is a crucial parameter controlling aqueous mobility of uranium and many redox sensitive fission products, such as iodine and technetium. Thus, understanding of these redox state controls is required for the evaluation and mitigation of consequences of potential waste container failure.

Hydrothermal corrosion experiments (150 – 250 °C) of (1) zircaloy, (2) waste container material, and (3) UO_2 individually in deionized (DI) water and simulated groundwater will derive baseline data of evolving redox potentials and the solubility of engineered barriers. The presence of newly formed solid corrosion phases will supply the system with competing redox pairs. The advanced hydrothermal experiments with cladding, waste container material and UO_2 in direct contact with each other in DI and synthetic ground water at elevated temperatures and pressures will be followed by structural and microstructural analysis. Advanced microscopy via transmission electron microscopy and Raman spectroscopy will provide insights about the secondary phase formation processes at the interfaces. *The corrosion experiments and phase identification of the secondary phases formed, will close knowledge gaps by understanding redox state controls to provide data relevant to permanent SNF disposal for generic deep geological environments evaluation and mitigation of potential waste container failure consequences. The experimentally derived data about secondary phase formation will be utilized for phase relationship analysis to decipher the redox conditions.* Performance assessments of DGRs rely on correct input data for transport modeling of potential radionuclide release. The here derived redox relationships are required as input for reference cases, e.g. argillite reference case. Thus, we will contribute to closing knowledge gaps about the aqueous mobility of uranium as well as other redox sensitive fission products present in SNF which are highly dependent on the prevailing redox conditions and buffer capacities of the system.