

Effect of Anoxic Iron Corrosion Products on the Dissolution of MOX Fuel under Repository-Relevant Conditions

Saleh, M.^{1,4*}; Darwish, E.¹; Hedberg, M.¹; Tam, P.L.¹; Spahiu, K.^{1,3}; Ekberg, C.¹

(1) Nuclear Chemistry / Industrial Materials Recycling, Chalmers University of Technology, Gothenburg, Sweden

(2) Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg, Sweden

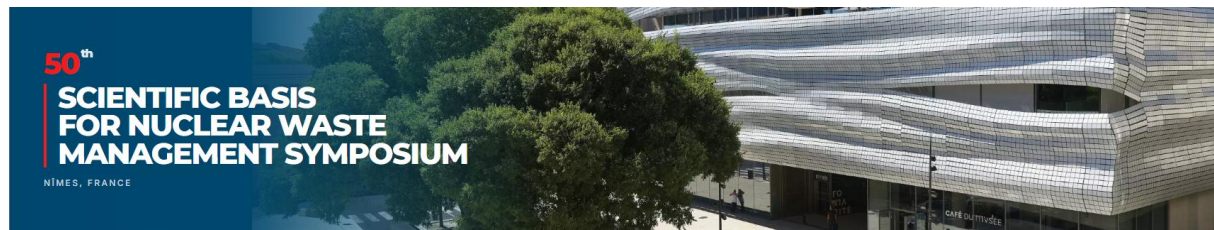
(3) Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden

(4) Studsvik Nuclear AB, Nyköping, Sweden

Abstract

Understanding the mechanisms that govern the stability of spent nuclear fuel under repository conditions is a key factor in evaluating the long-term safety of deep geological disposal systems. The dissolution of the $\text{UO}_2(\text{s})$ -based fuel matrix largely determines the potential release of radionuclides once the protective canister barrier is compromised. Although reducing groundwater environments, such as those anticipated in crystalline bedrock, are expected to maintain $\text{UO}_2(\text{s})$ in a thermodynamically stable state with very low solubility, the radiation field surrounding the fuel alters local redox conditions through water radiolysis. The interaction of α -radiation with water generates several reactive species, including oxidants such as H_2O_2 and O_2 , as well as reductants such as e-aq , $\text{H}^\cdot$, and H_2 . These species can significantly influence the redox chemistry at the fuel-water interface. In European deep geological repository concepts for spent nuclear fuel (SNF), massive copper canisters with cast iron inserts are designed to delay groundwater contact with the fuel.

In the event of a canister breach, fuel corrosion would occur under anoxic conditions at repository depth. Although reducing groundwater environments thermodynamically favour UO_2 stability, α radiolysis of water generates oxidizing species (e.g., H_2O_2) that can promote oxidative fuel dissolution. Concurrently, anoxic corrosion of iron produces Fe(II) and H_2 , which may buffer redox conditions and suppress radiolytic oxidation. While the mitigating role of actively corroding iron has been demonstrated, the long-term influence of iron corrosion products on fuel stability remains insufficiently understood. This study investigates the effect of two relevant anoxic iron corrosion products, magnetite (Fe_3O_4) and chukanovite ($\text{Fe}_2(\text{OH})_2\text{CO}_3$), on the dissolution behavior of unirradiated MOX fuel under repository-relevant conditions. Leaching experiments were conducted using MOX pellets containing 10 wt.% Pu (specific α -activity: 1.79 GBq g^{-1}) in simulated granitic groundwater representative of the Forsmark site (Sweden) under an argon atmosphere using an autoclave. The use of high- α -activity MOX provides a conservative assessment of radiolytic effects compared to aged spent fuel expected in a repository. The results show a pronounced inhibiting effect of chukanovite on MOX fuel dissolution, whereas magnetite did not significantly suppress radiolytic oxidation under the investigated conditions. The presence of chukanovite maintained elevated Fe(II) concentrations in solution, suggesting that aqueous Fe(II) plays a key role in reducing oxidizing radiolysis products and stabilizing U(IV) . In contrast, magnetite alone was insufficient to counteract α -radiolytic dissolution. These findings highlight the importance of specific Fe(II) -bearing corrosion products in buffering redox



conditions in the near-field of a geological repository. The results contribute to a better understanding of long-term fuel stability and radionuclide retention under anoxic repository conditions, supporting safety assessments of deep geological disposal systems.