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Radiolysis-Driven Redox Coupling Between Structural Fe in Bentonite and Dissolved Copper

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Many countries plan for high-level nuclear waste disposals using a groundwater-saturated, smectite-rich clay barrier, in direct contact with the metallic waste canisters. These clay barriers will therefore be unavoidably exposed to high doses of ionizing radiation. Because iron (mainly Fe(III)) is the only redox-active element in smectite-rich clay minerals, its redox behavior can potentially influence the redox state and mobility of other solutes, potential radionuclides, as well as impact corrosion rates of the metallic waste canisters, such as copper, as in the case of the Swedish KBS-3 concept for high-level nuclear waste disposal.

Previous γ-irradiation studies demonstrated substantial reduction of structural Fe(III) to Fe(II) in hydrated smectites [1–3] but did not resolve the reaction kinetics or the competition between oxidants and reductants generated by water radiolysis. Here, high-flux synchrotron X-rays are used to generate primary radicals *in situ* to quantify the time-resolved Fe redox kinetics using X-ray Absorption Spectroscopy. This approach directly probes electron transfer to and from structural Fe in smectite under controlled radiolytic conditions.

The study investigates radiation-induced reactions between structural Fe(II)/Fe(III) and Cu(I)/Cu(II) in copper-exchanged smectites and at the copper metal-smectite interface (**Figure 1**). This is achieved by a multimodal XRD–XAS approach at the Balder beamline (MAX IV), allowing monitoring of the structural evolution (XRD), local coordination and interatomic distances (EXAFS), and oxidation-state dynamics (XANES) as a function of radiation dose. Results reveal how radiolytically generated radicals mediate Fe–Cu redox coupling and shift redox equilibria within the clay barrier (**Figure 2**). Repository-relevant conditions were evaluated through complementary gamma-irradiation experiments conducted at representative total doses. These findings provide kinetic and mechanistic constraints on Fe–Cu interactions impacting the redox conditions at the clay buffer-waste canister interface in future deep geological repositories for nuclear waste.

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[3] D. Svensson and S. Hansen, *Clays Clay Miner*. 61, 566–579.

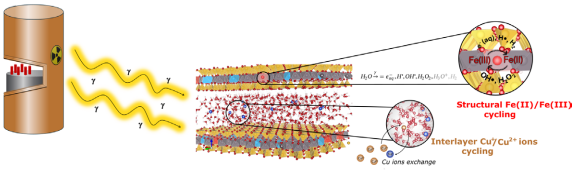

Figure 1: Schematic representation of structural Fe(II)/Fe(III) cycling with water radiolysis products and redox interactions with Cu solute

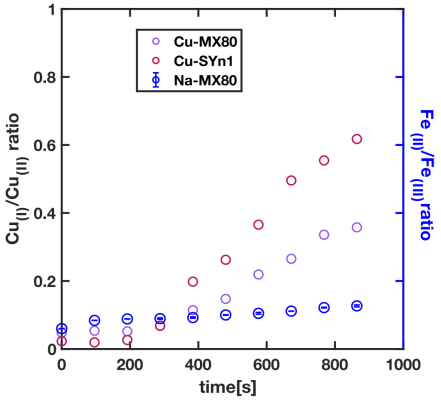

Figure 2: Cu(I)/Cu(II) ratios in excess of water for Cu-MX80 and Cu-SYn-1 (Fe-free smectite). Na-MX80 (blue cirlces) are the Fe(II)/Fe(III) ratios in the Cu-free sample, for comparison