

U(VI) sorption and nanoparticulate formation in secondary amorphous silica

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Spent nuclear fuel is dissolved in HNO₃ to reclaim reusable fission products. Historically, leaks to ground of this acidic (mol conc.) active liquor have occurred, and these leaks are expected to have altered subsurface geochemical and mineralogical properties that govern radionuclide mobility and fate. Understanding the processes occurring within leak zones is thus crucial when devising remediation strategies. Here we used batch experiments to assess acid-mineral interactions that mimic historical exposure of Sellafield sediment to acidity (0.01 - 10 M L⁻¹ HNO₃). The altered sediment was then used in sorption experiments to assess the impact of chemical weathering on the attenuation of U(VI).

Following a 2.5 mth reaction period, chlorite and easily reducible Fe-oxides were the only minerals to undergo complete dissolution when exposed to > 0.1 M L⁻¹ HNO₃. Sediment SEM and TEM also highlighted the presence of a secondary amorphous Si precipitate (Si_{am}) that likely formed by either: a) the non-stoichiometric dissolution of aluminosilicate surfaces leaving an amorphous Si framework, or b) an interfacial dissolution-precipitation mechanism that left hydrated silica layers on the primary mineral surfaces [1].

Despite the dissolution of key sorbing phases (Fe-oxides and chlorite), all reacted sediments were capable of sequestering U(VI) with a capacity equivalent to, or greater than, the unreacted sediment (at pH 5). TEM-EDX mapping showed U(VI) homogeneously distributed throughout Si_{am}, whilst HADDF-STEM images also highlight the presence of U(VI) hotspots/nanoparticles (2-3 nm) in the Si_{am}.

Overall our results show that HNO₃ induced mineral dissolution led to the formation of Si_{am}, which compensated for the loss of key U(VI) sorbing phases. We suggest that Si_{am} acted as: 1) a new sorption surface and, 2) a porous media that allowed U(VI) diffusion into pore spaces, creating a U(VI) supersaturated micro-environment, which led to the precipitation of a U-nanoparticle-like phase [2].

[1] Hellmann et al., (2003), *Phys Chem Miner* 30, 192-197.

[2] Singer et al., (2014), *Chem Geol* 390, 152-163.