Uranium incorporation into magnetite with varying Fe(II)/Fe(III) and U concentration

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The nuclear fuel cycle has left a significant legacy of contaminated land and radioactive waste. Many nations currently plan to dispose of their higher activity radioactive wastes within deep geological disposal facilities. However, it is predicted that over long timescales (1000's – 10,000's years), steel containers that encase the waste will undergo anaerobic corrosion, potentially leading to the release of radionuclides, including uranium. This process will result in the formation of a number of solid phases, including the iron oxide magnetite ($Fe^{II}Fe^{III}_2O_4$). Uranium is known to sorb to magnetite via various mechanisms, including surface mediated reduction to U(IV), and incorporation within the mineral structure. These sorption processes may significantly limit the migration of U within the repository system. Despite this importance, the mechanism(s) of U incorporation into magnetite, and the impact of U concentration and magnetite stoichiometry, are poorly understood.

In this study, magnetite was synthesised under anaerobic conditions via a direct precipitation process in the presence of U(VI). The concentration of U(VI) (0.3 - 3wt %) and the magnetite stoichiometry (Fe(II)/Fe(III) ratio, x = 0.5 - 0.8) were varied during the reaction. X-ray absorption spectroscopy (XAS) indicated that with increasing *Fe(II)/Fe(III) ratio(x),* an increasing fraction of U becomes directly incorporated into magnetite via substitution of octahedrally coordinated Fe. At x = 0.5, a mixture of incorporated U and $U(VI)_{(adsorbed)}$ is formed. With increasing x, a mixture of incorporated U and U(IV) is observed and with an increasing U(IV) contribution at x = 0.8. In addition, XANES data suggest the incorporated uranium is present as U(V). Dissolution experiments indicate that the majority of the U is strongly bound to the magnetite, supporting the findings from the XAS. These data suggest that U incorporation with magnetite may have an important impact on the mobility of U in an engineered geological disposal facility.