

Kinetics of Co-Mingled ⁹⁹Tc and Cr(VI) Removal From Nuclear Waste Streams Using Fe(OH)₂(s)

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During vitrification of nuclear waste containing technetium-99 (Tc) at the Hanford Site (WA, USA), a large fraction of Tc is expected to volatilize and be captured in a secondary (off – gas) waste stream. Remediation of Tc containing waste streams, before or after vitrification, has two major challenges: (i) reduction of Tc(VII) to less mobile Tc(IV) in the presence of co-mingled redox-sensitive chromium, Cr(VI), which is more readily reduced than Tc(VII); and (ii) immobilization of Tc in a stable phase that inhibits reoxidation and release. In an effort to overcome these challenges, the use of Fe(OH)₂(s) to simultaneously reduce Tc(VII) in the presence of Cr(VI), and immobilize Tc(IV) in Fe oxide/ oxyhydroxide minerals formed by Fe(OH)₂(s) oxidation has been successfully demonstrated. However, rate of Tc and Cr(VI) removal by Fe(OH)₂(s) depends on the composition of the nuclear waste stream, e.g. secondary constituents, pH, *E_h*. In this work, three simulated waste streams were studied to evaluate Tc/Cr(VI) removal kinetics over 24 hours: 1 M NaOH solution (control system), 5 M Na LAW (low activity waste) simulant, and off-gas simulant. Results from solution analysis of samples taken during the reaction, coupled with solid phase characterization, e.g. XAS and XRD, were used to identify trends in Tc and Cr(VI) removal rates and the resulting solid phase formed. Based on the results of this work, the majority of Tc and Cr(VI) reduction and removal occurs simultaneously within the first five minutes of simulant contact with Fe(OH)₂(s). However, the order in which Tc and Cr(VI) are completely removed from each simulant and the solid phases formed, e.g. magnetite and goethite, depends on the simulant chemistry. The implications of these trends on the treatment of nuclear waste streams will be discussed.