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A Review on Long-Term Stabilization Mechanisms of Tc/Re in Sorption and Immobilization Systems

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1. Introduction

As nuclear power generation is increasingly adopted as a low-carbon energy source, the generation of spent nuclear fuel becomes inevitable, leading to the production of technetium-99 (Tc-99). In aqueous environments, Tc-99 predominantly exists as the pertechnetate ($Tc(VII)O_4^-$), which exhibits high chemical stability and mobility, posing significant challenges for long-term safety in disposal systems. To mitigate its mobility, Tc-99 is commonly reduced to the $Tc(IV)O_2$, which is characterized by lower solubility. However, reduced Tc(IV) is susceptible to re-oxidation under oxidizing conditions, resulting in the recovery of high mobility.

Previous studies have reported that pristine zeolite Na-A exhibits high removal efficiency for perrhenate (ReO_4^-), particularly under alkaline conditions, without altering the oxidation state of rhenium (Re) [1]. Similarly, functionalized metal organic frameworks, such as PEI-modified MIL-101(Cr), have demonstrated high sorption capacities for ReO_4^- through electrostatic attraction and coordination with nitrogen-containing functional groups [2]. In both systems, spectroscopic analyses confirmed that Re remained in the +7-oxidation state after sorption, indicating that immobilization was primarily governed by surface complexation and electrostatic interactions rather than reductive precipitation. While these studies clearly demonstrated excellent short-term removal performance, systematic evaluations of long-term stability and remobilization behavior under varying geochemical conditions remain limited. In this study, short-term performance is defined as immobilization or sorption behavior evaluated within 7 days, corresponding to the typical duration of conventional batch sorption experiments, whereas assessments conducted beyond 7 days (up to approximately 100 days) are considered long-term evaluations. Deep geological disposal requires long-term safety under evolving conditions, and reduced Tc(IV) remains susceptible to re-oxidation. Therefore, short-term experiments alone are insufficient, and long-term stability assessments are essential for Tc immobilization strategies.

Therefore, ensuring the safe disposal of Tc requires not only effective short-term immobilization but also a thorough understanding of sorption mechanisms and systematic evaluation of long-term stability. As a result, we review previous studies that have conducted long-term stability assessments for Tc immobilization and aim to provide evaluation criteria for the stable disposal of Tc.

2. Reviews

2.1. Redox reaction [3]

A recent study proposed a combined bio mineral system employing the sulfate reducing bacterium Desulfovibrio vulgaris and pyrite (FeS_2) to stabilize highly mobile aqueous $Tc(VII)O_4^-$. The main mechanism of this system is a redox reaction that converts Tc(VII) to the less soluble and less mobile Tc(IV) species. The interaction between the microorganism and pyrite enhanced extracellular electron transfer, thereby significantly improving the rate and efficiency of Tc reduction. Notably, the reduction process was not limited to the formation of TcO_2. Sulfur associated species such as TcS_2 were suggested to form, which were interpreted to exhibit greater resistance to re-oxidation. Importantly, the study went beyond evaluating simple reduction efficiency by assessing the long-term stability of the reduced products. Repeated Tc(VII) injection experiments were conducted to verify sustained reduction capacity, and the reduced products were exposed to oxidizing conditions in air for 100 days to examine remobilization behavior. The results demonstrated that Tc re-oxidation and remobilization were significantly suppressed in the combined system, highlighting the critical role of redox-based immobilization mechanisms in achieving long-term stability.

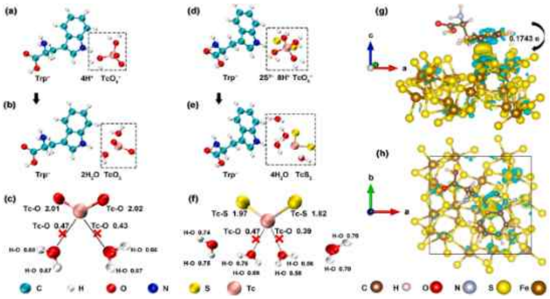

Fig. 1. Reduction of TcO_4^- by Trp^- and the role of pyrite. (a-b) Optimized structures showing TcO_4^- reduction to TcO_2 by Trp^-. (d-e) Optimized structures showing TcO_4^- reduction

to TcS_2 by Trp^- in the presence of sulfide. (c) and (f) Mayer bond order analysis supporting TcO_2 and TcS_2 formation, respectively. (g-h) Charge density difference showing electron transfer between Trp^- and FeS_2; Bader analysis indicates 0.1743 e^- transfer [3].

2.2. Precipitation [4]

This study evaluated the long-term immobilization of $Tc(VII)O_4^-$ in groundwater environments through reduction–precipitation mechanisms induced by slow-release electron-donating substrates. Under microbially reducing conditions, soluble Tc(VII) was converted to insoluble Tc(IV), and XANES and EXAFS analyses confirmed the formation of Tc(IV) oxide and sulfide precipitates, including hydrous TcO_2 and TcS_2. Sulfur-containing substrates promoted the formation of TcS_2 precipitates, whereas iron-containing substrates facilitated the precipitation of Tc(IV) as hydrous TcO_2 associated with Fe-bearing mineral phases. Long-term stability was assessed by exposing the reduced and precipitated samples to oxidizing conditions for approximately 120 days, followed by analysis of Tc remobilization and changes in oxidation state. The results demonstrated that Tc(IV) precipitates formed in the slow-release substrate systems exhibited significantly lower re-oxidation and remobilization compared to simple TcO_2 precipitates. These findings indicate that the chemical form of the precipitate and its association with mineral phases play a critical role in achieving long-term Tc immobilization.

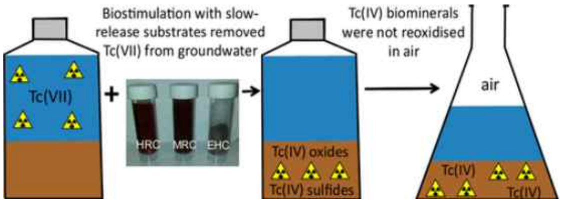

Fig. 2. Schematic illustration of long-term Tc immobilization via substrate induced reduction-precipitation pathways [4].

2.3. Structure incorporation [5]

A study employing chukanovite (Fe^{2+} hydroxy carbonate), a typical iron corrosion product, demonstrated that $Tc(VII)O_4^-$ can be reduced to Tc(IV) under anoxic conditions through Fe^{2+} mediated redox reactions. XANES and EXAFS analyses revealed that the immobilized Tc(IV) species exhibited pH-dependent stabilization mechanisms. At near-neutral to moderately alkaline conditions, TcO_2 dimers were bound to mineral surfaces via inner-sphere complexation, whereas at highly alkaline conditions, Tc(IV) became structurally incorporated into chukanovite-like phases. Importantly, long-term stability was evaluated by exposing the reduced and immobilized samples to oxidizing conditions in air for approximately 95 days, followed by analysis of Tc remobilization. The results showed minimal Tc release even after oxidative transformation of chukanovite into magnetite or goethite, indicating that structurally stabilized Tc(IV) species can remain largely resistant to re-oxidation. This study highlights that beyond simple reduction, structural incorporation of Tc plays a critical role in achieving long-term immobilization under oxidizing environments.

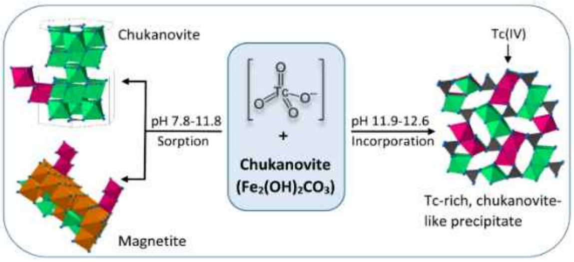

Fig. 3. Schematic illustration of Tc(IV) sorption and incorporation into chukanovite phases [5].

3. Conclusions

This review emphasizes that Tc immobilization strategies should not be limited short-term removal efficiency evaluations but must be accompanied by systematic assessments of long-term stability. Although previous studies have demonstrated decreased solubility through the reduction and precipitation of Tc(VII) to Tc(IV), such short-term performance evaluations do not sufficiently guarantee sustained stability under actual disposal conditions. The re-oxidation and remobilization behavior of Tc strongly depends on the chemical form of the precipitated species and their association with mineral phases. Therefore, future Tc disposal strategies should incorporate long-term stability evaluations under evolving redox conditions as an essential component. Furthermore, future studies should be conducted to evaluate Tc stability under conditions that realistically represent geological disposal environments. This includes long-term redox fluctuations, changes in groundwater chemistry such as pH, carbonate, and sulfide concentrations, and mineral transformation processes occurring over extended timescales. Such evaluations will be critical for accurately predicting Tc behavior and for developing reliable immobilization strategies for geological disposal systems.

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