Understanding the chemistry of low-valent technetium species relevant to their separation from Hanford tank waste

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The long half-life, complex chemical behaviour in tank waste, limited incorporation into glass waste form, and high mobility in subsurface environments make technetium-99 (Tc) one of the most difficult contaminants to dispose of and/or remediate. It is a major component of nuclear tank waste stored at the U.S. Department of Energy (DOE) site at Hanford, Washington, and is already present in the subsurface of Hanford from historic operations. Consequently, Tc is one of the largest risk contributors in the subsurface and deep vadose zone at Hanford. In solution Tc can have oxidation states ranging from +7 to +1, however it is most often observed as pertechnetate (TcO_4^-) (oxidation state VII) in strongly alkaline environments. In Hanford Tank waste, Tc exists predominately in the alkaline liquid supernatant and salt cake fractions, and therefore TcO_4^- is expected to be the dominant fraction. However, contrary to general expectations, our recent studies on Hanford tank waste as well as studies by other groups have demonstrated that a significant fraction of the soluble Tc in the waste supernatants occurs as low-valent Tc (oxidation state < +7).[1, 2] Most notably EXAFS observations have suggested the dominance of $Tc(CO)_3^+$ species in the presence of organic chelators, in addition to Tc(IV) and Tc(VI) which have also been observed. The objective of this work is to investigate aspects of the nature and chemistry of the non-TcO_4^- species derived from the $Tc(CO)_3^+$ coordination centre, specifically under the conditions typical for the alkaline liquid fraction of the tank waste and to gain better understanding and control over their redox behaviour. The observation of significant non-TcO_4^- species changes the paradigm of understanding of Tc thermodynamics, motivating systematic studies aimed at gaining a deeper insight into the mechanisms of the generation of these species *in-situ* as well as evaluating their *ex-situ* stabilities under ambient atmospheric conditions; these studies are key to designing new methods for effective Tc separation and remediation. In this regard, this presentation will also look at the possible mechanisms of formation/stabilization of low valent Tc species in the tank waste supernatants.

References:

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