

Technetium interaction with natural organic matter: complexation versus colloid/colloid association

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The redox-sensitive fission product technetium-99 (Tc) is of great interest in nuclear waste disposal studies because of its potential for contaminating the geosphere due to its very long half-life (2.13×10^5 year) and high mobility under oxidising conditions, where technetium forms pertechnetate (TcO_4^-). Under suitable reducing conditions, e.g. in the presence of an iron(II) containing solid phase which can act as an electron donor, the solubility can be limited by the reduction of pertechnetate followed by the formation of a surface precipitate.¹ However, by association with mobile humic substances (HS) or other associating/complexing species, the solubility of reduced Tc species may be drastically enhanced.²

Detailed multiple scattering analysis of EXAFS data of Tc(IV)/pyrogallol solutions based on DFT modeled reference structures has demonstrated the existence of a stable Tc-pyrogallol complex which is readily formed at pH 11 and remains stable towards technetium colloid or precipitate formation both as function of pH and time in the pH range between 11 and 4.³ The occurrence of stable, readily formed Tc-complexes with pyrogallol, a humic substance model compound, is a strong indication for the existence of similar complexes in natural systems containing dissolved organic matter. The formation of such complexes indicates an extra potential for migration of Tc(IV) in systems containing natural organic matter, in addition to the previously discovered Tc(IV) eigencolloids stabilized by dissolved HS through colloid-colloid interactions.²

The formation of stable Tc(IV)-NOM complexes was investigated as function of pH using dissolved Boom Clay organic matter. Pertechnetate was pre-reduced in supernatant solutions containing natural BC organic matter at different pH. After the pre-reduction and re-setting of the supernatant pH to pH 8.2, the predominant pH in the Boom Clay system, the supernatant solutions were contacted with the Boom Clay solid phases. Comparison of these systems with reference Boom Clay batch systems allows to evaluate the competition between the sorption of technetium on the BC solid phase and the formation of stable Tc(IV)-BC organic matter complexes and Tc(IV)-BC organic matter colloid/colloid associations.

¹Cui, D. Q. and T. E. Eriksen (1996). "Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material." *ES&T* 30(7): 2263-2269.

²Maes, A., K. Geraedts, C. Bruggeman, J. Vancluysen, A. Roßberg and H. Hennig (2004). "Evidence for the Formation of Technetium Colloids in Humic Substances by X-Ray Absorption Spectroscopy." *ES&T* 38(7): 2044-2051.

³Breynaert, E., Maes, A. (2007). Structure elucidation of Tc(IV) Pyrogallol Complexes. Migration Conference, Munich, Oral Presentation