Effect of natural humic substances on the dissolution and stability of reduced technetium and uranium

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Reductive precipitation and immobilization of soluble technetium (as pertechnetate, Tc (VII)O₄) and uranium (as uranyl, U (VI) O_2^{2+}) to sparingly soluble Tc (IV) and U (IV) species have been proposed as one of the promising remediation technologies to sequester uranium and technetium in situ in the subsurface. However, the dissolution and longterm stability of Tc (IV) and U (IV) are poorly understood, particularly in the presence of natural and synthetic organic ligands, which are known to cause the complexation and mobilization of certain metal ions and radionuclides. In this study, the kinetics of both ligand-promoted and oxidative dissolution of Tc (IV) and U (IV) are determined, and their mobility is evaluated in the presence of naturally occurring humic substances and synthetic ethylenediaminetetraacetate (EDTA). We found that EDTA and the humic acid are among the most effective in promoting the ligand-induced dissolution of Tc (IV) and U (IV) by complexation. However, EDTA is found to suppress the oxidative dissoltuion of Tc (IV) and U (IV), whereas the humic acid enhances the oxidative dissolution due to its redox reactive functional properties. Furthermore, the oxidative dissolution is found to be much quicker than the ligand-promoted dissolution by humic substances. Evaluation of the dissolution and stability of reduced U (IV) in a contaminated sediment column confirms that both the synthetic and natural organic ligands can cause the mobilization of U (IV) although the dissolution rate appears to be relatively slow. Our results suggest that the presence of both synthetic and natural organic ligands, as commonly observed at many comtaminated sites, can potentially impact the long-term stability and mobility of reduced Tc (IV) or U (IV).

Spectroscopic and DFT studies of pentachlorophenol reactions on Fe(III)-montmorillonite clay surfaces

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In situ FTIR methods and DFT cluster model calculations have been used to investigate the formation of octachlorodibenzodioxin (OCDD) from pentachlorophenol (PCP) on Fe (III) saturated smectite clay, which has been observed under environmentally relevant conditions [1]. The clay-facilitated single electron transfer from PCP to Fe (III) as the crucial step of the reaction pathway was proposed and examined by the combined techniques.



Figure 1: Comparison of calculated infrared spectra of PCP/Fe $(OH)(H_2O)_n^{2+}$ with experimental spectra. The calculated peak intensities and binding energies of PCP/Fe $(OH)(H_2O)_n^{2+}$ are linearly related to the number of coordination H_2O .

The formation of PCP radical cations on the clay surface as the reaction-initiating step is strongly supported by this combined spectroscopic and theoretical study. DFT calculations of PCP/Fe $(OH)(H_2O)_n^{2+}$ reproduce observed FTIR vibrational features, and demonstrate that they are a direct result of single electron transfer from PCP to Fe (III).

[1] Gu (2008) et al. Environ. Sci. & Technol. **42**(13), 4758–4763.