

## Theoretical calculations on the thermodynamics and kinetics of U(VI) homogeneous reduction by Fe(II)

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As uranium in the (VI) oxidation state is orders of magnitude more soluble than (IV), there is intense interest in promoting the (bio)reduction of uranium in remediation settings. Fe(II) is an environmentally ubiquitous reductant, however, inconsistencies have been experimentally reported on the thermodynamics and kinetics of U(VI) homogeneous reduction by Fe(II) [1,2].

Here, as a foundation for understanding its heterogeneous reduction behavior, we report on theoretical calculations of the thermodynamics and kinetics of the one electron reduction of monomeric U(VI) (hydrolysis) species by  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  in homogeneous solution. NWChem [3] was used to optimise the structures of the U and Fe monomers as well as inner- and outer-sphere complexes, pre- and post- electron transfer, by spin-unrestricted Kohn-Sham Density Functional Theory (DFT) and using the COSMO continuum solvation model. In addition to structure and free energy prediction, explicit calculation of the electronic coupling interaction was also performed, to estimate the electron transfer kinetics as defined by Marcus theory.

Calculations indicated that electron transfer via either an inner- or outer-sphere mechanism was only thermodynamically favourable for the second hydrolysis species  $\text{UO}_2(\text{OH})_2(\text{H}_2\text{O})_4^0$ . However, in both cases, electron transfer proceeded via a coupled electron-proton transfer mechanism – an immediate indication that electron transfer would be inhibitive slow. These results suggest that the homogeneous reduction of U(VI) by Fe(II) is either thermodynamically unfavourable or kinetically limited at environmentally relevant U and Fe concentrations at pH values < 7.

[1] Liger *et al.* (1999) *Geochim. Cosmochim. Acta* **63**, 2939-2955. [2] Du *et al.* (2011) *Environ. Sci. Technol.* **45**, 4718-4725. [3] Valiev *et al.* (2010) *Comput. Phys. Commun.* **181**, 1477.

## A generic approach to geochemical multi-surface modelling of the leaching of contaminated materials

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Geochemical modelling is increasingly being used in both scientific research and environmental risk assessment of contaminated materials. In this presentation an overview will be given of the development of a generic multi-surface geochemical modelling approach, to describe the speciation and solid/liquid partitioning (leaching) of major and trace elements in both soils and waste materials. The approach is based on the premise that the major reactive organic and mineral surfaces that are being considered, play a generic and determining role in the speciation and leaching of elements in these different materials.

The geochemical modelling approach is based on individual adsorption models for which generic binding parameters have been published for a wide range of elements. It currently includes reactions for aqueous speciation and mineral solubility, combined with sorption to organic matter (NICA-Donnan model), Fe/Al-(hydr)oxides (Generalized Two-Layer Model) and clay (Donnan model). As such, the model is fully based on published generic thermodynamic parameters for these different types of processes and used without any parameter fitting. Methods for the estimation of essential modelling parameters such as the potentially available/reactive fraction of elements of interest, and the type and amounts of reactive mineral and organic surfaces will be discussed. The performance of this modelling approach has been tested for a range of different elements and contaminated materials, particularly by comparing measurements and model predictions of the solid/liquid partitioning of elements over a wide pH range.

Examples will be presented of different model applications, illustrating similarities and differences in controlling processes and element speciation. These applications suggest very similar properties and contributions of the considered reactive mineral and organic surfaces in the speciation and leaching of elements among very different waste and soil materials. Finally, an outlook will be given on current work and ambitions to further develop and improve this modelling approach.