Partial-equilibrium concepts to model trace element uptake

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Uptake of trace elements into host minerals involves various mechanisms - from ion exchange and inner-sphere adsorption via surface entrapment or in-diffusion to structural incorporation upon precipitation or recrystallization. Even at long reaction time, their interplay may result in a metastable distribution of minor elements that deviates from complete aqueous- solid solution thermodynamic equilibrium. Uptake processes may proceed at widely different rates, e.g. fast (minutes to hours) for ion exchange and slow for re-crystallization (days to years), with important consequences for the reactive transport of contaminants. In this work, we explored how the rate-dependent uptake and metastability can be implemented in geochemical models using the partial equilibrium principle.

Thermodynamic models cannot be directly related to particular molecular mechanisms or their locations. Yet, some information can be retained in the model by introducing (i) multiple metastability constraints; (ii) mineral surface areas and site densities; and (iii) a set of 'layered', intrinsically metastable solid phases. In particular, the additional time-step-dependent metastability constraints [1] can be imposed on the amounts of solid solution end members. Because the specific free energy of the solid-aqueous interface is usually positive, solids with large specific surface area are metastable relative to coarse-crystalline counterparts. The surface free energy decreases due to adsorption, the extent of which is limited by the site density and the solid surface area. The limited adsorption can be modeled using the activity coefficient terms [2] or, more commonly, by adding the mass balances for surface- or permanent charge sites [3,4].

In usual aqueous - solid solution (AqSS) models, metastability constraints can only be set on bulk amounts of host and trace end members. In the new aqueous – layered solid (AqLS) model, 'seed' grains with defined specific surface, representing metastable cores of the solid, are enveloped by layers of the overgrown (or re-crystallized) solid solution phase. This 'overgrowth' part has its own metastability constraints linked to the surface area of 'seed' phase. The 'adsorption solution' phase can be linked to the surface area of either the 'layer' (in AqALS) or the 'seed' phase (AqAS).

These partial equilibrium concepts, combined with different models of uptake kinetics [5], have been implemented in the GEM-Selektor code (http://gems.web.psi.ch) and tested in simulations of uptake into carbonates, sulfates, and goethite. Major trends in the experimental data were reproduced well in all cases. A more detailed time-dependent distribution of trace elements in AqLS and AqALS models could be reconciled with the inferred uptake mechanisms.

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Application of iron nanoparticles for subsurface remediation: geochemical interaction and transfer

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Use of metallic nanoparticles in the groundwater treatment is a relatively new concept. Due to their small size nanoparticles exhibit both the critical necessities, a large surface area to volume ratio and ability to transport through finest porosity. Zero valent iron nano particles (nFe°) are perhaps the most used and kinetically efficient reactive material for in-situ groundwater treatment. Effective treatment ability of any reactive material does not depend only on maintaining reactive surface area and oxidation but also on the mobility through the finest pores within the sediment to be able to reach the targeted contaminants. Although there have been several studies recently, discussing the transport of nanoparticles in model porous media but the behaviour and interaction in real sediment is poorly understood. Geochemical interactions, non-uniform porosity and aggregation and oxidation of particles make it difficult to predict the effectiveness of treatment systems. We setup several bench scale flow through columns in laboratory to investigate the behaviour of the nFe° in subsurface transport. Several organic coatings were tested for surface modification to improve dispersion in aqueous media and mobility in sediment. Different porous media i.e. model sand, contaminated sediment and interaction with iron oxides were also tested for possible impact on mobility of nanoparticles. Oxidation kinetics of nanoparticles in aqueous medium was followed using different analytical tools like XAS, TEM and XRD analysis.

Our results show that the transfer of nanoparticles was largely affected by the geochemical interactions within the transfer medium. Transport of iron nanoparticles in model sand media was found to be largely different from the real sediment given the similar physico chemical parameters. We observed upto 95% transfer of nano particles in sandy porous media and upto 64 % in real sediment. The oxidation kinetics of nanoparticles after suitable surface coating in aqueous media was found to be relatively slow (~14 days), which allowed a relatively complete decontamination when tested against TCE contaminated groundwater in our experiments. Latest results will be presented.

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