

Reductive transformation of chlorinated hydrocarbons at iron minerals in the presence of organic sorbates

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Redox reactions at mineral surfaces play an important role in anoxic groundwater systems. Surface mediated transformation of natural and anthropogenic solutes were studied for various Fe(II)/Fe(III)hydroxide systems. Commonly, these studies investigated model systems devoid of organic matter. NOM may although affect the electron transfer processes as NOM may form complexes with iron both in aqueous solution and at the mineral surface. Thus, NOM sorption at iron hydroxides may compete with the formation of highly reactive Fe(II) surface sites. Otherwise, NOM is redox active and may enhance the electron-transfer across mineral surfaces.

In this study we therefore investigated the effect of redox *inert* (e.g. MOPS, HEPES) as well as redox *active* organic sorbates such as quinones and humic acids on the transformation of tetrachloromethane (CCl₄) at Fe(II)-goethite mineral surfaces. The addition of redox *inert* organic sorbates such as MOPS or HEPES resulted in a decrease (up to 3-fold) of CCl₄ degradation as well as in a 1.5-fold increase of aqueous ferrous iron. The decreased surface reactivity thus may be caused by competitive sorption of the organic sorbates, probably limiting the formation of highly reactive Fe(II) surface sites. In contrast, the presence of redox *active* quinones or humic acids led to a strong stimulation (up to 5-fold) of CCl₄ degradation at low DOC concentrations (10 mg DOC/L), while at higher levels (100 mg DOC/L) no stimulation was observed anymore in comparison to pure Fe(II)-goethite systems. These first results indicate that NOM – especially at environmentally relevant concentrations – might facilitate redox transformations of chlorinated hydrocarbons at mineral surfaces.

Pitzer parametrization constrained by density: application to natural and industrial systems

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Highly saline aqueous solutions are widely present in geological and industrial environments, particularly where water evaporation is strong. Among the various approaches that have been proposed in order to accurately describe the very complex chemistry of such systems, the Pitzer formalism can be successfully applied to determine aqueous solutions characteristics for high ionic strengths.

Determining a consistent set of Pitzer parameters is a difficult task, and available databases currently apply to rather limited chemical systems: developments have to be performed to extend their fields of application [1]. Estimation of Pitzer parameters requires to measure specific characteristics of aqueous solutions such as: activity of water (a_w), pH (for acid/base systems), osmotic coefficient (for completely dissociated electrolytes), aqueous speciation as an interpretation of Raman spectroscopy, mineral solubility, etc. However, depending on the system salinity, measurement of some of the above parameters can be problematic.

Therefore, the use of an additional characteristic for constraining the Pitzer parameter estimation procedure may be of interest. We propose here to use as a constraint the density of the aqueous solution, the measurement of which is rapid and easy. Each aqueous species of a solution contributes to the density according to its concentration and its partial molar volume. Density calculations can be performed in the framework of the Pitzer formalism [2].

Results obtained for specific volume calculations of complex electrolytic systems, up to a temperature of 100°C and for high salinities, demonstrate the relevance of newly established Pitzer parametrization.

[1] André *et al.* (2009) *GCA*, this vol. [2] Monnin (1994) *Chem. Geol.* **20**, 1435-1445.