

Abstract

The properties of the iron oxide/water interface are of utmost importance for the chemistry in natural aquatic environments as well as for processes related to the corrosion of metals. In these kinds of systems iron oxides are present as small particles precipitated on surfaces or suspended in solution. Inherent features of the iron oxide surface are for example the tendency to build up a surface charge and its capacity of sorbing various ionic species. These things and other related phenomena can be studied using the concept of surface complexation.

This thesis contains both experimental and theoretical surface complexation studies of the iron oxide/water interface. Colloidal particles of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$) have been prepared on lab scale and used as model substances in the experimental investigations. The charging properties of the suspended particles have been studied using potentiometric titration. In addition, the electroacoustic technique has been used to study the particles under the influence of a high frequency electric field. With this technique the so-called zeta-potential and the size of the suspended particles can be determined. Most of the experimental data were described satisfactorily using a 1-pK basic Stern surface complexation model. For the hematite particles in NaNO_3 solution it was necessary to account for ion pairing of electrolyte ions into the Stern plane.

Besides using existing surface complexation models a reformulation of the underlying theory has been performed using statistical mechanics. In this way a molecular description of surface complexation was obtained and with the new model it was possible to go one step beyond the equilibrium constants and the Gouy-Chapmann theory presently used in surface complexation. Included are descriptions of particle screening and specific binding of protons at surface sites. To account also for nonlinear electrostatic response a layer of condensed counterions was introduced. The new model was applied to titrated surface charge data of goethite at various background concentrations and a good agreement between the experimental data and the model was obtained. Both the size of the screening ions and the central particle size were shown to be of importance for the surface charge.

Because of its relevance in the nuclear power industry the sorption of cobalt(II) on hematite was also studied. Sorption data obtained from radioactive tracer measurements was combined with data from potentiometric titrations. This combination yielded valuable information on the pH dependence of both the amounts of cobalt sorbed on the surface and the number of protons released as a consequence of the sorption. The cobalt sorption was modelled with the 1-pK basic Stern model. By introducing a low concentration of high affinity surface sites for cobalt sorption it was possible to describe the sorption in very wide interval of cobalt concentrations, ranging from 10^{-8} M to 10^{-4} M. A simplified version of the model for cobalt sorption was used as a part of the interpretation of online radioactivity data from nuclear boiling water reactors.

Keywords: colloidal particles, potentiometric titration, surface charge, cobalt sorption, activity build-up, 1-pK basic Stern model, electrokinetics, electroacoustics, zeta-potential, site binding, statistical mechanics, corrected Debye-Hückel theory.