

Towards building a unified adsorption model for goethite based on variable crystal face contributions.

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Surface complexation models (SCMs) have been developed for at least 50 years to describe the interaction of mineral surfaces and other inorganic sorbents with ionic species in aqueous media through sorption processes. SCMs that depict the interfacial region using three electrostatic planes have been found to describe more comprehensively the adsorption behavior as a function of adsorbate concentration, pH and ionic strength. The reactive surface site density is an essential parameter in these models but has eluded accurate and independent determination. This has resulted in a lack of unified parameters for minerals of equal nature but different particle size. In the present work we will show that in the case of goethite (Fig. 1), one of the thermodynamically stable Fe(III) (hydr)oxides, and very abundant in natural environments, promising results have been recently obtained by describing with better accuracy the crystal face composition of their particles, especially as a function of particle size (Fig. 2). This has been made possible through a suite of high-resolution electron microscopy techniques, some of which focus on the surfaces at the atomic level. This ultimately has allowed empirical determination of the separate acidity constants for the reactive singly- and triply-coordinated hydroxyl surface sites on goethite, and in turn unified electrolyte-binding and heavy metal binding constants. Only the capacitance value, and the contributing surface stoichiometries and their respective affinity constants and charge distributions (CD) were left as optimizing parameters. This is very promising for the use of SCMs to progressively describe more complex systems, and to gradually approach the heterogeneities found in real environmental geochemical and engineered systems. This work will present the progress achieved in unifying proton, electrolyte, arsenate, phosphate, Zn(II) and Pb(II) binding constants on goethite, by independent determination of surface site densities.

Figure 1. Molecular structure of goethite crystal faces {101} (a), and {210} (b).

Figure 2: STEM HAADF image of a 42 m²/g (BET) goethite showing the Fe atom positions at the {101} crystal edge looking down the vertical axis. The steps and kinks are identified as

