The Role of Surface Structure in Goethite Adsorption Capacity

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Synthetic goethite (α-FeOOH) is known to increase its adsorption capacity significantly with decreasing specific surface area (SSA, determined by N_2-adsorption). Recent investigations on the possible effects of crystal size, habit, surface roughness, and oriented attachment in aqueous suspension and upon drying, were reported on two synthetic goethites with SSA of 40 and 100 $m^2.g^{-1}$[1] We have extended this study to include more intermediately-sized samples of 53 and 75 $m^2.g^{-1}$ to determine more thoroughly the relative effects of crystal size and surface roughness through Scanning Transmission Electron Microscopy (STEM) methods. As in the previous study, synthetic goethite crystallizes with {101} prism and {210} tip faces with one of the {101} faces greatly enlarged relative to its symmetry-related faces creating a tablet habit. Atomic-resolution STEM imaging of Fe columns imaged down [001] permitted observations of surface roughness along [010] perimeters. More than 2000 atomic pairs per crystal were counted to determine the proportion of {101} and {210} steps and terraces. Results show that surface roughness increases as the SSA increases. Steps oriented in the {210} configuration have a theoretical density of singly-coordinated surface sites of 7.5 /nm^2 available for adsorption of ions and protons, while {101} configured steps have 3.03 sites/nm^2. Thus, an increase of {210} steps will increase site density, while increases of {101} steps decrease site density. Calculations show that an replacement of 1/3 of prism terraces by {210} steps will increase the adsorption capacity by ~40%. This study emphasizes the need to understand the actual surface roughness of crystals when assessing the meaning of adsoption experiments.

[1] Livi, et al. (2017) *Langmuir*, **33**, 8924-8932, 10.1021/acs.langmuir.7b01814.