The influence of surface structure, habit, and oriented attachment on goethite adsorption capacity

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It is well established that the adsorption capacity of goethite (α-FeOOH) per m^2 increases progressively with decreasing specific surface area (SSA, determined by N_2-adsorption), below *ca*. 80 m^2/g. For example, the maximum adsorption of chromate increases three-fold as SSA decreases from 94 to 50 $m^2.g^{-1}$ [1]. In order to quantitatively model the site adsorption capacity, the exact nature of the crystal face orientations, their relative surface areas, the population of reactive steps present on the faces, and the degree of agglomeration of crystals during the adsorption experiment must be known. To this end, detailed electron microscopy observations were made on a suite of synthetic goethites with SSA ranging from 40 to 100 $m^2.g^{-1}$. All goethite crystals studied were elongated along the **b**-axis (Pnma setting). Atomic resolution transmission electron microscopy (TEM) and Scanning TEM determined that on the goethite prism faces there were significantly more {210} steps on large (40 $m^2.g^{-1}$) goethite crystals than on small (100 $m^2.g^{-1}$) crystals. The {210} steps (on tips and prism face steps) have more than double the reactive site density of {101} or {001} prism faces. This makes the 40 $m^2.g^{-1}$ sample considerably more reactive. In addition, oriented attachment of the prism faces observed by TEM increases the tip to prism face surface area ratio. CryoTEM of goethite in suspension will determine the extent of oriented attachment that occurs during adsorption experiments. Taken as a whole, an increase in reactivity of large goethite crystals may be explained by a combination of rough prism faces and an increase in tip:prism surface area. Therefore, habit, surface step population and *in vitro* agglomeration need to be considered when modeling adsorption capacity.

[1] Villalobos & Pérez-Gallegos (2008) *J. Colloid Interface Sci*. **326**, 307-323.