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Fe(III) oxide coatings: Physical properties depend on substrate and coating thickness

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The surface reactivity of hydrous Fe oxides may vary even among specimens with the same chemical formula. The purpose of this study was to investigate sorption-relevant changes in the physical properties of Fe(III) oxide coatings when the substrate mineral and coating thickness were varied. Three Fe(III) oxide coatings were prepared: one on quartz (α -SiO₂) and two on kaolinite (Al₂(OH)₂Si₂O₅). One of the kaolinite coatings was comparable to the quartz coating ('thin'), and one contained roughly ten times as much Fe ('thick'). The coating method was kept as consistent as was feasible in all three cases. Physical characteristics of these coated solids were probed by N₂ (g) adsorption/desorption assays and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS).

Physical adsorption results indicated some similarities between the coating on quartz and the thick coating on kaolinite. Desorption hysteresis and other evidence of porosity appeared in these two solids. In contrast, the thin coating on kaolinite exhibited no sign of porosity. The specific surface area (SSA) of the thinly-coated quartz and kaolinite were only slightly larger than those of the respective uncoated minerals, whereas the SSA for the thickly-coated kaolinite approached that of goethite (α -FeOOH). SEM-EDS analysis showed that the spatial distribution of the Fe(III) coating on quartz was distinctly different from that of the coatings on kaolinite. The Fe-to-substrate ratio for the quartz solid was spatially heterogeneous and significantly higher on edges, cracks, and pitted surfaces than on flat surfaces. Fe distribution on both of the kaolinite solids was significantly less heterogeneous. Some differences were also apparent between the thin and thick coatings on kaolinite; in particular, the thin coating showed markedly more uniformity of coating distribution than the thick coating on kaolinite. There was also some suggestion of differences in coating distribution on the edges and faces of kaolinite grains as a function of coating thickness.

These results demonstrate that the physical form of an Fe(III) oxide coating can vary with both the thickness of the coating and the properties of the substrate surface. This has implications for predicting the reactivity of Fe(III) oxide coatings with dissolved sorbates.

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An improved MUSIC model for gibbsite surfaces

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The point of multi-site complexation (MUSIC) models is to realistically describe the adsorption behavior of solid surfaces. However, in order to prevent these models from becoming simple curve-fitting exercises with little connection to reality, some parameters such as pK_a values and site densities must be constrained. Recently, Bickmore et al. (2004) [1] showed that currently used methods for pK_a prediction are flawed, and presented a new method based on *ab initio* bond length calculations. Also, Bickmore et al. (2002) [2] described a more accurate method for measuring particle morphology, which is needed to determine site types and densities. We are applying these new methods to predict adsorption behavior on gibbsite particles. We are creating a MUSIC model that incorporates these predicted pK_a values and accurate particle morphology measurements. This model will then be compared to data from potentiometric titrations of synthesized gibbsite particles with varying aspect ratios.

We are using the combined *ab initio*/bond-valence method of Bickmore et al. (2004) [1] to calculate the effective acidity of gibbsite surface functional groups. However, some of the necessary *ab initio* calculations involve relatively large numbers of atoms. Therefore, we are using the Fireball density functional theory code, which is designed to quickly optimize large systems [3]. The automated computerized image analysis routines of Bickmore et al. (2002) [2] will be used to quantitatively measure morphology of gibbsite particles. These routines can accurately measure the specific edge, basal, and total surface areas of gibbsite particles. The total specific surface area measurements will be compared to measurements made using the BET method.

References

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