

Surface Structural Model for Ferrihydrite

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Abstract – A structural model for the geometry of Fe(III) octahedra near the surface of poorly finely divided ferrihydrite was elaborated based on the bond–valence theory and by considering the interaction of water molecules in the 2 nearest hydration spheres. In contrast to bulk Fe atoms, which are bonded to bridging oxo (O) and hydroxo (OH) ligands, surface Fe atoms are also octahedral coordinated to H₂O ligands forming the 1st hydration shell ((H₂O)_I). In the wet state, external water molecules of the 2nd hydration shell ((H₂O)_{II}) are ingly H-bonded to (H₂O)_I, while they are doubly coordinated in the dry state. Accordingly, wet ferrihydrite contains twice as many sorbed water molecules as dry ferrihydrite, and the structural difference due to the 2nd hydration shell accounts quantitatively for the 15% increase of ferrihydrite weight experimentally measured in moist atmosphere. The interaction surface Fe atoms with their 2 nearest hydration spheres modifies the geometry of surface Fe octahedra as compared to bulk octahedra, and idealized Fe-OH and Fe-H₂O bond lengths in the wet and dry state were evaluated by the bond–valence theory. Our structural model provides a sound crystal–chemical basis to describe many apparent incongruities of Fe X-ray absorption near edge structure (*K*-XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopic data

that have led to differing interpretations of the coordination environment of Fe in ferrihydrite by various investigators.

Key words – EXAFS, Ferrihydrite, Hydrrous Ferric Oxide, XANES, X-ray Absorption Spectroscopy.