# Ferrihydrite Transformation Rate Modeling and its Mechanism in the Presence of Adsorbed Oxyanions

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Ferrihydrite (Fh) is a metastable iron hydroxide nanoparticle that, under oxic conditions, eventually transforms to less hydrated and more stable iron (hydr)oxides such as goethite (Gt) and hematite (Hm). These minerals are by far the dominant iron oxides in the surface environment, and due to their high specific surface area and high reactive surface sites readily make complexes with ion species such as oxyanions and control their cycling and behavior in soil and groundwater. We have developed a kinetic model that describes and predicts the effect of different types of surface complexation, from weak electrostatic outer-sphere for $NO_3^-$, to a mix of outer-sphere and inner-sphere for $SO_4^{2-}$, to predominantly strong bidentate inner-sphere for $H_2AsO_4^-$, on the mechanism of Fh transformation. Two sets of pure and adsorbed Fh samples were prepared, non-buffered and buffered at pH 5.5 ± 0.2, aged for up to 50 days at 70 ± 1.5°C, and then characterized using synchrotron x-ray total scattering and linear combination fitting (LCF) to identify phases and quantify phase abundances, respectively. The kinetic model showed that the rate of Fh transformation is not constant in the presence of $NO_3^-$ and $SO_4^{2-}$ such that the rate is slower at the beginning of the transformation where oxyanions are present on the surface before desorbing to the solution. Both buffered and non-buffered As-adsorbed samples were stable, with only < 2% transformed during 50 days of aging, suggesting a negative correlation between the rate of transformation and strength of the oxyanions bonding on the Fh surface. Also, results showed that the rate constant of transformation is almost twice in the non-buffered pure sample, showing the importance of constant pH in measuring the rate of Fh transformation.