
Influence of Citrate on the Kinetics of Fe(II) Oxidation and the Formation of Iron Oxyhydroxides¹

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Abstract: The rate of Fe(II) oxidation at a constant rate of oxygen supply in the presence of citrate was measured at pH 6.0 at various citrate/Fe(II) molar ratios at 23.5° C in 0.01 M ferrous perchlorate system. The kinetics followed a first-order reaction with respect to Fe(II) concentration at constant pH (6.0) and aeration (5 ml/min). The rate constant decreased exponentially from 41.3×10^{-4} to 7.6×10^{-4} /min with an increase in the citrate/Fe(II) molar ratio from 0 to 0.1.

The nature of the hydrolytic products formed after 120 min of oxidation was arrived at by X-ray powder diffraction (XRD), infrared spectrometry (IR), and transmission electron microscopic (TEM) analyses. In the absence of citrate, goethite (α -FeOOH) and poorly crystalline lepidocrocite (γ -FeOOH) were the oxidation products formed at pH 6.0. The formation of lepidocrocite was promoted at the expense of goethite at citrate/Fe(II) molar ratios of 0.0005 to 0.005. The formation of lepidocrocite was especially pronounced at a citrate/Fe(II) molar ratio of 0.001, as observed from the width at half height (WHH) and the area of the 020 XRD peak of lepidocrocite. At a citrate/Fe(II) molar ratio of 0.01, however, the crystallization was perturbed resulting in the formation of noncrystalline Fe oxides, and no precipitate was observed at a citrate/Fe molar ratio of 0.1. The strong complexation of Fe(II) with citrate retarded the kinetics of Fe(II) oxidation and the formation and hydrolysis of Fe(III). The complexation, electrostatic, and steric effects of the coexisting citrate anions in solution apparently influenced the oxygen coordination and the way by which the double rows of edge-sharing Fe(O,OH)₆ octahedra linked during crystallization, resulting in the formation of lepidocrocite.

Key Words: Citrate • Goethite • Hydrolysis • Iron oxyhydroxide • Lepidocrocite • Oxidation

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