Effect of Cysteine and Manganese on the Crystallization of Noncrystalline Iron(III) Hydroxide at pH 8

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Abstract: To provide a greater understanding of the crystallization of iron oxides under natural aqueous conditions, the combined effect of an inorganic ion (Mn^{2+}) and a reducing organic ligand (L-cysteine) on the conversion of noncrystalline ferric hydroxide to goethite and/or hematite was investigated at pH 8.

At cysteine: Fe ratios ≥ 0.2 , L-cysteine caused noncrystalline iron(III) hydroxide to transform rapidly into goethite at pH 8; in the absence of the organic ligand, hematite was the predominant reaction product. The presence of Mn (\geq 9 mole %) in the cysteine-ferric hydroxide system retarded crystallization and reduced the goethite-promoting effect of cysteine.

Polarographic measurements showed that the adsorption of cysteine on noncrystalline iron(III) hydroxide was immediately followed by the oxidation of cysteine to the disulfide with simultaneous reduction of a proportion of the interracial ferric ions. The partly reduced noncrystalline iron(III) hydroxide dissolved at pH 8 more rapidly than the original material, thus facilitating the formation of goethite. In Mn(II)-noncrystalline iron(III) hydroxide coprecipitates, the interfacial oxidation/reduction reaction with cysteine (and hence the partial reduction of the noncrystalline phase) was reduced, due to replacement of some interfacial Fe(III) by non-reducible Mn.

At pH 8, uptake of Mn by crystalline iron oxides was low (< 5 mole %). Mn precipitated preferentially as pure Mn phases, either rhodochrosite (in NaHCO₃ buffer) or hausmannite (in NH₄Cl/NH₃ buffer).

Key words: Crystallization • Cysteine • Ferrihydrite • Goethite • Iron oxides • Manganese

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