Influence of Chloride on the Formation of Iron Oxides from Fe(II) Chloride. I. Effect of [Cl]/[Fe] on the Formation of Magnetite

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Abstract: The formation of fine-grained magnetite ($\sim 0.1 \,\mu$ m) at pH 7 and 25° C from aeration of Fe(II) chloride solutions is presented. The magnetite converted at 105° C to maghemite with poorly developed superstructure lines. Under the experimental conditions employed, as the initial [Cl]/[Fe] ratio was increased from the stoichiometric value of 2, the final product contained increasing amounts of lepidocrocite. The degree of crystallinity of this phase, as measured by the width at half height of the 020 X-ray diffraction peak, also increased with this ratio. The hydrolysis rate (base consumption to maintain pH) showed a plateau whose position and extent changed with the initial [Cl]/[Fe] ratio. Through this plateau region the Eh decreased to a minimum value the position of which was directly related to the [Cl]/[Fe] value. The formation of lepidocrocite rather than magnetite is likely due to the high [Cl] where there would be increased difficulty for neighboring OH to condense and eliminate H₂O. The formation of Fe-O-Fe bonds in this condensation would be impeded by Cl substitution for OH either in the first formed green rust stage or during its oxidation.

Key Words: Akaganeite • Chloride • Green rust • Iron • Lepidocrocite • Maghemite • Magnetite • Synthesis

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