Chlorite Ion Removal by Ferrous Iron Addition [Project #633A]

This 2-part project resulted in two publications. #90627 is summarized below. #90633 is the publication for part 2.

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BACKGROUND
In drinking water treatment, the use of chlorine dioxide (ClO2) as an oxidant, disinfectant, or both is frequently considered when utilities seek to control trihalomethane concentrations. However, one major problem associated with its use is that much of the applied ClO2 often remains as residual chlorite (ClO2-). Concern about residual concentrations of ClO2, ClO2-, and chlorate (ClO3-) in drinking water have resulted in limitations on applied ClO2 dosages. Elimination of these by-products could greatly enhance the potential for ClO2 usage in drinking water treatment.

APPROACH
The overall goal of this research study was to investigate the potential to use ferrous iron (Fe2+) for the chemical reduction of ClO2- in drinking water. The specific research objectives are listed below:

• Evaluate both the stoichiometry and the reaction kinetics between Fe2+ and ClO2- as a function of solution pH, temperature, dissolved organic carbon (DOC) concentration, and O2(aq) concentration.

• Assess the potential for ClO3- formation as a by-product of the Fe2+-ClO2- reaction.

• Assess the fate of iron during treatment, including potential problems that may develop due to excess Fe2+ addition.

• Evaluate the impact of ferric hydroxide solids (formed as a by-product of the Fe2+-ClO2- reaction) on alum coagulation for turbidity and DOC removal.

RESULTS
Based upon data collected during the study, the following conclusions were formulated:

• The Fe2+-ClO2- reaction is kinetically rapid over the pH 5.0-7.0 range, with essentially complete ClO2- reduction occurring in reaction times as short as 5-15 seconds.

• Fe2+ doses of 3.0-3.1 mg Fe/mg ClO2- effectively promoted ClO2- reduction while producing minimal residual soluble iron. This stoichiometry reasonably predicts chloride ion (Cl-) as the by-product of ClO2- reduction by Fe2+.

• Excess dosages of Fe2+ could be removed by reaction with O2(aq) under neutral or alkaline pH conditions. However, stability of soluble iron may be a problem with excess Fe2+ doses under acidic pH conditions.
• There was no evidence of ClO₃⁻ formation as a by-product of the Fe²⁺-ClO₂⁻ reaction.

• The presence of Fe(OH)₃(s) solids formed as a by-product of the Fe²⁺-ClO₂⁻ reaction did not adversely affect the performance of alum as a primary coagulant for turbidity and DOC removal.

The experimental results indicate that Fe²⁺ can be used effectively for the control of residual ClO₂⁻ in drinking water facilities that utilize ClO₂ as an oxidant/disinfectant. Due to the rapid reaction kinetics observed during this study, the Fe²⁺ may be added at several points within the treatment train and still promote efficient ClO₂⁻ removal. While this study emphasized Fe²⁺ addition during rapid mixing, it is conceivable that Fe²⁺ could be added as late as in the filter-applied water. Water utilities contemplating such treatment should conduct pilot-scale testing to insure effective capture of the resulting Fe(OH)₃ solids within the filters.

An important issue is the proper dosing of Fe²⁺. Excess amounts of Fe²⁺ were readily removed from solution by O₂(aq) in the neutral pH range. Persistence of Fe²⁺ may be an item of concern under acidic pH conditions, and alternative oxidants for Fe²⁺ removal (eg., HOCl) may need to be considered.

The report also addresses practical issues such as the management of solution pH during treatment, impact of various sources of Fe²⁺ iron on process performance, and potential coagulation benefits (improved DOC removal, lowered coagulation dosages) that may be derived from by-product Fe(OH)₃(s) formation.