



Cyanide Destruction with Chlorine Dioxide

Introduction

Chlorine dioxide (ClO₂) is effective as both a disinfectant and an oxidant in water and wastewater treatment. Its selective reactivity makes chlorine dioxide a powerful non-chlorinating oxidizing agent useful in many water treating applications for which chlorine and other oxidizing agents are unsuitable. Unlike most oxidants, chlorine dioxide may be used over a broad pH range.

Application Description

Cyanides (CN⁻) are used to solubilize metal ions in basic solution. Consequently, cyanide compounds are found in wastewater streams from processes such as metal plating, steel case hardening, pickle liquor neutralizing, gold and silver ore refining and blast furnace stack gas scrubbing. Cyanide compounds are very toxic and must be removed from the wastewater prior to discharge.

Cyanide is an extremely strong chelating agent, reacting readily with transition metal ions, forming very stable complexes, which are extremely resistant to oxidation. Therefore, cyanide compounds can be classified as oxidizable and non-oxidizable cyanides.

Oxidizable cyanides: Comprising "weak acid dissociable cyanide" (WAD) cyanide, and labile metal-cyanide complexes. WAD cyanide includes free cyanide anion (CN⁻) and hydrogen cyanide (HCN). Labile metal-cyanide complexes include complexes of cadmium, copper, nickel, silver and zinc, which are easily broken down.

Non-oxidizable cyanides: Comprising non-labile metal-cyanides complexes, typically iron-cyanide complexes (Fe[CN]₆^{2- or 3-}), or cobalt.

Only oxidizable cyanides can be treated by chlorine dioxide or other oxidants.

Treatment Alternatives

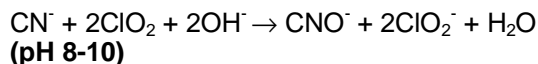
There are various methods available for the treatment of cyanides in wastewater. Oxidation should be considered when levels of oxidizable cyanide are too high to be processed by a biological treatment system.

Chlorine dioxide

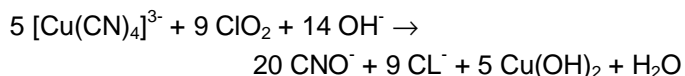
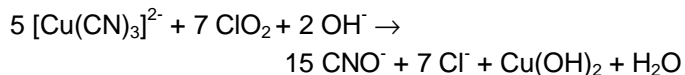
Chlorine dioxide is unique in its ability to be used at moderately basic pH's. All other oxidants require pH's greater than 12. In the case of chlorine this is necessary to hydrolyze toxic cyanogen chloride (CNCl) gas formed during treatment. Cyanogen chloride is not formed during chlorine dioxide treatment of cyanides.

Chlorine dioxide oxidizes simple cyanide to cyanate (a less toxic substance) and/or carbon dioxide and nitrogen. The end products depend on reaction conditions. With free cyanide the reaction with chlorine dioxide is reported to be instantaneous. Strongly alkaline conditions speed up the reaction between chlorine dioxide and oxidizable cyanides. However, excessive alkaline decomposition of chlorine dioxide to chlorate may occur at pHs above 10. The optimal pH range is therefore, 8-10, depending on pH discharge limitations.

In neutral and alkaline solutions below pH 10, an average of 2.5 mg/L by weight of chlorine dioxide oxidizes 1 mg/L of cyanide ion to cyanate. Chlorine dioxide has not been observed to form cyanogen chloride during the oxidation of cyanide.

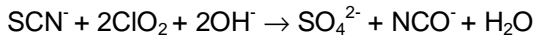


Cyanide is most commonly encountered in its complexed form, often with iron (and cobalt), which is not oxidizable by chlorine dioxide. The reaction of chlorine dioxide with various cyano complexes depends upon the relative ease of dissociation of cyanide from the complex. Cyanide complexes containing Ag⁺, Cu⁺, Zn²⁺, Ni²⁺, Pb²⁺, and Cd²⁺ dissociate fairly easily and are destroyed by chlorine dioxide as shown below.



The reaction of chlorine dioxide with cyanide complexes occurs in two stages. Stage one sees the conversion of cyanide to cyanate ion with the formation of chlorite. The second reaction is a catalyzed oxidation (by the transition metal ion) to chloride.

Chlorine dioxide also oxidizes thiocyanate to sulfate and cyanate. In neutral solutions, an average of 3.5 mg/L of chlorine dioxide oxidizes 1 mg/L of thiocyanate ion.



Alternative Oxidants

- **Alkaline chlorination** is effective for oxidation of all cyanides except iron complexes, noble metal, and cobalt complexes. Chlorine has the lowest chemical costs, but requires high pH to avoid cyanogen chloride formation. The presence of ammonia will also create a high demand for chlorine.
- **Hydrogen peroxide** is the most common oxidant, but requires high pH (through caustic addition) and is much more costly than alkaline chlorination.

Advantages of Chlorine Dioxide

- Chlorine dioxide does not form cyanogen chloride.
- Chlorine dioxide may be used without pH adjustment.
- Chlorine dioxide does not react with organics to form THMs.

Feed Requirements

For industrial applications dosages will vary depending on the application. Dose rates may be determined by completing a chlorine dioxide demand study.

For once-through systems, or systems where treated water may enter a US waterway, the concentration of residual chlorite ion should be monitored such that it does not exceed the requirements of the NPDES permit, and is in compliance with local, state and federal regulations.

Method of Feed

Chlorine dioxide is a gas produced by activating sodium chlorite with an oxidizing agent or an acid source. Sodium chlorite is converted to chlorine dioxide through a chlorine dioxide generator and applied as a dilute solution. Chlorine dioxide solutions should be applied to the processing system at a point and in a manner which permits adequate mixing and uniform distribution. The feed point should be well below the water level to prevent volatilization of the chlorine dioxide. Avoid co-incident feeding of chlorine dioxide with lime or powdered activated carbon.

Chlorine Dioxide Analysis

Residual chlorine dioxide concentrations should be determined by substantiated methods, which are specific for chlorine dioxide. Chlorine dioxide solutions can be analyzed by iodometric and amperometric titrations, and spectrophotometrically, with the standard DPD (N,N-diethyl-*p*-phenylenediamine) method. These methods are described in detail in *Standard Methods for the Examination of Water and Wastewater*¹.

4500-ClO ₂ B	Iodometric Method
4500-ClO ₂ D	DPD-Glycine Method
4500-ClO ₂ E	Amperometric Method II

Further Information

More detailed information on sodium chlorite is available on request through the OxyChem Technical Service Department. Call or write:

Technical Service Department
OxyChem
Post Office Box 12283
Wichita, Kansas 67277-2283
800-733-1165 option #1

www.oxy.com

References

1. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA and WEF, Washington, D.C. (20th Ed., 1998).

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