Treatment of Ammonia Plants with Chlorine Dioxide

Chlorine dioxide (ClO_2) is effective as both a disinfectant and an oxidant in water treatment. Chlorine dioxide is a broad-spectrum microbiocide effective over a wide pH range. Unlike chlorine, chlorine dioxide does not react with organic materials to form trihalomethanes (THMs). Chlorine dioxide is also non-reactive with ammonia-nitrogen and with most treatment chemicals (corrosion and scale inhibitors) present in cooling water systems.

Chlorine dioxide is effective in the control of microbiological growths in industrial cooling waters under conditions unfavorable to chlorine. It is particularly effective in systems having a high pH, ammonia-nitrogen contamination, persistent slime problems, or where the microbial contamination is aggravated by contamination with vegetable or mineral oils, phenols or other high chlorine-demand producing compounds

Application Description

Microbiological control of cooling systems in ammonia plants is especially difficult as nitrogen compounds and in particular ammonia is often present in the cooling water. The efficacy of the microbiological treatment program is dependent on the system conditions and the degree of contamination from nitrogen compounds present in the process stream.

Treatment Alternatives

Three oxidizing biocides are most commonly used for cooling tower treatment: chlorine, bromine and chlorine dioxide.

Chlorine

Chlorine (in all its forms) reacts rapidly with ammonia and amines to form chloramines, which have 1% the biocidal efficacy of hypochlorous acid. This is a stepwise reaction, which forms a mixture of mono-, di- and tri-chloramines. These reactions, which are summarized in Equations 1-3, require 7.6 parts of chlorine for every part of ammonia-N to form trichloramine or nitrogen trichloride (NCl_3).

(1) $HOCl + NH_3 \rightarrow NH_2Cl + H_2O$

(2) $HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$

(3) $HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$

The amount of chlorine that is required to overcome the ammonia demand and achieve a free residual is called 'breakpoint' chlorination. However, simply increasing the chlorine dosage in the presence of high pH or ammonia levels is not advisable since this causes increased metal corrosion, wood delignification and higher levels of Total Dissolved Solids (TDS).

Application Note

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Bromine

Bromine also reacts with ammoniacal compounds to form bromamines. There is a significant difference between the biocidal activity of bromamines and chloramines. Bromamines are potent biocides, while chloramines are not. However, like chlorine, bromine reacts with organic materials, whether treatment chemical or contaminants. Brominated organics may also be more harmful than chlorinated organics. Consequently, bromine overcomes only some of chlorine's deficiencies.

Chlorine Dioxide

Chlorine dioxide has specific reaction properties that make it ideally suited for use in ammonia plants. It is a very selective oxidizer and will not react with many of the compounds that readily react with chlorine and bromine

Advantages of Chlorine Dioxide

- Chlorine dioxide does not react with ammonia-nitrogen.
- Chlorine dioxide does not react with organics to form THMs.
- Chlorine dioxide does not react with triazole corrosion inhibitors.

The dosage required for biocidal control remains fairly constant over a wide range of cooling water conditions. This makes chlorine dioxide an excellent choice for cooling water that has a high pH, or that
has high levels of organic or ammoniacal contamination.

Feed Requirements

For control of bacterial slime and algae in industrial recirculating and one-pass cooling systems, the required dosages will vary depending on the exact application and the degree of contamination present. The required chlorine dioxide residual concentrations range between 0.1 and 5.0mg/L. Chlorine dioxide may be applied either continuously or intermittently. The typical chlorine dioxide residual concentration range is 0.1 - 1.0 mg/L for continuous doses, and 0.1 - 5.0 mg/L for intermittent doses. The minimum acceptable residual concentration of chlorine dioxide is 0.1 mg/L for a minimum one minute contact time.

For more information on dosage requirements specific to your application contact your Siemens Representative.

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

Chlorine Dioxide Analysis

Residual chlorine dioxide concentrations should be determined by substantiated methods, which are specific for chlorine dioxide. Two suitable methods are published in Standard Methods for the Examination of Water and Wastewater1:

4500-ClO_2 D	DPD-Glycine Method
4500-ClO_2 E	Amperometric Method II

References

1. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA and WEF, Washington, D.C. (20th Ed.,l998).

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