Pretreatment
Chlorine Dioxide

The following are general recommendations for chlorine dioxide removal prior to TRISEP® membranes. For additional instructions, please contact MANN+HUMMEL Water & Fluid Solutions Technical Service.

INTRODUCTION

Chlorine (Cl_2) has been used for many years to treat municipal and industrial wastewaters as a disinfectant, however free chlorine may react with the membrane surface leading to possible decline in membrane performance. Because of this, dechlorination prior to the reverse osmosis (RO) or nanofiltration (NF) membrane system is highly recommended to prevent oxidation of the membrane. Please refer to MANN+HUMMEL Water & Fluid Solutions' **Pretreatment – Dechlorination Using Sodium Metabisulfite** (TSG-C-012) guide for more information on dechlorination methods.

Chlorine is most commonly available as chlorine gas and the hypochlorites of sodium and calcium. In water, they hydrolyze to produce hypochlorous acid (HOCl):

$Cl_2 + H_2O \rightarrow HOCl + HCl$
$NaOCl + H_2O \rightarrow HOCl + NaOH$
$Ca(OCl)_2 + 2\ H_2O \rightarrow 2\ HOCl + Ca(OH)_2$

Hypochlorous acid dissociates in water to hydrogen ions and hypochlorite ions:

$HOCl \leftrightarrow H^+ + OCl^-$

The sum of Cl_2, NaOCl, $Ca(OCl)_2$, HOCl and OCl^- is referred to as free available chlorine (FAC) or free residual chlorine (FRC), given as mg/L Cl_2.

CHLORINE DIOXIDE

Chlorine dioxide is also an oxidizing biocide that is used for disinfection, color reduction and taste and odor control. It has been shown that less than 0.1 ppm of chlorine dioxide can successfully inactivate common water pathogens in only five minutes of exposure. Chlorine dioxide forms chlorite and chlorate, both of which are considered disinfection by-products (DBPs). In fact, the EPA has established a maximum contaminant level goal (MCLG) for chlorite of 0.8 ppm. Because 75% of chlorine dioxide that is applied to water forms chlorite, the maximum chlorine dioxide concentration allowable is 1.3 ppm unless a chlorate removal process is employed. While chlorate does not have a MCLG established, studies indicate that it is a potential health hazard.

Chlorine dioxide is a highly volatile compound and is not stable in concentrated solutions. This is because the gas may detonate upon compression. For this reason, it is recommended to generate carbon dioxide on site by mixing sodium chlorite with chlorine gas or hypochlorous acid:

$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$
$2\ NaClO_2 + HOCl + HCl \rightarrow 2\ ClO_2 + H_2O + 2\ NaCl$

The above mixing methods have the potential for leaving behind unreacted chlorine gas or hypochlorite which may damage RO membranes. Because of this, other methods of forming chlorine dioxide (or using pure chlorine dioxide) may be used:

$2\ NaClO_2 + H_2O_2 + H_2SO_4 \rightarrow 2\ ClO_2 + NaSO_4 + O_2 + 2\ H_2O$
$5\ NaClO_2 + 4\ HCl \rightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O$

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Despite the lack of free chlorine shown in the above equations, the effects of chlorine dioxide on the integrity of RO and NF membranes have yet to be fully understood. If used improperly or if in the presence of oxidant-demanding species such as iron, manganese or organics, the use of chlorine dioxide is capable of damaging RO and NF membranes.

Even though chlorine dioxide's many advantages including its biocidal effectiveness and lack of harmful by-products, it is recommended to remove all chlorine dioxide prior to the RO and NF systems or use another form of disinfectant to prevent membrane degradation.

Contact

Europe
Germany: +49 611 962 6001
Italy: +39 0721 1796201
info@microdyn-nadir.com

Americas
USA: +1 805 964 8003
sales.mnus@microdyn-nadir.com

Asia
Singapore: +65 6457 7533
China: +86 10 8413 9860
waterchina@mann-hummel.com

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