



FILMTEC™ Membranes Water Chemistry and Pretreatment: Biological Fouling Prevention

Chlorination / Dechlorination

Chlorine (Cl_2) has been used for many years to treat municipal and industrial water and waste waters to control microorganisms because of its capacity to inactivate most pathogenic microorganisms quickly. The effectiveness of chlorine is dependent on the chlorine concentration, time of exposure, and the pH of the water. Chlorine is used for treating potable water where a residual chlorine concentration near 0.5 mg/L is commonly used. In an industrial water treatment scheme, fouling of water intake lines, heat exchangers, sand filters, etc., may be prevented by maintaining a free residual chlorine concentration of 0.5–1.0 mg/L or higher, dependent on the organic content of the incoming water.

Chlorination for RO/NF pretreatment has been applied usually where biological fouling prevention is required (i.e., typically for surface waters). Chlorine is added continuously at the intake, and a reaction time of 20–30 min should be allowed. A free residual chlorine concentration of 0.5–1.0 mg/L should be maintained through the whole pretreatment line. Dechlorination upstream of the membranes is required, however, to protect the membranes from oxidation.

FILMTEC™ membrane can withstand short-term exposure to free chlorine (hypochlorite); however, its resistance is limited. The membrane can be used successfully in installations where system upsets result in temporary exposure to free chlorine. Eventual degradation may occur after approximately 200–1,000 hours of exposure to 1 ppm concentrations of free chlorine.

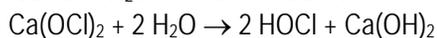
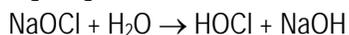
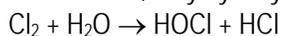
The rate of chlorine attack depends on various feed water characteristics. Under alkaline pH conditions, chlorine attack is faster than at neutral or acidic pH. Chlorine attack is also faster when iron or other transition metals are present either in the water or on the membrane surface; these metals catalyze membrane degradation. Because of the risk of membrane oxidation, chlorine is not recommended for intentionally sanitizing membrane systems.

Continuous chlorination and dechlorination of the feedwater has been standard for years. Biofouling problems downstream of the point of dechlorination, however, are quite common. It is believed that chlorine reacts with the organic matter in the water and breaks it down to more biodegradable fragments. Since there is no chlorine present on the membranes, microorganisms can grow with an enhanced nutrient offering, unless the system is sanitized very frequently. Therefore, the continuous chlorination/dechlorination method is becoming less popular.

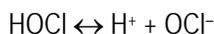
Instead of continuous chlorination, chlorine is preferably applied off-line to the pretreatment section periodically. During off-line chlorination, the feedwater has to be sent to drain prior to reaching the membranes. Before the system goes into operation again, all chlorine containing feed water has to be rinsed out carefully, and the absence of chlorine must be verified (e.g., by monitoring of the oxidation-redox potential (ORP)).

Chlorination Chemistry

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



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



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), expressed as mg/L Cl_2 . As discussed later, chloramines are formed from the reaction of chlorine with ammonia compounds present in the water. These chlorine-ammonia compounds are referred to as combined available chlorine (CAC) or combined residual chlorine (CRC). The sum of free and combined available/residual chlorine is called the total residual chlorine (TRC).

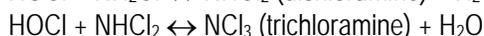
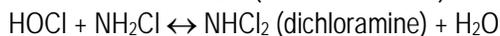
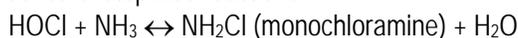
$$\text{TRC} = \text{FAC} + \text{CAC} = \text{FRC} + \text{CRC}$$

The germicidal efficiency of free residual chlorine is directly related to the concentration of undissociated HOCl . Hypochlorous acid is 100 times more effective than the hypochlorite ion OCl^- . The fraction of undissociated HOCl increases with decreasing pH.

At pH 7.5 (77°F (25°C), 40 mg/L TDS), only 50% of free residual chlorine is present as HOCl , but 90% is present at pH 6.5. The fraction of HOCl also increases with decreasing temperature. At 41°F (5°C), the HOCl mole fraction is 62% (pH 7.5, 40 mg/L TDS). In high-salinity waters, less HOCl is present (30% at pH 7.5, 25°C, 40,000 mg/L TDS).

Chlorine Demand

A part of the chlorine dosage reacts with ammonia nitrogen to combined available chlorine in a series of stepwise reactions:



These reactions are governed primarily by pH and chlorine-to-nitrogen weight ratio. Chloramine also has a germicidal effect, albeit lower than that of chlorine.

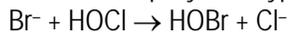
Another part of the chlorine is converted to nonavailable chlorine. This chlorine demand is caused by the reaction with reducing agents such as nitrite, cyanide, sulfide, ferrous iron, and manganese. Chlorine is also consumed by the oxidation of organic compounds present in the water.

To determine the optimum chlorine dosage, best point of injection, pH, and contact time to prevent biofouling, ASTM D 1291 /[33](#) should be applied to a representative water sample. For further details, the Handbook of Chlorination /[34](#) is recommended.

Seawater

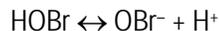
The major difference between the chlorination chemistry of seawater and that of brackish water is the presence of bromide in seawater in concentrations of typically 65 mg/L.

Bromide reacts rapidly with hypochlorous acid to form hypobromous acid:



Thus, in chlorinated seawater the biocide is predominantly HOBr rather than HOCl.

Hypobromous acid then dissociates to hypobromite ion as follows:



HOBr dissociation is less than HOCl dissociation. At pH 8, where 72% of HOCl is dissociated, about 17% of HOBr is dissociated. In other words, effective treatment can be performed at a higher pH than in brackish water, where no bromide is present.

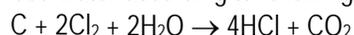
Both hypobromous acid and hypobromite ions interfere with free residual chlorine measurements and are included in the free residual chlorine value.

The reactions of HOBr with other compounds of the water are analogous to the reactions of HOCl. Bromamines and brominated compounds are the reaction products.

Dechlorination

When RO or NF membrane is used in the RO/NF process, the feed must be dechlorinated to prevent oxidation of the membrane. FILMTEC™ membranes have some chlorine tolerance before noticeable loss of salt rejection is observed. The first sign of chlorine attack on RO/NF membrane is loss of membrane flux followed by an increase in membrane flux and salt passage. Eventual degradation may occur after approximately 200–1,000 hours of exposure to 1 mg/L of free chlorine (200–1,000 ppm-h tolerance). The rate of chlorine attack depends on various feed water characteristics. Under alkaline pH conditions, chlorine attack is faster than at neutral or acidic pH. An acidic pH is preferred for better biocidal effect during chlorination. Chlorine attack is also faster at higher temperatures and higher concentrations of heavy metals (e.g., iron), that can catalyze membrane degradation. Since oxidation damage is not covered under warranty, FilmTec recommends removing residual free chlorine by pretreatment prior to exposure of the feed water to the membrane. Other oxidizing agents such as chlorine dioxide, hydrogen peroxide, ozone, and permanganate are capable of damaging RO/NF membranes also if not used properly.

Residual free chlorine can be reduced to harmless chlorides by activated carbon or chemical reducing agents. An activated carbon bed is very effective in the dechlorination of RO feed water according to following reaction:



Sodium metabisulfite (SMBS) is commonly used for removal of free chlorine and as a biostatic. Other chemical reducing agents exist (e.g., sulfur dioxide), but they are not as cost-effective as SMBS.

When dissolved in water, sodium bisulfite (SBS) is formed from SMBS:



SBS then reduces hypochlorous acid according to:



In theory, 1.34 mg of sodium metabisulfite will remove 1.0 mg of free chlorine. In practice, however, 3.0 mg of sodium metabisulfite is normally used to remove 1.0 mg of chlorine.

Chlorination / Dechlorination (cont.)

The SMBS should be of food-grade quality and free of impurities. SMBS should not be cobalt-activated. Solid sodium metabisulfite has a typical shelf life of 4–6 months under cool, dry storage conditions. In aqueous solutions, however, sodium bisulfite can oxidize readily when exposed to air. A typical solution life can vary with concentration as follows:

Concentration (wt %)	Solution life
10	1 week
20	1 month
30	6 months

Although the dechlorination itself is rapid, good mixing is required to ensure completion. Static mixers are recommended. The recommended injection point is downstream of the cartridge filters in order to protect the filters by chlorine. In this case, the SMBS solution should be filtered through a separate cartridge before being injected into the RO feed. Dechlorinated water must not be stored in tanks.

When RO/NF membranes are fouled with heavy metals such as Co and Cu, residual SBS (up to 30 ppm) partially converts to oxidants under the presence of excessive oxygen. When there is a heavy potential for metal fouling, SBS dosing amount control must be optimized and oxidation conditions of the concentrate must be monitored by an oxidation-reduction potential (ORP) meter [/35/](#).

The absence of chlorine should be monitored using an oxidation-reduction potential (ORP) electrode downstream of the mixing line. 175 - 200 mV threshold readings of the ORP have been typically applied. The electrode signal shuts down the high pressure pump when chlorine is detected.

FILMTEC™ Membranes For more information about FILMTEC membranes, call the Dow Water Solutions business:

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