

APPLICATION OF TWINOXIDE[®] TO PREVENT BIOFOULING OF RO MEMBRANES...

... AND TO PROVIDE AN EFFICIENT DISINFECTION PROCESS IN THE FEED STREAM OF THE REVERSE OSMOSIS UNIT.

Introduction

The membrane separation technology, especially reverse osmosis, is used as an alternative to water production with higher quality and also to wastewater treatment in industrial process for its reuse. However, the use of the membranes is limited by its lifetime which varies according to the species and amount of impurities present in the effluent and the frequency of cleaning.

Some impurities also can propitiate the development of microorganisms in the flow channels and on the surface of the membranes that, in some extend, will contribute for the membrane degradation, this phenomenon is known as biofouling. To prevent biofouling is necessary an efficient disinfection process in the feed stream of the reverse osmosis unit, to promote the death of the microorganisms and the oxidation of the organic matter. Chlorination is the practice adopted in many industries, but chlorine can cause environmental damage, health hazards in the industry and damages the polyamide membranes. Therefore, it is necessary to find a less aggressive agent to the environment and to the polyamide membranes.

TwinOxide[®] is less aggressive than any chlorinating agent and than free chlorine but is capable to reduce the total population of bacteria.

RO tolerance of TwinOxide[®]

Many experiments (mentioned below) had already been carried out in various laboratory scale to reverse osmosis units with chlorine dioxide generated by classical way. It was verified that chlorine dioxide is less aggressive than chlorine. And below 0.8 ppm of chlorine dioxide, carbon filters and RO equipments effectively removes chlorine dioxide and its by products.

When using TwinOxide[®] it is possible to use TwinOxide[®] before the RO-membrane without damaging the membrane. The function of adding TwinOxide[®] after the active coal and before the membrane is simple: by adding TwinOxide[®] in ppb dosage rates the water contains disinfection power at low dosage contributing positively to face the undesired fouling of RO systems. The degree and frequency of fouling varies widely from one membrane system to another. Fouling to the point of cleaning begin required can occur as limited as once per year or as frequently every day. The foulants can be classified into four main categories: dissolved solids, suspended solids, biological, and non-biological organics. Biological fouling continues to be a major unresolved problem for membranes and systems as the most common RO-membrane types in use today are attacked and degraded by chlorine and according to public literature by other oxidizing agents.

Chlorine is commonly used as a feed water disinfectant. However it must be removed from the feed water prior to entering the RO

system. Without a disinfectant present in the water, microorganisms colonize and form a biofilm in the RO system. Ultimately common practice is that the RO membranes have to be removed from service and cleaned. Thus the biofilm causes a reduction in membrane performance and membrane damage leading to higher maintenance and system operating cost. The main objectives of TwinOxide[®] disinfection treatment, is to efficiently treat a membrane separation system to control biofilm formation by extremely low levels of TwinOxide[®] 0.3% solution by not adversely affecting the RO membrane.

TwinOxide[®] test protocol

Firstly to sterilize an RO system a dosage rate of 25-100ppm of TwinOxide[®] is required with a circulate sterilization solution for 10-15 minutes. After that the system needs to be rinsed several times with tap water. The tap water needs to be renewed between rinses. After that the system needs to be rinsed 3-4 times with de-ionized water. Once drained, the system is ready for use and the membrane can be installed.

By dosing extreme low levels of TwinOxide[®] 0.3% solution in the feed water the depositing and growing of biofilm on membranes can be significantly reduced without damaging the membranes leading to increased salt passage. The dosage rate of TwinOxide[®] to the feed water will vary per RO system depending on the available biofilm in the RO system as well as the composition of the feed water.

The US Patent Application No. 20050061741 used the method wherein the chlorine dioxide concentration (Stabilized Sodium Chlorite) is used at 1 to 500 parts per billion. The effective range may be in the range of 1-900 parts per billion. Obviously TwinOxide[®] trial can be started at a dosage rate of 5 ppb of TwinOxide[®] 0.3% solution. To avoid the growth of biofilm a dosage rate on an average has to be determined depending on contamination level but below 1000 ppb. Further a dosage rate above ~1000ppb will provide a critical level of TwinOxide[®] where the membrane possibly might be affected by the oxidizing power of TwinOxide[®] (this variation depends on the feed water composition and quality and therefore an appropriate dosage rate must be determined by test). Further TwinOxide[®] can be used for normal disinfection control in the water treatment systems with RO installations to replace existing disinfectants (e.g. chlorine, ozone etc). For continuous dosing with TwinOxide dosing level can vary in between 0.05-0.08 ppm.

An appropriate sensor should control the TwinOxide[®] level in the system (chlorine dioxide sensor or potentiostatic analyzer) at ppb level. You can also manually check the concentration of chlorine dioxide by DPD kit or Strip. The dosing system that injects TwinOxide[®] in the feed water can also be automatically controlled by the monitoring sensor and stop dosing if levels exceed the maximum value to avoid damage to the membrane, for this you can

your equipment supplier to integrate the system towards atomization. Appropriate testing knowledge and monitoring by the customer is advisable.

Notes

- A dosage rate of TwinOxide® should never exceed the level of 1000 ppb and have a minimum of 5ppb. While using TwinOxide® the salt passage will not increase (a true and valid indicator that the membrane is not damaged).
- At near neutral pH TwinOxide® can be theoretically used at higher dosing levels also but this remains to be studied yet. Polyamide type membranes are generally resistant to chlorine dioxide at near-neutral pH. This chemical evidently attacks membranes at high pH by oxidation since no halogen uptake is observed.
- Never use TwinOxide® on celluloses membranes!

Various references and other background knowledge

Reference can be found in Desalination, 48 (1983) I-16, Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands, REVERSE OSMOSIS MEMBRANE SENSITIVITY TO OZONE AND HALOGEN DISINFECTANTS and J. GLATER, M.R. ZACHARIAH, S.B. MCCRAY AND J.W. MCCUTCHAN, Chemical, Nuclear and Thermal Engineering Department, University of California, Los Angeles, CA 90024 (USA).

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HALOGEN INTAKE OF EXPOSED B-9 MEMBRANE				
Disinfectant chemical	Concentration (ppm)	pH	Exposure time (h)	Polymer halogen content (% by wt.)
Cl ₂	30	3.0	8	13.4
	30	3.0	24	17.0
	30	3.0	40	17.7
	30	3.0	100	22.1
	30	8.6	112	0.1
Br ₂	70	3.0	40	22.2
	70	5.8	40	29.5
	70	8.6	40	19.1
ClO ₂	30	3.0	100	0.5
	30	8.6	48	0.3

The response of FT-30 and B-9 membranes to chlorine dioxide has been documented in earlier reports ^{1 2}. Both membranes show good resistance at near neutral pH but are severely damaged at pH 8.6. Chemical attack evidently occurs by a mechanism different from chlorination, however, since chlorine is not incorporated into the membrane polymer.

1] J. Glater, J.W. McCutchan, S.B. McCray and M.R. Zachariah, Halogen Interactions with Typical Reverse Osmosis Membranes, presented at the Water Re-Use Symposium II, August 23-28, 1981, Washington, DC.
2] S.B. M&ray, J. Glater and J.W. McCutchan, The Effect of pH and Halogens on the Stability of Reverse Osmosis Membranes, UCLA-ENG-8115, Water Resources Center Report 73, July 1981.

Glater et al tested chlorine dioxide concentrations of 3 to 30 parts per million. Adams, Desalination, 78 (1990) pages 439-453, titled: The Effects of Chlorine Dioxide on Reverse Osmosis Membranes, conducted 6-month compatibility tests using a feed water chlorine dioxide (generated in classical way) concentration of 1000 parts per billion and recorded measurable damage to the RO membranes.

Another innovation in the US patent application **20050061741** is the treatment of the membrane separation system such as an RO system and other membrane(s) with subpart per million levels of chlorine dioxide. It has been discovered that treatment of clean RO membranes with chlorine dioxide at a concentration of 1 to 500 parts per billion in the feed water is

effective in preventing the formation of biofilm on an RO membrane. Treatment under these conditions resulted in no damage to the RO membrane. This is contrary to results published by Glater et al, American Chemical Society (1981) titled: The Effects of Halogens on the Performance and Durability of Reverse-Osmosis Membranes. Glater et al tested chlorine dioxide concentrations of 3 to 30 parts per million. Adams, Desalination, 78 (1990) pages 439-453, titled: The Effects of Chlorine Dioxide on Reverse Osmosis Membranes, conducted 6-month compatibility tests using a feed water chlorine dioxide concentration of 1000 parts per billion and recorded measurable damage to the RO membranes.

An abstract of this patent is given in the annex:

Annex: Abstract of US Patent Application 2005006174

Disclosed is a method for preventing osmotic membrane fouling comprising treating reverse osmotic feed water and membranes with chlorine dioxide at an extremely low concentration, e.g., as low as one part per billion in the feed water. The effective range may be in the range of 1-900 parts per billion. Also disclosed is a membrane separation system in which fouling is prevented using ultraviolet, pH acid adjustment or an electrochemical generator to produce the chlorine dioxide.

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Please also check the full application of claims for your reference: <http://appft1.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PG01&p=1&u=%2Fnetahtml%2FPTO%2Fsrchnum.html&r>

1 liter of TwinOxide® 0.3% solution at 0.05 ppm disinfects 60,000 liters of water.
1 liter of TwinOxide® 0.3% solution at 3 ppb disinfects up to 1,000,000 liters of water!