A Literature Review of the Effects of ClO_2 and RO Membranes

There have been very few papers written in the literature concerning the effect ClO_2 has on RO membranes. The following bulletin summarizes the work completed to date by five researchers. Further work in this area is recommended.

Research Studies

1. Work by Vos

Vos, et. al.,[1,2] in 1966 and 1968, reported on the effect chlorine had on cellulose acetate (henceforth CA) membranes. Above 50 ppm Cl^2 will attack CA membranes after 1 week of continuous exposure. At 10 ppm for 15 days, no detectable change in performance was noted. ClO_2 was shown by Vos, et. al.,[1] to be unreactive towards CA membranes.

2. Work by Glater

In an effort to investigate other types of membranes, Glater, et. al.,[3] in 1981, reported that newer, thin film composites (henceforth TFC) were more susceptible to oxidative damage than was CA membranes.

There is some benefit to their work. However, there are also some major errors in their work. In their work they compared the oxidants on a molar basis instead of a practical use basis.

They compared the following:

Oxidant	Dose (ppm)
Cl_2	3.0
Br_2	7.0
I_2	11.0
ClO_2	3.0

That is, 3.0 ppm Cl_2 was considered to be equivalent to 3.0 ppm ClO_2, whereas in the real world, the concentration of ClO_2 that would be equivalent to 3.0 ppm Cl_2 would be approximately 1/4 to 1/5 of that amount, or 0.6 – 0.7 ppm. Similarly, bromine equivalency would probably be somewhat less than that shown.

Membranes tested are shown below:

Code	Manufacturer	Polymer type
U1	Fluid Systems	Poly(rther/urea) (TFC)
C2	Environgenics	CA-CTA 50/50 (homogeneous)
V1	Hydranautics	Homogeneous CA (coated with vinyl acetate)
A2	DuPont	Homogeneous Aromatic Poly-amide
X2	FilmTec	Polysulfone (TFC)

The CA membranes were resistant to all of the oxidants tested.

The U1 membrane appeared to be sensitive to all oxidants tested, being very sensitive to bromine and to ClO_2.

The other non-CA membranes tested, A2 and X2, showed good oxidant stability with ClO_2, except for pH 8.6. The reasons for this are not clear, except that the disinfection ability of ClO_2 appears to improve as the pH increases. We have also observed[4], that as the pH increases, ClO_2 tends to adsorb more strongly to surfaces than at lower pHs.

In summary, this article provides useful data regarding the impact Cl_2 has on various RO membranes. It does not, however, provide useful data regarding the relative impact other oxidants have, because the authors have made erroneous conclusions regarding how much of other oxidants are the equivalent to chlorine in real world use concentrations. For example, in relatively clean systems, i.e., surface water disinfection or other similar systems, the relative dose rate would be (San Jacinto unclarified river water - Houston) approximately 8 ppm Cl_2 and 2 ppm ClO_2 to meet demand.

Because the reaction chemistries are so different, as the level of contamination increases, the Cl_2/ClO_2 ratio changes. In some dirty systems, Cl_2 demand might increase, for example, to 20 – 30, while the increase in ClO_2 might only be to 3 to 4. That is, an increase in demand for Cl_2 will not result in a corresponding increase in demand for ClO_2, because the ClO_2 does not react in general with organics in the same way and to the same degree that Cl_2 does.

3. Work by Adams

Adams[5], in 1990, made similar observations and performed experiments on various RO membranes under more real-world conditions. Membranes he tested included DuPont's B-15, FilmTec's FT-30, Desalination systems' 2B, and UOP's MP and L.

In general, Adams stated that the common practice of using the concentration X time data (ppm oxidant X hrs of operation) to look at membrane life when exposed to oxidants is misleading. He also stated that high concentrations of ClO_2 are aggressive to membranes. However, he also stated that at concentrations < 1.0 ppm, membranes were found to have a much greater tolerance for ClO_2 than for Cl_2. This is important because ClO_2 is known to retain its excellent biocidal characteristics at that concentration. In addition, because ClO_2 is a gas, it can permeate through the membrane and can provide biocidal protection downstream of the RO unit.

4. Work by Bohner

Bohner and Bradley[6], in 1990, investigated the use of acidified chlorite to clean Polysulfone membranes. They found that ClO_2 can be used to disinfect RO membranes. ClO_2 was not found to be effective at removing inorganic deposits.

Bohner and Bradley[7], in 1991, investigated the use of ClO_2 as a sanitizer in ultrafiltration systems commonly found in dairies. In particular they were interested in determining the corrosivity various formulations containing ClO_2 would be if used intermittently.

They found acidified chlorite (acidified with HCl) was very aggressive to stainless (low pH and high chlorides), but that ClO_2 made from acid/bleach/chlorite was not corrosive.

Their work concluded that ClO_2 can be used safely for sanitation of UF systems at a concentration of 15 ppm and near neutral pH.

5. Work by Averett: In 2003, results were presented describing an effort to clean up a badly fouled RO membrane in a Southwestern Power Plant[8]. The following points were thought to be important.

a. An ounce of prevention is worth a pound of cure. That is, it is much easier, less time consuming, and much less costly to prevent or control bacterial biofilm buildup in an RO system than it is to try to clean up a severely fouled RO system.

b. Water to the RO should be very well disinfected – this will involve using either ozone or ClO_2, as these oxidants provide a much more complete kill than other oxidants.

c. Periodically provide a ClO_2 disinfection and soak program to multimedia filters during the backwash procedure. This will minimize the potential for the multimedia being a site of bacterial growth.

d. Provide a continuous feed of chlorine-free ClO_2, at a rate of ≤ 0.1 mg/L (preferably 0.01 – 0.05 mg/L). Even this low a ClO_2 residual has shown to be able to not only prevent, but clean up established biofilm in cooling tower fill, even when gray water is used as tower makeup.

e. With some routine, the frequency to be determined and dictated by the needs of the specific application, a periodic 'cleaning' procedure using ClO_2 sequentially with a good alkaline RO cleaner followed by a reverse-flow ClO_2 cleaning step, should be employed.

f. Chlorine dioxide chemistry is fairly complex. An in-depth knowledge of ClO_2 chemistry, generation, and analytical idiosyncrasies is essential for the production, application, and measurement of chlorine-free ClO_2. Therefore, any group or person that is consulted with for assistance in this area should have an established track record of experience with references.

Summary by Averett: ClO_2 can be used to prevent fouling of RO membranes. In addition, ClO_2 can be used very effectively to disinfect RO feed if ClO_2 is fed to a level slightly higher than demand, say 0.01 – 0.05 ppm above demand. ORP could be used to control these dosages very effectively.

6. Other work

Saad, M., "Biofouling Prevention in RO Polymeric Membranes Systems," Desalination, Proceedings of the NWSIA 1992 Biennial Conference, Volume 2, Presented at National Water Supply Improvement Association 1992 Biennial Conference, Desalting and Recycling, August 23-27, 1992, Newport Beach, CA.

> "One of the most promising alternatives to chlorine is ClO_2. Studies show the great potential of chlorine dioxide due to its biocidal effectiveness, lack of harmful by-products, and its relatively mild effect on polymeric membrane structures. Removal of ClO_2 may not even be needed ahead of the membranes, providing a continuous disinfection throughout the entire membrane system at low dosages (1-2 ppm)."

References

1. Vos, K., et. al., "Desalination, 5, 157(1968).
2. "Saline Water Conversion Report," U.S. Department of the Interior, Office of Saline Water, 232, 1966.
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4. Simpson, G., unpublished results, 1997.
5. Adams, W. R., "The Effects of Chlorine Dioxide on Reverse-Osmosis Membranes," Desalination, 78(3), 439 (1990).
6. Bohner, H., and Bradley, R., "Effective Control of Microbial Populations in Polysulfone Ultrafiltration Membrane Systems," Journal of Dairy Science, 73, 2309(1990).
7. Bohner, H., and Bradley, R., "Corrosivity of Chlorine Dioxide Used as a Sanitizer in Ultrafiltration Systems," Journal of Dairy Science, 74, 3348(1991).

Averett, W., Simpson, G., and Miller, J., "Cleaning RO Membranes with Chlorine Dioxide," Southwest Chemistry Conference, sponsored by TXU Energy, Dallas, Texas, July 28 – August 1, 2003.

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