Reducing the Fouling Rate of Surface and Waste Water RO Systems

WAYNE T. BATES, Hydranautics, Rockton, IL. USA

IWC-98-08

Keywords: fouling, reverse osmosis, membranes, surface water, waste water, biocides

Summary: This paper discusses technical advances to reduce the rate of fouling due to organic, colloidal and biological foulants. These advances will focus on a new low fouling composite polyamide RO membrane with a neutral surface charge and the institution of biological control programs.

INTRODUCTION

This paper will focus on recent technical advances on how to reduce the rate of organic, colloidal and biological fouling of Reverse Osmosis (RO) systems for notoriously difficult feed water sources. Market applications of RO technology will become more accessible for the treatment of surface waters, municipal secondary or tertiary waste waters, landfill leachate, laundry gray water, and industrial process waste waters. Areas of discussion include:

- A review of critical RO system design and operating considerations.
- The use of a new low fouling composite polyamide RO membrane that has a neutral surface charge for reduced organic fouling.
- A review of RO pretreatment for reduced colloidal and biological fouling.

It has been observed that the use of a neutrally charged Low Fouling Composite (LFC) polyamide membrane reduces the rate of attraction of charged organic and colloidal material from the feed water. This is the same observation seen in the past when a neutrally charged Cellulose Acetate (CA) membrane operated on difficult feed waters. A significant reduction in fouling rate and improved cleanability has been observed using this LFC membrane, without sacrificing the advantages of higher salt rejection, lower feed pressure, higher flux, and a broader pH range associated with commercially existing negatively charged Composite Polyamide (PA) membranes.

Biological control programs will be discussed in conjunction with the use of this new LFC membrane. The LFC membrane has a similar chlorine tolerance level as existing PA membrane and have to be protected from biological fouling.

RO SYSTEM DESIGN AND OPERATING CONSIDERATIONS

A conservative, carefully planned out total system design is required for an RO system treating difficult waters. Competent application engineering comprised of a series of sound engineering decisions and proper on-site operations will increase the chances of a successful application. The following criteria must be addressed :

1. Feed Water Characterization: The importance of a detailed water analysis showing minimum, maximum and average levels of ions and potential foulants cannot be over emphasized, especially when the feed source can experience seasonal or process fluctuations. A pilot plant may be prudent for the development of the optimal pretreatment scheme and RO design parameters.

2. RO Pretreatment: The most important design consideration is proper pretreatment for the removal and control of foulants. When dealing with difficult feed waters, the engineer must make a decision as to whether to use conventional pretreatment techniques or to use crossflow MF or UF systems to minimize RO fouling due to colloidal, organic and biological foulants. Included in this is the need for a carefully planned biological control program to minimize the rate of biological fouling for biologically active feed waters.

3. RO Element Selection: .A large number of choices exist when selecting an RO element. This includes evaluation of membrane type, membrane surface charge, fouling resistance, active membrane area in the element, feed pressure requirements and rejection levels of dissolved ions and organics.

4. Flux Rate: The rate of membrane surface fouling is a function of the permeate flux rate, measured as GFD (Gallons per square Foot of membrane area per Day). The lower the flux rate, the lower the rate of fouling. The relationship of fouling rate to the flux has been demonstrated both during laboratory tests and in field operation. The most recent university research work was reported by Elimelech [1,2] from the University of California, Los Angeles. This report concluded the increase in fouling rate with higher flux is a result of higher concentration of organics at the membrane surface and a higher drag force perpendicular to the membrane surface

5. Cross Flow Velocity: The higher the cross flow velocity parallel to the membrane surface, the lower the rate of fouling. Foulants are flushed away from the membrane surface by the higher shearing action. Higher area membrane elements allow for the use of fewer pressure vessels and higher feed and concentrate flows.

6. System Flushes and Shutdown: The biological fouling rate can increase dramatically when the system is idle and no water is flowing. The system should be flushed to remove foulants on shutdown, startup, and even intermittently during standby. The best low-pressure flushes are performed at high crossflow velocities using RO permeate quality water. A RO soaked with permeate quality water can help loosen existing foulants.

7. Normalize Data: To understand how the RO is operating when process variables fluctuate, the operator logged data must be normalized to determine the rate of system fouling. Normalization programs have been developed that calculates and charts normalized feed-to-reject pressure drop, normalized permeate flow and normalized per cent salt passage. These normalized parameters are calculated by comparing current conditions to those in the first day of operation with adjustments made for changes in major variables such as temperature, feed TDS, recovery and pressures.

8. Proper Cleaning Operation: Operators must be instructed to run the RO system properly by cleaning when mildly fouled, not severely fouled. The RO should be cleaned whenever the normalized pressure drop increases by 15%, the normalized permeate flow decreases by 15%, or the normalized per cent salt passage increases by 15%. A well

designed cleaning operation includes the ability to clean stages separately to achieve optimal crossflow velocities.

A LOWER FOULING RO MEMBRANE

The best RO element to reduce fouling rates is one that has a neutrally charged surface to minimize the attachment of charged foulants, can be used with a biocide to control biological fouling, and has a high surface area to decrease flux and increase cross-flow velocity. In the past, the cellulose acetate (CA) membrane with its neutral surface charge and a resistance to biocidal chlorine up to 1 ppm or 26,280 ppm-hours, exhibited the best fouling resistance for difficult water applications. However, the CA membrane had pH limitations, higher feed pressure requirements, and higher salt passage when compared to the popular negatively charged composite polyamide (PA) membranes. Today, a new generation of Low Fouling Composite polyamide (LFC) membrane is available. The LFC membrane has the unique advantages of equivalent rejection and feed pressure requirements of a durable PA membrane and the neutral surface charge of the CA membrane (see Figure 1). A limitation to the LFC membrane is that being a polyamide membrane it has a chlorine tolerance level similar to PA membranes of approximately 1,000 ppm-hours.

Figure 1: Comparison of RO Membranes

	LFC	PA	CA
Membrane polymer	Polyamide	Polyamide	Cellulose acetate
Surface charge	Neutral	Negative	Neutral
NaCl rejection	99%	99 to 99.7%	95 to 98%
Organic rejection	Similar	Similar	Lower
Test Pressure	225 psi	225 psi	420 psi
Specific flux (gfd per 100 psi of NDP)	13	13	5 to 6
Feed pH range	3 to 10	3 to 10	4 to 6
Temperature limit	113 F (45 C)	113 F (45 C)	104 F (40 C)
Chlorine tolerance	1000 ppm-hr	1000 ppm-hr	26,280 ppm-hr
Hydrophilicity	47° angle	62° angle	50° angle

The reduced fouling capability of the LFC membrane is the result of new membrane chemistry. The membrane is permanently modified during the casting process to produce a neutral surface charge and a more hydrophilic membrane surface. The combination of a neutral surface charge and increased hydrophilicity minimizes the adsorption of hydrophobic organic foulants (e.g. humic matter) onto the membrane surface. Flux degradation due to the build up of foulants that are organic in nature, hydrophobic metal gels (e.g. iron), and charged colloidal material is minimized. Just as important for long term operational stability is the enhanced ability to remove foulants and restore the system flux with periodic flushings and/or chemical cleanings.

The LFC membrane can operate with either acidic or basic feed waters and still maintain its neutral surface charge. The surface charge of three membranes over a pH range of 3 to 10 were analyzed quantitatively by measuring the Zeta Potential using Laser-Doppler electrophoresis equipment. The LFC membrane maintained a relatively neutral surface charge of –3 to +5 millivolts (mV). The conventional PA membrane has a negative charge of –5 to –21 mV between a pH of 4 to 10 due to the disassociation of the carboxylic groups in the polyamide chain. Interestingly, the PA membrane at a pH less than 4 actually exhibits a positive charge due to the disassociation state of the amine groups in the polyamide chain. [3] (See Figure 2).

The LFC membrane, in the same fashion as the CA membrane, can operate with foulants of varying charges with minimal or no loss of flux. The conventional negatively charged (anionic) PA membranes are notorious for a dramatic irreversible loss of flux when exposed to cationic (positively charged), amphoteric (either positively or negatively charged based on pH conditions) and neutral polyelectrolytes which are so popular as potential pretreatment and cleaning chemicals (e.g. coagulants, flocculants, surfactants, detergents). Figure 3 depicts the excellent flux stability of the LFC membrane when challenged with cationic, anionic, amphoteric and neutral surfactants. [3]

The LFC membrane is being operated on a tertiary municipal effluent at the waste water treatment plant at San Pasqual, Ca USA. The pretreatment prior to the RO consists of capillary ultrafiltration. The LFC membrane is being compared to an ESPA membrane, a low-pressure negatively-charged composite polyamide membrane. The system is operated at a flux rate of 10 gfd (17 l/m^2hr). Figure 3 shows the ESPA membrane starts at 25% less feed pressure when clean due to its lower specific flux. However, within days the LFC operates at lower feed pressure due to organic fouling of the negatively charged ESPA membrane. Both membranes have established stabilized fluxes, but the LFC operates at 30-35% less feed pressure. The salt rejection for both membranes after 2000 hours of operation have stayed above 99%. [3]

RO PRETREATMENT SYSTEMS

Any paper on the use of RO membranes for difficult water sources would be remiss without a discussion on critical pretreatment requirements. In general terms, the application engineer should design the pretreatment for LFC to the same standards as if a conventional PA membrane was being used.

Organic Fouling: The LFC membrane offers significant advantages in long term and recoverable flux stability when compared to conventional PA membranes when the foulant is an organic. This capability makes removal of organics in the pretreatment less of an issue than in the past. Though no definitive level of acceptable organic content in a RO feed water exists, an alert level for the designer to consider LFC over a PA membrane could be considered to be 3 ppm TOC (Total Organic Carbon as C), 6 ppm BOD (Biological Oxygen Demand as O_2) or 8 ppm COD (Chemical Oxygen Demand as O_2).

Colloidal and Suspended Fouling: This pretreatment requirement includes the filtration of colloidal and suspended particles to turbidities of less than 1.0 NTU and a 15-minute SDI (Silt Density Index) value of less than 4.0. Excessive volumes of colloidal and suspended material will plug the RO element feed path, regardless of the membrane type.

Conventional pretreatment schemes in the past have utilized a myriad of technologies such as clarifiers, lime softeners, sand filters, carbon filters, iron filters, multimedia filters, and chemical feeds to flocculate and coagulate. In the last few years, there has been a greater acceptance in the industry to the use of cross-flow microfiltration (MF) and ultrafiltration (UF) membrane systems. The increased use of MF and UF have been driven by a number of factors. Capillary membrane technology has always produced RO feed water of significantly better and predictable quality than conventional pretreatment systems, but now is being recognized as being both cost-effective and capable of stable operation.

Biological Fouling: This pretreatment requirement is difficult to characterize or quantify in the design phase of an RO system. It can be expected that in RO systems where biological activity results in slimy biofilm formations, the problem can be found in the pretreatment system back to the point where no biocide is present and in the RO. This type of fouling process will plug the RO element feed path, irrespective of the membrane type. Permeate flux will decrease and the feed-to-concentrate pressure drop will increase. Excessive pressure drop may result in mechanical damage of the RO elements. Design wise, minimizing piping dead-legs and avoiding the use of carbon filters can minimize biological fouling. Operationally, sanitizing the RO pretreatment equipment and RO equipment prior to loading RO elements and continuous running of the RO system after start up is important in minimizing the build up of the biofilm.

The long-term answer in controlling biological fouling lies in the institution of a “biological control program”. The program has two major parts:

- Control biological fouling during the service and offline modes using a continuous or periodic introduction of a biocide.
- Establish an effective sanitization and clean

up regiment after the RO becomes biologically fouled.

To date, there is no “perfect” biocide for use with the LFC or PA membrane. The “perfect” biocide for these membranes would have the following properties:

- Does not damage the membrane.
- Controls and kills all strains of bacteria and biofilms
- Physically breaks up existing biofilms
- Compatible with all system components
- Non-toxic and easy to handle
- Easily disposed of and bio-degradable
- Easily monitored and injected
- Disinfects the permeate side of the membrane
- Inexpensive

Chlorine: The LFC membrane, like the PA membrane, has limited chlorine tolerance of approximately 1,000 ppm hours and requires that the RO feed be dechlorinated to less than 0.1 ppm. Normally, membrane life is defined as three years and/or when salt passage doubles. Chlorine tolerance is further reduced by the presence of insoluble iron, which acts as a catalyst in the oxidative attack of chlorine. Chlorine damage of the membrane is easily identifiable by decreased salt rejection, increased flux, and by a factory dye test. Presence of chlorine damage will effectively void the membrane warranty. However, in recent years there have been some field experiments using continuous and intermittent chlorination during the service mode by end-users who have experienced severe bio-fouling problems. These end-users have had to assess and assume the risks mentioned above versus the benefits of chlorine as a biocide. The benefits of chlorine is that it is an effective biocide, inexpensive, controls the volume of the biofilm mass, a portion of it passes through the membrane to sanitize the permeate side, it could extend the useful life of the membrane by sparing it from harsh cleanings and irreversible fouling conditions, or at least reduce the hassles of frequent cleanings and sanitizations. One train of thought for systems with a biofilm suggests that by controlling the chlorine dosing, the amount of chlorine that actually makes it to the membrane can be minimal as the chlorine is consumed by the biofilm. One end-user has reported that a “chemotherapy” approach of chlorine shock dosing at 0.25 ppm for four hours per day has reduced his cleanings by a factor of ten over a period of 15 months, with no reportable loss of salt rejection when compared to a test train that had no chlorine introduced. [4] The passage of chlorine into the permeate will vary by system, but has been observed at 20 to 50% of the feed level.

Chloramines: The use of non-oxidizing chloramines as a continuously fed biocide has gained interest recently. Typically, LFC and PA membranes can have a chloramine tolerance of 150,000 to 300,000 ppm-hours before a noticeable increase in salt passage. The 300,000 ppm-hours level correlates to a chloramine level of 11.4 ppm for an operating period of 3 years. RO designers are cautioned that it has been observed in a few applications that this chloramine tolerance can be much lower due to the catalytic effects of high temperature, low pH, or presence of transition metals. Chloramines are produced by adding ammonia to chlorinated water. If the mix is not perfect, there can be either residual free chlorine or ammonia. The residual free chlorine would require dechlorination using a sodium bisulfite feed or carbon filtration, but this can also result in dechloramination with a resulting increase in ammonia gas or ammonium ion levels. Caution is required in that the increased presence of sodium bisulfite or ammonia or ammonium can invite biofilm growth if all the chloramines were removed. Ammonia is known to be corrosive to any downstream non-stainless steel metal fixtures. The passage of chloramines into the permeate is relatively high, and has been observed at up to 80% of the feed level. The passage of ammonia into the permeate is 100% since it is a gas. Since ammonium is a monovalent cation, it is well rejected.

Isothiazalon: The use of non-oxidizing isothiazalon as a continuously or intermittently fed biocide (or slimicide) has also gained interest recently as it is causes no degradation of the LFC or PA membrane. Isothiazalon is available under the Rohm & Haas brand name Kathon, Betz brand name Slimicide C-68, or Argo brand name Rogun 781. This biocide is hazardous, so special handling precautions are warranted and should not be used for systems producing potable water. Typical dosing on a continuous basis can be 3 to 5 ppm of active ingredient, but actual dosing should be based on achieving a near zero residual in the reject stream. Intermittent shock dosing levels of 15 to 25 ppm for at least a couple of hours can be effective, but rapid regrowth of the biofilm is possible if conditions are proper. There is basically no passage of this biocide into the permeate due to its large molecular weight. This biocide is expensive to buy, but the savings in reduced cleanings, longer membrane life and more stable operation of the RO over time should result in a justifiable payback.

Hydrogen Peroxide/Paracetic Acid: The use an oxidizing type biocide solution of hydrogen peroxide and paracetic acid for offline sanitizations has been popular since the 1980's for PA membranes, especially for RO systems having to meet FDA or potable drinking water requirements. Hydrogen peroxide alone could be used as a biocide at a 2,000 ppm dosage, but the addition of 450 ppm of paracetic acid dramatically improves its rate of bacterial disinfection to less than one hour and breaks down a biofilm in about four hours. Temperature has to be maintained between 20 and 25 °C for an effective disinfection while protecting the membrane. Special care must be taken that transition metals (e.g. iron or manganese) are not present in the feed water and the membrane surface is cleaned of these metals as they can catalyze an oxidative attack of the membrane.

Other biocides and biological cleaning chemicals: The industry's best hope in developing better "biological control programs" resides with specialty RO chemical suppliers. The development of new biocide products (e.g. enzyme based slimicides) and their proper application will be important in operating LFC and PA membrane systems on difficult water sources.

CONCLUSION

As the water treatment industry enters the new millennium, the ability to treat difficult surface and waste waters that are notorious for having high organic, colloidal and biological fouling potential using membrane technology will open a number of new markets. The introduction of LFC, the first neutrally charged polyamide RO membrane, addresses the issue of how to accommodate organic foulants. The increased popularity of capillary MF or UF membranes addresses the issue of how to accommodate colloidal foulants. Advancements are being made in the development of biological control programs using biocides of different types to accommodate biological foulants.

References:

1. X. Zhu and M. Elimelech. "Fouling of Reverse Osmosis Membranes by Aluminum Oxide Colloids". Journal of Environmental Engineering, December 1995, 884-892.
2. S Hong and M. Elimelech. "Fouling of Nanofiltration Membranes by Natural Organic Matter", proceedings of 1996 ADA Conference, Monterey, Ca. USA, August 1996, 717-727.
3. R. Gerard, H. Hachisuka, M. Hirose. "New Membrane Developments Expanding the Horizon for Application of Reverse Osmosis Technology", proceedings of 1997 Aquatech 98 in Amsterdam, the Netherlands.

4. B. Karnaugh, J. Jaminet, B. Shelton. "Biofouling Management of the TIME DI Water RO Plant by Direct Periodic Chlorination", Ultrapure Water July/August 1998.

Figure 2: pH Effects on Membrane Surface Charge

Figure 3: Membrane Exposure to Surfactants

Figure 4: LFC Flux Stability at San Pasqual