Pretreatment for Membrane Processes

Reverse osmosis (RO) and Nanofiltration (NF) have long been utilized for desalination, softening and contaminant removal. As the available ground water, fresh water and "clean" water sources are depleting globally, RO/NF technologies are being applied to surface waters, wastewater and ground waters. These types of source waters have substantially more particulate matters, organic substances and other solids which may not be compatible with RO/NF membrane processes. Both technologies are manufactured, designed and built for "salt" and dissolved ion removal and not particulate matter. Therefore, proper pretreatment plays a critical role in the performance, life expectancy and the overall operating costs of these systems.

Although the salt rejection characteristics of RO/NF membranes are well known to the industry since the 1980's, compatibility of feed water particulate matter, fouling/scaling rates, impact on membrane life and membrane degradation due to "poor" source waters are still being analyzed by engineers, manufacturers and end users. Unfortunately some of these problems are found after facilities are built and put in service. This is a crime, since multi-million dollar investments are at stake and improper application gives membranes a bad name. In fact, those of us involved in the membrane industry strongly believe that it is not the membranes that fail, it is improper application or inadequate pretreatment which causes failures.

Since the manufacturing process, element properties and to some degree behavior of NF spiral wound elements are the same as RO, most of the discussion in this article applies to NF systems as well as RO systems.

Source Water Assessment
The first and most important step in RO system planning and design is to assess the source water quantity and quality. For the water quality, which is our focus here, it is crucial to get adequate information, not just a snapshot, but a historical view of the source water quality. Table 1 is the minimum extent of water quality analysis required. For some of the parameters such as TOC, TSS, temperature, pH etc, historical data is required to establish the minimum, average and maximum expected values to be able to properly plan and design the system. For some of the parameters as noted, measurement should be done on site

Table 1: Minimum Required Water Quality Analysis	
Aluminum*	Ortho Phosphate
Ammonia	Potassium
Arsenic	Selenium
Bacteriological (coliform)	Silica Colloidal (as Sio2)
Bacteriological (Total)	Silica Soluble (as Sio2)
Barium *	Silver
Bicarbonate	Sodium
Cadmium	Strontium*
Calcium	Sulfate
Carbonate	Total Alkalinity (m value)
Carbonate Alkalinity (p value)	Total Dissolved Solids
Chloride	Total Hardness
Chlorine	Total Iron*
Chromium	Total Organic Carbon
Color	Total Phosphate
Conductivity	Total Suspended Solids
Copper	Turbidity (NTU)
Dissolved Iron*	Zinc
Fluoride	
Free Chlorine	PRIMARY & SECONDARY MCL's
Lead	
Magnesium	**On Site Measurements**
Manganese	Temperature
Nickel	PH
Nitrate	Carbon dioxide
	Hydrogen Sulfide
* Recommended to be measured in ug/L	

since the property will change with time and method of sample handling.

Pretreatment Objectives
The primary objective of pretreatment is to make the feed water to the RO compatible with the membrane. Pretreatment is required to increase the efficiency and life expectancy of the membrane elements by minimizing fouling, scaling and degradation of the membrane.

Fouling refers to entrapment of particulates, such as silt, clay, suspended solids, biological slime, algae, silica, iron flocs and other matter on the surface, or even worst, within the membrane pores. Typically fouling occurs in the lead elements of the first stage initially and then it works itself through the following elements. Depending on the operating conditions and water chemistry some metals, such as soluble iron and manganese, oxidize once they are within the membrane system and can precipitate anywhere throughout the RO system. Similarly,

microbes can grow and spread throughout an entire RO system. Microbiological and organic fouling are perhaps the most common types of foulants and more difficult to control in surface water and wastewater applications.

Scaling refers to precipitation and deposition of sparingly soluble salts such as Calcium Sulfate, Barium Sulfate, Calcium Carbonates, Silica, Calcium Fluoride and any other super saturated salt on the immediate surface of the membrane. Typically scaling starts on the tail elements of the last stage (on the reject side), since they are treating water with the highest concentrations of ions. Once a crystal of scale forms within the membrane element, it acts as a nucleation site for additional scales to form and the rate of scale formation increases exponentially.

Inadequate pretreatment often necessitates frequent cleaning to restore product flux and salt rejection. This results in excessive chemical cleaning costs, increases system downtime, and in severe cases will result in permanent loss of performance, membrane degradation and therefore shorter membrane life.

Table 2: Guidelines for Acceptable RO / NF Feed Water

Parameter	Recommended Maximum Value
Turbidity	0.5 NTU
TOC	2 mg/L
Iron 1	0.1 mg/L
Manganese	0.05 mg/L
Oil & grease	0.1 mg/L
SDI 15	3
VOC's 2	In ug/L range

1- If absolutely no chance of air entry / oxidation and pH< 7, values as high as 1-2 mg/L may be acceptable.
2- Higher concentrations may damage the element glue line.

Pretreatment Guideline
The proper pretreatment of raw water to make it compatible as a feed water to RO must involve a total system approach for continuous, consistent and reliable operation.

The type and extent of a pretreatment system will depend on the type of source (i.e. well water, beach wells, open sea, surface water or partially treated wastewater). The major difference is not only the feed water composition, but also water quality variability by seasonal factors, climate conditions and/or activities on the surface waters.

Table 2 is a general "loose" guideline for acceptable feed water to an RO/ NF system. It should be noted that there is not a set standard among the industry for such a criteria. One of the reasons is that system design and operational parameters do play a role on potential fouling/scaling of an RO system. For example systems with higher recovery tend to foul quicker and may have a higher potential for scaling due to the fact that membrane actually sees a higher concentration of ions and impurities.

Most element manufacturers have similar guidelines but may not be as stringent since their recommendations are an absolute maximum, meaning if they are exceeded the warranty will be void. In general terms, the lower these values are the more reliable the performance, coupled with less frequent cleaning and longer membrane life. The recent generation of "low fouling" elements is believed to have more tolerance to some of the parameters listed in Table 2. Please refer to the element manufacturers for their guidelines.

Silt Density Index (SDI) test is generally viewed as an indicator for potential colloidal fouling. The standard SDI test (ASTM D-4189) is inexpensive, quick and simple to perform. However, there is significant disagreement in the RO industry on its usefulness and scientific validity. Moreover, although it is not the most scientific test, it is a good indicator of changes in the feed water and visual inspection of the membrane pad may reveal potential upstream problems early.

Pretreatment Options
RO pretreatment typically consists of "none" to a complex, comprehensive system for poor raw waters. The pretreatment systems can be chemical, mechanical or a combination. Tables 3 and 4 present a list of potential pretreatment options which are routinely utilized for RO systems.

Pretreatment is generally considered to be sufficient when membrane cleaning is limited to 3-4 times per year or less,

Table 3: Potential RO/NF Chemical Pretreatment Options

Technique	Purpose
Coagulants / polymers	Added as a part of coagulation / flocculation process to improve solid removal
Scale Inhibitors	Allow new compounds to be formed which have a better solubility properties and some absorb to the surface of the micro-crystals thereby reducing further crystal formation
Antifoulants	Help keep some compounds such as Iron in suspension
Acids	To lower pH and therefore reduce scaling potential of some compounds such as Carbonates
Bisulfites	Dechlorination

Table 4: Potential RO/NF Mechanical Pretreatment Options

Technique	Purpose
Pre-Screens	Large objects and sand removal
Cartridge Filter	Protection of membrane elements
Clarifier	Suspended Solids reduction
Media filtration	Suspended Solids removal
Activated carbon	Organic removal and dechlorination
Greensand Filters	Iron / Manganese reduction
Ozone	Organic removal and reducing biological activities
UV	Reducing biological activities
Full conventional plant (coagulation, flocculation, sedimentation and media filtration)	Particulate, organic and biological activity removal
Microfiltration / Ultrafiltration	Particulate and bacteria removal and organic reduction

1- If absolutely no chance of air entry or oxidation and pH<6.5 (reduced state), values as high as 1-2 mg/L may be acceptable.
2- Higher concentrations may damage the element glue line.

membrane elements last over 5 years and the productivity and salt rejection are maintained within the expected ranges.

The more comprehensive and complex the pretreatment becomes, the more it should be viewed as a separate system and not a side process component.

Seawater RO Pretreatment
Pretreatment for Seawater RO is often more critical than groundwater, because most large seawater plants use open intakes that supply raw water possessing more pollutants (oil & grease, algae, phytoplankton), fluctuations in turbidity, organic content and biological activities (Red Tide for example).

Raw water variations can significantly impact the SDI measured from the pretreatment system. Fluctuating and often high turbidities combined with frequently high levels of organic, microbial and colloidal constituents are the root cause of the ailments of open-intake based SWRO pretreatment systems. Recent studies have found that inadequate pretreatment, including coagulant addition and biofouling mitigation, may account for over 60% of SWRO system failures as shown in Figure 1. The impact of inadequate or ineffective pretreatment can be any or a combination of the following:

- Accelerated increase in net driving pressure

- Accelerated reduction in normalized permeate flow

- Accelerated increase in pressure drop across the vessel
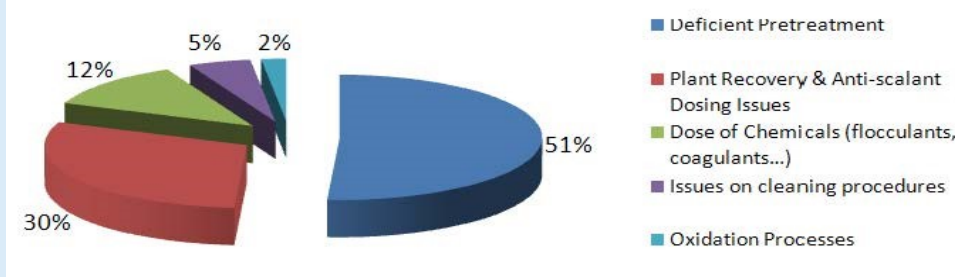
- Increase in the RO cleaning frequency

- Reduced RO membrane life as a result of increased RO cleaning

- Reduced plant availability as a result of increased RO cleaning.

The result of these operation impacts is a direct increase in the operational costs of the seawater RO (SWRO) facility.

In the past two decades there have been many large seawater RO plants constructed, with various types of pretreatment, ranging from direct filtration to Integrated Membrane Systems (IMS) which utilizes MF or UF as a pretreatment to SWRO.

The degree of pretreatment and unit processes depends on the source water variability and quality as discussed. Three major unit processes currently utilized in SWRO pretreatment are as follows:

Direct Filtration: The most common method of providing pretreatment for SWRO is the use of coagulation, inline flocculation and dual-media filtration. This method generally is very effective at treating good quality seawater to SDIs of less than 4. When treating degraded seawater, the addition of sedimentation basins may be required for reliable |performance of the filters. Increasingly, treatment of pretreatment residuals prior to liquid discharge is required, particularly in North America and Australia. The cost associ-

ated with adding thickening and dewatering in seawater resistant materials is substantial (5%-10% of facility cost) and can often be avoided or minimized if coagulant is not required.

Dissolved Air Flotation (DAF): Various studies and full scale plants on seawater indicate that DAF can enhance the performance of downstream unit processes. The use of DAF as pre- treatment in seawater desalination may possess additional advantages over conventional coagulation/flocculation/filtration by preferentially removing oil & grease, plankton, algae and Red Tide organisms from the raw water.

Figure 2: Growth in MF/UF Pretreatment Capacity in SWRO

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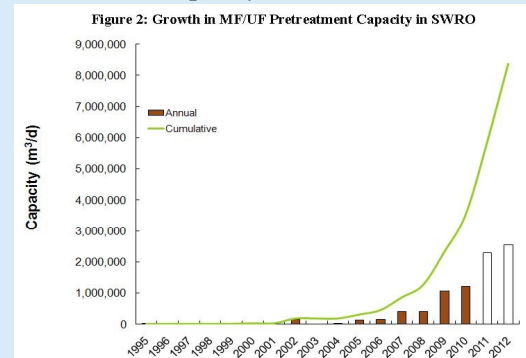
Integrated Membrane Systems (IMS): Although the application of low pressure membrane technology has been documented to provide superior pretreatment to RO seawater desalination systems, the increased capital and sometimes operating costs and limited full-scale experience (on seawater) associated with these technologies have constrained their application in full-scale facilities in the past. In recent years, continued reduction in costs have resulted in MF/UF technologies being cost competitive with conventional treatment processes. As a result, the total installed capacity has grown significantly as shown in Figure 2. As a result, more installations are enjoying the advantages of MF/UF pretreatment, which include filtrate with very low and consistent turbidity and SDI,

Figure 1: Causes of SWRO Failure

in most cases superior to that of conventional filtration.

It is important to conduct pilot studies when deciding on the optimum pretreatment to evaluate the ability to reliably clean the MF/UF membrane over its projected life. Much of the early literature published on the use of MF/UF as pretreatment for SWRO focuses on MF/UF system filtrate turbidity and SDI. It is critical to ensure that the fouling problem has not just been transferred from the SWRO to the pretreatment process.

Various MF/UF pretreatment technologies are being applied in SWRO applications, with ten different suppliers of either spiral-wound or hollow-fiber technologies. This number is anticipated to grow as ceramic membranes and new technologies from developing markets are implemented.

The following are just a few examples on how pretreatment impacts the RO and post treatment.

Example A: Overdosing of coagulants in a coagulation/filtration pretreatment may in fact cause RO element fouling by the iron flocs carried over from the pretreatment to the RO system.

Example B: If chlorination is used to control microbiological growth in the pretreatment, overfeeding will cause degradation of Thin-Film Composite RO elements.

Example C: An activated carbon pretreatment used for organic removal or dechlorination may actually encourage biological growth due to the tendency of carbon beds to incubate microbes.

Example D: Frequently, metals such as Iron, Aluminum, Cobalt, and sometimes Arsenic are found as impurities in pretreatment chemicals. Care should be taken to specify proper chemicals with strict limitations on impurities.

Example E: Microfiltration / Ultrafiltration as a part of an Integrated Membrane

System have been shown in pilot studies and full scale applications to provide the most suitable feed water to downstream RO systems. However, care should be taken to view, design and operate the MF/UF pretreatment as a separate system with its own consideration for fouling, and not "solve" the RO fouling problem by transferring it upstream to the MF/UF system.

Example F: Selection of pretreatment may impact post treatment. A good example would be if acid is used to lower the pH of the feed water (for reducing scaling potential), the carbonate will convert to the CO_2 which may need to be removed with a degasifier process in the post treatment.

Example G: Some cationic polymers used in the pretreatment process may actually co-precipitate with negatively charged scale inhibitors and increase fouling potential.

Example H: If a substantial amount of sulfuric acid is added to reduce feed water pH, it may increase sulfate scaling potential due to additional sulfate from the acid.

Conclusion

There is not a single solution for an acceptable RO/NF pretreatment system. The solution depends on raw water composition, seasonal and historical water quality changes and the RO/NF system operational parameters. The "loose" guidelines given in this article are suggestions only and are subject to debate, as has been common in the membrane industry for over 20 years!

However, the importance of a system approach and adequate pretreatment needs cannot be over emphasized. It has also been proven that relying on frequent cleaning to "wash away" the pretreatment inadequacy is not the optimum solution and is definitely not an industry acceptable practice.

This material has been prepared as an educational tool by the American Membrane Technology Association (AMTA). It is designed for dissemination to the public to further the understanding of the contribution that membrane water treatment technologies can make toward improving the quality of water supplies in the US and throughout the world.

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