utilization of chemical treatments to maintain and restore membrane performance

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abstract

A reverse osmosis unit's reliability is an important consideration for anyone dependent on its smooth operation. Good maintenance practices improve reliability and reduce operating costs. Treatment chemicals can be an important part of a comprehensive maintenance program. Preventative maintenance can be enhanced through the targeted use of chemicals to minimize fouling, deposition and precipitated scales. When circumstances call for remedial action to restore performance, specialized chemicals can bring a system back to acceptable operation at a reasonable use cost. These materials can be applied on-site by the user, or the process can be performed off-site with several additional benefits.

introduction

When a new set of reverse osmosis elements is installed, performance begins to decline immediately. Membrane manufacturers tell us that normalized flux declines by roughly 10% in the first 30 days of operation. This is truly a best-case scenario, as it takes into account only the properties of the reverse osmosis membrane itself and does not take into account the many physical, chemical and biological processes that may combine to further reduce membrane performance.

Feedwater quality is a major determinant in the rate of performance decline a membrane system experiences. Suspended materials present in the water source foul elements beginning with the first stage. This can result in increased pressure differential and reduced flux. Dissolved minerals are concentrated as the feed passes through the brine-side of the membranes. As the mineral concentrations increase beyond saturation, salts precipitate. These salts tend to form in the tail elements first. The result is reduced flux and increased pressure drops in the final array. Bacteria can grow in any water, but they grow best in warm waters, and their optimal growth range overlaps with the typical feedwater temperature of reverse osmosis systems. Also, bacterial slimes can form in any part of the system. In practical experience, no one type of fouling occurs in isolation. In fact, each can influence the others, and it is common to have more than one problem foulant.

planning for success

The problems described above are well known among equipment designers and experienced system operators. There is no good reason for any of these problems to get out of control and compromise system reliability if they are considered and addressed before the system is commissioned and again regularly during its operation. Sound analysis, appropriate countermeasures and continual monitoring are required to maintain efficiency. Suspended solids, dissolved minerals, and biological activity each warrant its own treatments.

Suspended solids in a feed source are commonly measured by turbidity or SDI. The preferred levels for reverse osmosis feed are turbidity less than 0.1 NTU or SDI less than 5. These values are most commonly achieved by pretreatment equipment. Multimedia filters, activated carbon, bag filters, and cartridge filters are all intended to reduce particulate loading on reverse osmosis elements. During the design phase, there is a great deal of flexibility in the specification of the types, qualities, and sizes of filters. Frequently, water quality changes after the design is finalized. In other cases, the performance of the pretreatment equipment may not be as high as anticipated. Once the equipment is installed, there is very little flexibility in the equipment itself. The media in the multimedia filter or the cartridges in the pre-filter can be changed, but

generally there is no ability to add new unit operations. In this case, chemicals can be successfully applied to a multimedia filter.

Coagulant chemicals, sometimes called filter aids, are injected prior to the multimedia filter, and increase particle size so that solids are more readily captured by the filter. There are a number of common coagulants, but they all belong to one of a few groups.

- Inorganic coagulants are metal salts that react with alkalinity and precipitate as metal hydroxides or carbonates. The resulting precipitates interact with suspended solids forming larger particles. Common metal salt coagulants are ferric chloride, aluminum sulfate, aluminum chloride, and poly-aluminum chloride.

- Organic coagulants come in two classes. First, there are soluble, charged polymers. The positive charges on these polymers interact with the negative charges that naturally occur on colloids. The interaction leads to particle growth. The second group is self-precipitating organic polymers. These novel materials form a seed floc similar to inorganics. In either case, the mechanism of particle growth is one of charge-neutralization and agglomeration. As this is a complex process, it will not be covered in detail here. The net effect is that more suspended material is removed by the multimedia filter, and as a direct result outlet turbidities, and SDI's are reduced. As a rule, low-turbidity/high-SDI waters respond better to metal salt/polymer mixtures, while high-turbidity/high-SDI waters respond better to soluble polymers. Feed rates are typically 0.5 to 5 ppm. When a filter aid is used, backwash frequencies are generally increased, though the change is usually manageable, and the system performance benefit is worth the additional water use.

If chemical feed is not an attractive option for SDI reduction, there is a novel filter media that has shown promise as a replacement for the garnet, quartz, and anthracite that are commonly employed in multimedia filters. The media are glass beads that are chemically modified to maintain cationic charge without continuous chemical feed. The media has demonstrated particle size reductions on the order of 0.05 microns, which is similar to microfiltration. Conventional backwash is used to maintain the media,

and several times per year it is necessary to chemically clean and recoat the media.

Mineral scales can be formed by a number of materials, but the most common are calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, calcium fluoride, ferric hydroxide, aluminum hydroxide, and silica in its various forms. The saturation level of any given salt varies with temperature, with the concentration of other ions and often with pH. These factors must be taken into account when designing or monitoring a system. Table 1 shows the saturation constant (K_{sp}) for the most common salts, as well as empirical concentration limits[1] for some of the materials. Also included is the maximum treatable range using commercially available antiscalant chemicals. These chemicals can contain phosphonates, dispersant polymers or a mixture of the two. Phosphonates act by disrupting the process of crystal formation, while dispersants impart an anionic charge to suspended or precipitated materials, thereby causing them to repel each other.

It is important to note that it may not be possible to achieve maximum treatable levels on all materials concurrently. For example, it may not be possible to sustain barium sulfate at 105 times saturation and simultaneously maintain iron at 1 mg/l. Salts and antiscalants interact, and that interaction is dependent on pH, temperature, the concentration, and nature of the antiscalant compound. In order to maintain an effective antiscalant program, it helps to be able to model the chemistry of the system under a variety of conditions. The calculations involved would make this unwieldy to do on paper, but the impact of treatment chemicals can be readily modeled using software programs provided by chemical suppliers. A good software package will take into account the effect of the variables mentioned above and will permit the user to evaluate different scenarios with respect to system recovery, throughput, pH, temperature, and mineral concentrations.

Bacteria are literally everywhere. They are in feedwater, on equipment surfaces and on the hands of the person changing cartridge filters. They grow well in warm water with organic material in it. They can grow in 18 megaohm water where one would think the water is too clean to support life. They are on membranes, feed spacers, and piping, and if they proliferate, they cause operational problems.

Table1. Guidelines for Mineral Scales in Reverse Osmosis Systems

Material	Limit without Treatment	Maximum Treatable in Brine
Calcium Carbonate	LSI or S&D Index** = 0.0	LSI or Stiff & Davis Index 3.0
Calcium Sulfate	Ksp 9.1×10^{-6}***	2.4 x's K_{sp}
Barium Sulfate	Ksp 1.1×10^{-10}	65 to 105 x's K_{sp}
Strontium Sulfate	Ksp 3.2×10^{-7}	30 to 35 x's K_{sp}
Calcium Fluoride	Ksp 5.3×10^{-9}	100 to 13,000 x's K_{sp}
Iron	0.05 mg/l at pH >7	0.5 to 1mg/l****
Manganese	NA	0.5 to 1mg/l
Aluminum	NA	0.5 to 1mg/l
Silica	120 mg/l at pH 7, 25ºC[2]	240 ppm at pH 7

**   Langelier Saturation Index is used in waters with TDS less than 10,000. Stiff and Davis Index is applied to waters with TDS over 10,000.

*** K_{sp} values from Lange's Handbook of Chemistry[3].

**** In some cases, iron can be maintained as high as 4 mg/l in the brine.

Bacteria are actually not that harmful. They generally do not degrade the membrane physically or damage the equipment. They only present a problem when they generate a colony sufficient to restrict the path of flow or sufficient to restrict transport through the membrane. That said, most membrane systems experience some degree of biological fouling.

Cellulose acetate systems permit easy control of microorganisms through chlorination. Unlike the more common polyamide thin-film composite (TFC) membrane, cellulose acetate tolerates chlorine well. Biological control is as simple as maintaining a free chlorine residual. TFC membranes, however, degrade in the presence of chlorine. The effects are cumulative and proportional to the concentration and exposure times. Therefore, bio-control in a TFC system requires a bit more planning and monitoring.

Bacterial control should be taken into account when a system is in the design stage. Often the rate of growth is slow enough that system performance can be maintained via routine clean-in-place (CIP). Factors promoting rapid bio-growth are a ready food source, such as feedwater bearing organics, optimum pH conditions between 5 and 9, and a temperature above about 60°F (15°C). Surface waters are more prone to rapid fouling than ground waters, and mill supply is more prone than municipal supply.

When evaluating water at risk for biofouling, there are several strategies that can be applied. One is the application of non-biocidal materials that clean bacteria and the exocellular polymers they excrete from the surfaces. Since extremes of pH can kill bacteria, it is common to perform routing cleanings with low-pH cleaners, and high-pH cleaners applied alternately. If the rate of fouling is relatively low, this approach can be successful. If the rate of fouling is high, it may be impractical to clean frequently enough to maintain system performance. A second strategy is to apply biocide chemicals to the system, either off-line in shock treatments or on-line in continuous low-level treatment.[5] Both methods of dosing with biocides have proven successful in practice, and the selection of a method often depends on the intended use of the product water. For industrial waters not intended for human or animal consumption, continuous on-line dosing is an option. If the water will be used in pharmaceutical, beverage or similar applications, off-line treatment is the only option.

In planning a reverse osmosis maintenance program, the benefits of chemical treatments should be weighed and implemented where warranted. Chemicals can improve long-term RO performance by improving feedwater quality, preventing mineral scale, and solids deposition or by minimizing bacterial growth. A well thought out and properly executed maintenance program including chemicals can greatly extend the run-time between cleanings and generally improve system reliability.

recovering from trouble

The system is well designed. Water quality has been evaluated. Pretreatment is generating quality feed water. The system is reliable for months at a time. However, eventually the effect of hundreds or thousands of hours of operation are felt. As a result, system pressures increase and normalized flow decreases. It is time to bring the system back to optimum performance.

Virtually all of the major membrane manufacturers agree on the following statements: (1) membranes should be cleaned when normalized flow decreases by 10% from the initial acceptance test conditions, (2) membranes should be cleaned when the overall pressure drop increases by 15% over the initial acceptance test conditions. These two simple, explicit statements often go ignored, despite the fact that it has been demonstrated that the optimum cleaning response is achieved when these guidelines are followed. It can be difficult to recover performance if the system operates in a fouled condition for an extended period of time. Perhaps part of the problem is the mystery that surrounds the proper use of the CIP skid supplied at start-up. Or perhaps it is not knowing how to clean or what materials to use. There certainly are plenty of options.

Reverse osmosis element cleaning can be carried out in a number of ways. The optimum way is determined by the nature of the foulants and by the time, manpower, and resources available. The first question is not a minor one. A cleaning can be performed at just the right time, flow, and temperature, and it can still fail if the chemistry applied is not appropriate for the specific foulant. For that reason, it is wise to spend some time before a cleaning is needed to determine your most likely foulants. Increased pressure drops in the first stage indicate colloidal fouling from either organics or inorganics in a system, and it can also indicate bacterial fouling. This type of fouling tends to benefit from a low-pH soak followed by an alkaline cleaning. If the final stage pressure drops are elevated, it is an indication of mineral deposition. To properly address this type of fouling, it is necessary to know what minerals are most likely to deposit. System projections or antiscalant projections can be useful here, as can a new mineral analysis on both the feed and concentrate. These types of deposits may require low-pH cleaners for carbonate scales, or alkaline chelant cleaners for sulfate scales.

Besides evaluating the type of fouling to be removed, the user must decide between mixing their own cleaner from a number of open market chemicals or using packaged cleaners designed for the membranes and foulants of concern. The advantages of packaged cleaners are many. A quality packaged cleaner will be pH-buffered to protect the membrane and to maintain optimum pH throughout the cleaning. Buffering ensures a consistent pH whether the chemical is applied at a relatively low dosage for maintenance cleaning or at an elevated dosage for severe fouling. It will also be designed to be safe for the membranes, will minimize excessive chemical handling and will minimize the number of MSDS to be reviewed by the users.

When resources are limited, reverse osmosis system users now have the option to send their membranes out to be cleaned. It seems the trend for the past 15 years has been to reduce maintenance and operations staff to minimal levels. In this lean environment, it is frequently more cost effective to remove the elements from the system and ship them off-site for foulant removal than it is to perform a CIP. There are a few reliable suppliers in this field. Some provide basic cleaning and others provide a higher level of performance and documentation. One novel process provides a detailed flow test both before and after processing. The information is recorded by serial number so the end user has documentation of performance improvement for each specific element. The test information includes element pressure drop at a standard test flow, normalized permeate flow, and normalized salt rejection. Armed with this information, the user can decide which elements should be loaded into each array in order to optimize permeate quality or flow characteristics.

In addition to routine cleanings, this unique process can often take membranes that cannot be cleaned onsite and restore them to the manufacturers specifications for flux and salt rejection. If a decision has already been made to replace membranes, this process can serve as an inexpensive source of spare membranes. Rather than discarding the old elements, they can be sent for processing. If the process is successful, the elements are then being preserved, sealed in bags and packaged in boxes. The user can then keep them in storage as spares.

recommendations for maintenance and operation

Keeping in mind that each system is unique, it is nevertheless helpful to have general maintenance guidelines for reverse osmosis systems. With that in mind, Table 2 summarizes some useful guidelines that can be implemented in any facility.

recommendations for clean-in-place

Successful CIP requires planning and proper control of key system parameters. The most important parameters for cleaning are the cleaning chemistry, solution temperature, flow rate per vessel, pressure drop, and use of soak times. Frequently, the effects of temperature, flow and soak times are ignored. Table 3 summarizes key parameters for successful cleaning. Bear in mind that most reverse osmosis systems experience mixed deposits, so a single cleaning may not be effective.

conclusions

The reliability of a reverse osmosis system is a significant benefit of the technology. Smooth operation depends on feedwater characteristics, fouling tendencies and the ability to recover performance after it has declined. Chemicals enhance the operation of reverse osmosis pretreatment equipment, reduce the fouling nature, and bacterial activity of the feedwater and can reliably restore membrane performance when applied properly. Effective use of chemicals requires knowledge of the system's weaknesses and monitoring for signs of trouble. When used properly, chemicals make a membrane system more reliable and extend the life the system.

Table 2. Guidelines for Reverse Osmosis Maintenance

Parameter	Acceptable	Preferred
Feedwater Turbidity	<0.2 NTU	<0.1 NTU
Feedwater SDI	<5	<3
Mineral Saturation	Per guidelines in Table 1	Per recommendations of antiscalant supplier
Microbiological Control	Monitor pressure differentials. Apply biocide as required.	NA
Clean-In-Place	Normalized flow decreased by 10% or pressure drop increased by 15% to 25%[6]	NA

Table 3. Key Parameters for Successful CIP

Parameter	Guideline
Temperature	TFC: 105 to 120ºF (40 to 49ºC), Consult with manufacturer. CA: 90 to 95ºF (32 to 35ºC), Consult with manufacturer.
Flow per Vessel	4" Vessel > 10 gpm [7] 6" Vessel > 25 gpm 8" Vessel > 35 gpm
Recirculation Time	45 to 60 minutes per array
Soak Times	Low pH soak 1 to 24 hours High-pH soak 1 to 8 hours Consult with the chemical supplier and/or membrane manufacturer for guidance.
Comments	Most foulants are not homogeneous. Sequential cleaning with both low-pH and high pH is effective for mixed deposits. [8]

references

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