

# The Inherent Risks of Using Generic Chemicals In RO Applications

(July, 1996) By David L. Kronmiller, Ph.D. and Stephen R. Dunham

## Introduction

The efficiency and quality of RO operations is often dependent on the thoroughness of membrane cleaning procedures and the effectiveness of system pretreatment. The earliest forms of membrane cleaners and preventative maintenance chemicals such as citric acid, caustic potash, and sodium hexametaphosphate provided some relief from incessant membrane fouling. Ironically, these generic materials, in many cases, contributed to membrane fouling or merely gave the short-lived illusion of solving the operator's fouling problem.

Today, the generic materials of the 1960's are used with little consideration of their inherent side-effects and the risks to successful long-term RO operations. The complexities of membrane fouling and the potential adverse effects of generic materials must be considered by RO operations personnel.

With a practical knowledge of the chemical and physical interactions between water constituents, foulants, and chemical additives operators may avoid further complicating an existing foulant problem.

Supplementing this practical knowledge with a basic understanding of why properly designed RO chemicals are preferable to generics will enable operating personnel to select treatments which are more appropriate and more effective for their specific RO operating conditions.

## Membrane Cleaning

Membrane cleaning is recommended when feed pressures increase by 10% to maintain the same product flow or when a 10% drop in product flow occurs at a constant pressure. Such changes in normalized RO performance result from foulant accumulation on the membrane surface.

Whether the fouling occurs on the lead membranes from colloidal silt, colloidal silica, and ferric iron, or at the last membranes of an array from calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, ferrous iron, silicates, and other scale, it is important that all inorganic, organic, and biological foulants be removed from the membrane surface.



# The Inherent Risks of Using Generic Chemicals In RO Applications

## Generic Cleaners

The most common generic inorganic acids used for membrane cleaning are hydrochloric acid (industrial grade is known as muriatic acid) and sulfuric acid. Both have been used for removing light membrane scale including calcium carbonate, calcium phosphate, iron oxides and metal sulfates. Hydrochloric acid has been used for calcium carbonate removal but its fuming characteristics make it less convenient to safely use on-site. While sulfuric acid is less problematic on-site, it may encourage insoluble calcium sulfate formation which may cause RO system set-back.

Citric acid (2-hydroxy-1,2,3-propane tricarboxylic acid) is a common organic acid which is used to remove calcium carbonate and iron-based scale. Use of citric acid often gives the illusion of a successful cleaning. However, while this common generic acid may desorb calcium carbonate and sequester iron fouling, it is also known to cause severe set-back by precipitating an insoluble ferrous iron compound, usually starting on the back half of the lead membrane.

Other generic cleaners such as formic acid, hydroxyacetic acid and tartaric acid share these same adverse characteristics.

Oxalic acid, a dibasic acid, is effective for removing deposits containing iron. However since oxalic acid causes other metal salts to be insoluble, its use often causes more harm than benefit.

The use of such acids to dissolve foulants stemmed from an adjunct of detergent theory called the principal of sequestration. Sequestration is defined as the phenomenon of binding metal ions in soluble complexes. The sequestering agent is commonly referred to as a ligand and usually has at least one electron pair in a sigma orbital which is not already directly involved in the bonding.

These electrons may then form a coordinate bond between the ligand and the metal ion. When one bond can form with the metal, the ligand is called inidentate. If two positions are available, the ligand is bidentate. EDTA (ethylenediaminetetraacetate), a ligand used in RO cleaning, has six coordinating pairs.

Sequestering agents with amino and carboxylate ions are the most common organic generics and polyphosphate anions are the principal inorganic ligands.



# The Inherent Risks of Using Generic Chemicals In RO Applications

Ligands including aminocarboxylic acid, hydroxyalkylaminocarboxylic acid, aminophosphonic acid and polycarboxylic acid have been used since the introduction of RO technology. In fact, sequestration is used by detergent manufacturers to control the hardness of the makeup wash water so that the surfactants used in detergency can work properly.

Another common generic material used in RO cleaning is tripolyphosphate along with trisodium and monosodium phosphate. The detergent manufacturers have been reformulating their products to eliminate phosphates and phosphonates for many years because of their adverse environmental impact(3). Franz Guenter et al. (2) point out the hazards posed by the contamination of the aquifers and public waters by photostable EDTA ligands with toxic metals found in waste treatment plants.

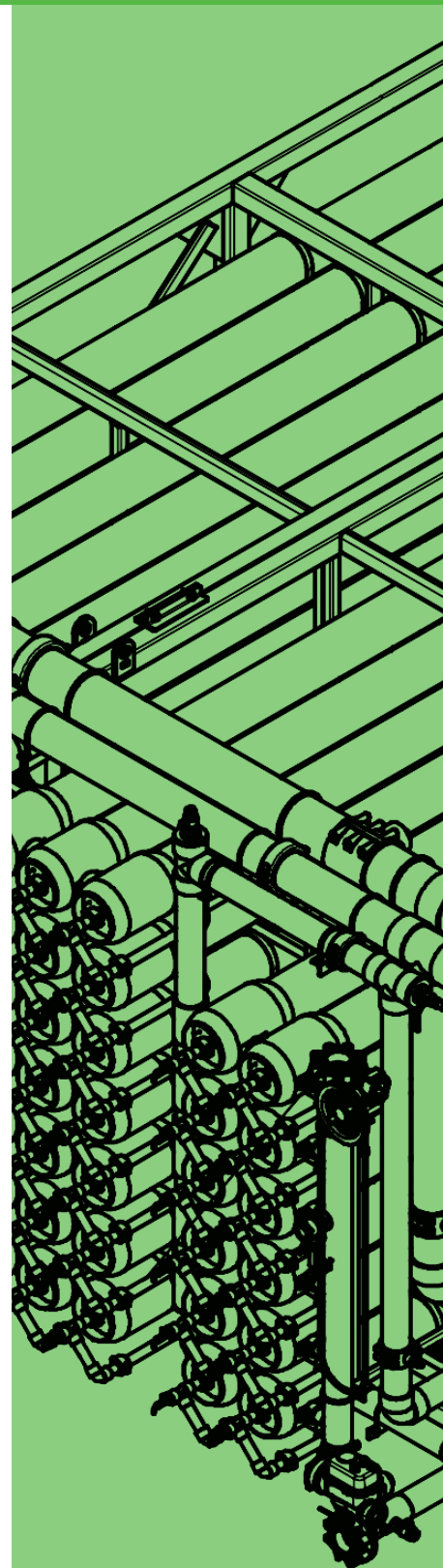
These compounds then contaminate and remain stable in the aquifer and public drinking waters. However, many RO specialty chemical companies still use phosphates and phosphonates in their antiscalants and cleaners.

There are several important factors that affect sequestration including (1):

1. **Attainment of equilibrium**
2. **Specific metal cation and its concentration**
3. **Specific sequestering anion and its concentration**
4. **Specific precipitating anion and its concentration**
5. **Presence of other metal ions**
6. **Total ionic strength**
7. **Solution pH**
8. **Solution temperature.**

Sequestration can only be accomplished with ionized metals. RO foulants are usually in molecular (either inorganic or organic) form and have already precipitated onto the membrane. Sequestration is normally used in the formulation of laundry detergents to reduce the hardness of the water used for the wash. Although theoretically the substances could, through equilibrium, redissolve into their ionic forms, the energetics are extremely low for this process to occur.

For redissolving to occur the free metal ion concentration for the complex must be lower than that of the precipitate. Most precipitates are highly insoluble and therefore tend to remain on the membrane surface as residual foulants.





# The Inherent Risks of Using Generic Chemicals In RO Applications



The effect of pH on sequestration is important. At high pH values (pH 11- 12) a ligand generally exists in a free or fully ionized state. Lowering the pH adds protons to the ligand in a stepwise fashion until there is no ionic species capable of sequestration. Essentially, the hydrogen ion, which is a cation itself, competes for the ligand. Examples of commonly used sequestration agents are sodium tripolyphosphate which tends to perform best at pH of 9 or higher and sodium nitrotriacetate which typically performs better at pH 10 or higher. Formulations including these sequestering agents with sodium or potassium hydroxide is commonly considered. However, the metal ion tends to interact with the hydroxide ion leading to insoluble metal hydroxides which may heavily foul the membrane.

Temperature has an impact on the effectiveness of the ligand-sequestrant complex stability which is related to the distribution of thermal energy within the complex (thermodynamically known as the «equipartition of energy»). Structures of the ring type tend to be less sensitive than the cage type structure.

## For Effective Membrane Cleaning

In the case of RO membrane foulants, cations such as calcium are already ionically bonded to anions such as sulfate and exist in

agglomerate and crystalline form. Sequestering agents (typically used to control hardness in laundry detergents) do not necessarily break down the aggregates and crystals fouling the RO membrane. If a sequestration agent is used in a cleaner formulation, it should be part of a system that chemically and physically modifies the foulant and does not cause the precipitation of insoluble compounds.

It is often necessary to chemically and physically modify the structure of a foulant in several steps which lead to the conversion of the foulant into a stable form that may be removed from the RO system without redeposition, or set-back. The physical processes involved are usually dispersion, deflocculation and peptization of divided inorganic solids as well as organic foulants.

Figure 1.0 illustrates a simple foulant system. RO foulants accumulate on the membrane in several characteristic ways. Calcium carbonate scale develops above the membrane surface while metallic silica foulants wet out the membrane surface, spreading into the pores of the membrane surface.

# The Inherent Risks of Using Generic Chemicals In RO Applications

Other foulants such as barium sulfate or strontium sulfate tend to exist on or slightly above the membrane surface depending on the interfacial energies or tensions. Such an accumulation results in numerous physical irregularities over the membrane surface due to the pools of foulants which have accumulated.

Successful foulant removal begins with the transport of a compound or compounds to the foulant/water and foulant/membrane interfaces by hydration of the foulant surface. Next, the foulant mass must be complexed. As complexing occurs, the foulant/membrane interface is modified, encouraging desorption of the foulant from the membrane surface. Following the desorption of the foulant, it must become complexed with a dispersant which stabilizes the foulant, allowing its effective removal from the system. The energetics of foulant removal from the membrane surface can be expressed as follows (also see Figure 2):

$$DG = g_{WF} + g_{SW} - g_{SF}$$

DG is the Gibbs free energy of the system which is the sum of the water/foulant and surface/foulant surface tensional forces less the surface/foulant forces.

For this condition to be spontaneous the surface/foulant forces must be greater than or equal to the sum of the water-foulant and surface-water forces or:

$$g_{SF} > g_{WF} + g_{SW}$$

The mere addition of a single surfactant can not cause a decrease in the water/foulant and surface/water energies without causing a concomitant change of the surface/foulant energies and thereby not satisfying the greater than or equal to requirement. Once the foulant has been modified and lifted off the membrane surface it must be stabilized until removed from the RO system. The successful RO cleaning chemical requires a system of specialized colloidal electrolytes and specialty chemicals having varying charges, chemical potentials, physical shapes and stability.

## Biological Fouling:

Biological fouling occurs throughout the arrays of many membrane systems and may result from a variety of environmental conditions. Conditions which affect biological growth include temperature, presence of inorganics such as iron or sulfates, seasonal changes in feedwater chemistry, pretreatment such as carbon filters and chemical additives containing phosphonates.





# The Inherent Risks of Using Generic Chemicals In RO Applications



Species commonly identified in RO systems (11) include:

## 1. Fungi

Fusarium  
Trichoderma  
Penicillium

## 2. Bacteria

Pseudomonas vesicularis  
Acinetobacter calcoaceticus  
Staphylococcus warneri  
Mycobacterium  
Chromobacterium  
Bacillus  
Arthrobacter  
Lactobacter  
Micrococcus.

Although fungi and bacteria have some differing characteristics, similar approaches may be used to control both. For the sake of space and simplicity, we will discuss only bacteria control in this article. Bacteria cells are bound by a pair of membranes walls with different passive permeability properties (see Figure 3). The outer membrane is a porous shield more permeable to small molecules. This porosity is conferred by specific porin proteins allowing solutes of molecular weight 700 to 10,000 (6) to pass.

Between the two membranes of the bacteria, adhesion sites exist. Adhesion sites mediate the transfer of newly synthesized lipids and lipopolysaccharides from the inner membrane to the outer membrane.

These lipopolysaccharides are the cause of «biofilm» known in the RO industry as bio fouling or slime. The transfer of lipopolysaccharides from the inner membrane to outer membrane requires energy which the cell attains from its transduction proteins in the inner membrane. For biogenesis of the bacterial cell envelope to occur, secretion of proteins made in the inner cytoplasmic membrane (and into the outer membrane of gram negative organisms) must occur.

The export from the bacterial cytoplasm requires energy with the leader peptide and other protein factors. These are necessary for the polypeptide conformational changes which must accompany the transition from a cis-polar aqueous phase (e.g. cytoplasm) to the nonpolar membrane bilayer phase or the transpolar phase. Energy, the leader peptide and other protein factors are also necessary for the individual ionic amino acids through the nonpolar membrane bilayer.

The energy source for the export from the bacterial cytoplasm has been found to be the membrane potential  $\Delta\psi$  or the electrochemical gradient involving the chemical gradient of the  $H^+$  ions,  $\Delta\mu_{H^+}$  and adenosine-5' -triphosphate (ATP) (7). Figure 4 illustrates the mechanism for protein translocation.

# The Inherent Risks of Using Generic Chemicals In RO Applications

Bacteria generally maintain  $K^+$  concentrations greater than their environmental medium. The higher internal osmolarity gives rise to turgor (osmolarity gradient) pressure which is necessary for normal bacterial growth (8). The cell walls of the bacteria are strong enough to maintain large osmotic gradients. This system is referred to as the high affinity Kdp system.

The high affinity Kdp system for  $K^+$  allows the cells to scavenge the  $K^+$  necessary for growth in conditions where the external  $K^+$  concentration is extremely low. It is for this reason that cells can grow in high purity water where  $K^+$  concentrations are very low. Figure 5 illustrates the uptake systems for  $K^+$  needed for the normal metabolism of the escherichia coli.

The e. coli Kdp system consists of three intrinsic inner membrane proteins, KdpA, KdpB, and KdpC, with molecular weights of 59,189, 72,112, and 20,267, respectively (9). Loss of the osmolarity gradient (turgor) caused by an increase in external osmolarity leads to a large uptake in  $K^+$  that results in an expression of the Kdp operon. However if the external osmolarity rises too high, the cell is protected by the fact that the high ionic strength shuts down the  $K^+$  uptake by inducing the expression

of the genes coding for the uptake of the «compatible solutes» proline and betaine (10).

## Problems with Generic Chemicals for Controlling Biological Fouling

Generic biological control products, such as chlorine, peracetic acid, or formaldehyde are oxidizers which lance and rupture cells. By rupturing the cell and releasing the cell contents, generics will increase the concentration of low molecular weight TOC materials, which may precipitate onto the membrane surface. The cell remnants may then serve as sites of nucleation for further biological and/or inorganic membrane fouling. Oxidants also attack thin film composite type membranes by oxidizing the glue lines and membrane surface, reducing salt rejection. Such damage to the membrane surface is irreparable and reduces useful membrane life.

## For Effective Prevention of Biological Fouling

The proper approach for the control of biofouling is to interrupt the mechanism for the  $\gamma$  and ATP utilization which produces the biofilm and the uptake systems for  $K^+$  needed for the survival of each of these cellular systems. After cell metabolism has been interrupted and the cell is neutralized, it must then be chemically controlled so adherence



# The Inherent Risks of Using Generic Chemicals In RO Applications



The proper approach for the control of biofouling is to interrupt the mechanism for the  $\gamma$  and ATP utilization which produces the bio-film and the uptake systems for  $K^+$  needed for the survival of each of these cellular systems. After cell metabolism has been interrupted and the cell is neutralized, it must then be chemically controlled so adherence of the cell to the membrane and brine channel spacers is eliminated. By inhibiting cell adherence onto the membrane and brine spacers, fouling by microorganisms may be eliminated.

## Inorganic Scale Prevention

When higher concentrations of inorganic water constituents exist, they have a tendency to coalesce and form larger agglomerations or crystals which fall out of solution and foul the membrane. Crystal growth is the formation of a new solid phase from the dissolved liquid phase of the constituents. In the absence of foreign surfaces which may serve as sites of nucleation, small clusters of molecules naturally form, then grow by accretion to form droplets or an amorphous precrystalline soup.

As the concentration of droplets increases, crystallites begin to form and coalesce to yield massive amounts of a new crystal phase.

The onset of the crystalline phase, however, does not occur at saturation. Instead, conditions for the phase change may be exceeded considerably. Impedance of new phase formation is associated with the extra surface energy of the small clusters which form an energy barrier. Such small clusters have been called germs (12). If they are somewhat larger and recognizable as precursors to the new phase they are called nuclei.

Once nuclei form in the super-saturated soup, they begin growing by accretion but at the same time the concentration of the remaining material drops creating a competition for material between the process of nucleation and crystal growth. The more rapidly nucleation occurs, the larger the number of nuclei form before the supersaturation disappears. This results in a larger number of smaller crystals (13).

## Problems of Generics for Scale Control

Some generic pretreatments are known to promote biological growth. S.R. Ahmed et. al. (4) point out that an inorganic antiscalant, sodium hexametaphosphate (SHMP) is not only the source of microorganisms but also a source of nutrients for biofilm to occur.



# The Inherent Risks of Using Generic Chemicals In RO Applications

In addition, the instability of SHMP in the stock solution inhibits its effectiveness in an RO system. Winters et. al. (5) point out that sodium thiosulfate used to neutralize chlorine can also be a nutrient for bacteria. Sodium metabisulfite also can contribute to biological growth and sulfate scale.

The use of crystal modifying antiscalants is also problematic. By absorbing polymer onto the surface of the growing crystal, growth is disrupted by the adsorption and redistribution on the surface of the material. Large pristine crystal growth may be inhibited but new planes form by surface deposition and migration on the edges of the crystal (14). This causes a chemical dynamics shift that yields a large number of smaller crystals instead of fewer greater-sized crystals. A higher concentration of smaller but growing crystals has greater overall crystal surface area. The result is more crystal precipitation over more of the membrane surface thus creating more sites of nucleation. The sites then become larger as other constituents have an affinity for the preexisting foulant and fouling accelerates.

Some antiscalants which rely solely on the substoichiometric control of cations as a method of controlling crystal growth may also prove problematic.

Although some cations are scavenged by the polymer's functional groups, metal ions such as iron or aluminum cause the formation of an insoluble compound which precipitates onto the membrane.

## **For Effective Control of Inorganic Membrane Fouling**

For effective prevention of inorganic fouling, the pretreatment must prevent or retard the small pre-crystalline molecular clusters from forming while increasing the energy barrier of those that develop before the crystalline phase is established. Dispersant properties are further beneficial so colloidal silt, ferric iron, colloidal silica, etc. are controlled, reducing membrane fouling in the first membranes of an array.



# The Inherent Risks of Using Generic Chemicals In RO Applications

## Conclusion

Though the generic chemicals of the 1960's are available to RO operating personnel today, it is important that the potential side-effects of generics and their risks to long-term RO operations be carefully considered.

A proper energetic design of RO maintenance and preventative maintenance products ensures more effective performance without contributing to or aggravating an existing RO fouling problem. With proper RO chemicals and an effective RO management program, operators may run their RO systems more efficiently and economically.