FOULING IN MEMBRANE DESALINATION: A WESTERN AUSTRALIAN PERSPECTIVE

by R. ROBINSON and G. E. HO

SUMMARY
The purification of water by membrane processes alters feedwater equilibrium in the separation phase which has the tendency to promote a decline in the performance and eventually to complete blockage, or fouling, of the membrane. This paper investigates the main agents causing fouling in the reverse osmosis (RO) membrane, and methods for their control or elimination by pretreatment of the feedwater.

A summary table of fouling causes and remedies has been compiled. Recommendations for treatment of typical Western Australian brackish groundwater for drinking use are proffered.

INTRODUCTION
Membrane fouling, through its many forms and mechanisms, is probably the most formidable obstacle to be overcome in the implementation of membrane processes for water purification. Fouling may be defined as the process of blocking the passage of fluid through a permeable membrane or aperture such that the rate of fluid flow is diminished for a given driving force (Belfort, 1984). In RO systems this blockage is reflected in the decline of the recovery ratio, the ratio of the permeate through the membrane to the flow rejected by the membrane, and alteration of the salt passage through the membrane at a given temperature and pressure of the feed water.

Fouling can be caused by a number of feedwater constituents or by the deterioration of the membrane structure itself, and may be reversible or irreversible in its effects.

PART 1. CAUSES OF FOULING
Common causes of fouling may be outlined as:

i) Concentration polarization is a fully reversible phenomena inherent in all mass separation processes. Concentration polarization is caused by the buildup of a concentration gradient adjacent to the membrane surface due to the preferential rejection of solute and removal of solvent by the membrane. This higher concentration at the film interface reduces permeate flux and quality due to a higher local osmotic pressure for a given pressure driving force. The polarization process applies to dissolved salts as well as colloidal and suspended matter (Lepore and Ahlert, 1988). Although not a fouling process itself, concentration polarization is usually a precondition for fouling in membranes.

ii) Gel formation – Membrane fouling is often caused by the formation of gels at the film surface. They may be classified as compacted or non-compacted in nature. The latter commonly consist of humic substances, biosilmes, and macromolecules such as proteins, carbohydrates, greases, oils and tannins. Non-compacted gels are commonly calcium compounds, metal hydroxides, and amorphous silica. These compounds block the membrane pores as they leave the bulk solution. Charged particles such as surfactants have additional fouling potential as they often are hydrophobic and adsorbed to the charge of the membrane surface, changing the barrier layer such that the water flux of the membrane is greatly reduced. Gel formation may be temporary or permanent depending on the constituent involved.

iii) Precipitation – Many of the sparingly soluble minerals cause precipitation as their solubility constant is exceeded in the process of the removal of the solvent in reverse osmosis. This forms a scale on the membrane surface which reduces its permeability. Among the ions commonly encountered in precipitates are calcium, magnesium, carbonates, sulfates, silicas and most forms of iron. It follows that precipitation is worst in high recovery membrane systems. Scale is partially reversible if flushed or cleaned with suitable solvents.

iv) Plugging – In membrane processes is generally caused by finely dispersed or suspended solids. Major foulants causing plugging include iron, organic and inorganic colloids, and humic substances. Clays are generally the greatest contributor to fouling of membranes utilizing surface waters, and their charge characteristics can make them especially difficult to remove (Swinton 1985). Colloids attain a stability in suspension due to their charge and double layer thickness which can become destabilized leading to flocculation due to changes in concentration, ionic strength or pH during separation processes. This makes predictive studies of colloidal fouling very difficult (Lepore and Ahlert, 1988). Plugging can be worsened by allowing particles greater than one-fifth the size of the membrane water channels into the system – hence the standard 5 or 10 micron cartridge pre-filter for RO systems.

v) Biological fouling – There are two mechanisms of biological fouling. One is blocking, much like that due to particles and precipitates, but caused by cell and cell by-products of biological activity. The second mechanism is direct microbial attack of the membrane, causing decomposition. This occurs typically with cellulose acetate membranes. The later aromatic polyamide membranes are less susceptible to biological growth. Once occurring, biological growth is difficult to remove – even if the organisms are killed, the cell material remaining is a major source of plugging of the membrane (Jonsson, 1988).

REMEDIES FOR REVERSE OSMOSIS FOULING
Preventing fouling is technically feasible in most instances but limited by economics. Basically two approaches can minimize fouling-effective design and pretreatment. Post-fouling treatment and rehabilitation of the membrane remains a less desirable remedy.

i) Design – A significant source of contamination, thus fouling, is introduced from the materials of construction of the water supply, storage or pumping system. The role of nucleating agents, such as metal hydroxides, in catalyzing fouling means that these contaminants often contribute to the fouling problem to a large degree at only very small concentrations. The preferred material of construction for brackish water or seawells is non-porous. Materials such as polyvinyl chloride (PVC), polyethylene, fibre reinforced vinyl ester and epoxy fiberglass are acceptable for pipes and well casings. Reinforced concrete piping is viable for certain applications. Pumps with high pressure applications require alloys of stainless steel or other non-corrodible material, plastics being too weak for over about 400 kPa head delivery (Applegate & Sackinger, 1987).

Designing the system suited for an application often involves a tradeoff between system efficiency and minimizing the fouling problems. Choosing the appropriate membrane configuration is one factor, for example; a one-stage membrane treatment step may only give a NaCl removal of 80%, but will be preferable to a two-stage
configuration removing 98% NaCl and hardness but producing ionic concentrations exceeding saturation values. A systems approach, isolating the limiting factors in terms of fouling potential, then adapting system configuration to suit, helps determine the appropriate tradeoff of pretreatment costs versus efficiency.

Turbulence at the feed side of the membrane should be considered as another factor in controlling fouling. Polarization effects, precipitation and scaling can all be reduced by maintaining turbulence through high velocities of the feed stream, hence minimizing boundary layer thickness (Belfort, 1984). This may involve the use of reject stream recycling or membrane pressure vessel designs to promote turbulence at the membrane surface.

ii) Pretreatment — The forms of pretreatment used in RO systems range in size, cost and complexity. In smaller plants, cost effectiveness often favours membrane replacement, either periodically or when performance falls to an unacceptable level, in lieu of pretreatment. Systems with a capacity of less than 2500 litres/day usually need little pretreatment beyond cartridge filtration, but at the expense of membrane life (Lepore & Ahlert, 1988). In larger plants it is more important to maximize membrane life and system efficiency.

Generally pretreatment falls into two categories eg removal of the fouling species before membrane separation, or inhibition of the formation of the foulant while passing through the RO plant.

iii) Membrane Cleaning — Of importance to the maintenance of a RO system is the cleaning regime used to remove any foulant already adhering to the membrane. It has been demonstrated by many researchers and practitioners of RO that if a membrane is allowed to foul beyond a certain level that effects can be irreversible, even to the point of discarding the membrane (Degremont, 1973). It is for this reason that most manufacturers specify a maximum level of performance decline before membrane cleaning is to be initiated, usually no greater than 10-20% of the original performance of the membrane.

SPECIFIC FOULANTS AND THEIR PREVENTION

The type of foulant likely to be encountered in reverse osmosis desalination of natural waters is well documented in research and industry. Table 1 summarizes these.

PART 2. ANTI-FOULING PRETREATMENT FOR TYPICAL WESTERN AUSTRALIAN GROUNDWATERS

The propensity for fouling of a RO system is dependent upon the specific qualities of the water to be treated, and to a large degree can only be proved with trials using that particular water (Lepore & Ahlert, 1988). Knowing the characteristics of typical Western Australian groundwaters, however, general choices can be made in the system requirements, given the design requirements of a low-maintenance system for remote area drinking water production. Table 2 summarizes borewater water quality problems experienced from a number of remote sites in Western Australia, based on Australian Standards for drinking water (National Health and Medical Research Council, Australian Water Resources Council, 1987).

From this data it appears that the predominant problems are the presence of iron and manganese at levels which cause taste, odour and staining problems, as well as causing scaling in pipes, especially in hot water systems in conjunction with hardness.

TABLE 1: CAUSES AND REMEDIES OF FOULING IN MEMBRANE DESALINATION SYSTEMS:

<table>
<thead>
<tr>
<th>FOULING TYPE</th>
<th>SOLUTION</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) METAL HYDROXIDES</td>
<td>- Iron Oxides</td>
<td>- Iron hydroxides</td>
</tr>
<tr>
<td></td>
<td>- Iron sulphides</td>
<td>- Manganese Oxides</td>
</tr>
<tr>
<td>iii) PRECIPITATION OF SALTS:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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</tr>
</tbody>
</table>
Typical Water Quality Problems for EQULING TYPE • SOLUTION

moulds. These organisms and their products often cause membrane fouling and pore plugging.

Reverse osmosis modules provide a large surface area for the attachment and growth of bacterial slimes and other microorganisms. Diatoms, aerobic bacteria, and iron bacteria may also contribute to fouling. In some instances, the combination of high turbidity and low pH may result in the formation of mineral scales, such as calcium carbonate and barium sulfate, which can cause membrane fouling and pore plugging.

Diatoms
Aerobic bacteria
Iron bacteria

Alginic acid used in feed streams:
Solutions
Calcification

Not suitable for polysulfone membranes without activated carbon filters (Rogers, 1984).

Continuous dosing > 1 mg/L. Requires pH control (Light et al., 1988).


For chloramine sensitive membranes (Belfort, 1984).

Continuous dosing preferred for low mineralization sites (Hulme & Wood, 1974).

Sustained reducing environment (Johnson, 1986).

5 mg/l of 80% plant tissue for chlorite-sensitive membranes (Winters et al., 1984).

For low turbidity waters only (Lepore & Ahlert, 1988).

Regular cleaning/disinfection

Required in the absence of, or preferably accompanying, algicide dosing.

Table 2 – Typical Water Quality Problems for WA Groundwaters (Robinson, 1990)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>No.</th>
<th>Total No.</th>
<th>Percent</th>
<th>Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (incl. Silica)</td>
<td>20</td>
<td>111</td>
<td>18</td>
<td>25 NTU</td>
</tr>
<tr>
<td>T.S.</td>
<td>54</td>
<td>140</td>
<td>24</td>
<td>1500 ppm</td>
</tr>
<tr>
<td>Hardness</td>
<td>23</td>
<td>129</td>
<td>&gt; 600</td>
<td>ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>48</td>
<td>125</td>
<td>&gt; 1.5</td>
<td>ppm</td>
</tr>
<tr>
<td>Manganese</td>
<td>10</td>
<td>125</td>
<td>&gt; 0.1</td>
<td>ppm</td>
</tr>
<tr>
<td>Fluoride</td>
<td>23</td>
<td>125</td>
<td>&gt; 1.5</td>
<td>ppm</td>
</tr>
<tr>
<td>Nitrate (as NO3)</td>
<td>26</td>
<td>125</td>
<td>&gt; 45 mg/L</td>
<td></td>
</tr>
<tr>
<td>pH Too Low</td>
<td>28</td>
<td>126</td>
<td>&lt; 6.5</td>
<td></td>
</tr>
<tr>
<td>BACTERIOLOGICAL (below figures not mutually exclusive):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total colif.</td>
<td>23</td>
<td>122</td>
<td>20</td>
<td>120 tot colif/100 ml; E. coli. 12 120 2 E. coli/100 ml;</td>
</tr>
<tr>
<td>Fecal strept.</td>
<td>9</td>
<td>122</td>
<td>7</td>
<td>Salmonella 3 122 2 zero</td>
</tr>
<tr>
<td>AVERAGE DEPTH TO WATER: 32 METRES.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

High salinities, hardness, low pH in the Kimberley clay areas, and bacterial contamination all appear to be quality problems. High nitrates and fluoride were found in many areas. Records of sulfates were not available for many bores, but it can be surmised that in the high iron and hardness areas that sulfates and probably hydrogen sulfide would be encountered (Robinson, 1990). Overall, classic highly mineralized waters are typical of most inland semi-arid regions of WA, ranging from the low pH, high turbidity clay waters of the Kimberley to the hard, high iron content of the Goldfields region.

Appropriate Pretreatment Systems – Given the requirements of a low pressure, low maintenance RO system to desalinate WA groundwaters, the two options of systems design and pretreatment were adapted to these constraints.

Design of the system using low pressure RO membranes will allow a relatively high flow rate into the system for the pressure ratio (8-101/min @ 1200 kPa for a Desal low-pressure 65 mm diameter membrane). This, in conjunction with a low recovery ratio, around 8-25%, dependent on pressure, is the main strategy for coping with waters of high fouling potential. The recovery ratio of the system will be set according to the degree of fouling potential induced by the concentration of dissolved ions in the reject stream. This design option allows the need for extensive pretreatment to be eliminated for the loss of some system efficiency—a sacrifice which enhances the long term reliability and simplicity of servicing of the system.

The second design option, presently being tested at Murdoch University by the authors, is the use of a pressure vessel accumulator linked with a pressure switch placed in front of the prefilter/membrane components. This design is primarily tailored to accumulate variable inputs from a renewable energy pump (wind, in this case) but has the benefits of inducing a surge of pressure and flow during the discharge cycle, which has been shown to reduce fouling in RO systems through increased turbulence promotion at the membrane surface (Goel & McCutchan, 1976; Allen & Shippey, 1978).

i) Metal hydroxide fouling is expected, given the levels of mineralization of Western Australian groundwaters, particularly of iron (up to 150 ppm in some Central Reserves water supplies) and manganese. The treatment strategy favoured is to exclude air and oxidizing chemicals where possible to keep ions in their soluble state. This appears straightforward but in practice is very difficult for usage in remote outback areas. The addition of sequesterant through automatic dosing [see section (iii) below] will assist this process by minimizing iron catalysis of other precipitation reactions such as that of silica (George, 1979). The addition of an oxygen scavenger such as sodium sulfite would help maintain iron solubility. The exclusion of ferrous materials in the pump and delivery system is straightforward for a low-pressure system. Sanitation of drilling and downhole equipment should prevent the reformation of iron-oxidizing bacteria in such isolated settings. In a non-attended facility this strategy, with or without additional sequestrant and/or deoxygenation, remains the only feasible one, the alternative of the oxidation and removal of iron/manganese through batch or continuous processing being too cost and labour intensive.

ii) Colloidal fouling from groundwater sources is not common for a properly established bore but is very common from surface waters. The use of a borehole lined with sand and screen allows the connection to a surface water source is effective in eliminating a large proportion of colloidal foulants as well as bacterial contamination. Humic and fulvic acids, where present, can be easily filtered by this 'de-facto' slow sand filter (Huisman & Wood, 1974). The dosing of dispersants such as sodium hexametaphosphate should reduce the coagulation of the mineral based colloids where they are present, allowing their rejection by the RO membrane into the waste stream (Belfort, 1984; Lepore & Ahlert, 1988). A pair of 50 cm length, 5 m cartridge filters are considered standard for this type of unit, and should need replacement only every six months given typical borewater inputs (Lepore & Ahlert, 1988). These provisions, in conjunction with appropriate separation and flow/surging design features already mentioned, should eliminate colloidal problems; the degree of effectiveness can only be ascertained on a site specific basis by installation and monitoring.

iii) Precipitation of salts presents a major problem for highly mineralized groundwaters. Even at a 10% recovery ratio it is expected that many of the solubility constants of salts will be exceeded. Taking the Langelier Index of scaling and applying this to a reject stream for averaged and maximum calcium carbonate levels for each region the results in Table 3 were determined:

Similar scaling propensities will no doubt be generated by other ions in solution, which must be corrected by pretreatment in addition to design changes.

Large scale pretreatment of groundwaters for RO is unusual unless only one inorganic solute is involved, cartridge prefiltration being sufficient. Carbonate and non-carbonate hardness can usually be treated by the use of sequesterants, a number of "designer" brands being available for particular scaling problems which allow over 200% solubility limits and a LSI value

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affect silica polymerization. Silica scaling varies with pH but is unpredictable; a "safe" upper limit of 120 ppm of amorphous silica in the reject stream should dictate the recovery ratio of the system. The exclusion of metal oxides in the feedwater should be undertaken according to (i) above to minimize polymerization.

Acid dosing could prove dangerous and expensive and requires an accurate continuous monitoring of pH, often too impractical for field conditions unless carefully handled by qualified personnel.

iv) Biological fouling is predominantly a problem of surface waters, or where contamination of groundwater has occurred due to animal and/or human effluent; as in the majority of cases of remote community water supply contamination (Public Works Dept of W.A., 1982). Careful placement of aeration facilities and fencing of bores from animals is the first step in controlling contamination. Where biological fouling is a risk, chlorination is only feasible after the RO treatment due to the sensitivity of most modern membranes to chlorine. In this case it is recommended that sodium metabisulphite be dosed to a residual 1–2 ppm to maintain a reducing environment, preventing aerobic bacteria and maintaining the solubility of oxidizable iron as suggested in point (i) above. If anaerobic bacteria are present, ultraviolet radiation pretreatment by the use of a 40 Watt solar powered UV lamp system developed by the Murdoch University Energy Research Institute (formerly Solar Energy Research Institute of WA) for use in remote area water supply systems may prove feasible (January 1983). Automated shock dosing systems may be tried as a less favoured option where extreme contamination is repeatedly experienced.

CONCLUSION

Steps to ensure minimal fouling of a membrane treatment system include good design, pre-treatment of feed waters, the addition of chemical anti-fouling agents and membrane cleaning. These treatments all involve costs, whether that of reliability, expense or complexity. The choice of treatments to prevent fouling in RO systems must minimise these costs. This represents the greatest challenge to the developer of desalination systems for typical Australian groundwaters.

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