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The effects of feed water de-gassing on the permeate flux of a small scale SWRO pilot plant

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ABSTRACT

The effects of pressure release on feed water cavitation have been studied using a small pilot scale SWRO system. The presence of dissolved atmospheric gases in seawater leads to a potential for cavitation within the porous membranes used in high pressure processes. The rapid application and release of applied pressures in the range of 10–60 atm was found to cause visible cavitation throughout the bulk solution phase. This phenomenon was not related to increased gas solubility under the applied pressure, since no additional gases were allowed into the system. It was found that almost complete removal of the initial dissolved atmospheric gases prevented this cavitation. Earlier laboratory scale studies had reported that removal of cavitation by feed water de-gassing enhanced permeate flow rates by 3–5% but this level of improvement was not observed in the pilot scale study operating at an applied pressure of 38 atm with seawater feed. It is possible that larger effects may be observed with the use of more hydrophobic membranes and at higher working pressures. Pre-heating seawater feed to enhance RO efficiency may also lead to greater cavitation within the RO membrane. This study has also demonstrated that pre-treatment using hollow-fibre membranes with efficient vacuum pumping systems can readily produce a high flow rate of 99.5% de-gassed seawater. Feed water de-gassing at these high levels also has the advantage of reducing both inorganic and biological fouling and reduces oxidative degradation of the polymeric membranes.

Keywords: Desalination; Degassing; Seawater; Reverse osmosis

1. Introduction

The efficiency of the fundamental process of desalination produced by forcing water through an asymmetric polymer matrix membrane from a salt solution via the application of high pressures depends on many factors. One factor which has received relatively little attention is the potential for cavitation caused by rapid pressure release within the nanoporous, slightly hydrophobic, porous RO membrane. The presence of dissolved atmospheric gases is often ignored; however, under atmospheric pressure 1 L of water dissolves about 20 ml of gas (at atmospheric pressure). Increasing salt levels and increasing temperature both reduce this solubility and this effect can also be important. In SWRO membrane processes, separation occurs because of the different levels of favourability, within the polymer membrane matrix, for various components present in the feed water. Increasing the applied pressure (P) on the feed solution increases the chemical potential (μ) of all the components in the mixture, via the relation: $\delta\mu = V_m \delta P$. Of the three components, salt, water and dissolved gases, the latter are the most weakly bonded within

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the solution and so will have the lowest activation energy (ΔE) for penetration into the membrane. This activation energy will determine the distribution function for each component, through the relation:

$$C_{\mathrm{PM}} = C_{\mathrm{FS}}\left(-\frac{\Delta E}{kT}\right) \tag{1}$$

where C_{PM} is the concentration within the polymer matrix (PM) and C_{FS} is the concentration within the feed solution. For example, for electrolyte ions such as Na^+ and Cl^-, the distribution between RO membrane and seawater is typically about 1/20 to 1/25 and therefore this corresponds to an activation energy ΔE of about +3 kT.

The magnitude of the activation energies will follow the series: ions > water >> dissolved (inert) gas molecules.

This is because ions are strongly bonded to water molecules in the feed solution by ion-dipole forces and in the PM they are in a much lower dielectric constant material, which will increase their Born energy. Water molecules are strongly bonded to other water molecules by hydrogen bonds in the feed solution. Dissolved nitrogen and oxygen molecules are bonded to water via weaker van der Waals forces and it is possible that they could be in a lower energy environment within the PM (which could even produce a negative value of ΔE).

Hence, although the dissolved gases are present at much lower concentrations in the feed solution they could be more highly favoured within the PM. Hence, the concentration of dissolved gases in the water entering the PM should be higher than in the feed solution, whereas, by comparison, the salt concentration will be much lower. As the pressure is rapidly reduced within the surface layer of the RO membrane these dissolved gases, in the presence of hydrophobic moieties, could cavitate within the membrane, partially restricting permeate flow. Typical commercial RO membranes contain aromatic groups which will present suitable, i.e. hydrophobic, cavity nucleation sites within the polymer matrix. In the study reported here we have also examined the hydrophobicity of some typical commercial RO membranes.

It is interesting to speculate whether the application of a high (60 atm) applied hydrostatic pressure followed by its rapid release will have any effect on cavitation in bulk solution, that is, without allowing additional gas dissolution at the higher pressures. It is likely that pressurising the salt solution feed will tend to force dissolved gas molecules into clusters — to reduce their impact on the optimum packing structure for liquid water under high pressure. We know that at atmospheric pressure non-polar solutes induce ice-like structures in surrounding water — which will be of lower density. At higher applied pressures these solutes will be forced together to free this structured water to reduce the volume (i.e. increasing its density). Water cavitates much more readily, under suction pressure, when it is saturated with dissolved air [1] and is exposed to hydrophobic groups [2]. It is actually very difficult to cavitate pure, gas-free water in a clean, smooth vessel.

If we make the reasonable assumption that a phase change occurs when a spherical cavity of 1 nm radius is created in water, then we can easily estimate the suction pressure required. The total energy (E_T) of a cavity of radius r is given by the sum of the negative work done by the suction pressure (i.e. ΔP negative) on the cavity volume and the surface tension (γ) work done on creating the surface of the cavity. Thus, the total cavity energy is given by:

$$E_T = \frac{4}{3}\pi r^3(\Delta P) + 4\pi r^2\gamma \tag{2}$$

A diagram of the behaviour expected for water is shown in Fig. 1. If we make the assumption that 1nm is the critical radius (r_c) of cavity formation, i.e. when $dE_T/dr = 0$, then it follows that we can estimate the critical suction pressure using the Laplace pressure equation:

$$\Delta P = -\frac{2\gamma}{r_c} \tag{3}$$

For pure water this gives a critical suction pressure of about –1,460 atm. By comparison, the largest suction pressure observed experimentally for de-gassed water was –1400 atm [3], which is close to theoretical predictions.

In most practical situations contaminants and real, rough surfaces facilitate the nucleation of cavities in water at much lower suction pressures than this. The presence of dissolved gases and hydrophobic groups also substantially reduce the cavitation pressure. For example, experimental cavitation pressures are typically about –1 atm for distilled water, saturated with air, and –200 atm for 99.98% de-gassed water [1] (Fig. 2). Thus it

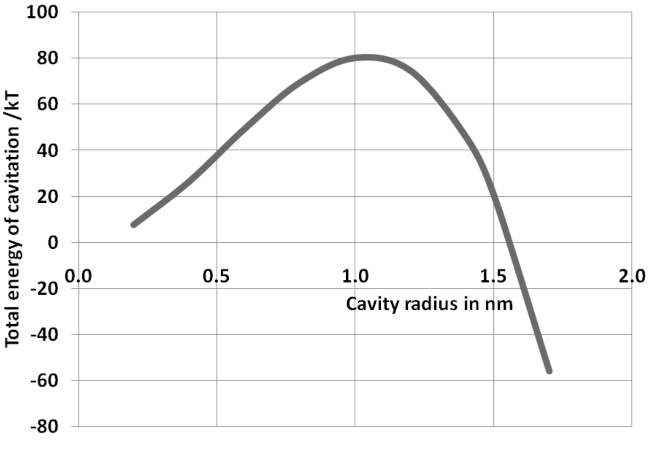

Fig. 1. Theoretical calculation of the energy (in kT units) required to form a spherical cavity of radius r in pure water under ideal, de-gassed conditions, in the absence of nucleation sites, with an applied suction pressure of –1400 atm.

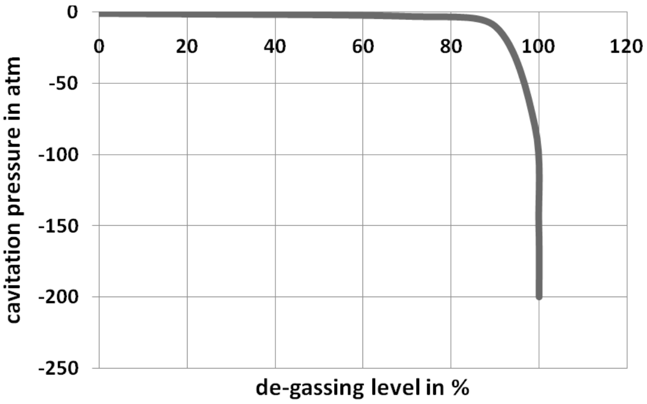

Fig. 2. Cavitation pressures extracted and re-plotted from the data published by W.J. Galloway [1].

is clear that the de-gassing of water and salt solutions strongly inhibits cavitation.

The high pressure differential established across the thin surface skin layer of an RO membrane, during the reverse osmosis process, could give rise to cavitation within the porous polymer network. This cavitation could then affect the permeate flow rate. The polymers used in modern composite RO membranes contain hydrophobic moieties, such as saturated and unsaturated hydrocarbon rings. These groups can form nano-size surface regions of hydrophobicity within the polymer matrix of the membrane, which could nucleate cavities in water. In addition, different RO membranes have different levels of hydrophobicity, hence, for normal (gassed) feed water, gas cavitation is expected as the pressure is released within the porous matrix structure of the surface layer of an RO membrane and will be inhibited by de-gassing. These effects were studied in the work presented here.

In earlier experiments we used a small laboratory scale commercial RO unit to study the effects of de-gassing on permeate flow rate [4]. In these experiments the feed solution was de-gassed using commercial Teflon hollow-fibre filters with a vacuum to withdraw the dissolved gases to a level of about 99.5% de-gassed. The results obtained with this system indicated that a 3–5% increase in permeate flow rate was produced by feed water de-gassing at an RO pump pressure of 55 atm. These results gave supporting evidence for the proposition that cavitation does indeed occur in RO membranes, due to the rapid release in applied pressure within the membrane, restricting permeate flow. The current project was aimed at extending this study and on scaling up the size of the SWRO unit. The basic postulate is that since dissolved gases are the most favoured component to be forced out from a pressurised salt solution into the porous structure of an RO membrane, they will form gas cavities as the pressure is rapidly reduced within the porous skin layer of the RO membrane and these cavities will reduce the permeate flow. De-gassing the feed water will prevent this — especially when de-gassed over 98%.

In this study we have examined the effect of rapidly released applied pressure on salt solutions and the effects of de-gassing on permeate flux in a small scale commercial type SWRO system. We have also studied the effect of commercial high pressure piston pumps on dissolved gas levels in the pressurised feed water and have studied the effect of prior de-gassing on gas cavitation, upon pressure release for bulk salt solutions.

2. Methods and materials

The feed water used for this study was seawater, sourced from the Perth Seawater Desalination Plant. The seawater for the Perth Seawater Desalination plant is sourced from Cockburn sound. The intake water varies with a salinity ranging from 35,000 mg/L to 37,000 mg/L with the intake temperature fluctuating from 16 to 24°C between seasons [5–7]. This water had been subjected to routine pre-treatment processes, including flocculation, and various stages of coarse, fine and microfiltration. The treated seawater had an average measured conductivity of 45.1±2 mS/cm and a measured turbidity of 0.22±0.1 NTU. The feed water was stored in a 28 m^3 tank, and pH and conductivity were found to maintain their original values for up to three months, during storage. The water was pumped from the tank using a Davey Torrium centrifugal pump. It was then fed through a Waterco Micron W300 MkII sand filter, and a membrane microfilter, to protect the reverse osmosis membrane, by removing any suspended solids. The feed water was then delivered to a pair of Liquicel 4×28 hollow fibre modules, with X50 fibres, arranged in series.

During the tests with the degassed feed water, a vacuum was applied to the hollow fibre membranes, initially with an Elmo-Rietschle Vacfox VC75 single stage rotary vacuum pump, and later with an Edwards E2M40 two stage rotary vacuum pump. Vacuum pressure was monitored using an Endress-Hauser Cerabar-S digital pressure gauge, the gauge measured in kPa to two decimal places (quoted error ±0.075%) [8]. The dissolved oxygen level and temperature of the feed water was recorded as it left the hollow fibres, using a Mettler-Toledo InPro 6900 trace-level dissolved oxygen probe, connected to an M700 transmitter.

The feed water was then delivered to a high pressure, three-cylinder Catpumps 1057 Triplex pump, driven by a 4 kW Monarch Alloy electric motor, which was controlled by a Santerno Sinus M variable frequency drive, allowing the pump speed to be varied and controlled precisely. A pulsation damper was used to limit rapid pressure variations from the piston pump. Industrial scale RO plants more commonly use centrifugal pumps to push water through the membranes; however, centrifugal pumps are not readily available for small-scale systems, such as this one. Therefore, a triple piston pump was used in this pilot study. Use of this type of pump also enabled us to control the flow-rate, via the piston frequency, separate to the applied pumping pressure. This pump was used to pressurise the feed water to pressures of up to 65 bar, which was then delivered to a Filmtec SW30-4040 reverse osmosis membrane, housed in a Codeline fibreglass pressure vessel. A needle valve was used to generate and control the pressure by restricting the reject output flow. A bypass valve was used to allow low-pressure rinsing of the system.

The feed pressure was measured in the sand filter, and in the feeds to the hollow fibre modules and the high pressure pump, to a precision of ±10 kPa, and in the reverse osmosis membrane, to a precision of ±0.5 bar, with Wika mechanical pressure gauges. The flow rate was monitored at the inlet to the hollow fibre modules, and at the reject outlet from the reverse osmosis system, using Bürkert digital flow meters. The Bürkert flow meter measured in m^3/h (for feed and reject flows) to two decimal places or L/h to one decimal place (for permeate flow). The quoted error for the flow meters was ±0.5%. The pressure difference between the high-pressure reverse osmosis inlet and high-pressure reject streams was monitored with an Endress–Hauser Databar-S digital pressure gauge. A schematic representation of the experimental apparatus is shown in Fig. 3.

Unfortunately, it was found that the high-pressure pump created slight (i.e. a few %) variation in both feed rate and pressure. These pressure pulsations occurred even though the pump system was fitted with a pulse damper. This effect caused the flow meters to fluctuate. Because of this problem, the permeate flow rate was measured both using the flow meter and also by diverting the permeate stream into a temporary storage vessel, where its weight could be continuously monitored — giving short-run flow rates (typically over 5 min intervals). This allowed a more accurate time weighted average of the permeate flow rate to be collected. Both types of data are given on the permeate flow rate graphs.

During runs, the reject flow was stored in a 10 m^3 holding tank, until the end of each experiment, whereupon the permeate was also added to this tank. After each experiment, the mixed content of this tank were returned to the 28 m^3 storage tank, by means of a Davey Dynapump centrifugal pump.

Several experiments were carried out at feed water pressures ranging from 30 to 60 bar, without degassing, to determine uniform, baseline operating conditions. Baselines were also determined each time a new spiral wound membrane was used in the RO pilot, as initial flow rates through new membranes can be inconsistent. Each run was begun by bypassing the needle valve pressure control, and rinsing the system with the treated seawater

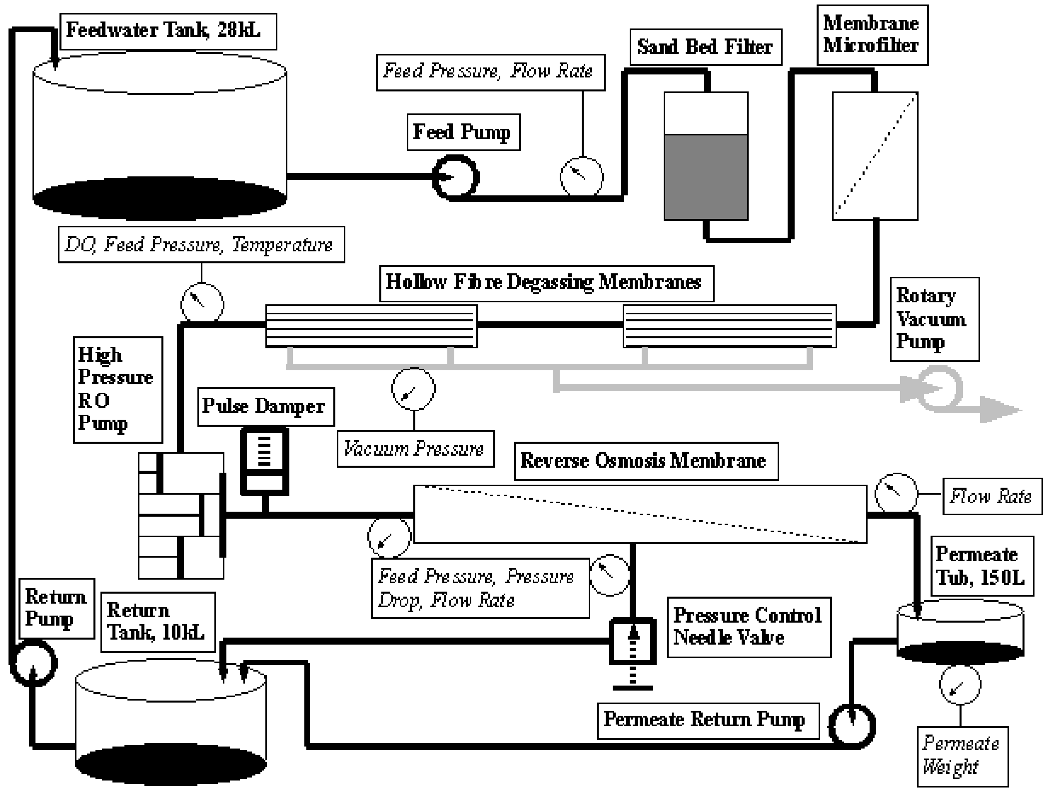

Fig. 3. Schematic diagram of the pilot scale reverse osmosis system.

feed, using only the low pressure Davey feed pump. The output flows were diverted to waste, until no flow was observed from the permeate line. This indicated that the membrane was filled with high osmotic pressure seawater, at which point, the output flows were diverted back to the 10 m^3 holding tank. The high-pressure, reverse-osmosis pump was then activated, and the needle-valve bypass was closed. The high-pressure pump speed and needle valve were adjusted until the desired flow rate and feed pressure were achieved. The system was then run for 90 min, with measurements being taken every 5 min. After the conclusion of the measurements, the pressure was reduced, the needle valve bypassed, and the pumps switched off. For storage, the system was rinsed with tap water, which was treated with sodium metabisulphite, to prevent damage to the membranes due to residual chlorine in the tap water.

A similar method was used for the experiments with degassed feed. The system was run with the same procedure as before for the first 30 min of each 90 min experiment. After 30 min, the vacuum pump was switched on to produce a vacuum on one side of the hollow fibre membranes. A vacuum level of about 1 kPa or lower was typically achieved within about 10 min. This corresponds to a de-gassing level of 99% or better. The actual de-gassing level achieved with time was monitored continuously using a dissolved oxygen (DO) probe. After 30 min of degassed operation, the vacuum was removed, and the hollow fibres were vented to the atmosphere. The DO levels returned to atmospheric levels within a 5–10 min. The system was then run for a further 30 min under gassed conditions. This method allowed the performance of the system under gassed conditions to be contrasted directly with the performance of the system under degassed conditions, gained under otherwise identical conditions. Degassed experiments were performed at feed water pressures of 38, 40 and 55 bar. When the vacuum pump was used, water vapour was transferred across the hollow fibre membrane with the dissolved atmospheric gases. At these low vacuum pressures, the water vapour acts as a carrier gas for the other atmospheric gases. To protect the vacuum pump, several traps filled with pre-dried silica gel were set up just before the inlet to the vacuum pump. The silica gel in these traps had to be replaced regularly.

Observations of cavitation were made by setting up and running the reverse osmosis system, with the reverse osmosis pump speed kept constant, and the needle valve used to increase the applied pressure in increments of 10 bar, from 10 bar to 60 bar. At each pressure, several samples of the reject stream were taken, examined visually, and photographed with a Nikon D40x digital SLR camera, immediately following pressure release to atmosphere. The same procedure was repeated with the feed under gassed and degassed conditions. The obvious presence of a high density of small bubbles in the reject water samples was taken as an indication of cavitation. Feed solutions included the pre-treated seawater, tap water, and simulated seawater solutions, made using tap water and curing salt (West Australian Salt Refinery). The simulated seawater had a conductivity of about 49 $mScm^{-1}$. Tap water feed solutions were treated with sodium metabisulphite to ensure an oxidation-reduction potential below 175 mV, to prevent oxidative degradation of the reverse osmosis membrane.

Further tests were carried out to observe the effect, if any, of bicarbonate/carbon dioxide pressure cavitation. Both seawater and treated tap water contain significant quantities of bicarbonate ions, at a level of about 2 mM. Removal of dissolved CO_2 gas from such a solution, using the hollow fibre membranes, will not have much effect on the level of dissolved bicarbonate and carbonate ions. In order to determine whether the observed cavitation was affected by dissolved HCO_3^-, CO_3^{2-} or dissolved CO_2, or was due entirely to the presence of the dissolved atmospheric (inert gases) O_2 and N_2, samples of simulated seawater were prepared, using laboratory-quality deionised water, with 35 gL^{-1} of refined NaCl salt. Laboratory deionised water has much lower levels of dissolved HCO_3^- and CO_3^{2-} ions. These solutions had an electrical conductivity, in all cases, of between 48 $mScm^{-1}$ and 51 $mScm^{-1}$. These solutions were also sparged with ultra-high purity N_2, supplied by BOC gases, to remove any residual dissolved HCO_3^- and CO_2. The pH of these sparged solutions was between 7 and 8, and the dissolved O_2 level was found to be below 50 ppb (that is, less than 0.5% of atmospheric equilibrated levels). This water was then used as feed for the pressure tests described earlier. These higher quality samples did not need sand filtration and so this process was bypassed, which also reduced the volume needed for rinsing the system. The hollow fibres were flushed with N_2 gas, and then sealed, to prevent regassing with atmospheric CO_2, during the course of the experiment. The feed water reservoir was also bubbled continuously with N_2 gas throughout the course of the experiment, to prevent re-dissolution of atmospheric CO_2.

Water droplet contact angles were measured on various RO membrane samples housed within a sealed glass vessel, using a syringe to enlarge a sessile drop on a flat segment of each membrane. The advancing angle was recorded as the highest observed angle before the edge of the drop advanced. The drop was then reduced until the edge could be seen to recede, to measure the receding angle. The angle of the interface was recorded using a horizontally mounted microscope with an eyepiece fitted with a crosshair and a protractor.

Initial measurements showed considerable variations, with measured advancing angles typically being very low. This suggested the presence of surfactant contamination on the membrane surface. This was confirmed when samples of the membranes were placed in a clean tube with de-ionised water, and shaken. Foaming was observed, indicating the presence of surfactant. The reported measurements were recorded for samples of membrane that were pre-soaked in de-ionised water, rinsed thoroughly, and then air-dried in a laminar-flow clean air cabinet, to remove any residual surfactant coating.

3. Results and analysis

The results of an initial study of the variation in hydrophobicity of some typical commercial membranes, measured through water droplet contact angles, are summarized in Table 1. The variation observed is consistent with heterogeneous surfaces which could offer nucleation sites. The range of these results supports the view that there could be a correlation between an improved permeate flow rate and the level of hydrophobicity of the RO membrane.

Seawater was passed through the reverse osmosis pilot unit under de-gassed conditions and the feed, permeate and reject were monitored for their dissolved oxygen levels using the DO probe. These measurements were used to determine whether the high pressure pump introduced dissolved gas into the de-gassed feed water. In these experiments, the feed water dissolved oxygen level was about 150 ppb (98.4% degassed), whereas the reject was typically slightly higher at about 175 ppb (98.1% degassed). The permeate water had a significantly higher level, typically about 460 ppb (95% degassed). The higher levels observed in the permeate was expected because air cannot easily be excluded from the product side of the RO membrane cartridge. These results show that the high pressure (piston) pump only added a small degree of re-gassing, of about 25 ppb, which corresponds to a re-gassing level of only about 0.3% of dissolved gas levels at normal atmospheric pressure (of about 9000 ppb).

The effect of rapid pressure release, via a needle valve, from 10–60 atm to atmospheric pressure, was examined by visual inspection. A uniform distribution of fine bubbles, as seen in Fig. 4 (left), was produced following rapid pressure release for the gassed seawater feed. The tap water feed produced no visible cavitation, but this was attributed to the low osmotic pressure of the solution, which prevents the application of feed pressure, due to the very high permeate flux. When NaCl was added to the tap water, to simulate normal seawater, cavitation was observed identical to that seen in the pre-treated seawater feed. Similar cavitation was observed in NaCl solutions made up with deionised water and purged with nitrogen, demonstrating that cavitation occurred even in the absence of dissolved CO_2 gas, bicarbonate or carbonate ions. By comparison, there was no visual evidence of bubble formation for any feed solution, once it had been 99.5% de-gassed.

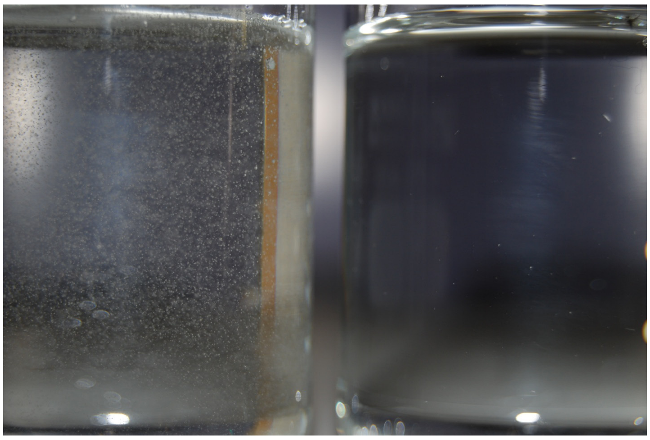
Atmospheric seawater feed Degassed seawater feed

Fig. 4. Photographs of the effect of rapid pressure release (from 40–50 atm to 1 atm) on gassed (normal) seawater and 99% de-gassed seawater. The cleaned seawater used in these experiments was obtained from the Kwinana RO plant. It is the feed supply prepared for their RO units.

In experiments to study the effect of cavitation on the permeate flow rate for the pilot scale system, baseline gassed performance was determined at 38 atm, at a recovery rate based on that used in industrial SWRO plants (7–10%) [9]. Consistent performance was recorded at 38 atm and a typical example is given in Fig. 5. This data was obtained using the 5 min interval weighing method. When the reverse osmosis system was operated at pressures closer to industrial plant conditions, of around 55 atm, it was not possible to obtain consistent baseline performance with the needle valve control system because the permeate flow rate varied by up to 5% within minutes. Because of this, the permeate flux results reported here were based on feed water pressures limited to about 38 atm.

Table 1
Contact angles of water droplets measured on a range of cleaned, dried, commercial RO membranes

Membrane type	Advancing contact angle (°)	Average advancing contact angle (°)	Receding contact angle (°)
Dow Filmtec SW30-HR	20–35	27.8	0
Dow Filmtec BW	40–90	67.5	0
Toray SWRO	58–64	59.5	0
AD-M GE WPT	73–77	75.7	0

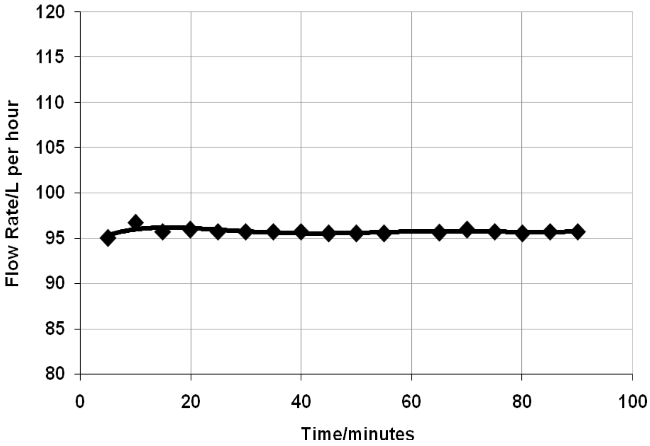

Fig. 5. Permeate flow rate data measured using the 5 min weight method, at a feed water pressure of 38 atm, and at a pump speed of 44.00, for gassed feed water.

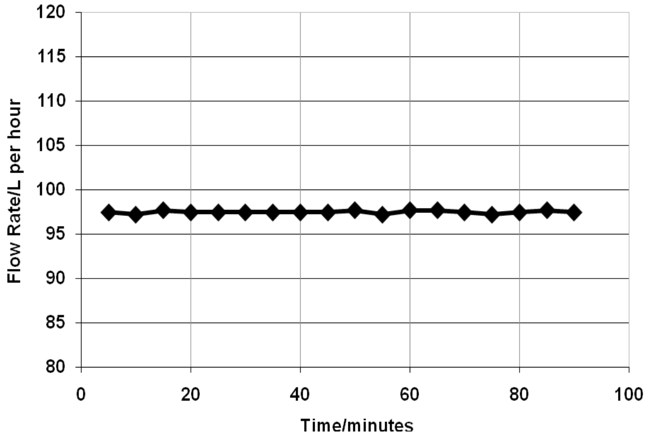

Fig. 6. Results obtained at a feed water pressure of 38 atm, (at a pump speed of 44.00), using the 5 min weighing method. The results obtained showed no significant change in permeate flow rate when the feed water was de-gassed to 98.9% at 30 min and then re-gassed at 60 min.

Table 2 presents a summary of typical permeate flow data collected at 38 atm, with feed water degassing. Although there were occasional experiments with increased permeate flow rates on de-gassing, the bulk of the experiments showed no increase and sometimes even a reduction in flow rate. Fig. 6 shows a typical result where there was no change in permeate flow rate on degassing to 98.9%. Table 2 also shows that the feed water temperature dropped when vacuum was applied across the hollow fibres, due to water evaporation. This caused the temperature of the feed water to drop, in some cases, by as much as a 0.11°C (Table 2). Permeate flux increases by about 2% per °C temperature rise [10], apparently due to the reduction in viscosity of water with temperature, from Hagen–Poiseuille's law [11]. Hence, a reduction in temperature of 0.11°C corresponds to a permeate reduction of about 0.2%, which will have only a slight effect on the permeate flow data given in Table 2.

Fig. 7 gives an example, observed in a few experiments, where the permeate clearly increased on degassing the feed water. In this case there was a modest

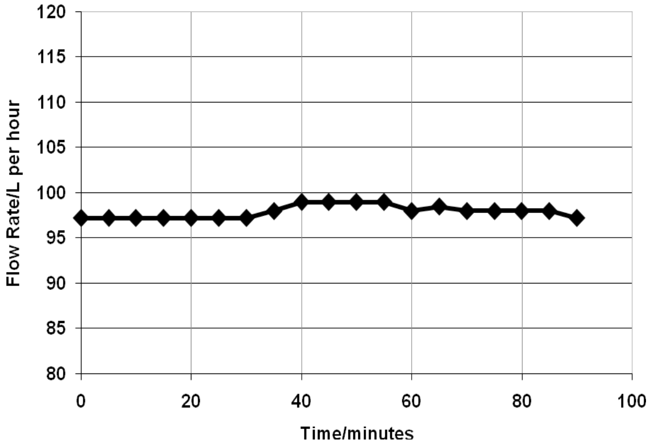

Fig. 7. Results obtained at a feed water pressure of 38 atm, at a pump speed of 44.06, and using the flow meter for the permeate rate. The permeate flow rate was found to increase when the feed water was de-gassed to 98.3%, at 30 min and then returned to the previous rate when the feed water was re-gassed (after 60 min).

Table 2

Typical changes in permeate flow observed at a feed water pressure of 38 atm, using the 4 inch RO pilot, with feed water degassing. Permeate flow was converted from weight data (which is accurate to ±10 g) to units of feed and reject flow.

Maximum degassing level achieved (%)	Average permeate flow (gassed) (m^3/h)	Average permeate flow (degassed) (m^3/h)	% change in permeate flow rate	Change in temperature upon degassing (°C)
98.8	0.06296	0.06288	–0.13	–0.03
98.9	0.08108	0.08072	–0.45	–0.01
99.0	0.09944	0.09924	–0.3	–0.07
99.1	0.09504	0.09632	1.3	–0.01
99.4	0.10032	0.10176	1.4	–0.04
99.6	0.06316	0.06316	0.0	–0.08
99.6	0.06632	0.06472	–2.5	–0.11

increase of about 2% when the feed water was degassed to 98.3%. After 60 min, when the feed solution was regassed, the rate returned to a similar level to the baseline rate prior to de-gassing.

When the vacuum applied to the hollow fibre unit reached values below the vapour pressure of water, at that temperature, substantial amounts of water vapour were drawn across the HF membrane. These vacuum levels were needed to produce de-gassing levels at 99% or greater. Under these conditions, the water vapour acts as a carrier gas, assisting in the removal of other dissolved atmospheric gases. At a vacuum pressure of 1 kPa, which produces a de-gassing level of about 99%, 4.5 L of water vapour was transferred per hour. In these experiments the water was condensed and collected using silica gel traps to protect the vacuum pump. The condensed water passed through the HF membrane is also desalinated and of high purity. This high quality water corresponds to a significant amount, roughly 4–6% of the RO permeate produced, and in a commercial process this water would represent an additional product to be collected.

4. Discussion

The results reported here clearly demonstrate that the application of high mechanical pressure to salt solutions, that is, without the opportunity for enhanced dissolution of gases (through Henry's law), followed by rapid release back to atmospheric pressure, via a needle valve, produces significant cavitation effects. It has also been established that de-gassing the water, up to 99.5% degassed, prior to pressurization, completely removes this effect. Further experiments, reported here, indicate that this cavitation process is due to the presence of dissolved inert gases, oxygen and nitrogen in the feed water rather than due solely to the presence of high levels of bicarbonate in seawater, naturally and in tap water, by design. As reported, the cavitation effect occurs even at relatively low applied pressures, such as 10 atm. Since, in these experiments, no additional atmospheric gases are allowed into the system, which would then readily dissolve, the applied pressure and its release through a needle valve must cavitate using the dissolved gases already present. The non-polar nature of dissolved oxygen and nitrogen molecules will mean that adjacent water molecules will tend to have a higher degree of bonding with neighbouring water molecules, even producing a local ice-like structure similar to that observed with hydrocarbons, which drives the self assembly of surfactant molecules in aqueous solution [12]. By comparison, dissolved 'inert' gas molecules apparently create nucleation sites for cavitation, during pressure-release flow processes. A re-examination of the behaviour of the laboratory scale RO system [4] running at 55 atm with a slow piston pump (with a slow pumping cycle of 2 s) confirmed that with tap water salt solution as feed (with similar bicarbonate levels to seawater) no cavitation was observed in the reject solution. However, this observation is not inconsistent with the current study because of the much slower and uneven pumping rate and the fact that the laboratory system had an energy recovery pumping system which would release the pressure more gradually, and well before it was released to visual observation.

The nature of the membrane RO process leads directly to the suggestion that dissolved gas cavitation may readily occur within the thin porous skin layer where the pressure release occurs because of the presence of hydrophobic moieties within the polymeric membrane which can act to nucleate bubbles. RO membranes have a range of wetting properties indicative of the local hydrophobic moieties which are well suited to support this nucleation process. The hydrophobic nature of the membranes is important for their function and is related to their low dielectric constant which supports ion rejection from the membranes. The selection of RO membrane polymers is influenced by their degree of hydrophobicity.

It seems very likely that the cavitation observed in bulk will also occur within the polymer matrix of RO membranes, however, the effect this will have on permeate flux is less clear. Earlier studies using a small scale 55 atm Filmtec unit indicated that de-gassing the feed improved permeate flux by up to 5% [4]. However, the small scale pilot studies reported here showed no effect at a pressure of about 38atm using similar membranes. Both systems used piston pumps and a range of different feed water. The Filmtec membranes are the least hydrophobic (Table 1) and the effect may well be greater for the other, more hydrophobic membranes. The observations of cavitation following restricted pressure release in bulk water, strongly suggest that cavitation could occur within these membranes. Unfortunately, only modest pressures were achievable with the pilot used here (at about 38 atm) and because of the presence of salt on the high pressure side of the membrane, the chemical potential of water on both sides of the membrane would have been much closer for the pilot unit than with the laboratory scale unit. It is possible that this had the effect of reducing the cavitation levels in the pilot study.

The use of pre-heated feed water to enhance permeate flow [10] apparently is effective because of the reduction in viscosity of water with temperature, from Hagen–Poiseuille's law [11]. This will lead to improved efficiency in SWRO plants using waste industrial heat, solar or geothermal heat. Unfortunately, dissolved gas solubility decreases with temperature and so rapid preheating will also cause increased supersaturation of the dissolved gases within the feed water, which will enhance cavitation in the RO membrane. De-gassing the feed water will prevent this. There are several other additional advantages in feed water de-gassing. Removal of dissolved oxygen will reduce the enhanced bio-fouling expected at the higher operating temperatures. De-gassing also has the advantage of reducing oxidative degradation of the RO membranes. The development of hydrophobic carbon nanotube membranes may also require the use of feed water de-gassing to improve their stability and to prevent pore cavitation within these hydrophobic materials. There may also be other advantages in feed water de-gassing from its effect on the pumping process itself and on the energy recovery processes used by commercial SWRO plants. Cavitation will be inhibited by the use of high level de-gassing and this may improve the efficiency of these mechanical processes [13]. Advice from our commercial partners [14] indicates that an improvement of the order of about 5% in permeate flow rate would be required to offset the costs involved in the membrane de-gassing process, although this estimate does not include the additional advantage of the pure water distillate produced by the hollow fibre de-gassing process.

5. Conclusions

The results presented here demonstrate that cavitation will occur in a small scale RO pilot when run under normal conditions. Feed water degassing at high levels (above 99%) completely prevents this cavitation effect. However, no consistent improvement in permeate flux was observed using a Filmtec membrane, in this pilot study. Some of the experiments indicated an improved permeate flow rate on de-gassing but the effects observed at the low feed water pressures used in this study were only quite modest. There are some clear advantages in high level feed water de-gassing, for example to reduce oxidative degradation and bio-fouling. Also, more hydrophobic membranes, such as cellulose triacetate and eventually CNT composite membranes may display a more pronounced cavitation effect. The results presented here indicate that future studies should focus on higher applied pressures, where the cavitation effect should be more prevalent. The use of more hydrophobic membranes may also produce more significant effects.

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