On the asymptotic flux of ultrapermeable seawater reverse osmosis membranes due to concentration polarisation

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Abstract

Just as thermodynamic considerations impose a finite limit on the energy requirements of reverse osmosis, concentration polarisation imposes a finite limit on flux, or equivalently, on system size. In the limit of infinite permeability, we show the limiting flux to be linearly dependent on the mass transfer coefficient and show this to be true for low recovery systems just as well as moderate and high recovery single stage and batch reverse osmosis system designs. At low recovery, the limiting flux depends on the logarithm of the ratio of hydraulic to bulk osmotic pressure and at moderate or higher recovery, the relationship with this pressure ratio is a little more complex but nonetheless can be expressed as a simple formula. For a single stage seawater reverse osmosis system operating at a hydraulic pressure, recovery ratio, and value of mass transfer coefficient that are typical today, the flux asymptote is roughly 60 L m$^{-2}$ h$^{-1}$ – roughly four times where average fluxes in seawater reverse osmosis systems currently stand.

Keywords: reverse osmosis, seawater, ultrapermeable membranes, flux, batch

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1. Asymptotic flux, as compared to asymptotic energy consumption

Even with infinitely permeable reverse osmosis membranes, there are finite limits on the flux that can be achieved in the future. We quantify the asymptotic limit on flux imposed by concentration polarisation—the phenomenon whereby solvent flux through the membrane results in the elevation of solute concentration, and hence osmotic pressure, at the membrane surface. We show that the limiting flux depends linearly on the mass transfer coefficient in the feed water channel and also in a logarithmic fashion on the ratio of the applied hydraulic pressure to the feed osmotic pressure.

In recent years, considerable discussion has been directed to the potential impact of highly permeable (ultrapermeable) membranes [1, 2, 3, 4, 5, 6, 7], which one might consider to be membranes with permeability above 10 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. In particular, authors have examined how ultrapermeability might affect the energy consumption of seawater reverse osmosis and concluded that as membrane permeability improves, there are strongly diminishing returns in the form of energy savings [4, 6, 7]. Indeed, as illustrated in Fig. 1, at ultrapermeabilities, specific energy consumption (per unit volume of permeate), $E_s$, in a single stage seawater reverse osmosis system reaches an asymptote.

Also presented, but receiving less coverage, is the impact of higher membrane permeability on average membrane flux (or system size), in which form diminishing returns also occur as membrane permeability becomes very high [4, 7, 8], as represented in Fig. 2. In this work, we show and explain that there is a finite limit on flux that results from concentration polarisation and derive analytical expressions for that limit. Just as thermodynamic limitations impose a finite limit on energy consumption, transport based limitations impose a finite limit on flux. Interestingly, it might be said that the thermodynamic limitations on energy consumption are more strongly felt in seawater RO systems today than the transport based limitations on flux, i.e., while there is little room for improvement in energy consumption, there is still substantial room for improvement in flux. To a significant extent, this is an artifact of the conventional...
Figure 1: Impact of permeability on specific energy consumption at constant average flux for single stage reverse osmosis (based on the model developed in Section 3)

Figure 3 illustrates a comparison of the osmotic pressure profiles and net pressure profiles (hydraulic minus osmotic) for membranes of finite and infinite permeability. The centerline osmotic pressure is equal in both cases, but the osmotic pressure at the membrane surface is higher for the membrane of infinite permeability, as a result of higher concentration polarisation. The net pressure at the centerline is also the same regardless of permeability. However, the net pressure at the membrane’s inner surface is finite and positive when permeability is finite, but zero when permeability is infinite. For infinite permeability, conditions on either side of the membrane are in thermodynamic equilibrium (in the sense that the chemical potential of water is the same).

2. Asymptotic limits on flux at infinitesimal (or low) recovery

We seek to understand why concentration polarisation imposes a finite limit on flux. One way to do so is to combine a solution-diffusion model [9] for
membrane permeability and a stagnant film model\textsuperscript{2} \cite{11} for concentration polarization, and to do this for infinitesimal recovery – whereby the quantity of product water removed from the feed is small enough to consider the feed osmotic pressure constant. For such a model of reverse osmosis (assuming 100% salt rejection), water flux is given by:

\[ J = A_m \left[ P - \pi_F e^{J/k} \right], \]  

(1)

with \( P \) the hydraulic pressure, \( \pi_F \) the osmotic pressure of the feed and \( k \) the mass transfer coefficient. This may be rearranged to give\textsuperscript{3}:

\[ A_m = \frac{J}{\left( P - \pi_F e^{J/k} \right)}. \]  

(2)

To understand what happens to flux at very high permeability, we can take the limit of flux as permeability, \( A_m \), goes to infinity. Doing this, which is equivalent

\textsuperscript{2}Mathematical justification for the use of a stagnant film model is provided by Zydney \cite{10}.

\textsuperscript{3}More generally, the same result may be obtained without the need for the solution diffusion model. By assuming thermodynamic equilibrium of water across the membrane – true if the membrane is infinitely permeable to water – the net hydraulic pressure must exactly balance the osmotic pressure at the feed side surface of the membrane (i.e., \( P = \pi_F e^{J/k} \)).
Figure 3: Profiles of osmotic pressure and net pressure (hydraulic minus osmotic) for flux through membranes of finite and infinite permeability. The applied hydraulic pressure, the osmotic pressure of the feed and the mass transfer coefficient are equal in each case.
to finding the zero of the denominator in Eq. (2), leads to:
\[ J_\infty = k \cdot \ln(P/\pi_F). \]  

(3)

Figure 4a is a log-linear plot of Eqs. (1) and (3) for a fixed ratio of hydraulic pressure to osmotic pressure of the feed. The implication for membrane development is that, for fixed hydraulic pressure, flux will not increase indefinitely if one increases permeability – the flux approaches an asymptotic value. The implication for system operation with high permeability membranes is that, for any value of permeability (even infinite), an increase in hydraulic pressure will always yield an increase in flux – but the increase in flux depends on the logarithm of the hydraulic to osmotic pressure ratio. In contrast, the limiting flux rises linearly with the mass transfer coefficient.

Dimensionless quantities may also be defined in the following manner:

\[ J^* \equiv \frac{J}{k} \]  
\[ P^* \equiv \frac{P}{\pi_F} \]  
\[ A_m^* \equiv \frac{A_m \pi_F}{k} \]  
\[ E^* \equiv \frac{E_s}{\pi_F} \]  

leading to an even simpler form for Eq. 3:
\[ J^* = \ln(P^*). \]  

(8)

For comparison with Fig. 4a, this dimensionless form is shown in Fig. 4b. As a matter of reference, for a typical seawater membrane permeability (1 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)), a typical mass transfer coefficient (5\(\times\)10\(^{-5}\)) and a typical seawater osmotic pressure (25.6 bar), the dimensionless permeability of membranes today is roughly 0.14. We note that \(J^*\) is sometimes called the modified Péclet number [8, 12].
3. Asymptotic limits on flux at moderate or high recovery

3.1. Asymptotic flux of a single stage seawater reverse osmosis process

A common implementation of seawater reverse osmosis systems today is in a single stage configuration where the recovery is roughly in the range of 30-50% (Fig. 5a). We now derive an expression for the asymptotic flux in such systems, which is somewhat different than for systems with infinitesimal recovery. For single stage reverse osmosis, assuming constant fluid density, the incremental recovery of permeate along the feed flow path may be written as

\[ \dot{V}_F \, dRR' = J(RR') \, dA' \]  

where \( RR' \) is the volume fraction of the feed flow rate, \( \dot{V}_F \), recovered as permeate all of the way up until some intermediate point on the one-dimensional flow path, and \( dA' \) is the incremental membrane area. In this formulation, streamwise viscous pressure drop in the feed is neglected (i.e., \( P \), the hydraulic pressure in the single stage process, is not a function of \( RR' \)) and the mass transfer

\[ k = 5 \times 10^{-7} \frac{m}{s} \]  
\[ \alpha = 25.0 \text{ bar}, \, \beta = 35.0 \text{ bar} \]

Some systems may adopt a dual pass configuration whereby the permeate from a first pass is processed by a second pass. For the present discussion, it is sufficient to focus on a single pass system, or the first pass of a two pass system.
coefficient is assumed to be constant$^5$. The average flux $\bar{J}$ is equal to the total permeate flow divided by the total membrane area $A$

$$\bar{J} = \frac{\dot{V}_P}{A} = RR \frac{\dot{V}_F}{A},$$  \hspace{1cm} (10)

$^5$In practise, the mass transfer coefficient, which depends on the velocity of the concentrate, will fall along the flow path as the velocity falls due to the removal of permeate.
and, if the membrane is impermeable to salt and osmotic pressure is assumed to vary linearly with solute concentration\(^6\)

\[
\pi_F \dot{V}_F = \pi_C \dot{V}_C 
\]

\[
= \pi_C (\dot{V}_F - \dot{V}_P) 
\]

\[
\implies \pi_C = \frac{\pi_F}{1 - RR'}, \quad (13)
\]

with \(\pi_C\) the concentrate concentration at a recovery ratio \(RR'\). With these results, Eq. 9 may be integrated to yield the following expression for average flux as a function of permeability

\[
\bar{J} = \frac{RR}{\int_0^{RR'} \frac{dRR'}{J(RR')}} 
\]

with the local flux given by the following generalisation of Eq. (1):

\[
J(RR') = A_m \left[ P - \frac{\pi_F}{1 - RR'} e^{J(RR')/k} \right]. 
\]

Defining a dimensionless average flux, \(\bar{J}^* \equiv \bar{J}/k\), these equations may also be written as:

\[
\bar{J}^* = \frac{RR}{\int_0^{RR'} \frac{dRR'}{J^*(RR')}} 
\]

\[
J^*(RR') = A_m^* \left[ P^* - \frac{1}{1 - RR'} e^{J^*(RR')/k} \right]. 
\]

In practice, the value of the mass transfer coefficient (and thus the dimensionless permeability) will be a function of distance along the flow path because of changing cross flow velocity as permeate. (Recent studies have also shown that the mass transfer coefficient may be affected by the development of the flow within the channel, for low or moderate values of the Reynolds number at which turbulence mixing has not become important [15, 16], including cases with obstructions similar to spacers.) Here, we approximate the mass transfer to be constant along the flow path, knowing this will be more accurate at lower

\(^6\)In most cases of interest, the osmotic pressure is a weakly nonlinear function of salinity [13, 14].
recoveries and less accurate at very high recoveries. With this approximation, and letting $A_m$ tend to infinity gives the asymptotic flux for single stage reverse osmosis:

\[
\bar{J}_\infty = \frac{RR}{\int_0^{RR} \frac{dRR'}{k \ln \left[\frac{(P/\pi F) (1 - RR')}{(P/\pi F) (1 - RR)}\right]}}
\]

or, in dimensionless form:

\[
\bar{J}_\infty^* = \frac{\frac{P^* RR}{\text{li}(P^* F) - \text{li}(P^*/\pi F)} - (P/\pi_{\text{out}})}{\text{li}(P^*/\pi F) - \text{li}(P^*/\pi_{\text{out}})}
\]

where $\text{li}$ is the logarithmic integral\(^7\) and $1 \leq P/\pi_{\text{out}} = (P/\pi F)(1 - RR) \leq P/\pi F$. Equation (20) is an interesting display of the logarithmic weighting of the flux driving force. As $RR \to 0$, Eq. (20) may be shown to Eq. (3). The limit as $P \to \pi_{\text{out}}$ is discussed in the Appendix.

As for systems with infinitesimal recovery, the asymptotic flux at finite recovery depends linearly on the mass transfer coefficient. The dependence of flux on permeability, for fixed hydraulic pressure and recovery, is shown in Fig. 5b. This figure provides a picture of how flux could be improved with technological improvements in membranes, were concentration polarisation (and not fouling) to be the limiting factor affecting flux. Today’s membranes (those employed in seawater desalination plants today) exhibit permeabilities of roughly 1 L m\(^{-2}\) hr\(^{-1}\) bar\(^{-1}\) for high rejection seawater membranes or 2 L m\(^{-2}\) hr\(^{-1}\) bar\(^{-1}\) for high flow seawater membranes [18, 19]. As seen in Fig. 5b, the concentration polarisation based limit, if we are to consider a mass transfer coefficient that is typically employed today\(^8\), is roughly four to five times where average

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\(^7\)li($x$) $\equiv \int_0^x \frac{dt}{\ln t}$ where the integral is taken as a Cauchy principal value [17].

\(^8\)Based on typical flow rate and concentration polarisation values reported in the Dow Technical Manual [20].
flux is today.

3.2. Asymptotic limits on the flux of an idealised batch seawater RO process

To better understand the fundamental limits on reverse osmosis performance, one might additionally consider an idealised batch process where the applied hydraulic pressure is adjusted in time to match the rise in osmotic pressure as water is removed from the feed, as discussed in [21] and [22]. For a given permeability, this condition implies a constant flux during the process. One may think of a stirred cell type system, with a stir bar providing convection at the membrane surface and a piston capable of controlling volume flow rate and the applied pressure, \( P^b \) (Fig. 5a). One means of comparing this batch process to a single stage process is to do so at the same recovery ratio and the same energy consumption per unit of permeate produced. In a single stage RO process with no viscous pressure drop and perfectly efficient pumps and pressure recovery devices, the energy consumption per unit volume of permeate, \( E_s \), is simply given by the applied pressure, \( P \) (typically converted to units of kWh/m\(^3\)). In a pure batch process, the energy would be given by the integral of pressure as a function of recovery ratio, divided by the recovery ratio (to express energy on a unit permeate rather than unit feed basis):

\[
E_s = \frac{1}{RR} \int_0^{RR} P^b(\RR') \, d\RR' = \frac{1}{RR} \int_0^{RR} \left( \frac{J^b}{A_m} + \frac{\pi_F}{1 - \RR} \right) \, d\RR'
\tag{22}
\]

where \( J^b \) is the constant flux in the batch process and Eq. (15) has been applied in substituting in for \( P^b \). Integrating this expression and equating energy in the single stage and batch processes, leads to the following implicit solution for \( J^b \)

\[
P = \frac{1}{RR} \left[ \frac{J^b}{A_m} + \pi_F e^{J^b/k} \ln \left( \frac{1}{1 - RR} \right) \right],
\tag{23}
\]

which asymptotes, in the limit of infinite permeability, to

\[
J^b_{\infty} = k \cdot \ln \left[ \frac{P}{\pi_F \ln \left( \frac{RR}{1-RR} \right)} \right],
\tag{24}
\]
or, in dimensionless form:

\[
J_{\infty}^{b,*} = \ln \left[ P^* \frac{RR}{\ln \left( \frac{1}{1-RR} \right)} \right].
\]  

(25)

Again, for this idealised batch process, the asymptotic flux depends linearly on the mass transfer coefficient. As \( RR \to 0 \), Eq. (24) limits to Eq. (3). Also, \( RR < RR^* \), where \( RR^* \) is given by the solution to \(-\ln(1 - RR)/RR = P^*\); in words, for a fixed energy consumption, there is a maximum recovery ratio at which the flux reaches zero.

Equation 24 is plotted in Fig. 5b. Of note is the improved flux, for the same energy consumption, of a batch process compared to a single stage process. This increased flux at equal energy consumption is symmetric to the reduced energy at equal flux that has previously been described [21]. For reference, in Fig. 5c, typical values of dimensionless permeability, \( A_{m}^* \), are on the order of roughly 0.1-0.2. The utility of this dimensionless representation is that we can also draw conclusions for more general processes, for example, brackish water processes where the feed osmotic pressure may be a factor of ten lower than seawater but membrane permeability may be a factor of two higher. Approximating mass transfer coefficients as being the same in seawater and brackish water applications, a typical range for the dimensionless permeability might be roughly 0.02-0.04 for brackish applications, much lower than seawater. From Fig. 5c, it is then seen that transport imposes much less on of a limit, for brackish applications relative to seawater applications, on the flux enhancement that may be achieved with ultrapermeable membranes.

3.3. Summary of asymptotic limits

As a form of summary, expressions for the asymptotic flux due to concentration polarisation provided in Tables 1 and 2, in dimensional and dimensionless form, respectively. The minimum energy requirement is also shown; if the system is operated at a higher pressure (i.e. \( P > \pi_f/(1 - RR) \) for single stage RO), more energy will be consumed.
Table 1: Dimensional form of the asymptotic limits as $A_m \to \infty$ of flux at constant energy and minimum energy per unit volume of permeate at infinitesimal average flux.

<table>
<thead>
<tr>
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<th>Asymptotic Flux, $J_\infty$</th>
<th>Minimum Energy, $E_s$</th>
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</thead>
<tbody>
<tr>
<td>RR→0</td>
<td>$k \cdot \ln (P/\pi F)$</td>
<td>$\pi F$</td>
</tr>
<tr>
<td>Single stage RO</td>
<td>$k (P/\pi F) RR \frac{\text{li}(P/\pi F) - \text{li}[(P/\pi F)(1 - RR)]}{(1 - RR)}$</td>
<td>$P F \frac{\text{ln} \left( \frac{1}{1 - RR} \right)}{1 - RR}$</td>
</tr>
<tr>
<td>Batch RO (fixed flux)</td>
<td>$k \cdot \ln \left[ \frac{P}{\pi F \ln \left( \frac{1}{1 - RR} \right)} \right]$</td>
<td>$P F \frac{\text{ln} \left( \frac{1}{1 - RR} \right)}{1 - RR}$</td>
</tr>
</tbody>
</table>

Table 2: Dimensional form of the asymptotic limits as $A_m \to \infty$ of flux at constant energy and minimum energy per unit volume of permeate at infinitesimal average flux.

<table>
<thead>
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<th>Asymptotic Flux, $J^*$</th>
<th>Minimum Energy, $E^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR→0</td>
<td>$\ln (P^*)$</td>
<td>$1$</td>
</tr>
<tr>
<td>Single stage RO</td>
<td>$P^* \cdot RR \frac{\text{li}(P^<em>) - \text{li}[P^</em> \cdot (1 - RR)]}{(1 - RR)}$</td>
<td>$1 - RR$</td>
</tr>
<tr>
<td>Batch RO (fixed flux)</td>
<td>$\ln \left[ P^* \frac{RR \ln \left( \frac{1}{1 - RR} \right)}{1 - RR} \right]$</td>
<td>$\frac{1}{RR} \ln \left( \frac{1}{1 - RR} \right)$</td>
</tr>
</tbody>
</table>

4. Mass transfer coefficients for UPMs

Fane et al. [8] have pointed out the importance of limiting the modified (or transverse) Pécellet number, $J^* = J/k$, in order to control concentration polarisation for UPMs. The nondimensionalizations of the preceding section may be used to isolate this variable as a function of other parameters. Specifically, Eq. (15) can be written as [cf. Eq. (17)]

$$\frac{J(RR')}{k} = \left( \frac{A m \pi F}{k} \right) \left[ \frac{P}{\pi F} - \frac{e^{J(RR')/k}}{1 - RR'} \right].$$

Similarly, Eq. (23) may be written

$$\frac{J^b}{k} = \left( \frac{A m \pi F}{k} \right) \left[ RR \frac{P}{\pi F} + e^{J^b/k} \ln (1 - RR) \right].$$
Both results show that for any given feed pressure and recovery, the mass transfer coefficient must be raised in direct proportion to $A_m$ if the modified Péclet number is to held fixed. Rohlfs et al. [15] have recently modeled the streamwise development of mass transfer coefficients for high transverse Péclet number.

5. Implications and limitations

There are several factors that can limit increases in the operating flux of RO, including concentration polarisation, fouling, scaling by sparingly soluble salts (whether compounded by effects of concentration polarisation or not), and increased viscous pressure in the feed channel due to increased flow rates. The purpose of this note is provide an explanation for the flux asymptote that arises due to concentration polarisation when employing ultrapermeable membranes.

The simple formulas derived herein make this limit clear for both single stage and batch processes.

We have projected the values of transport-based flux asymptotes holding system operating parameters at values that are employed in systems today. These asymptotes illustrate that, while improvements in flux scale less than linearly as permeability increases, the limit imposed on average flux by transport is roughly four times where average flux is today for seawater desalination and roughly twenty times where it is today for brackish desalination. Operating conditions will change with time, but the dimensionless analysis, charts and results are robust to such changes and allow for flux asymptotes, imposed by transport limitations, to be continuously updated.

6. Acknowledgements

The authors would like to thank Dr. Gregory P. Thiel for insightful discussion of this note.
Appendix A. Asymptotic flux for single stage RO as $P \to \pi_{\text{out}}$

As $P \to \pi_{\text{out}}$, the logarithmic integral approaches a singular value, and $|\text{li}(P/\pi_F)| \ll -\text{li}(P/\pi_{\text{out}})$. To understand the behavior of Eq. (20) in this limit, we need the asymptotic behavior of $\text{li} x$ as $x \to 1^+$, which may be obtained from the series representation

$$\text{li} x = -\gamma + \ln(\ln x) + \sum_{n=1}^{\infty} \frac{(\ln x)^n}{n \cdot n!} \text{ for } x > 1$$

where $\gamma = 0.5772156649\ldots$ is the Euler-Mascheroni constant [17, Eqs. (5.1.3) and (5.1.10)]. Hence, we have:

$$\text{li} x \sim -\gamma + \ln(\ln x) \text{ as } x \to 1^+$$

(A.2)

Thus, with Eq. (20), $\bar{J}_\infty$ has the behavior

$$\bar{J}_\infty \sim k \frac{(P/\pi_F) - (P/\pi_{\text{out}})}{\gamma + \text{li}(P/\pi_F) - \ln[\ln(P/\pi_{\text{out}})]} \text{ as } P/\pi_{\text{out}} \to 1$$

(A.3)

Of course, this means $\bar{J}_\infty \to 0$ as $P/\pi_{\text{out}} \to 1$.

References


URL http://web.mit.edu/seawater/


URL http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08db/0901b803808db77d.pdf
