



# Theoretical framework for energy analysis of hypersaline pressure retarded osmosis



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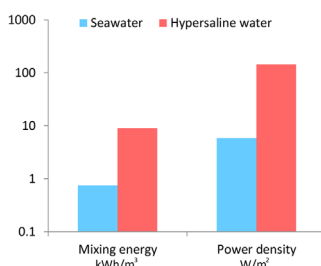
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## HIGHLIGHTS

- We present the theoretical foundation for calculations on hypersaline osmotic power.
- Mixing energy, extractable energy and power densities are examined.
- Increasing draw salinity will dramatically increase both energy and power density.
- For hypersaline draws, traditional PRO systems may operate at low efficiencies.
- Energy can be more efficiently extracted by applying PRO systems in series.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Pressure retarded osmosis (PRO) has traditionally been focused on the mixing of seawater and river water, but in pilot scale tests, this mixing scheme has been found to be economically unattractive due to power densities that are too low. One way of obtaining higher power densities may be through use of hypersaline draw solutions. In this work, the theoretical framework for calculation of the free energy of mixing, the maximum extractable work in batch and co-current PRO systems, and the potential power densities of hypersaline solutions is presented. Calculations show that very high values in all categories are realizable. By diluting 26 wt% (saturated NaCl) to seawater concentration, 15.7 kW h/m<sup>3</sup> draw is released and a maximum power density of 143 W/m<sup>2</sup> membrane can be obtained with a commercially available FO membrane. In cases where the hypersaline solution is the limiting solution, large losses of energy can be expected if the process is carried out as a constant pressure single stage operation. To minimize losses, a serial setup can be applied. Although the practical challenges for hypersaline PRO may be greater than for seawater based PRO, the high potential gains may make hypersaline PRO a more promising way of making the PRO concept realizable.

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## 1. Introduction

To mitigate climate change it has been recognized that a broad portfolio of alternative energy technologies is required (Hoffert et al., 2002). One of these technologies can be salinity power, in which a salinity gradient between two solutions is used to produce energy when mixing the two solutions under controlled

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conditions. One of the most promising methods for harvesting this energy is pressure retarded osmosis (PRO) (Yip and Elimelech, 2014). In the PRO process, a membrane is used to separate the two solutions, and the difference in osmotic pressure between the solution of high salinity (the draw) and the solution of low salinity (the feed) is used to induce a flow of water across the membrane from the feed to the draw. By applying pressure to the draw side, a pressurized flow of water is realized, and this can be converted into electricity by passing the pressurized water through a turbine (Achilli and Childress, 2010; Klaysom et al., 2013). Typically, the pressure on the draw side is held constant in which case the process can be called constant pressure retarded osmosis (C-PRO).

The most studied PRO scenario has been the mixing of river and seawater (Achilli et al., 2009; Chou et al., 2012; Gerstandt et al., 2008; Skilhagen et al., 2008; Thorsen and Holt, 2009; Yip and Elimelech, 2011), but so far it has not been possible to make this process economically viable. The main reason for this is that the amount of power that can be generated per square meter membrane (power density) with currently existing membranes is lower than  $5 \text{ W/m}^2$  (Skilhagen, 2010), which is the power density that the Norwegian energy company, Statkraft, has estimated will be necessary before commercial PRO can be realized (Gerstandt et al., 2008). A second challenge is that for a PRO scheme mixing seawater and river water, it has been estimated that only 0.192 kW h can be realized per cubic meter mixed solution, and this leaves little energy for pretreatment and pumping (Lin et al., 2014). One way of increasing both power density and the energy density is by using draw solutions of higher salinity than seawater. These are called hypersaline solutions.

The main work on hypersaline draws has been carried out on RO brine solutions (salinity  $\approx 6 \text{ wt}\% \approx 1.0 \text{ M NaCl}$ ) (Achilli et al., 2009; Chou et al., 2012; Kim et al., 2015a; Kim et al., 2015b; Saito et al., 2012; She et al., 2012; Wan and Chung, 2015), but also experiments with concentrations up to 12 wt% ( $\approx 2.0 \text{ M NaCl}$ ) (Kim and Elimelech, 2013, 2012; Kim et al., 2015a; She et al., 2012; Straub et al., 2013), as well as a single study with a draw concentration of 3.0 M NaCl ( $\approx 16 \text{ wt}\%$ ) (Straub et al., 2013), have been conducted. In these studies it has been found that although negative effects such as concentration polarization become increasingly important at higher salinities (McCutcheon et al., 2006), the higher salinity gradients make it possible to obtain power densities well above  $5 \text{ W/m}^2$ . The maximum reported experimental values are as such  $24.3 \text{ W/m}^2$  for 1.0 M NaCl (Zhang et al., 2014),  $39.4 \text{ W/m}^2$  for 2.0 M NaCl (Straub et al., 2013) and for  $59.7 \text{ W/m}^2$  3.0 M NaCl (Straub et al., 2013). The two last power densities were even obtained by using a commercially available membrane (Straub et al., 2013). Adding to that, theoretical investigations have estimated that by using highly concentrated hypersaline draws from salt lakes (33 wt%) power densities can potentially reach up to  $696 \text{ W/m}^2$  (Helfer et al., 2014). From a cost perspective, a higher power density is interesting since it will allow for use of fewer membranes and less material thereby reducing capital costs. These cost savings can be significant, and it has been estimated that capital cost PRO plants based on hypersaline draws could be up to 40 times less compared to seawater based PRO plants (Helfer et al., 2014). The harsher condition may however increase operational costs, especially if frequent membrane replacement is required. Finally, by using hypersaline draws, the salinity of the feed can be increased as well (Kim and Elimelech, 2013), and this could be very important in areas with limited fresh water resources.

To accurately estimate the realizable energy from hypersaline PRO schemes, and hereby evaluate the potential of the hypersaline PRO process, it is necessary to first calculate the free energy of mixing, which represents the theoretical maximum energy available, and then determine the irreversible losses in order to find the

actual extractable work. The theoretical framework for the detailed analysis for mixing of river and seawater has been outlined in the work of Yip and Elimelech (2012). However, in their approach, a number of assumptions were made that limits the use of the model to waters of seawater salinity ( $\sim 3.5 \text{ wt}\%$ ). In this work, we present the theoretical framework for determining the PRO energy potential for salinities (based on NaCl) up to 26 wt% (6 molal, 5.3 M, the saturation limit for NaCl solutions), and use it to evaluate the hypersaline PRO process. We use the same approach to determine the maximum extractable work as outlined by Yip and Elimelech (Yip and Elimelech, 2012), which is only strictly valid for laboratory recirculation setups and co-current PRO systems. A second approach to estimate the extractable work in counter-current PRO systems has been outlined by Reimund et al. (2015).

## 2. General mixing theory

When two solutions, A and B, of different compositions are mixed to yield a mixture, M, free energy is released. The amount of energy that is released in the process depends on both the specific composition of each of the solutions, and the relative ratio in which the solutions are mixed. The free energy of mixing is given by Eq. (1).

$$-\Delta G_{\text{mix}} = RT \left( \left[ \sum x_i \ln(\gamma_i x_i) \right]_M - \phi_A \left[ \sum x_i \ln(\gamma_i x_i) \right]_A - \phi_B \left[ \sum x_i \ln(\gamma_i x_i) \right]_B \right) \quad (1)$$

where  $x_i$  is the mole fraction,  $\gamma_i$  the activity coefficients of each of the species present in the solution, and  $\phi_A$  and  $\phi_B$  are the ratios of the moles in solution A and B respectively to the total moles in the system ( $\phi_A + \phi_B = 1$ ).  $R$  is the gas constant and  $T$  is the absolute temperature in Kelvin.

If solutions A and B consist solely of water and salt (NaCl), and  $\phi = \phi_A$ , Eq. (1) may be rewritten as:

$$\begin{aligned} \frac{-\Delta G_{\text{mix}}}{RT} &= x_{w,M} \ln(\gamma_{w,M} x_{w,M}) + \nu \cdot x_{s,M} \ln(\gamma_{s,M} x_{s,M}) \\ &\quad - \phi (x_{w,A} \ln(\gamma_{w,A} x_{w,A}) + \nu \cdot x_{s,A} \ln(\gamma_{s,A} x_{s,A})) \\ &\quad - (1 - \phi) (x_{w,B} \ln(\gamma_{w,B} x_{w,B}) + \nu \cdot x_{s,B} \ln(\gamma_{s,B} x_{s,B})) \end{aligned} \quad (2)$$

where the subscript w refers to water and s to salt.  $\nu$  is the dissociation constant for the salt, which for NaCl is 2.

## 3. Mixing theory for mild saline solutions

When working with mild saline solutions, a number of assumptions can be made to simplify Eq. (2). In the work of Yip and Elimelech (2012) the molar mixing energy in Eq. (2) was converted to a volumetric mixing energy by assuming that the solution mixed ideally, so that the molar ratio,  $\phi$ , was equal to the volumetric ratio. Further, it was assumed that the activity of water could be neglected because the activity, the product of the mole fraction and the activity coefficient, was very close to 1. Following these assumptions, it is possible to reduce Eq. (2) to:

$$\frac{-\Delta G_{\text{mix},V,A}}{\nu RT} = \frac{c_{s,M}}{\phi} \ln(\gamma_{s,M} c_{s,M}) - c_{s,A} \ln(\gamma_{s,A} c_{s,A}) - \frac{1 - \phi}{\phi} c_{s,B} \ln(\gamma_{s,B} c_{s,B}) \quad (3)$$

Here the mixing energy is calculated per unit volume of solution A. In a river/seawater scheme this is practical since solution A is taken to be the feed solution, the river, which will be the limiting solution relative to the seawater of which there is plenty.

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