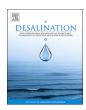


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Pressure retarded osmosis from hypersaline solutions: Investigating commercial FO membranes at high pressures



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ABSTRACT

The hypersaline PRO process was investigated in laboratory scale at pressures up to 70 bar and draw solution salinities up 5 M NaCl to evaluate the power potential and the practical application of the process. Five commercial FO membranes were tested to evaluate the potential of different types of FO membranes, but also the potential of applying already existing membranes in the hypersaline PRO process. The results showed that with commercially available FO membranes, the PRO process could be operated at pressures up to 70 bar with power densities significantly above the 5 W/m^2 , which is the estimated cost efficiency level. Of the tested membrane materials, the cellulose membranes showed highest performance at pressures above 20 bar. Below this pressure, the highest performance was found with the thin film membranes. This study also showed that high pressures negatively influenced the membrane resistance and salt permeability, which therefore should be focus points in future development of high pressure PRO membranes.

1. Introduction

To mitigate climate change and air pollution, renewable energy technologies must be developed and improved, and it is generally recognized that a broad portfolio of technologies is necessary to completely substitute fossil fuels [1]. One of the potential technologies that is still largely untapped is salinity power [2]. In this technology, concentration gradients between two water bodies like a river (fresh water) and the ocean (salt water), are used to extract energy through one of several schemes. At the moment the technique known as pressure retarded osmosis (PRO), is regarded as being the best available solution [3]. Compared to wind and solar power, salinity power has the advantage that it can deliver a constant base-load of energy, independent on whether the sun is shining or the wind is blowing. Furthermore, salinity power plants can be placed underground, something which might actually benefit the process, and in this way be less visible in the environment [4]. The last years have seen a large and increasing number of publications on salinity power, but now the feasibility is being questioned due to the fact that with current PRO systems only 0.192 kWh per mixed solution can be extracted when mixing seawater and river water, which leaves little room for further losses, energy for pretreatment and inefficiencies [5].

A large part of the work on PRO has focused on scenarios where

One way to overcome both challenges and potentially make PRO cost efficient, is to apply draw solutions of higher salinity, also known as hypersaline draw solutions [10]. In the Japanese Mega-ton Water System project, seawater desalination brine was used as draw solution, and with this it was possible to obtain $> 13 \text{ W/m}^2$ [11]. Chung et al. also desalination brine in a small pilot study, with which it was possible to obtain 14 W/m^2 [12]. In laboratory studies investigating hypersaline draw solutions, power densities above 5 W/m^2 , have consistently been found, with Straub et al. reporting a power density of 60 W/m^2 when using a 3.0 M NaCl draw [13]. The energy potential measured as kWh per cubic meter fresh water also increases markedly from 0.7 kWh for

river water and seawater are used. In 2009, the Norwegian energy company Statkraft constructed the world's first osmotic power plant based on such a scheme [6]. However, in 2013, Statkraft decided to terminate their work on PRO due to the fact that they could not produce power densities above 5 W/m² membrane area. 5 W/m² is now generally accepted as the level that must be surpassed for PRO schemes to become cost efficient [2]. Since the Statkraft project, power densities above 5 W/m² obtained with hand cast membranes have been reported [7,8], and recently Maisonneuve et al. reported a power density of 7.1 W/m² using a newly developed commercial membrane [9]. However, even though membranes are improving, the low energy density of the PRO process may still limit it use in river water/sea water schemes.

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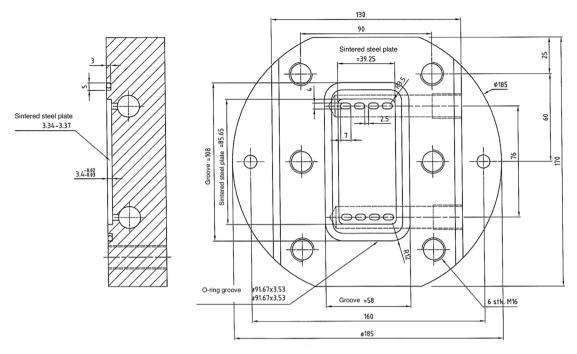


Fig. 1. Design of high pressure cell for PRO.

seawater (3.5 wt%) to 9 kWh for saturated NaCl solutions (26 wt%)

In this work, the use of hypersaline NaCl solutions and the effect of both draw concentration and feed concentration on the power density were investigated. Draw concentrations up to 5 M NaCl are used. This is close to the saturation limit of pure NaCl solutions and the highest reported for PRO studies. To fully take advantage of the hypersaline draw, it is necessary to operate at high pressures. Previous studies have used pressures up to 55 bar, but in this study we have designed a PRO system capable of operating at pressures up to 70 bar. This setup is used to investigate how very high pressures influence the membrane performance by measuring changes in water and salt permeability as well as the structural coefficient. Also, we investigate the applicability of five commercially available FO membranes for high pressure hypersaline PRO. Four of these has not previously been investigated for use in hypersaline PRO.

2. PRO theory

In pressure retarded osmosis, two solutions with different osmotic pressure are pumped on opposite side of a semi-permeable membrane. Due to the difference in osmotic pressure, water will flow from the solution of lowest salinity (the feed solution) to the solution of highest salinity (the draw solution). This transport of water can be described with Eq. (1).

$$J_w = A(\Delta \pi - \Delta P) \tag{1}$$

where J_w is the flux of water (L m⁻² h⁻¹), Δm is the membrane water permeability constant (L m⁻² h⁻¹ bar⁻¹), Δm is the osmotic pressure difference of feed and draw solution and ΔP is the difference in the applied pressure across the membrane.

To produce energy, the flow of water through the membrane is retarded by applying pressure to the draw solution. As long as the applied pressure is lower than the osmotic pressure difference, there will be a net flow of water to the draw solution, and this increases the volume of the pressurized solution. Energy can be realized e.g. by sending the pressurized solution to a turbine.

A key performance parameter of the PRO process is the power density, which is the number of watt produced per square meter

membrane. It can be calculated as the product of the draw pressure and the water flux as described by Eq. (2).

$$W_p = J_w \cdot P \tag{2}$$

Since the process is driven by an osmotic gradient it is important to determine the osmotic pressure accurately. In traditional seawater based PRO, it is sufficient to use the Van't Hoff equation to determine the osmotic pressure, but for hypersaline solutions, this equation becomes too inaccurate. Instead osmotic pressure can be calculated from the water activity, a_{w} , as shown in Eq. (3).

$$\pi = \frac{RT}{V_{w}} \ln(a_{w}) \tag{3}$$

here R is the gas constant, T the absolute temperature and V_m the molar volume. We have previously described how V_m and a_w may be determined by using the Pitzer equations [10].

3. Materials & methods

3.1. Osmotic membranes

Five different commercial forward osmosis membranes were used in the study. For the investigation of the effect of draw and feed salinity an asymmetric cellulose acetate (CTA) membrane from Hydration Technology Innovations (HTI, Albany, OR) was used. The other membranes were: Membranes harvested from a HTI spiral membrane module (an HW-40 membrane in an OsMem 2521 FO-FS module), CTA and TFC membrane from Fluid Technology Solutions (FTS, Albany, OR) and aquaporin based membranes from Aquaporin A/S (Copenhagen, Denmark). The membranes from FTS and Aquaporin has not previously been investigated for use in hypersaline PRO.

3.2. High pressure PRO cell and setup

To access high pressures, specially designed membrane cells and tightly woven spacer materials are required [13–17]. For this study, a membrane cell was constructed with symmetric feed and draw channels with the following dimensions $85.7 \times 39.3 \times 3.4$ mm. From previous studies it was known that the in- and outlet of the feed channel were

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