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Evaluating the potential for zero discharge from reverse osmosis desalination using integrated processes – A review

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ABSTRACT

Desalination processes used worldwide produce a large amount of waste concentrate, the disposal of which can have significant environmental impacts. As such, there has been research carried out into the development of zero liquid discharge technologies which recognise that the waste concentrate streams contain valuable salts, minerals and water. These technologies include the proprietary SAL-PROC systems, as well as other integrated systems that use a variety of different technologies for the extraction of salts and minerals from waste concentrates. Research has also been conducted on using forward osmosis as a means of treating the waste concentrate in order to produce additional product water and thus reduce the volume of waste concentrate. This article provides a review of these technologies and evaluates the potential for achieving zero liquid discharge by combining these technologies with conventional desalination technologies into integrated processes.

Keywords: Forward osmosis; Recovery; Desalination; Reverse osmosis; Flux

1. Introduction

Freshwater sources are becoming stressed in many countries including the United States, Middle East North Africa and Australia. It is widely recognised that the desalination of brackish groundwater and seawater will become a reliable solution to the water shortages being experienced by these countries (Goosen, Al-Hinai, & Sablani, 2001; Purnama & Al-Barwani, 2006; Sethi, Walker, Drewes, & Xu, 2006; Tang & Ng, 2008). Whilst Middle Eastern countries such as Oman have been using desalination technology now for decades as a source of potable water (Goosen, et al., 2001), the implementation of desalination in the United States has been hindered by several factors (Lauer, 2006). These factors include high-energy requirements, high-treatment costs and the production of a large volume of waste concentrate. The latter of these factors is perhaps the most significant, with approximately twenty to fifty percent of the feed stream being wasted as by-product or concentrate from conventional desalination processes (Sethi, et al., 2006). The waste concentrate often contains inorganic compounds and has a much greater salt concentration than the feed water (Younos, 2005). Due to these properties, the disposal of waste concentrate poses a significant environmental and regulatory problem for desalination plants. Currently the methods of disposal include disposal to surface waters, deep well injection, land application and evaporation ponds (Younos, 2005). Whilst many methods of disposal exist, they all have various limitations and associated environmental issues depending on the volume and characteristics of the concentrate produced. As such, there has been research carried out into the development of zero liquid discharge (ZLD) technologies which recognise that the waste concentrate streams contain valuable salts, minerals and water. As such, novel approaches using integrated chemical and evapo-cooling systems and relatively new technologies such as forward osmosis (FO) have been investigated

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with the aim of recovering both salts and water whilst significantly reducing concentrate output. This paper examines technologies for both salt and water recovery from reverse osmosis desalination plant concentrate and proposes an integrated system which has the potential to achieve ZLD.

2. Salt recovery

The valuable salts that can potentially be recovered from the discharge concentrate of desalination plants vary depending on the feed water. Gypsum, sodium chloride, magnesium hydroxide, calcium chloride, calcium carbonate and sodium sulphate are some of the common products that have been identified (Ahmed, et al., 2003; Arakel, Mickley, & Stapleton, 2004). Methods for the recovery of these salts and minerals have been developed and include the SAL-PROC and Reverse-Osmosis-SAL-PROC (ROSP) systems, evapo-cooling systems and other integrated systems.

2.1. SAL-PROC and ROSP systems

The SAL-PROC technology developed by Geo-Processors achieves ZLD by integrating sequential reaction and evapo-cooling stages in a closed process to cause the precipitation and crystallisation of valuable chemical compounds (Arakel, et al., 2004). SAL-PROC technologies can be used either in conjunction with Reverse Osmosis (RO) desalination – ROSP – or as a standalone option to directly treat saline wastewater. Both of these technologies have been implemented in two case studies to treat saline waters in Lake Tutchewop, Victoria and water produced from the extraction of coal bed methane in Queensland.

Lake Tutchewop receives an annual salt load of approximately 64,000 tonnes per annum from irrigation discharge and saline groundwater discharge. The SAL-PROC technology was employed to design a full-scale plant capable of extracting products from the lake in order to balance the incoming salt load. The products recovered experimentally consisted of high grade magnesium hydroxide, sodium chloride, fine grained gypsum-magnesium hydroxide slurry and a concentrated calcium chloride solution (Arakel, et al., 2004). The SAL-PROC process route that was applied for this particular study is detailed schematically in Fig. 1. Similarly, a proposed coal bed methane (CBM) extraction operation in Queensland required the simultaneous extraction of large volumes of water that were saline and had elevated bicarbonate concentrations, making the water unsuitable for direct discharge into the environment. The ROSP technology was used as a treatment system for the saline water produced by the operation and is shown schematically in Fig. 2. The products produced by the process consisted of calcium carbonate, sodium sulphate and sodium chloride. Data obtained from pilot and demonstration scale facilities in the field at both sites were used to generate cost estimates including capital, operating and potential sales of chemical product. These are presented for both case studies in Table 1. From these figures, it is evident that both processes provide significant payback.

In addition to these two case studies, a feasibility study of salt production from an inland RO desalination plant was conducted by Ahmed *et al*. (2003). Three different treatment options using the ROSP technology were proposed to treat the reject concentrates from four different RO desalination plants operated by Petroleum Development Oman (PDO). The schematic diagrams of the three treatment options are shown in Fig. 3. It was found that sodium chloride, magnesium hydroxide, gypsum, calcium chloride, calcium carbonate and sodium

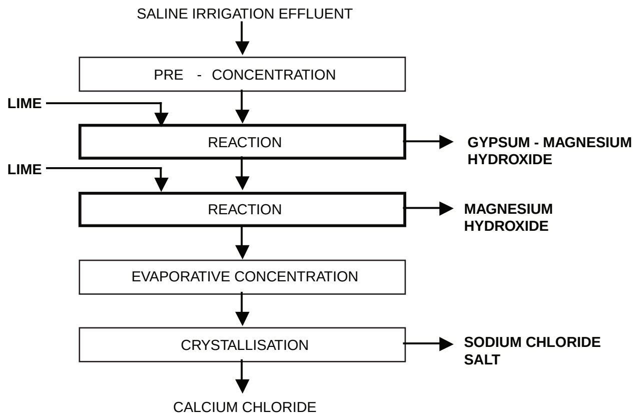

Fig. 1. SAL-PROC process route for treatment of waters from Lake Tutchewop (Arakel, et al., 2004).

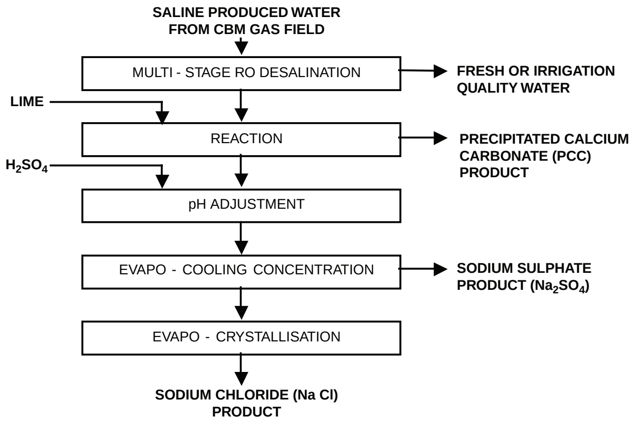

Fig. 2. ROSP process route for treatment of waters from the CBM extraction operation (Arakel, et al., 2004).

Table 1
Full scale project cost benefit analysis summaries of case study 1 and 2 (Arakel, et al., 2004).

Case study	1	2
Effluent type and location	Irrigation effluent, Victoria, Australia	Saline CBM produced water, Queensland, Australia
Nominal throughput volume, m^3/h	110	333
Water recovery	N/A	85%
Design operating hours p.a.	7,200	8,640
Feed salinity, g/L TDS	82	7.5
Salt load removal capacity, tpa	65,280	21,600
Annual product output, tpa	94,460	25,211
Total fixed capital cost	$15,044,008	$11,987,862
Total annual operating cost	$3,810,685	$4,816,166
Gross annual income from 100% sale of products	$9,810,800	$10,473,580

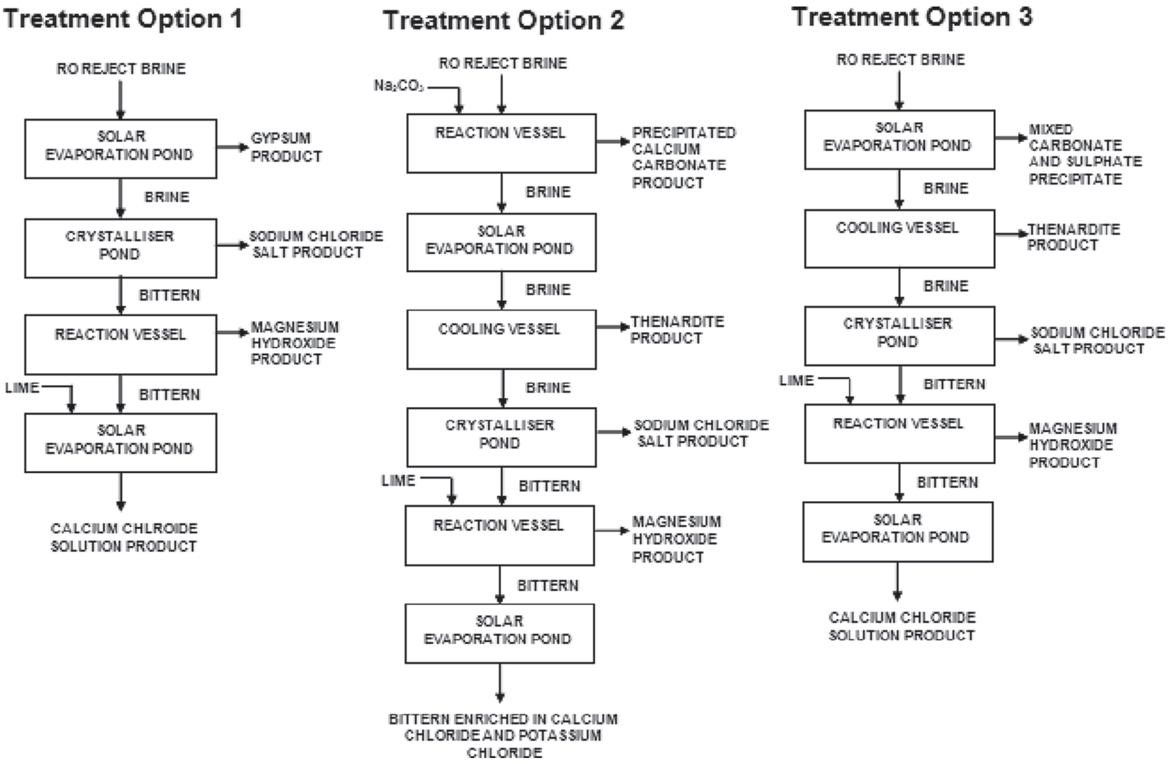

Fig. 3. Three proposed treatment options for reject concentrates from PDO operated desalination plants (Ahmed, et al., 2003).

sulphate could be produced from the reject concentrate of the RO desalination plants using the ROSP treatment methods. The projected annual product yield from each of the four PDO operated RO desalination plants for the selected treatment method was calculated and is shown in Table 2. Based on these product yields, it was estimated that US $895,000 could be gained from the sale of products from these four RO desalination plants.

Finally the studies conducted by Ahmed *et al.* (2003) and Arakel *et al.* (2004) both showed that it is economically feasible to treat saline wastewaters and recover valuable salts either by treating the saline water directly using the SAL-PROC technology, or by treating the desalination plant concentrate using the ROSP technology.

2.2. Other systems

Integrated systems using a variety of different technologies such as membranes, chemical precipitation,

Table 2
Projected annual product yield from each RO desalination plant (Ahmed, et al., 2003).

Products	Bahja 1 & 2	Rima	Nimr 1 & 2	Marmul 1 & 2
Treatment option 1				
Gypsum (t)	350	204	475	
Sodium chloride salt (t)	1000	510	1385	
Magnesium hydroxide (t)	75	68	97	
Calcium chloride (t)	240	295	385	
Treatment option 2				
Precipitated calcium carbonate (t)	370	320	532	
Sodium sulphate (t)	225	130	304	
Sodium chloride salt (t)	1100	560	1850	
Magnesium hydroxide (t)	35	36	51	
Bittern (ML)	1.5	1.0	2.5	
Treatment option 3				
Gypsum & magnesium carbonate (t)				220
Sodium sulphate (t)				180
Sodium chloride salt (t)				115
Magnesium hydroxide (t)				37
Calcium chloride (t)				55

crystallization and centrifuging exist for the extraction of salts and minerals from waste concentrates. For example, Drioli *et al.* (2004) developed a system which aimed to recover calcium carbonate, sodium chloride and magnesium sulphate from nanofiltration waste concentrate. The system consisted of membrane contactor and crystallizer technology used in conjunction with chemical precipitation. A schematic diagram of the integrated system is shown in Fig. 4. Drioli *et al.* (2004) found that the process was capable of recovering calcium carbonate using precipitation as well as sodium chloride and magnesium sulphate via membrane crystallization. The process recovered 35.5 kg/hr of sodium chloride, 2.95 kg/hr of calcium carbonate and 8.4 kg/hr of hydrated magnesium sulphate from a feed flow rate of 1 m^3/hr. The integrated system also improved the fresh water recovery factor of the nanofiltration up to 95% from 64%.

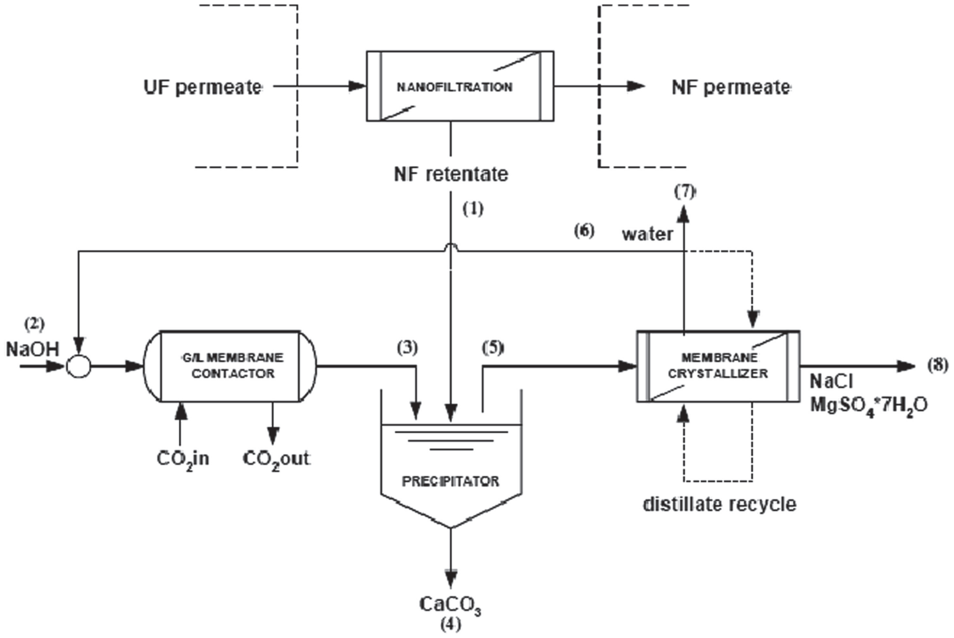

Fig. 4. Schematic diagram of an integrated membrane system for the recovery of dissolved salts from NF retentate (Drioli, et al., 2004).

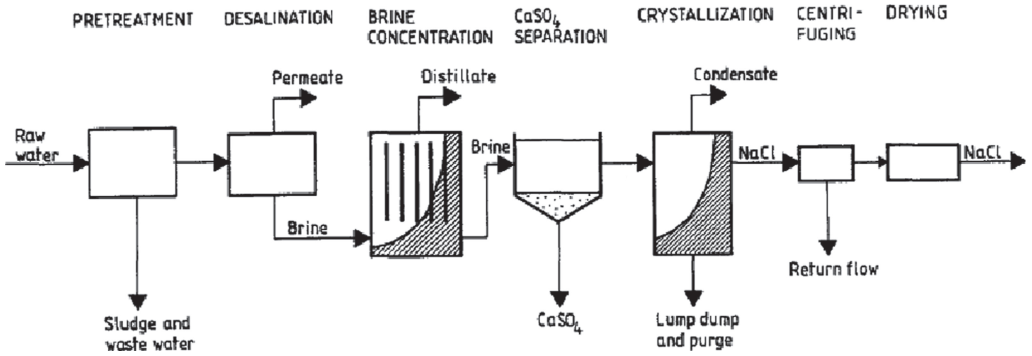

Fig. 5. Schematic diagram of the integrated process for recovery of salts from Debiensko coal mine wastewaters in Poland (Ericsson & Hallmans, 1996).

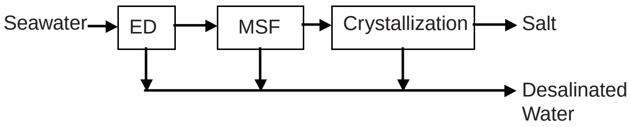

Fig. 6. Schematic diagram of the ED-MSF-crystallisation system for desalination-salt production (Turek, 2003a).

Another integrated system utilised by Ericsson & Hallmans (1996) was capable of recovering sodium chloride salt from saline wastewater at the Debeinsko coal mines in Poland whilst achieving near ZLD. The process consisted of brine concentration, calcium sulphate precipitation, crystallization, centrifuging and drying to produce sodium chloride salt from the RO concentrate of mine wastewaters. A schematic diagram of the process is shown in Fig. 5. A total of 4570 m^3/d of high-salinity water was processed, consisting of a mixture of raw coal mine discharge and RO concentrate with a salinity of 70 to 110 g/dm^3. The system recovered 12.5 t/hr of sodium chloride salt, with a salt purity of >99.6%.

Other integrated systems for salt production were investigated by Turek (2003a) and Turek (2003b) which utilised electrodialysis (ED) and a hybrid membrane-thermal process respectively. The ED system consisted of ED followed by multi-stage flash distillation (MSF) and crystallisation. A schematic diagram of the system is shown in Fig. 6. Two-step ED was used in countercurrent flow mode to perform desalination, with a water recovery rate of 90%. The estimated costs of the ED-MSF-crystallisation system for the production of desalinated water and salt for both low resistance and high resistance membranes are detailed in Table 3. Finally, it was found that desalinated water could be produced at a cost of \$0.44/m^3 by the ED-MSF-crystallisation system with an estimated salt production of 23.7 kg/m^3 of desalinated water. The hybrid membrane-thermal systems on the other hand utilised ultrafiltration (UF)-nanofiltration (NF)-MSF-crystallisation and UF-NF-RO-MSF-crystallisation to produce both salt and desalinated water. Schematic diagrams of the two systems are detailed in Fig. 7 and Fig. 8 respectively. This study found that the UF-NF-MSF-crystallisation system was capable of producing desalinated water at a cost of \$0.71/m^3, whereas the UF-NF-RO-MSF-crystallisation system achieved a cost of \$0.43/m^3. Both systems produced salt at 17.1 g/m^3 of desalinated water.

Similar to the SAL-PROC and ROSP systems, the integrated systems have been found to be effective at recovering salt and water either directly from saline wastewaters or desalination plant concentrate.

Table 3
Estimated costs of desalination-salt production in an ED-MSF-crystallisation system per 1 m^3 of desalinated water (Turek, 2003a).

	High resistance membranes	Low resistance membranes
Optimum value of first step ED current density, A/m^3	500	700
Electric energy consumption in ED stage, kWh/m^3	7.42	6.59
Electric energy cost in ED stage, \$	0.445	0.395
Investment and maintenance cost of ED stage, \$	0.450	0.377
MSF cost, \$	0.190	0.190
Crystallisation cost, \$	0.189	0.189
Total cost, \$	1.274	1.151
Value of produced salt, \$	0.710	0.710
Desalinated water cost, \$	0.564	0.441

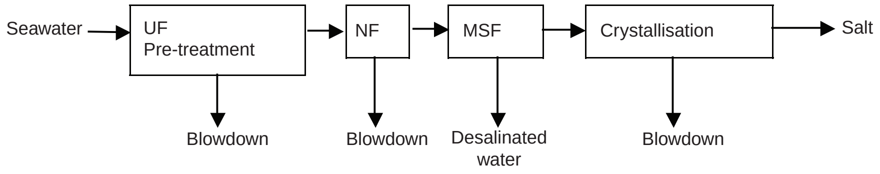

Fig. 7. Schematic diagram of desalination-salt production in an UF-NF-MSF-crystallisation system (Turek, 2003b).

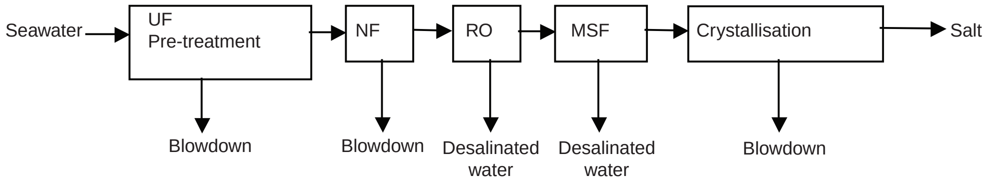

Fig. 8. Schematic diagram of desalination-salt production in an UF-NF-RO-MSF-crystallisation system (Turek, 2003b).

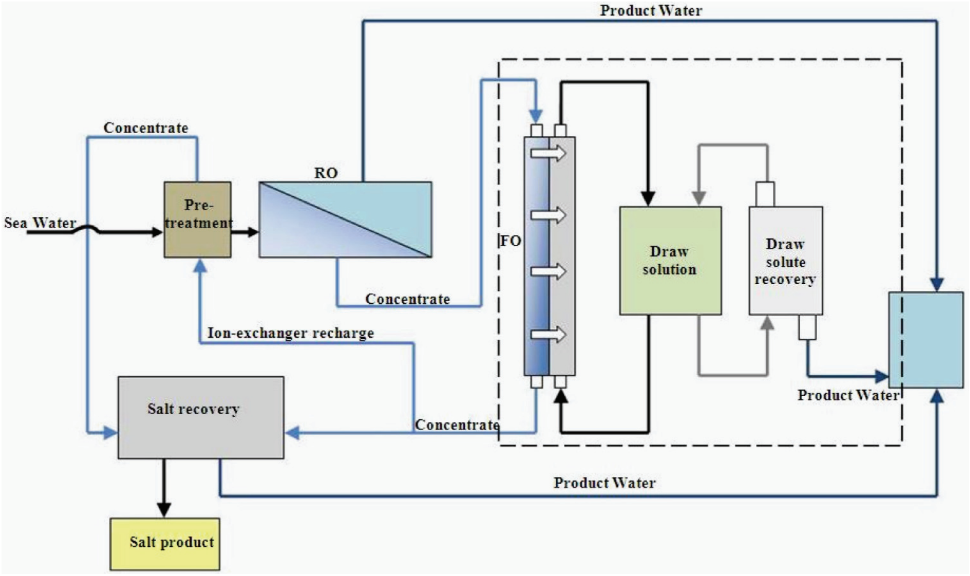

Fig. 9. Schematic diagram of proposed integrated process to achieve ZLD.

3. Water recovery via forward osmosis

Forward osmosis (FO) has been proposed as a means of desalinating water and as a method for reducing the waste concentrate produced from desalination plants by researchers over the past 40 years. FO differs from RO because the osmotic pressure differential ($\Delta\pi$) across the membrane is the driving force for the transport of water through the membrane, rather than the hydraulic pressure differential as in RO (Cath, Childress, & Elimelech, 2006). As such, FO utilises a highly concentrated solution generally referred to as the draw solution to generate a large osmotic pressure differential across the membrane, thus resulting in the transport of water from the less concentrated feed stream to the highly concentrated draw solution. A schematic diagram of a general FO process which incorporates draw solute recovery and recycling is shown within the dotted line in Fig. 9.

3.1. Draw solutions

Since the draw solution is the driving force behind the FO process, the solute within the draw solution must meet several criteria in order to be suitable for the FO process. These criteria for an ideal draw solution have been identified in the literature and are as follows (Cath, et al., 2006; McCutcheon, McGinnis, & Elimelech, 2005):

High osmotic efficiency: In order to achieve high osmotic efficiency, the draw solute must be highly soluble in water whilst having a low molecular weight. This allows the draw solution to generate a high osmotic pressure at lower concentrations than a less efficient draw solution. The generation of a high osmotic pressure is important because a higher osmotic pressure will produce a higher water flux and water recovery rate from the feed solution.

Easily and economically separated and recycled: The draw solute must be easily and economically separated from the permeate stream in order to produce potable product water. It is also important that the draw solute can be recycled to reduce operating costs.

Non-toxic: The draw solute must be non-toxic, as trace elements may be present in the product water after the separation of the draw solute.

Chemically compatible with the membrane being used: The draw solution must be chemically compatible with the membrane being used, as the draw solution can potentially degrade the membrane and impact upon flux and rejection rates.

A wide range of draw solutions which meet some or all of these criteria have been used in previous studies. These have included sulphur dioxide (Batcheldor, 1965; Glew, 1965), aluminium sulphate (Frank, 1970), fructose (Stache, 1989), a two step process using potassium nitrate and sulphur dioxide (McGinnis, 2002) and ammonium bicarbonate (McCutcheon, et al., 2005). Of these studies, only the more recent ones by McGinnis (2002) and McCutcheon, et al. (2005) have utilised draw solutes which have satisfied all of the criteria listed above.

3.2. Flux

The flux across a FO membrane has been found to be comparable to the flux across an RO membrane. The typical flux achieved by a seawater RO desalination plant is between 12 and 15 L/m^2.h for open water intake and 15 to 17 L/m^2.h for beach well intake, where the salt concentration is around 1.0 M NaCl, at operating pressures of between 55 and 80 atm (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009). In comparison to this, a flux between 3.2 and 23 L/m^2.hr was achieved for FO for a 0.5 M NaCl feed solution for bulk osmotic pressure differentials of 22 to 214 atm respectively. Whilst a flux was achieved between 4 and 7.2 L/m^2.h for FO for a 2.0 M NaCl feed solution for bulk osmotic pressure differentials of 79 and 125 atm respectively (McCutcheon, McGinnis, & Elimelech, 2006).

3.3. Water recovery, salt rejection and energy efficiency

Water recoveries between 38 and 86% have been realised for FO experiments depending on the feed water. Water recoveries between 60% and 86% where achieved for batch FO experiments using concentrates obtained from brackish water RO desalination with approximately 0.5 and 0.2 M salt concentrations respectively as the feed streams. Total water recoveries for the combined brackish water RO-FO processes for the two different feed streams were found to be greater than 95% and 96% each (Martinetti, Childress, & Cath, 2009). In this case the draw solution was 1.25 M NaCl. Similarly, the recovery for FO experiments using 1 M NaCl as the feed stream and 5 M fructose as the draw solution was found to be 56.8% after 18 hours of operations. The recovery for 2 M NaCl as the feed stream and 5M fructose as the draw solution was 38.5% (Tang & Ng, 2008). Since the feed solutions used by Tang & Ng (2008) are representative of concentrates obtained from seawater RO desalination, their results can be used to determine the total recovery of a seawater RO-FO desalination process. Using an average recovery rate of 45% for seawater RO desalination (Greenlee, et al., 2009), it can be calculated that the recovery rate can be increased to between 66% and 76% from 45% by using a seawater RO-FO desalination process.

The typical salt rejection of an FO membrane is generally greater than 97% according to Cath, et al. (2006). This is consistent with the salt rejection attained by McCutcheon, et al. (2006) of between 95% and 99%, with the higher rejection obtained at higher water flux. Finally, the energy requirements of the FO process are much lower than those of current desalination technologies. The energy savings of the ammonia-carbon dioxide FO process proposed by McCutcheon, et al. (2004), on an equivalent work basis, were projected to range from 72% when compared to RO up to 85% when compared to MSF distillation (McGinnis & Elimelech, 2007).

4. Integrated processes for ZLD

The salt recovery processes discussed earlier were effective at recovering valuable salt products which were able to substantially offset the costs of the desalination process while significantly reducing the quantity of waste concentrate produced. Similarly, the FO process has been shown to be capable of increasing the water recovery from abrackish water RO desalination plant up to 96% and up to an estimated 66% for a seawater RO desalination plant. By integrating the salt recovery and FO processes with conventional RO desalination, increased water recovery and the recovery of valuable salt products could be achieved, resulting in ZLD. A schematic diagram of a potential integrated process is detailed in Fig. 9. In this process the RO concentrate would be treated using a FO process in which further product water would be recovered and the draw solute fully recovered and recycled. The concentrate stream from the FO process could then be used to recharge the pre-treatment ion-exchange resins, after which all FO concentrate would be treated using a salt recovery process to recover valuable salts and further product water, using one of the methods as discussed earlier. The particular salt recovery process that would be used would depend upon the various species of salts present in the concentrate water.

5. Conclusion

The technologies to recover salt and greater volumes of product water from the desalination process are currently available. The salt recovery systems have proven to be effective through laboratory and pilot-scale experiments. Currently there is insufficient data pertaining to FO, as a desalination process, to critically evaluate the process as an effective method of recovering further product water. However, despite FO being in the early stages of development, it has shown the potential to be an effective means of desalination to improve product water yield when used in conjunction with RO. Further research is needed in order to improve this technology and to adequately determine the advantages and disadvantages of an integrated process compared to conventional desalination processes. Some of this research is already in progress, such as the construction of a pilot-scale FO plant at Yale University (Elimelech, 2007). Finally, with further research into FO, the integration of these technologies with existing RO desalination methods has the potential to achieve ZLD whilst producing salt products and additional product water.

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