Abstract

A photovoltaic powered ultrafiltration and reverse osmosis system was tested with a number of natural groundwaters in Australia. The objective of this study was to compare system performance at six remote field locations by assessing the impact of water composition and fluctuating energy on inorganic contaminant removal using a BW30-4040 membrane. Solar irradiance directly affected pressure and flow. Groundwater characteristics (including TDS, salts, heavy metals, and pH), impacted other performance parameters such as retention, specific energy consumption and flux. During continual system operation, retention of ions such as Ca$^{2+}$ and Mg$^{2+}$ was high (> 95%) with each groundwater which can be attributed to steric exclusion. The retention of smaller ions such as NO$_3^-$ was affected by weather conditions and groundwater composition, as convection/diffusion dominate retention. When solar irradiance was insufficient or fluctuations too great for system operation, performance deteriorated and retention dropped significantly (< 30% at Ti Tree). Groundwater pH affected flux and retention of smaller ions (NO$_3^-$ and F) because charge repulsion increases with pH. The results highlight variations in system performance (ion retention, flux, specific energy consumption) with real solar irradiance, groundwater composition, and pH conditions.

Keywords: brackish groundwater; photovoltaics; reverse osmosis; specific energy consumption; solar energy

1. Introduction

Water treatment and recycling are key issues with increasing water scarcity. Membranes can purify drinking water effectively; however processes are often energy intensive due to pumping requirements, especially when high pressures and flow rates are required. The coupling of membrane technology with renewable energy sources is thus an excellent option for desalination and remote community water supplies (Schäfer et al. 2005).

A main treatment concern is the removal of naturally-occurring inorganic salts and contaminants (World Health Organization 2008; Montgomery and Elimelech 2007). Reverse osmosis (RO) and nanofiltration membranes remove many such dissolved contaminants via several mechanisms (including size exclusion, charge repulsion, diffusion, convection, adsorption, precipitation). However, filtration behaviour is not yet understood, especially with regard to complex groundwaters and fluctuating energy.

Renewable energy membrane filtration (RE-membrane) systems were first used approximately 30 years ago (Petersen et al. 1981) and technology has developed since the first protocols into systems for remote areas which are now cost-competitive with other water supply technologies (Mathioulakis et al. 2007; Ghernandi and Messalem 2009). Systems of varying sizes operated with photovoltaic (PV) and/or wind energy have now been tested across the world in Australia (Robinson et al. 1992; Harrison et al. 1996), Saudi Arabia (Alawaji et al. 1995), Jordan (Gocht et al. 1998), Hawaii (Liu et al. 2002) and Gran Canaria (Herold and Neskakis 2001).

In order to avoid the effect of energy fluctuations on operational performance, most RE-membrane systems have used batteries to provide a constant energy source (Robinson et al. 1992; Alawaji et al. 1995; Harrison et al. 1996; Gocht et al. 1998; Herold and Neskakis 2001; Weiner et al. 2001). However, batteries are also undesirable for several reasons: decreased system efficiency; decreased performance at high temperatures and thus higher maintenance costs; difficulty and expense of replacing batteries in remote locations; and higher life-cycle costing (Richards et al. 2008). Additionally, not using batteries eliminates the chance of the system’s batteries being used for other purposes and thereby rendering such a drinking water production system useless. Therefore, it is better for system cost and efficiency to operate the system with no energy storage and such systems have subsequently been developed (Liu et al. 2002; Schäfer et al. 2007; Mohamed et al. 2008; Richards et al. 2008), but the effect of fluctuating operation on the performance of RE-membrane systems is to date not well understood.

The performance and operation of the RE-membrane system considered in this study has been the subject of ongoing research effort. The major publications on the system relevant to remote locations include: (1) design details in Schäfer et al. 2007; (2) a comparison of membrane type with fluctuating energy at one location in Richards et al. 2008; (3) removal of inorganic contaminants at one location and different membranes in Richards et al. 2011; and (4) social and community issues were considered in Werner and Schäfer 2007. The objective of this current study was to compare system performance with fluctuating energy (no energy storage) at six field locations (each with different groundwater), with regard to (1) ion retention; (2) specific energy consumption; and (3) groundwater characteristics (pH and composition).
2. Methods

Field trials were conducted at six locations in Central (Aileron, Aluyen, Harry Creek, Pine Hill, Ti Tree) and South (Coober Pedy, low salinity borehole) Australia (Werner and Schäfer 2007) in October 2005. These locations were deemed ideal for the field study due to high average solar irradiance, problems of water scarcity as a result of low precipitation, and no access to grid electricity (Australian Government, 2005). Locations were selected based on water quality data available.

The system was two-stage membrane filtration (ultrafiltration followed by reverse osmosis/nanofiltration) powered by PV. This system was designed to provide roughly 1000 L of drinking water plus about 9000L of disinfected water for other purposes (depending on feed water quality) per (solar) day for communities with 50 – 100 people. The system was designed to operate every day of the year, given that a significant volume of drinking water was produced on an overcast & rainy day (as demonstrated in Richards et al. 2008). Long term limitations will be adequate control of membrane fouling which would build up over time, although this is expected to be delayed due to ultrafiltration pretreatment. Details of the system design and experimental setup have been published elsewhere (Schäfer et al. 2007). The RO membrane used was a 4” Dow Filmtech BW30-4040 module (Dow, 2008).

Two types of experiments were conducted:

- **Solar experiments at constant pH**: Solar experiments assessed the impact of fluctuating energy on membrane performance at each of the six groundwaters at the natural pH. During the solar experiments, samples were taken hourly and solar irradiance (SI) varied from 0.01 – 3 kW.m\(^{-2}\), motor power from 50 – 200 W, transmembrane pressure (TMP) across the brackish water reverse osmosis/nanofiltration membrane from 2 – 12 bar, and feed flow from 90 – 500 L.h\(^{-1}\) depending on location and operation.

- **pH experiments at constant energy**: The pH experiment at Ti Tree varied the pH step-wise from 3 to 11 under constant energy conditions (from a diesel generator, Honda Eu10i 1kVA) so that flow (400 L.h\(^{-1}\)) and pressure (9 bar) remained constant. Adjustment of pH was made with 1M NaOH and HCl and samples taken after adjustment and equilibrium achieved (typically 30 – 60 minutes).

Samples were collected from feed, permeate, and concentrate streams (permeate and concentrate were recirculated to the feed). Ion analysis was conducted using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma atomic mass spectroscopy (ICP-MS) (cations), ion chromatography (IC) (anions), ion selective electrodes (F\(^-\) and NO\(_3\)\(^-\)) and standard pH and conductivity meters (TDS estimated as previously described (Schäfer et al. 2007)). All instrumental and analytical details such as preservation, spiking agents, internal standard, detection limits, instrument location are described elsewhere (note that some analysis was conducted with different instruments and thus detection limit varied) (Richards et al. 2011).

3. Results and Discussion

3.1. Groundwater Quality

Water quality analysis at the different field locations is shown in Table 1. The most saline water was Pine Hill (total dissolved solids (TDS) = 5700 mg.L\(^{-1}\)) and the least saline was Ti Tree (TDS = 1080 mg.L\(^{-1}\)). All groundwaters have a pH between 7.8 and 8.5. Australian Drinking Water Guidelines for NO\(_3\)\(^-\), Se, SO\(_4\)\(^2-\) and U (health-based) and CT, Mn\(^{2+}\), Na\(^+\) and TDS (esthetic) were exceeded at some locations (marked in **bold** font on Table 1). All locations exceeded guidelines for at least one contaminant.

![Table 1](image)

It is important to note that groundwater quality can be affected throughout the year by weather trends (in particular rainfall and temperature) and anthropogenic activities (ex: contamination and agriculture). For example, contaminant concentrations could be higher in very dry and hot conditions than when rainfall is high and temperatures are lower due to more dilution and less evaporation.

Average weather information is available for Alice Springs (site number 015590), which is the nearest major town to these field locations (Australian Government, 2005). This field study was conducted in October, where the average temperature is 30.9 °C and average monthly rainfall is 21.8 mm. The average monthly temperature varies from 19.7 °C (July) to 36.4 °C (January), and the average monthly rainfall varies from 8.6 mm (September) and 44.3 mm (February). When considering these monthly averages, October has higher than the yearly average temperature and approximately average rainfall. While it is expected that contaminant concentrations could be higher at certain points throughout the year, the hottest months (January and February) actually occur when the rainfall is highest too. When these conditions are considered, October seems to be a fair representation of average annual water quality. From an operational standpoint, it is also worth mentioning the daily sunshine averages too. In October, this was estimated to be 10.0 hours/day – with a minimum of 8.4 (June) and maximum of 10.3 (January). Besides averages, the month of October 2005 experienced the first rain in 18 months and very unusual amounts of it. Hence the data may well be different than what one expects based on averages. However the actual performance data is presented and the fluctuations observed have demonstrated interesting findings.

3.2 Effect of Fluctuating Energy on System Performance

As a result of no energy storage, SI directly impacted all aspects of operation: pressure, flow, flux and the quantity and quality of permeate produced (see Figure 1). At Ti Tree, the system turned on at approximately 07:00 with 0.04 kW.m\(^{-2}\) SI. The SI (1A) increased as the day progressed from 07:00 to 10:00 causing increased feed flow (1A), flux (1B), pressure (1B), and production (1C). From approximately 10:00 to 14:00, feed flow stabilized around 450 L.h\(^{-1}\), pressure at 10 bar, and permeate flow at 220 L.h\(^{-1}\) (corresponding to a recovery of nearly 50%). This recovery was much higher that the manufacturer’s test condition of 15% recovery (Dow), which is good from a short-term production standpoint but potentially could be damaging to the membrane module with long term operation. System operation became intermittent when significant cloud cover occurred from 14:00 because solar irradiance became insufficient for operation. When this happened, the system shut off and feed flow and pressure dropped; hence no more permeate was produced (note that sample collected is an average over intermittent operation). Operation was intermittent for the remainder of the day due to partial cloud coverage. Temperature increased from 24 to 33°C during the day due to ambient conditions and pumping heat resulting from recirculation. Specific energy consumption (SEC) (data not shown on Figure 1) did not change with SI and was 1.0 kW.m\(^{-2}\).

Retention was impacted by fluctuating energy (see Figure 1D) as a result of changes in flow and pressure affecting convection/diffusion mechanisms. Retention was stable during...
consistent system operation but dropped significantly (from >70% to 20-30%) for all contaminants when operation was intermittent (see sample taken at 18:00). During stable system operation, retention for Ca²⁺, Mg²⁺, Sr, K⁺, Na⁺, F⁻, NO₃⁻ and TDS was above 90%. Retention of multivalent ions (Ca²⁺, Mg²⁺ and Sr) was higher than monovalent ions (K⁺, Na⁺, F⁻, and NO₃⁻) which is consistent with RO principles (Peeters et al. 1998). Permeate water quality was acceptable according to guidelines for all contaminants during normal system operation (from 07:00 to 14:00) and not acceptable when operating intermittently due to cloud cover.

[Figure 1]

3.3 Comparison of Operation at Different Locations

Similar experiments to the Ti Tree experiment were repeated at five other locations. At a particular location, the same trends with regard to the direct correlation of solar irradiance with operational parameters were observed, and a summary of the main performance parameters follows in Table 2.

<table>
<thead>
<tr>
<th>Location</th>
<th>Flux Rate (L/h.m²)</th>
<th>Recovery (%)</th>
<th>SEC (kW.m²)</th>
<th>Volume Produced (L/day)</th>
<th>Permeate Flow (L/h.m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aileron</td>
<td>18.3</td>
<td>&gt; 90%</td>
<td>2.3</td>
<td>1720</td>
<td>38</td>
</tr>
<tr>
<td>Harry Creek</td>
<td>1510</td>
<td>&gt; 90%</td>
<td>3.2</td>
<td>2650</td>
<td>38</td>
</tr>
<tr>
<td>Ti Tree</td>
<td>9.1</td>
<td>&gt; 90%</td>
<td>1.0</td>
<td>600</td>
<td>38</td>
</tr>
</tbody>
</table>

The weather conditions varied at the different locations, making direct comparisons by daily averages difficult. The experiments at Coober Pedy and Harry Creek were fully sunny and thus are the easiest to directly compare. Experiments at Aluyen, Pine Hill and Ti Tree were affected by partial cloud cover during the day and rain occurred at Aileron. SI directly correlated with TMP at each of the locations (as solar availability determines SI rather than feed water). Aileron had the least solar irradiance and TMP reached a maximum of 6.7 bar during the day, whereas the averages for all other locations were all greater than 9.0 bar. The maximum TMP achieved was 11.6 bar at Harry Creek.

The rest of the parameters on Table 2 (flux, recovery, SEC, volume produced, permeate flow, and retention) were dependent on the feed water in addition to SI. Because of the similar full-sun weather conditions, Coober Pedy and Harry Creek are compared in detail with regard to water composition. The average flux at Coober Pedy (9.1 L/h.m²) was significantly less than at Harry Creek (18.3 L/h.m²) which can be attributed to high TDS at Coober Pedy (4780 mg/L) than Harry Creek (1510 mg/L, see Table 1) and thus higher osmotic pressure barrier. The difference in TDS (and consequential osmotic pressure barrier) also explains the lower recovery, higher SEC and lower permeate flow at Coober Pedy than Harry Creek. In addition to Coober Pedy’s higher TDS, concentrations of Mg²⁺, Mn²⁺, Ca²⁺, K⁺, Na⁺ and Sr were all higher than Harry Creek (Table 1) which further explains the lower flux observed. Although the difference in weather conditions affects the TMP, a similar impact of lower TDS leading to high flux, high recovery and lower SEC was observed with Ti Tree and Aluyen where recoveries were again far above the manufacturer’s test condition of 15% (Dow, 2008).

SEC is particularly interesting and of vital importance for RE-membrane systems (Robinson et al. 1992) because of the implications on capital cost and ability to compare treatment technologies. SEC values range from 1.0 (Ti Tree) to 3.2 (Coober Pedy) kW.m², which was comparable with low range SECs achieved with other renewable energy brackish water desalination processes (Ghermandi and Messalem 2009). As clearly observed with the comparison between Harry Creek and Coober Pedy, SEC is a function of feed water characteristics such as TDS and concentrations of heavy metals and salts, in addition to solar availability (determines power consumed by the pump).

Average daily TDS retention for each location was above 90%, despite occasional low retention obtained during intermittent operation (for example the drop from >90 to 20-30% as observed at Ti Tree and discussed previously). Likewise, TDS retention dropped to 40% at one sampling point with the poor weather conditions at Aileron, but the daily average remained above 90%.

The differences in selected ion retention for each location are shown in Figure 2. The highest retention at all locations occurred with multivalent ions Mg²⁺, Ca²⁺, and Sr, which was similar to what was observed at Ti Tree and expected due to charge and size exclusion. When operation was continuous (no system shut off), retention was above 85% for these contaminants at each of the groundwaters which is sufficient to meet drinking guidelines. This is of particular interest because the variation of TDS in the groundwater (between 1080 and 5700 mg/L) did not reduce retention to unacceptable levels despite the clear impact on parameters such as flux and SEC (Table 2). Similarly, variations in Mg²⁺ concentration (169 mg/L at Coober Pedy versus 38 mg/L at Ti Tree) did not affect Mg²⁺ retention (> 99.5% for both).

Interestingly, retention of NO₃⁻ followed SI at both Aluyen and Pine Hill, with retention lowest at the lower solar availability (early and late day). SI impacts convection/diffusion retention mechanisms because of changes in flow and pressure, which consequently affects transport of NO₃⁻ (a relatively small ion). However, this trend was not observed at Coober Pedy. This could be explained because Coober Pedy has higher concentrations of large hydrated ions such as Ca²⁺ and Mg²⁺ which could build an ionic boundary layer (concentration polarization) of these larger molecules on the membrane surface and effectively shield the impact of changing operating conditions on smaller ions such as NO₃⁻.

In very cloudy conditions (Aileron) retention dropped to between 40-50% for one sample at 09:00 due to severe fluctuations but the remainder of samples were retained > 93%. At Ti Tree, retention dropped at 18:00 due to system shut off as discussed previously. A comparison of Aluyen (some fluctuating SI) with Coober Pedy (no SI fluctuations) shows no difference in retention, indicating that occasional fluctuations (with a duration of several minutes maximum, occurring every couple of hours) did not impede system performance with regard to contaminant retention, as long as the fluctuation does not cause the power to shut off (as with Ti Tree where the system did not recover). Harry Creek has no data after approximately 12:00 due to the system being down.

Depending on how water is being used/stored, though, periods of unacceptable retention may not have much effect as long as the volumes produced during significantly cloudy/rainy periods are relatively small as compared to when the system is operating well. This is usually the case due to low pressure and hence low flux during reduced energy periods. For example, because the water is treated to such high levels during continuous operation, mixing of ultra high quality water with a small proportion of water that is not treated as well does not make much difference. The issue of intermittent operation is of ongoing research interest (Park et al. 2011).
3.4. Impact of pH on System Operation

The impact of pH on system operation was also evaluated (see Figure 3), as the natural pH of groundwaters can vary widely. At high pH (above pH 9), flux decreased nearly by 50% and SEC increased almost 200% from 0.95 to 1.8 kW.m⁻³. The precipitation of carbonate-based contaminants (such as MgCO₃, MnCO₃ and CaCO₃) is theoretically predicted by speciation modelling at high pH (Richards et al. 2009). However, precipitation of these compounds was not observed, as the retention of these large multivalent ions (Ca²⁺ and Mg²⁺) did not change with pH (Figure 3B). This is an interesting and unexpected result, and the subject of ongoing investigations. The flux decline could be explained by the increased osmotic pressure barrier caused by the addition of NaOH for pH adjustment.

Although the natural pH of the waters in this study only varied from 7.8 to 8.5 (see Table 1), some locations have much higher pH where flux decline and precipitation could be a major operational issue. For example, alkaline groundwaters have been identified from pH 9.1 in Tanzania (Nkotagu 1996) up to pH 12 in Korea (Lee et al. 2008). Although precipitation was not observed in Ti Tree, this has been observed in similar groundwaters (Richards et al. 2011). In such locations, contaminant retention may be unreliable and flux decline, fouling and membrane cleaning would be major operational barriers.

4. Conclusions

The main conclusions of the results presented here are as follows:

1. RE-membrane performance parameters (retention, flux, SEC, pressure, flow) correlated with groundwater composition (TDS, heavy metals, salts, pH) and solar availability.

2. During continuous system operation, retention of Ca²⁺, F⁻, NO₃⁻, Mg²⁺, Sr and TDS was high (~85%) for all groundwaters tested, despite differences in groundwater composition and solar availability. However, during periods of severe energy fluctuations (range from 0.02 to 0.8 kWh/m² lasting nearly two hours at Ti Tree), the system shut off and retention dropped significantly to unacceptable levels. This decreased performance during extreme fluctuations has practical implications, especially in locations where such extreme locations are frequently occurring. Because the benefits of not using batteries are tangible, current systematic investigations on fluctuations and determining a safe operating window are ongoing.

3. Retention of NO₃⁻ followed SI in some locations (Aluyen and Pine Hill) but not in others (Coober Pedy) which is attributed to higher concentrations of other ions (such as Mg²⁺, Ca²⁺ and TDS) in Coober Pedy which lead to concentration polarization. This illustrates the importance of considering groundwater composition in performance evaluation.

4. Flux, SEC and retention of NO₃⁻, F⁻ and TDS were impacted by pH (due to increased charge repulsion) but the retention of large ions (such as Ca²⁺ and Mg²⁺) were pH independent due to the dominant steric exclusion mechanism.

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References


Table 1. Groundwater quality at each of the six field locations in Australia. Concentrations exceeding Australian Drinking Water Guidelines (National Health and Medical Research Council, 2004) are marked in bold.

Table 2. Comparison of RE-membrane operating parameters by daily average at different field locations. Note that extensive details of operation at Pine Hill (Richards et al. 2008; Richards et al. 2011) and Coober Pedy (De Munari et al. 2009) have been published elsewhere.

Figure Captions

Figure 1. Performance of RE-membrane system at Ti Tree using BW30 membrane with operating parameters and ion retention over a solar day (afternoon partial cloud coverage).

Figure 2. Ion retention (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Sr, TDS, K\textsuperscript{+}, Na\textsuperscript{+}, F\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}) and solar irradiance (SI) at each of the six field locations over a solar day.

Figure 3. Impact of pH on flux, SEC and ion retention at Ti Tree using BW30.

<table>
<thead>
<tr>
<th>Parameter (mg L\textsuperscript{-1})</th>
<th>Aileron</th>
<th>Aluyen</th>
<th>Coober Pedy</th>
<th>Harry Creek</th>
<th>Pine Hill#</th>
<th>Ti Tree#</th>
<th>Aust. Guideline#</th>
<th>WHO Guideline#</th>
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<tr>
<td>TDS</td>
<td>2500</td>
<td>1540</td>
<td>4780</td>
<td>1510</td>
<td>5700</td>
<td>1080</td>
<td>500#</td>
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<td>pH (-)</td>
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<td>8.4</td>
<td>8.1</td>
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<td>F</td>
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\#Aesthetic-based guideline; \#Provisional guideline due to scientific uncertainties regarding toxicology/epidemiology and/or due to difficulties regarding technical achievability; \#Guideline recommended to protect against methaemoglobinemia in bottle-fed infants (short-term exposure); n/a: not analysed; *(Richards et al. 2011); ° National Health and Medical Research Council, 2004; ¤World Health Organization, 2008.
### Table 2

<table>
<thead>
<tr>
<th>Location</th>
<th>Weather</th>
<th>SI (kW.m(^{-2}))</th>
<th>TMP (bar)</th>
<th>Flux (L.h(^{-1}.m(^{-2}))</th>
<th>Recovery (%)</th>
<th>SEC (kWh.m(^{-3}))</th>
<th>Volume Produced (L.day(^{-1}))</th>
<th>Permeate Flow (L.h(^{-1}))</th>
<th>TDS Retention (%)</th>
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</table>

*Normalized to 12 hour solar day

### Figure 1

![Graph showing various parameters over time](image-url)
Figure 2

Retention (%) vs. SI (kW.m⁻²) for various locations:
- Aileron
- Aluyen
- Coober Pedy
- Harry Creek
- Pine Hill

Figure 3

Flux (L/h/m²) vs. Retention (%)

Retention (%) vs. pH for various ions:
- Ca²⁺
- Mg²⁺
- Sr
- Na⁺
- F⁻
- NO₃⁻
- TDS

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