University of Wollongong

Research Online

Faculty of Engineering and Information
Sciences - Papers: Part A

Faculty of Engineering and Information
Sciences

1-1-2015

Coal seam gas produced water treatment by ultrafiltration, reverse osmosis and multi-effect distillation: a pilot study

Long D. Nghiem

University of Wollongong, longn@uow.edu.au

Christian Elters

University of Wollongong, ce654@uowmail.edu.au

Alexander Simon

University of Wollongong, asimon@uow.edu.au

Taguchi Tatsuya

Sasakura Engineering Co. Ltd

William Price

University of Wollongong, wprice@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/eispapers>

Part of the [Engineering Commons](#), and the [Science and Technology Studies Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Coal seam gas produced water treatment by ultrafiltration, reverse osmosis and multi-effect distillation: a pilot study

Abstract

This study evaluates the technical feasibility of a pilot treatment train of ultrafiltration, reverse osmosis (RO), and multi-effect distillation (MED) for coal seam gas (CSG) produced water treatment. A total of 12,000 L of CSG produced water was processed from the Gloucester Basin in New South Wales (Australia). The results demonstrate the technical feasibility to obtain an overall clean water recovery of 95% and a final brine containing mostly sodium bicarbonate up to of 48 g/L. Stable operations of the pilot RO and MED systems at 76% and 80% recovery, respectively, were achieved. The results show that anti-scalant addition could effectively prevent scaling during MED operation. Mass balance analysis and analytical measurement suggest that precipitation of calcium, magnesium and silica might have occurred. Indeed, mineral deposition on the sight glass of the MED evaporative chamber became visible after 3 days of continuous operation. However, no evidence of mineral precipitation or scaling could be observed on the evaporative tubes of the MED system. In addition, the mineral deposition on the sight glass was completely removed by chemical cleaning at the end of the pilot evaluation program. The obtained RO permeate and MED distillate were of high quality and could be blended with UF filtrated CSG produced water for irrigation to reduce the treatment demand.

Disciplines

Engineering | Science and Technology Studies

Publication Details

Nghiem, L. D., Elters, C., Simon, A., Tatsuya, T. & Price, W. (2015). Coal seam gas produced water treatment by ultrafiltration, reverse osmosis and multi-effect distillation: a pilot study. *Separation and Purification Technology*, 146 94-100.

**Coal seam gas produced water treatment by ultrafiltration,
reverse osmosis and multi-effect distillation: a pilot study**

Revised Manuscript Submitted to

Separation Purification Technology

Long D. Nghiem^{1,*}, Christian Elters¹, Alexander Simon¹, Taguchi Tatsuya², and William Price³

¹ Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental
University of Wollongong, Wollongong, NSW 2522, Australia

² Sasakura Engineering Co., Ltd.
7-32 Takejima 4-chome, Nishiyodogawa-ku, Osaka 555-0011, Japan

³ Strategic Water Infrastructure Laboratory, School of Chemistry
University of Wollongong, Wollongong, NSW 2522, Australia

* Corresponding author: Long Duc Nghiem, Email longn@uow.edu.au; Tel: +61 2 4221 4590

Abstract

This study evaluates the technical feasibility of a pilot treatment train of ultrafiltration, reverse osmosis (RO), and multi-effect distillation (MED) for coal seam gas (CSG) produced water treatment. A total of 12,000 L of CSG produced water was processed from the Gloucester Basin in New South Wales (Australia). The results demonstrate the technical feasibility to obtain an overall clean water recovery of 95% and a final brine containing mostly sodium bicarbonate up to of 48 g/L. Stable operations of the pilot RO and MED systems at 76 and 80% recovery, respectively, were achieved. The results show that anti-scalant addition could effectively prevent scaling during MED operation. Mass balance analysis and analytical measurement suggest that precipitation of calcium, magnesium and silica might have occurred. Indeed, mineral deposition on the sight glass of the MED evaporative chamber became visible after 3 days of continuous operation. However, no evidence of mineral precipitation or scaling could be observed on the evaporative tubes of the MED system. In addition, the mineral deposition on the sight glass was completely removed by chemical cleaning at the end of the pilot evaluation program. The obtained RO permeate and MED distillate were of high quality and could be blended with UF filtrated CSG produced water for irrigation to reduce the treatment demand.

Keywords: Coal seam gas (CSG) produced water, reverse osmosis (RO), multi-effect distillation (MED), brine minimisation, and scaling.

1 Introduction

Coal seam gas (CSG), which is also known as coal bed methane (CBM), is a form of natural gas. CSG is essentially methane and can be used in the same way as conventional gas. Unlike coal and petroleum oil, the global distribution of CSG is geographically dispersed. Significant CSG reserves have been identified in Australia, Canada, China, Eastern Europe, India, and the USA [1-3].

As a notable example, Australia has seen some of the most significant CSG developments in the world [4]. Australia is on track to become the world's largest liquefied natural gas (LNG) producer by about 2018 [2]. It is estimated that 70% of the global LNG capacity under construction is taking place in Australia to tap into its vast CSG reserve [2]. CSG also plays an important role in the domestic market. CSG is expected to supply at least 30% of the Australian domestic energy market by 2030. CSG developments in New South Wales and Queensland will potentially contribute 78% of natural gas reserves in the eastern states [5].

Electricity generation from natural gas emits significantly less greenhouse gases and air pollutants than coal. According to the US EPA Emissions & Generation Resource Integrated Database, natural gas produces only 50, 33, and 1% of carbon dioxide, nitrogen oxides, and sulfur oxides at the power plant, respectively, compared to coal-fired electricity generation. Thus, CSG is expected to play a major role in the global energy mix to lessen the impact of fossil fuel on global warming and the environment while renewable energy is being developed [2].

CSG exists in almost all underground coal seams (typically 300–600 m below the surface) where it adsorbs to coal matrix and is held in place by water pressure. Groundwater extraction is required to depressurise the target coal seams and allow CSG to flow to the surface. Thus, CSG extraction usually involves the co-production of water, known as CSG produced water [6].

CSG produced water is essentially saline groundwater. The actual composition and volume of CSG produced water varies greatly from one region to another [3, 7]. In Australia, CSG produced water consists predominantly of sodium, bicarbonate (HCO_3^-), and chloride. Due to the high salt content, direct discharge of CSG produced water to inland water bodies may entail a range of adverse effects to the environment [1, 8]. For example, because of the high sodium content, the use of untreated CSG produced water for irrigation can lead to a gradual decrease in the permeability of soil, eventually causing infiltration problems and other form of soil degradation [9].

The state-of-the-art technology for CSG produced water management currently includes pre-treatment (e.g. coagulation, pH adjustment, ultra- (UF) or micro filtration) and reverse osmosis (RO) [4, 6, 10]. RO can achieve about 75% water recovery, depending on the salinity (hence osmotic pressure) and the fouling potential of the CSG produced water. RO also produces a volume of even more concentrated CSG produced water called brine [11]. RO brine is a major challenge for the sustainable produced water management in the CSG industry [6]. In Australia, this RO brine is usually stored in evaporation ponds. However, the use of evaporation ponds is costly and is only a temporary measure. For new developments the use of evaporation basins is unlawful in most states unless there are no alternative solutions. Given the possible leakages of the brine into the environment, regulators in Australia have actively encouraged the CSG industry to phase out the use of evaporation ponds for CSG RO brine storage [4]. This policy has encouraged several recent attempts to develop techniques to reduce the volume and/or to beneficially extract the minerals from CSG RO brine [4, 12, 13]. A noteworthy example is the recovery of soda ash from the CSG RO brine, which is being developed by Penrice (Penrice Soda Holdings Limited, Australia) in collaboration with GE (General Electric, Australia) and QGC (QGC Pty Limited, Australia). Another possibility is to use the sodium rich brine as feedstock to profitable generate sodium hydroxide by membrane electrolysis [14]. Both of these approaches require the CSG RO brine to be further concentrated to as close to saturation as possible to reduce downstream processing cost. Given the high osmotic pressure and scaling potential of CSG RO brine, the use of several thermal separation processes such as multi-effect distillation (MED) and membrane distillation to undertake this additional concentration step have been suggested in the literature [3]. These processes consume primarily thermal energy and thus they can be readily integrated with a solar thermal collection system. Indeed, solar-assisted MED systems for seawater and brackish water desalination have been demonstrated in several recent studies [15, 16]. However, to date, the technical feasibility of MED to further concentrate CSG RO brine has not been systematically investigated either at laboratory or pilot scale level.

This study aims to evaluate the use of UF, RO and MED at pilot scale level for CSG produced water treatment with respect to process stability and scaling potential. In addition, permeate, distillate and brine chemistries as well as possible process optimisations were reported and discussed.

2 Materials and Methods

2.1 Pilot treatment train

The pilot treatment train consisting of UF pre-treatment, RO filtration, and MED used in this study is shown in Figure 1. The UF and RO systems (Figure 1b) were constructed by OsmoFlo (Adelaide, SA, Australia) specifically for pilot evaluation purposes and were housed in a 20 ft shipping container. The UF system consisted of two hollow fibre polyacrylonitrile UF membrane modules (Ultra-Flo U860 Cartridge), each with a total membrane surface area of 96.6 m². The UF membrane had a nominal pore size of 25 nm and permeability at 20 °C of 93 L/m² hbar. The RO system was equipped with three 4-inch brackish water membrane modules (AG4040FM, General electrics, USA), each with an active membrane surface area of 23.7 m². The nominal NaCl rejection and water permeability of the RO membrane was 99.5% and 3.09 L/ m²hbar (at 25 °C and 2 g/L NaCl), respectively. Two cartridge filters (2 x 20" BB) with pore size of 1 µm were installed before the RO membrane modules for their protection from accidental intrusion of small objects or suspended solids to the feed reservoir. This is the standard design in an industrial RO system.

The pilot MED system (Figure 1c) was designed and constructed by Sasakura Engineering Co., (Osaka, Japan). It consisted of a heating chamber, an evaporating chamber, and a condenser. The system was equipped with a supervisory control and data acquisition (SCADA) system, and thus, was fully automated.

Figure 1: (a) Process diagram, (b) the pilot UF and RO system, (c) the MED system.

2.2 Experimental protocol

CSG produced water was collected and used immediately from a pilot gas well in the Gloucester Basin located along the lower north coast of New South Wales (Australia). The produced water was from a gas well known as Waukivory 03, which was being flow tested to assess gas production and the variability in produced water quality [17]. This CSG gas field is in a coal basin, generally described as part of the Hunter Coalfields or the Northern Sydney Basin [18].

The UF system was operated in the dead end mode. Each filtration cycle consisted of 17 minutes of production, followed by 40 seconds of air scouring and 30 seconds of back-flushing. The trans-membrane pressure of the UF was below 0.55 bar to prevent any irreversible membrane blocking. An industrial grade anti-scalant (Osmotreat, Osmoflo, Adelaide, SA, Australia) was added to the UF filtrate to obtain 5 mg/L prior to RO filtration. The feed flow rate to the RO system was 1 m³/h and the transmembrane pressure was set at 17 bar to obtain 76% water recovery, which is comparable to a full scale system typically deployed for CSG produced water treatment. The RO brine was fed into the MED system via an equalising tank.

The MED system was operated continuously throughout the pilot program. The temperature and absolute pressure in the evaporative chamber were 70 ± 2 °C and 25 ± 1 kPa, respectively. Two anti-scalants, namely Belgard EV2030 (BWA, USA) and Accent 1131 (DOW Chemical, USA), were added to the RO brine to obtain 5 and 10 mg/L each, respectively. The RO brine feed flow rate to the MED system was 20 L/h and water recovery was set at 80%. This set point was selected to achieve an overall recovery of 95% from CSG produced water.

At the conclusion of the pilot program, as a precautionary measure, the evaporative chamber of the MED system was chemically cleaned with 30 L sulfamic acid (0.3 M) followed by 30 L sodium hydroxide (0.9 M). Each cleaning solution was circulated for 1 hour at 60 °C and followed by a rinsing step using distillate water.

2.3 Analytical methods

2.3.1 Total organic carbon and bicarbonate

Total carbon (TC) and total organic carbon (TOC) was analysed using a Shimadzu TOC/TN-V_{CSH} analyser (Shimadzu, Japan, Kyoto). The TOC measurement was conducted by acidifying the sample to pH 1.5 using hydrochloric acid and subsequently air sparging for 5 minutes to remove all inorganic carbon in the form of carbonate. The bicarbonate concentration was calculated from the measured TC, TOC and the individual sample pH using a Bjerrum plot for carbonate systems [19].

2.3.2 Anion analysis

The concentrations of anions were determined using an Ion Chromatography system (LC-20AC, Shimadzu, Japan). The IC system was equipped with a Dionex Ion Pac AS23 anion-exchange column (Thermo Scientific, USA). The eluent consisted of 4.5 mM Na₂CO₃ and 0.8 mM NaHCO₃. The sample injection volume and eluent flow rate were 10 µm and 1 mL/min, respectively. The system was calibrated using standards of 5, 10, 50 and 100 mg/L of each ion.

2.3.3 Cation analysis

An Agilent 7500 CS (Agilent Technologies, Wilmington, DE, USA) inductively-coupled plasma mass spectrometer (ICP-MS) was used to measure the concentrations of Boron, Mn²⁺, Al²⁺, Na²⁺, K⁺, Mg²⁺, Ca²⁺ and Fe²⁺. The samples were diluted with 2% Suprapur nitric acid. The ICP-MS was tuned prior to each analysis batch by using a multi-element tuning solution, containing 10

µg/L of Li, Y, Ce, Tl and Co [20]. Triplicate analysis was conducted, and the variations were always less than 5%.

2.3.4 Other water quality parameters

Silica (SiO₂) concentration was measured using a Pocket Colorimeter II (Hach, Colorado, USA). Samples from RO and MED brine were diluted up to 10 times using Milli-Q water to avoid possible interferences from the high salinity of the sample. The silt density index (SDI) of the raw CSG produced water and UF filtrate was measured based on the standard method D4189. Turbidity was measured using a Hach 2100Qis portable turbidity meter (Hach, Colorado, USA). Conductivity and pH were measured using an Orion star A325 portable pH/conductivity meter (Thermo Scientific, USA).

3 Results and discussion

3.1 Water characteristics

The CSG produced water used in this study was slightly brackish (Table 1). Sodium (1,351 mg/L) and bicarbonate (1,717 mg/L) were the two dominating ionic species in this CSG produced water. Concentrations of other common cations and anions in this CSG produced water were either very low or undetectable. In particular, the chloride concentration of 62.2 mg/L is significantly lower than that reported from other CSG fields in Queensland (Australia) [6]. The concentrations of calcium and magnesium are also insignificant, possibly due to a hydro-chemical process along the groundwater flow path and the old age of this produced water (Table 1). The high sodium adsorption ratio value (SAR) of 89.6 of this CSG produced water renders it unusable for irrigation without dilution, treatment or chemical amendment. The organic content of this CSG produced water is very low (1.7 mg/L). Thus, the propensity of organic fouling associated with this CSG produced water is negligible. The high turbidity (32 NTU) and SDI₁₅ value (6.3) of this CSG produced water (Table 1) could be attributed to its high iron content. Further details of this CSG produced water are available elsewhere [17]. It is noteworthy that iron precipitate was observed a few hours after the CSG produced water was extracted to the surface. When CSG produced water is brought to the surface, due to the oxidation of ferrous into ferric which forms a precipitate, the dissolved iron content of the CSG produced water is relatively low. Nevertheless, the high turbidity and SDI₁₅ value reported here suggest that this CSG produced water cannot be fed directly to the RO process. Aeration is recommended to ensure complete removal of dissolved iron prior to membrane filtration.

188 **Table 1:** Characteristics of the CSG produced water.

General characteristics	
Conductivity	4.449 mS/cm
Turbidity	32 NTU
pH	8.4
Total organic carbon	1.7 mg/L
SAR	89.6
Silt density index (SDI ₁₅)	6.3
Ion concentration (mg/L)	
Bicarbonate	1717.4
Chloride	62.2
Sodium	1351.2
Magnesium	4.8
Potassium	29.0
Calcium	26.5
Iron	43.6
Silica	18.0

189 **3.2 Water balance of the combined UF-RO-MED treatment train**

190 The overall water balance of this pilot programme is shown in Figure 2. Water recovery of the
 191 UF/RO process was set at 76%. The RO brine was fed to the MED process to obtain an
 192 additional water recovery of 80%, resulting in a total recovery of 95%. The overall treatment
 193 efficiency in term of conductivity removal is also summarised in Figure 2. A total of 12,000 L of
 194 CSG produced water was treated in this pilot study. The performances of the individual
 195 processes in this treatment train are discussed in the subsequent sections.

196 **Figure 2:** Water balance of this pilot study.

198 **3.3 Process stability**

199 During the pilot program, no discernible reduction in the water production rate was observed
 200 with the UF/RO and MED process (Figure 3). The automatic air-scoring and backwashing cycle
 201 described in section 2.2 was able to maintain the UF permeate flux at about 50 L/m²h (Figure 3a).

UF pre-treatment reduced the CSG produced water turbidity from 32 NTU to less than 0.5 NTU. However, SDI_{15} of the UF treated CSG water was only reduced to 4.8. Despite this high SDI_{15} value after UF pre-treatment, no flux decline was observed with the RO process. Results reported here suggest that the SDI_{15} value may not be a suitable parameter to measure fouling propensity in RO applications for CSG produced water treatment. The results also indicate the effectiveness of the added anti-scalant to the UF filtrate.

Figure 3: (a) Permeate flux of the UF and RO system and (b) Feed, distillate and brine flow rate of the MED system as a function of time.

Operation of the MED system was fully automated. Except the first day of operation, the flow rates of the feed (i.e. RO brine), distillate, and MED brine were constant throughout this pilot testing program (Figure 3b). Results from Figure 3b suggest that the addition of anti-scaling reagents to the MED feed (i.e. CSG RO brine) could effectively prevent the formation of any scale on the evaporative tubes. Overall, the results from Figure 3 show that a treatment train of UF, RO and MED could recover over 95% water from CSG produced water, without any notable evidence of fouling or scaling.

3.4 Scaling assessment and effectiveness of chemical cleaning

The risk of RO and MED scaling can also be assessed by comparing the analytically measured concentrations of mineral salts to those obtained from a mass balance calculation. As expected, the concentrations of all mineral salts in the RO permeate and MED distillate are either negligible or below the detection limits (Table 2). The measured concentrations of monovalent ions such as Na^+ , Cl^- , K^+ are consistent with values from mass balance calculation. On the other hand, the measured concentrations of Mg^{2+} and Ca^{2+} in the MED brine are 186 and 680% lower,

respectively, than values obtained from mass balance calculation (Table 2). A similar observation can also be seen with silica. The calculated mass balance of SiO₂ closely matches the measured value during RO. However, there is a significant deficit of 210% of SiO₂ during MED.

Table 2: Distribution of key elements in within the treatment train (mg/L).

Elements		Na ⁺	Cl ⁻	Mg ²⁺	K ⁺	Ca ²⁺	Si
UF Filtrate		1165	67	4	14	34	18
RO brine (76% recovery)	Mass balance	4832	279	17	58	142	75
	Analytically measured	4450	187	13	39	140	68
RO permeate		7	0	0	0	0	0
MED brine (80% recovery)	Mass balance	22238	935	65	195	700	340
	Analytically measured	21242	798	21	154	25	108
MED distillate		3	0	0	0	0	0

The deficit of Mg²⁺, Ca²⁺, and SiO₂ in the MED brine suggests that some precipitates involved these minerals have been formed. In fact, on the third day of MED operation, some precipitate deposition was observed on the sight glass (Figure 4). By the end of the pilot testing program, the entire sight glass was observed with a thin layer of mineral precipitates (Figure 4c). The formation of a thin layer of precipitate on the sight glass can be attributed to the high affinity of silica to glass, which also contains a large portion of SiO₂ in its chemical composition.

It is noteworthy that no evidence of scaling on the evaporative tubes could be observed when the evaporative chamber was inspected at the end of the pilot program. This observation is consistent with the very low concentration of sparingly soluble minerals in the RO brine (Table 2).

Chemical cleaning using 0.3 M sulfamic acid followed by 0.9 M sodium hydroxide was conducted and the thin layer of mineral deposition on the sight glass was completely removed (Figure 4d). While scale was not observed in this pilot program, it is prudent to note that scaling may still develop during an extended MED period of operation. Nevertheless, results reported here also demonstrate that scaling can be effectively controlled by preventative chemical cleaning.

Figure 4: Mineral deposition on the sight glass of the MED evaporator. (a) at the beginning of the process, (b) after 3 days of operating the MED, (c) at the end of the process, and (d) after chemical cleaning using 0.3 M sulfamic acid followed by 0.9 M sodium hydroxide.

3.5 Produced water and brine quality during the process

3.5.1 Total dissolved solids

The total dissolved solid (TDS) content of CSG produced water varies from one coal seam to another and TDS concentrations from 0.01 g/L up to 300 g/L have been reported. In Australia, typical TDS concentration of CSG produced water from coal seam range between 1 – 6 g/L [6]. The TDS of the produced water used in this pilot study was 2.51 g/L and consisted mainly of sodium and bicarbonate (Table 1). No impact on the TDS concentration by UF was observed in this study. On the other hand, the rejection of TDS by RO and MED was 94.4 and 100%, respectively. Therefore, the TDS concentration of the RO and MED brine increased proportional to the water recovery or concentration ratio (Figure 6). At a water recovery of 74% using RO, TDS concentration in the brine increased from 2.51 to 9.61 g/L. A further 80% water extraction by the MED process produced in a final brine solution containing 48.41 g/L TDS, resulting in the overall fresh water recovery of 95%.

In this study, the conductivity of the raw produced water was 4.449 mS/cm (Table 1), and UF filtration had no impact on the water conductivity (Figure 5a). RO filtration and MED distillation

resulted in a stable conductivity rejection of 99.7% and 99.9% throughout the study, respectively (Figure 5a). Consequently, the increase in conductivity in the RO and MED brine was proportional to the water recovery (i.e. concentration ratio). It is noteworthy that although the MED process accounted only in 19.2% of the total process water recovery (Figure 2), it increased the brine conductivity most notably by 71% (Figure 5a).

Figure 5: Impact of UF, RO and MED treatment on a) conductivity and b) pH of the CSG water brine over six successive operating days. No data on day 3 were taken.

While UF filtration and subsequent concentration by RO had no impact on pH of the brine, a significant increase in the pH of the brine solution was observed following the MED process (Figure 5b). The pH of produced water depends on the ratio of acid and base components in the solution and therefore, the increase in MED brine pH can be associated to enhanced degassing of carbon (in the form of CO_2) from the brine. Due to the high MED process temperature (i.e. 70°C), and likely supported by the low vacuum (i.e. 25 kPa), more CO_2 can evaporate, which resulted in a shift of the solution pH towards a more basic condition. By contrast, the absorption of carbon dioxide, which forms carboxylic acid, to the RO permeate and MED distillate can shift

the solution pH towards an acidic condition due to the lack of pH buffering minerals (Figure 5b). Results reported here suggest that post treatment or blending is required to correct the pH of the RO permeate and MED distillate before beneficial consumption.

3.6 Total organic and inorganic carbon concentration

Similar to all other properties of produced water, the concentration of TOC and bicarbonate varies depending from basin to basin and from one coal seam to another. Although TOC concentration in CSG produced water is generally low, their composition is often complex and their impact on the environment not very well understood [21]. TOC in natural produced water was found to consist of polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds, alkyl phenols, aromatic amines, alkyl aromatics (alkyl benzenes, alkyl biphenyls), long-chain fatty acids, and aliphatic hydrocarbons [21]. In this study, TOC concentration was as low as 1.7 mg L^{-1} and was largely unchanged after UF pre-treatment (Figure 6a). In addition, a very low rejection of TOC was also found by RO. This result indicates that the organic fraction in this CSG produced water consist of mostly small molecular weight organic compounds, which are readily permeable through low pressure RO membranes [22, 23]. On the other hand, the MED process could offer a near complete removal of TOC. Indeed, TOC in the MED distillate was consistently below the detection limit of 0.3 mg/L (Figure 5a). Unlike the RO process, MED is a phase separation process, and thus, organic removal is not dependent on their molecular weight. The results reported in Figure 5a also suggest that the organic fraction of this CSG produced water is non-volatile.

The bicarbonate concentration before and after UF, RO and MED treatment was calculated first by measuring the total inorganic carbon (i.e. $\text{TC} - \text{TOC}$), then using a Bjerrum plot for carbonate [19]. At the pH of the raw produced water, UF and RO brine (i.e. pH 8.4), 97% of the total dissolved inorganic carbon exists as bicarbonate and 3% as carbonate. On the other hand, as the pH of the MED brine increased to 9.6, the ratio of bicarbonate decreased to 90% in favour of carbonate. No bicarbonate was found in the RO permeate and MED distillate (Figure 6b). Consequently, the bicarbonate concentration increased proportional with the water recovery of the process and eventually reached a concentration of 25500 mg/L in the MED brine. Results show stable rejection of both, TOC and bicarbonate throughout the study by RO and MED.

Figure 6: Impact of UF, RO and MED treatment on a) TOC and b) bicarbonate concentration of produced water treatment over 6 successive operating days. No data on day 3 were taken.

3.7 Feasibility consideration

Results reported here demonstrate the technical feasibility to achieve a water recovery of 95% by a combination of UF, RO, and MED treatment process over a sustained period of one week. The pilot MED system used in this investigation consisted of only one evaporative chamber and was not equipped with an energy recovery unit. Thus, it was not possible to evaluate the exact energy consumption of the proposed treatment train. Nevertheless, MED can utilise either solar thermal or waste heat from CSG compression as the primary energy source. In fact, the integration of solar thermal collection with MED for brackish water desalination has been reported [24]. Such solar driven MED system includes parabolic collectors (sun tracking), synthetic oil as heat transfer fluid and a thermal storage system. In addition, due to the high quality of the produced purified water, raw CSG produced water (i.e., UF filtrate) could be blended with the desalinated water to reduce the overall energy requirement and to condition the RO permeate and MED distillate. It is also noteworthy that the final MED brine obtained in this study contains enough

sodium for the extraction of saleable minerals through membrane electrolysis. According to Simon et al. [14], a sodium bicarbonate solution of 50 g/L (which is about half its solubility limit and is comparable to the strength of the MED brine obtained here) can be used as the feed stock to membrane electrolysis to produce commercial grade sodium hydroxide. Using the final brine as feedstock for membrane electrolysis could facilitate zero liquid discharge and at the same time off-set the overall treatment cost from the sale of sodium hydroxide. Overall, the blending ratio, revenue from saleable clean water and sodium hydroxide, and the availability of waste heat and space for solar thermal collection will influence the operating cost of the proposed treatment train. Although it is not possible to obtain a detailed economic analysis from the results presented here, these factors can significantly off-set the total cost of CSG brine management.

4 Conclusion

The obtained results demonstrate the technical feasibility to treat CSG produced water by a pilot treatment train of UF, RO, and MED and achieve 95% water recovery over a sustained period. In total, 12,000 L of CSG produced water was treated by the proposed treatment train. No evidence of scaling and process instability associated with the RO or MED processes could be observed. Indeed, detailed inspection of the evaporative chamber of the MED at the end of the experiment confirmed the absence of any precipitates on the evaporative tubes. Nevertheless, mass balance analysis and analytical measurement suggest that the precipitation of calcium, magnesium and silica might have occurred. Indeed, mineral deposition on the sight glass of the MED evaporative chamber was visible after 3 days of continuous operation. It is noteworthy that the mineral deposition on the sight glass was completely removed by chemical cleaning at the end of the pilot evaluation program. The desalinated water can be blended with the UF filtrate to reduce the overall energy requirement of CSG produced water treatment and condition the RO permeate and MED distillate for beneficial reuse.

5 Acknowledgment

This study was supported by the National Centre of Excellence in Desalination Australia, with industry support from AGL Energy (Sydney, Australia), Sasakura Engineering Co., Ltd. (Osaka, Japan), and OsmoFlo (Adelaide, Australia). Technical assistance from Mr Taner Ozdemir and Mr Wayne Taylor (OsmoFlo) during the study is gratefully acknowledged.

6 References

1. Hamawand, I., T. Yusaf, and S.G. Hamawand, Coal seam gas and associated water: A review paper. *Renewable and Sustainable Energy Reviews*, 2013. 22(0): p. 550-560.
2. World Energy Outlook 2011: Are We Entering A Golden Age of Gas? 2011, International Energy Agency: Paris. p. 1-131.
3. Plumlee, M.H., J.-F. Debroux, D. Taffler, J.W. Graydon, X. Mayer, K.G. Dahm, N.T. Hancock, K.L. Guerra, P. Xu, J.E. Drewes, and T.Y. Cath, Coalbed methane produced water screening tool for treatment technology and beneficial use. *Journal of Unconventional Oil and Gas Resources*, 2014. 5(0): p. 22-34.
4. Jia, H. and J. Poinapen, Coal seam gas associated water treatment and management: Opportunities and limitations. *The APPEA Journal*, 2013. 53: p. 185.
5. Stammers J, Coal Seam Gas: Issues for Consideration in the Illawarra Region, NSW, Australia. 2012, University of Wollongong.
6. Nghiem, D.L., T. Ren, N. Aziz, I. Porter, and G. Regmi, Treatment of coal seam gas produced water for beneficial use in Australia: A review of best practices. *Desalination and Water Treatment*, 2011. 32: p. 316–323.
7. Dahm, K.G., K.L. Guerra, P. Xu, and J.E. Drewes, Composite Geochemical Database for Coalbed Methane Produced Water Quality in the Rocky Mountain Region. *Environmental Science and Technology*, 2011. 45(18): p. 7655-7663.
8. Navi, M., C. Skelly, M. Taulis, and S. Nasiri, Coal seam gas water: potential hazards and exposure pathways in Queensland. *International Journal of Environmental Health Research*, 2014: p. 1-22.
9. Zhao, H., G.F. Vance, M.A. Urynowicz, and R.W. Gregory, Integrated treatment process using a natural Wyoming clinoptilolite for remediating produced waters from coalbed natural gas operations. *Applied Clay Science*, 2009. 42(3-4): p. 379-385.
10. Abousnina, R.M., L.D. Nghiem, and J. Bundschuh, Comparison between oily and coal seam gas produced water with respect to quantity, characteristics and treatment technologies: a review. *Desalination and Water Treatment*, In Press. DOI:10.1080/19443994.2014.893541.

11. Fritzmann, C., J. Löwenberg, T. Wintgens, and T. Melin, State-of-the-art of reverse osmosis desalination. *Desalination*, 2007. 216(1-3): p. 1.
12. Duong, H.C., A.R. Chivas, B. Nelemans, M. Duke, S. Gray, T.Y. Cath, and L.D. Nghiem, Treatment of RO brine from CSG produced water by spiral-wound air gap membrane distillation — A pilot study. *Desalination*, In Press. DOI: 10.1016/j.desal.2014.10.026.
13. Coday, B.D., P. Xu, E.G. Beaudry, J. Herron, K. Lampi, N.T. Hancock, and T.Y. Cath, The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. *Desalination*, 2014. 333(1): p. 23-35.
14. Simon, A., T. Fujioka, W.E. Price, and L.D. Nghiem, Sodium hydroxide production from sodium carbonate and bicarbonate solutions using membrane electrolysis: A feasibility study. *Separation and Purification Technology*, 2014. 127: p. 70-76.
15. Stuber, M.D., C. Sullivan, S.A. Kirk, J.A. Farrand, P.V. Schillaci, B.D. Fojtasek, and A.H. Mandell, Pilot demonstration of concentrated solar-powered desalination of subsurface agricultural drainage water and other brackish groundwater sources. *Desalination*, 2015. 355(0): p. 186-196.
16. de la Calle, A., J. Bonilla, L. Roca, and P. Palenzuela, Dynamic modeling and simulation of a solar-assisted multi-effect distillation plant. *Desalination*, 2015. 357(0): p. 65-76.
17. Sardella C, Flow Testing of Craven 06 and Waukivory 03 Gas Wells. 2014, Parsons Brinckerhoff.
18. McVicar T.R, Langhi L, Barron O.V, Rachakonda P.K, Zhang Y.Q, Dawes W.R, Macfarlane C, Holland K.L, Wilkes P.G, Raisbeck-Brown N, Marvanek S.P, Li L.T, and Van Niel T.G, Context statement for the Gloucester subregion. Product 1.1 from the Northern Sydney Basin Bioregional Assessment. 2014, Department of the Environment, Bureau of Meteorology, CSIRO, and Geoscience Australia.
19. Pedersen, O., T.D. Colmer, and K. Sand-Jensen, Underwater photosynthesis of submerged plants – recent advances and methods. *Frontiers in Plant Science*, 2013. 4.
20. Tu, K.L., L.D. Nghiem, and A.R. Chivas, Coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes. *Chemical Engineering Journal*, 2011. 168(2): p. 700-706.

- 412 21. Orem, W., C. Tatu, M. Varonka, H. Lerch, A. Bates, M. Engle, L. Crosby, and J.
413 McIntosh, Organic substances in produced and formation water from unconventional natural gas
414 extraction in coal and shale. *International Journal of Coal Geology*, 2014(0).
- 415 22. Bellona, C., J.E. Drewes, P. Xu, and G. Amy, Factors affecting the rejection of organic
416 solutes during NF/RO treatment - a literature review. *Water Research*, 2004. 38(12): p. 2795-
417 2809.
- 418 23. Nghiem, L.D. and P.J. Coleman, NF/RO filtration of the hydrophobic ionogenic
419 compound triclosan: Transport mechanisms and the influence of membrane fouling. *Separation*
420 *and Purification Technology*, 2008. 62(3): p. 709-716.
- 421 24. Milow, B. and E. Zarza, Advanced MED solar desalination plants. Configurations, costs,
422 future — seven years of experience at the Plataforma Solar de Almeria (Spain). *Desalination*,
423 1997. 108(1-3): p. 51-58.