# Elsevier required licence: © 2020

This manuscript version is made available under the CC-BY-NC-ND 4.0 license

http://creativecommons.org/licenses/by-nc-nd/4.0/

The definitive publisher version is available online at

https://doi.org/10.1016/j.jece.2020.104122

# Simulation of High pH Reverse Osmosis Systems for Desalination of Coal Seam Gas Associated Water

<sup>1</sup>Caleb Hirsimaki, John G. Outram and \*Graeme J. Millar

Institute for Future Environments and <sup>1</sup>School of Mechanical, Medical and Process
Engineering, Science and Engineering Faculty, Queensland University of Technology (QUT),
Brisbane, Queensland 4000, Australia

&

#### <sup>2</sup>Ali Altaee

<sup>2</sup>University of Technology in Sydney, 15 Broadway, Ultimo, Sydney, NSW 2007, Australia

This study has revealed the potential for a high pH reverse osmosis system to desalinate coal seam gas (CSG) associated water. The hypothesis was that the application of this technology in the CSG industry has been hindered by a lack of insight as to the water treatment plant design and process economics. Therefore, AqMB software was used to simulate three water compositions. Higher total dissolved solids content promoted the need for more resin and regenerant chemicals plus larger sized equipment. The use of hydrochloric acid to regenerate weak acid cation resin was prohibitively expensive (up to A\$17,554,687 per annum). Moreover, the use of acid converted the alkalinity to dissolved carbon dioxide, which required air stripping to remove. The power consumption for the air stripper represented 70 % of total process demand, and as such, it was not recommended. Acid solutions also required large amounts of sodium hydroxide (up to A\$4,546,682 per annum) to reach pH 10 wherein silica species were soluble. Use of a sodium chloride regenerated resin plus removal of the air stripping stage substantially improved economics to the point that the operational expenditure was predicted to be A\$417 per ML of water treated; a value comparable to conventional reverse osmosis desalination units.

**Key Words:** coal seam gas; coal bed methane; reverse osmosis; simulation; desalination

\*Corresponding Author

Professor Graeme J. Millar

Science and Engineering Faculty, Queensland University of Technology, P Block, 7th Floor, Room 706, Gardens Point Campus, Brisbane, Queensland 4000, Australia ph (+61) 7 3138 2377 : email graeme.millar@qut.edu.au

# <u>Highlights</u>

- Demonstration of HERO process to treat a range of CSG associated water types
- Logical election of unit operations to improve remediation performance
- Reduction of process costs to values comparable to conventional reverse osmosis
- Rapid acceleration of optimal HERO design for CSG associated water treatment

## 1. Introduction

The demand for energy is increasing globally due to factors such as growing population and higher levels of industrialization. Consequently, the development of unconventional resources such as coal seam gas (CSG) [1] or shale oil & gas [2] has accelerated in recent years. For example, Australia has substantial CSG reserves which are located mainly in Queensland and northern New South Wales [3]. Challenges arise in the CSG industry due to the production of by-product water which is collected as a result of depressurization of the coal seams during the gas extraction process [4]. CSG associated water typically comprises of relatively high concentrations of dissolved salts which can be detrimental if directly discharged to the environment [5]. Sodium chloride and sodium bicarbonate are invariably the main species in CSG associated water along with lesser amounts of alkaline earth ions, dissolved silicates, potassium, boron, fluoride, and sulphate [6-8]. To facilitate beneficial reuse of the CSG associated water for applications such as livestock watering and irrigation, a treatment process is required to meet environmental regulations.

Reverse osmosis (RO) has become the dominant desalination technology in Australia [9] with the USA preferring ion exchange due to the fact that water mainly contains sodium bicarbonate [10, 11]. With regards to the RO process, there has been a growing trend towards increasing the water recovery rates with the ultimate goal to achieve zero liquid discharge due to tightening regulations and costs of discarding waste [12]. As such membrane distillation has been evaluated for CSG associated water treatment due to the potential high recovery of water (>90 %). Duong et al. [13] conducted a pilot plant study for the treatment of RO brine from CSG associated water by spiral-wound air gap membrane distillation and demonstrated high water recoveries (> 95 %). Zhang et al. [14] studied membrane distillation treatment of RO brine derived from desalinating CSG associated water with high bicarbonate content and low hardness. These authors observed fouling of the membrane surface by silicate species which promoted a decline in water flux even after relatively short operational times such as 150 h. Duong et al. [15] advocated reducing the feed temperature to alleviate fouling of the membrane surface; albeit, this strategy resulted in a significantly lower water flux rate (ca. 10 L/m<sup>2</sup>/h) and decreased energy efficiency. Hence, membrane distillation requires further development with regards to CSG associated water desalination.

An alternate approach to enhancing water recovery when desalinating CSG associated water is the application of high pH RO systems [16]. Mukhopadhyay [17] described a high-efficiency reverse osmosis (HERO) process which initially involved a weak acid cation (WAC) resin to remove alkaline earth ions and some alkali metals. Subsequently, the low pH conditions resultant from the ejection of protons from the resin exchange sites diminished solution alkalinity. The dissolved carbon dioxide was then purged by air in a degassing unit. Finally, the pH was raised to in excess of 10 as these conditions dissolved silicates. Water recovery rates were at least 90 % using HERO. Moftah [18] added that the HERO system might also utilize: lime softening if hardness levels are high; use of a strong acid cation (SAC) resin or zeolite instead of WAC resin; sodium cycle softening instead of acid exchange resins; membrane contactors to strip dissolved carbon dioxide instead of conventional blown air degasser units. The HERO process, therefore, appears potentially suitable to treat GSG associated water. Nevertheless, application of high pH reverse osmosis has not been reported for the treatment of coal seam gas associated water despite the potential benefit of high water recovery rates.

A means to change the outlined situation may be to demonstrate the viability of high pH RO treatment of CSG associated water using process modelling strategies. Process modelling can accelerate the selection of appropriate unit operations for a wide variety of CSG associated water compositions. For instance, Vedelago and Millar [19] applied computational methods to evaluate the feasibility of both pH amendment/chemical addition and cation resin decarbonisation of three high alkalinity CSG associated water (total dissolved solids (TDS) ranged from 776 to 3463 mg/L). It was concluded that pH amendment was only compatible with CSG associated water concentrations < ca. 1000 mg/L. At higher CSG associated concentrations, the accompanying addition of anions to the treated water caused problems with respect to plant growth when the water was used for irrigation purposes. Whereas, Wicks et al. [20] examined the applicability of ion exchange using synthetic resins to remediate CSG associated water. Four different treatment scenarios were modelled for CSG associated water with a TDS value of 5054 mg/L. It was determined that a combination of the weak acid cation (WAC), strong acid cation (SAC) and strong base anion (SBA) resins were optimal. A degassing system was required to remove dissolved carbon dioxide after the

cation resin stage. In addition, the final adjustment of solution pH and the addition of micronized gypsum was necessary to ensure water quality compliance.

Significantly, no process modelling of high pH reverse osmosis treatment of CSG associated water has been published. Therefore, this study aimed to develop an appropriate process design for CSG associated water treatment using a high pH RO unit. A key outcome was an understanding of the effectiveness of high pH RO systems to treat a variety of coal seam gas associated water compositions encountered in the CSG industry. The underlying hypothesis was that: "if computational methods can be developed then the design and feasibility of high pH reverse osmosis systems in the CSG industry may be accelerated". Specific research questions addressed to support this hypothesis were: (1) how does the CSG associated water composition impact the viability of high pH RO? (2) what is the optimal process configuration? (3) what are the estimated operational parameters and costs? (4) is there any variation in predictions of different simulation software packages? The primary software tool used was AqMB which is a new water process engineering design package.

# 2. Materials and Methods

## **2.1 CSG Associated Water Compositions**

Three CSG water compositions were used in this study to investigate the viability of high pH RO systems for desalination purposes. From the published data of Rebello *et al.* [21] which presented an analysis of 150 wells from an operating CSG basin in Queensland, water compositions were chosen to encompass the variation in water quality encountered.

Table 1: Water compositions for simulated CSG associated water

	CSG 1	CSG 2	CSG 3	Units
TDS	4528	8785	10080	mg/L
pH	8.26	8.01	7.95	8/ =
SAR	46.2	108.4	80.7	
Conductivity	6130	14916	17282	microS/cm
Suspended Solids	5	153	7	mg/L
Turbidity	1.4	70	29	NTU
Total Alkalinity	1696	415	228	mg/L CaCO₃
Flow Rate	100	100	100	m³/h
Ammonia	0.9	1.54	2.7	mg/L (as "N")
Barium	1.12	4.89	8.92	mg/L
Bicarbonate	1943	460	264	mg/L
Boron	0.35	0.17	0.17	mg/L
Calcium	64.05	44	106	mg/L
Carbonate	61.8	22.9	7.2	mg/L
Chloride	1110	4900	5890	mg/L
Fluoride	2.2	1	0.4	mg/L
Iron	0.19	0.52	2.43	mg/L
Magnesium	4.32	15.2	33.1	mg/L
Manganese	0.002	0.033	0.11	mg/L
Potassium	6.48	16.3	20.1	mg/L
Silica	17.9	14	14.0	mg/L
Sodium	1414	3272	3713	mg/L
Strontium	1.90	10.24	18.6	mg/L
Sulphate	0	5	0	mg/L
<b>Total Organic Carbon</b>	<1	<1	<1	mg/L

For modelling purposes, a flow of 100 m<sup>3</sup>/h of CSG associated water was assumed as was a water temperature of 25 °C.

## 2.2 Modelling Software

#### 2.2.1 AqMB

AqMB (Aqueous Material Balance) is a new water treatment process modelling software package [22]. A critical aspect is a fact that it includes a wide range of unit operations encompassing both pre-treatment and desalination of contaminated water samples. AqMB software uses well known and accepted models for each unit operation which have been published in previous literature.

## 2.2.2 WAVE

An established commercial software termed "Water Application Value Engine" (WAVE) supplied by Dow Water & Process Solutions, was also employed for simulation purposes [23]. WAVE primarily focusses on the performance of ultrafiltration, reverse osmosis and ion exchange resins. In this study, AqMB was used to predict the performance of the pretreatment unit operations; and then the effluent was desalinated by a reverse osmosis system in WAVE. The outputs of both AqMB and WAVE reverse osmosis modeling were compared.

## 2.3 CSG Associated Water Treatment Unit Operations

## 2.3.1 Settling Pond

Once the CSG associated water is pumped from the well-heads, it is transferred into a treatment pond which is typically located adjacent to the desalination plant [4]. For simulation purposes the pond water quality was evaluated using the following constraints: (1) a net zero evaporation rate per annum; (2) a 10 mg/L increase in organic matter present per annum; (3) solids removal of 80 %; (4) a vertical wall height of 5 m; and (5) an average residence time in the pond of 240 hours.

## **2.3.2** Lime Softener

To model the performance of the lime softening unit, it was necessary to simulate a thickener on the basis that the solids content of the pH adjusted CSG associated water was relatively high. The thickener modelled in the simulation was constrained by the following assumptions: overflow solids 10/mg/L; minimum underflow solids (0.5 w/v %); surface loading rate 5 m/h; and floc/contact zone detention 20 min. The target pH was fixed as 10

based upon the study of O'Donnell *et al.* [24] which indicated that higher values promoted the presence of dissolved calcium ions.

## 2.3.3 Microfiltration/Ultrafiltration

Both micro- and ultrafiltration unit operations were input to the process design. Any particulate matter present in the CSG associated water following line softening was expected to be removed by this process configuration. The microfiltration system comprised of 5 micron absolute filters with solids retention capacity of 0.15 kg/m². The ultrafiltration unit operation was comprised of polyvinylidene fluoride (PVDF) Suez ZeeWeed (ZW1500-550) ultrafiltration membranes each with 51 m² area. The nominal pore size cut-off was 0.02 microns, and the design flux was 68 L/m²/h. The system was set to operate at 93 % recovery rate and cleaning involved in a combination of water backwashing and air scouring.

## 2.3.4 Ion Exchange with Weak Acid Cation Resin

The AqMB ion exchange unit was designed to incorporate a bed of DOW MAC-3 weak acid cation (WAC) resin in the H<sup>+</sup> form. The operating capacity was set to 1.8 eq/L when a linear velocity of 30 m/h was simulated. The WAC resin was regenerated by using reverse-flow configuration and exposure to 5 wt% hydrochloric acid. The regeneration stoichiometric ratio was assumed to be 2. Acid consumption figures are presented as 100 % basis.

## 2.3.5 Degasification

A degasification unit was included to strip dissolved carbon dioxide present after the acid cation stage. Air stripping involved a packed column gas adsorption tower wherein CSG associated water was distributed over packing material while air was counter-currently flowed. The process was assumed to operate at an air temperature of 30 °C; a pressure of 101.3 kPa; and a gas water ratio of 5 kg gas/kg liquid.

## 2.3.6 pH Adjustment

A chemical dosing unit was installed following the degasification step to adjust pH. Sodium hydroxide was dosed until the pH attained a value of 10.

#### 2.3.7 Reverse Osmosis

The membranes used in the simulation software were for brackish water DOW BW30HRLE-440 membranes which have a membrane area of 40.88 m². Based upon a feed flow rate of 100 m³/h, the desired recovery rate of ca. 75 % and a target flux rate of 22 L/m²/h it was estimated that a minimum 83 membrane elements were required. Assuming 6 membrane elements per pressure vessel this equated to 14 pressure vessels. The staging ratio was calculated from Equation 1.

Equation 1: 
$$R = \left[\frac{1}{1-Y}\right]^{1/n}$$

Where R is the staging ratio, Y is the desired system recovery expressed as a fraction and n is the number of stages. For CSG associated water which is typically brackish 2 stages were deemed sufficient to target a water recovery of 75 %. Hence, the staging ratio was calculated to be 2. Based upon typical constraints for 8 inch vessels (8 to 12 m³/h flow rate in the first stage per vessel and a minimum concentrate flow rate > 3.6 m³/h in the last stage) it was decided to use 10 vessels in the first stage and 5 vessels in the second stage.

## 2.4 Process Design

A summary of the process design which was simulated is shown in Figure 1.

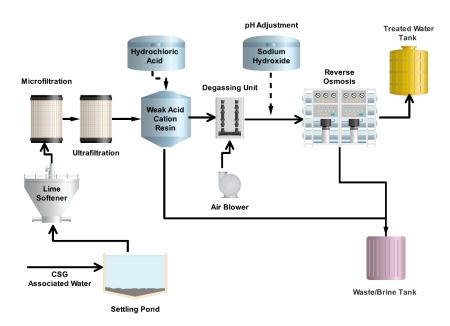


Figure 1: HERO process flow diagram

# 2.5 Technoeconomic Analysis

The following cost basis from AqMB was used (apart from sodium chloride which cost from the study by Micari *et al.* [25]) concerning estimating the operational costs for CSG associated water treatment *via* the HERO process [Tables 2 & 3]. The plant lifecycle period was set to 20 years, and plant availability was 96 %.

Table 2: Summary of costs used for chemicals and consumables

Table 2. Sammary of costs asca for enemicals and consumables								
		Cł	nemical Costs					
Lime (95 %)			297		A\$ per	tonne		
Sodium Hydroxide	(32 %)		414		A\$ per	tonne		
Hydrochloric Acid	(32 %)		300		A\$ per	tonne		
Sodium Chlori	de		133		A\$ per	tonne		
	<u>.</u>	C	Consumables					
Item	Unit	Life	Escalation	N	umber of	Effective		
	cost		rate	repl	acements in	escalation		
				•	cle period (n)	rate (i)		
	\$	years	%			%		
RO Membranes	450	3	3.0		6	9.3		
IX Resin	5	3	3.0		6	9.3		
UF Modules	1,800	5	3.0	4 15.9		15.9		
	Power							
Electricity		0.15			A\$/kWh			

Table 3: Breakdown of electricity consumption estimation

Unit Operation Type	Equipment Description	Equipment Type
Cartridge Filter	Feed Pump	Centrifugal Pump
Clarification (Solids Contact)	Feed Pump	Centrifugal Pump
Clarification (Solids Contact)	Recycle Pump	Slurry Pump
Clarification (Solids Contact)	Sludge Pump	Progressive Cavity Pump
Clarification (Solids Contact)	Flocculation Mixer	Mixer
Clarification (Solids Contact)	Rake Drive Motor	Axial Motor Drive
Ion Exchange	Feed Pump	Centrifugal Pump
Ion Exchange	Regen/Displacement Pump	Centrifugal Pump
Ion Exchange	Backwash Pump	Centrifugal Pump
Ultrafiltration	Feed Pump	Centrifugal Pump
Ultrafiltration	Backwash Pump	Centrifugal Pump
Ultrafiltration	Air Scour Blower	Centrifugal Blower
Reverse Osmosis	HP Booster Pump	Multistage Pump
Reverse Osmosis	HP Booster Pump	Multistage Pump
Storage Tank	Effluent Pump	Centrifugal Pump
Gas Absorption (Packed Column)	Feed Pump	Centrifugal Pump
Gas Absorption (Packed Column)	Air Blower	Blower

## 3. Results and Discussion

## 3.1 Pre-treatment of CSG Associated Water

#### 3.1.1 CSG Associated Water 1

The AqMB software package was used to examine a typical pre-treatment strategy for the HERO process when applied to CSG associated water sample 1 [Table 4]. When stored in the settling pond, the CSG associated water increased in pH, carbonate and total organic carbon (TOC). In contrast, a decrease in TDS, conductivity, level of suspended solids, turbidity, total alkalinity, barium, bicarbonate, calcium, carbon dioxide, iron and manganese was observed. The key phenomenon appeared to be the decarbonisation of the pond by the exchange of oxygen from the atmosphere (thus explaining the decrease in dissolved carbon dioxide and accompanying raising of the pH as the acidic material was desorbed). Increasing the solution pH favoured the formation of carbonate species instead of bicarbonate ions according to Equation 2.

Equation 2: 
$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$$

The settling period of 240 h was predicted to allow sedimentation of 77.5 % of the originally suspended solids in the CSG associated water, which correspondingly reduced the solution turbidity. A small fraction of barium ions were removed when the solution pH was increased by precipitation as barium carbonate (BaCO<sub>3</sub>). Calcium carbonate (CaCO<sub>3</sub>) also precipitated at a predicted rate of 65.5 mol/h due to the elevated pH conditions, in agreement with the accepted fact that calcium carbonate can precipitate at a pH > 9 [26, 27]). Similarly, iron also precipitated as ferrihydrite (FeOOH) at a considerably lower rate of 0.05 mol/h; which reflected the lesser abundance of iron compared to calcium in the CSG associated water sample. An even smaller amount of birnessite ((Mn<sup>4+</sup>, Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>.1.5 H<sub>2</sub>O) was formed which explained the removal of manganese from solution.

Lime softening to a target pH of 10 further reduced conductivity, suspended solids, turbidity, barium, bicarbonate, calcium, carbon dioxide, iron, and total organic carbon. Again calcium was removed in the form of solid calcium carbonate (734.1 mol/h in the underflow), Mohammadesmaeili *et al.* [28] also reported significant calcium carbonate formation according to Equation 3, when they added lime to a reverse osmosis brine solution.

Equation 3: 
$$Ca(HCO_3^-)_2 + Ca(OH)_2 \rightarrow 2 CaCO_3 + 2 H_2O$$

Table 4: AqMB simulation of pre-treatment for CSG associated water sample 1

	CSG 1	Exit of Settling Pond	Exit of Lime Softener	Exit of MF/ UF	Exit of WAC Resin	Degasser then pH adjustment	Units
		1 3.1.4	<b>Jonathan</b>		Column	to 10	
TDS	4528	4199	3782	3782	2466	1865	mg/L
рН	8.37	9.14	9.92	9.92	1.99	10	
SAR	46.2	61.7	102.3	114.1	277.6	462.7	
Hardness	170	99.7	36.2	29.0	0.46	0.46	mg/L CaCO₃
LSI	1.80	2.40	2.48	2.27		-1.49	
Conductivity	6168	6013	5903	5900	6897	3635	microS/ cm
Suspended Solids	112.8	25.43	10.0	0	0	0.008	mg/L
Turbidity	56.4	12.7	5.0	0	0	0.004	NTU
Total Alkalinity	1675	1606	1555	1548	0	23.6	mg/L CaCO₃
Flow Rate	99.98	99.95	79.33	73.58	73.84	73.89	m³/h
Ammonia	0.9	0.9	0.9	0.9	0.9	0.9	mg/L (as "N")
Barium	1.12	1.10	0.89	0.88	0.008	0.008	mg/L
Bicarbonate	1897	1395	587.7	587.8	0.06	0.60	mg/L
Boron	0.35	0.35	0.35	0.35	0.35	0.35	mg/L
Calcium	60.8	32.8	7.39	4.53	0.036	0.036	mg/L
Carbonate	70.0	270.6	630.5	626.2	0	0.59	mg/L
Carbon Dioxide	14.3	1.20	0.09	0.09	882.4	0	mg/L
Chloride	1111	1112	1112	1112	1111	1111	mg/L
Fluoride	2.2	2.2	2.2	2.2	2.2	2.2	mg/L
Iron	0.18	0.06	0.005	0.005	0.005	0.005	mg/L
Magnesium	4.32	4.32	4.32	4.32	0.09	0.09	mg/L
Manganese	0.002	0.000	0.000	0.000	0	0	mg/L
Potassium	6.48	6.48	6.48	6.48	6.48	6.48	mg/L
Silica	17.9	17.9	17.9	17.9	17.9	17.9	mg/L
Sodium	1414	1415	1415	1415	432.9	721.6	mg/L
Strontium	1.90	1.91	1.90	1.90	0.04	0.04	mg/L
Total Organic Carbon	0.18	0.45	0.27	0.14	0.14	0.14	mg/L
Resin volume					121900		L
HCl Consumption					33790		kg
NaOH Consumption						115.8	kg
Lime Consumption			52.07				kg/h

Notably, not all the calcium ions were removed from solution by the lime softening process which was consistent with the fact that minimum solubility of calcium carbonate (*ca.* 8 to 10 mg/L) is *ca.* 9.3 [29]. As there was a small quantity of dissolved carbon dioxide in the pond effluent stream, the possibility of lime reacting with carbon dioxide was deemed to occur [Equation 4] [29]. The reduction in carbon dioxide from 1.20 to 0.09 mg/L was consistent with this proposition.

Equation 4: 
$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

No removal of magnesium ions was predicted when lime was added to adjust the solution pH to 10. This calculation was consistent with the knowledge that magnesium ions typically do not precipitate until pH values above 10 [29, 30]; wherein insoluble magnesium hydroxide usually forms. Similarly, strontium ions were also not decreased by lime addition which was not expected based upon the study of O'Donnell  $et\ al.$  [24]. These authors conducted a series of detailed experiments relating to the removal of strontium from drinking water. Strontium ions could precipitate at a pH of 10 (ca. 50%) if an excess of calcium ions and inorganic carbon were present. Indeed, this was the case in this study; hence, it may be that the software has not taken this complexity into account.

In contrast, barium ions were slightly reduced in concentration (1.10 to 0.89 mg/L), and AqMB indicated that barium carbonate was precipitated at a rate of 0.17 mol/h in the underflow. As described by Rioyo *et al.* [31], barium carbonate has a very low solubility product and is favoured to precipitate in the presence of solution alkalinity under high pH conditions [Equation 5].

Equation 5: 
$$Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3$$

Table 4 indicated that a slight decrease in solution conductivity occurred after lime was added. This observation was in accord with the fact that lime softening typically reduces solution conductivity [30]; with the magnitude depending upon factors such as solution composition and pH employed. For example, Ordóñez *et al.* [30] found that lime dosing of reverse osmosis brine resultant from the treatment of paper mill wastewater, reduced conductivity by *ca.* 40 to 60 %. In the illustrated example, precipitation of calcium and magnesium species was the main factor responsible for the conductivity decrease.

The downstream microfiltration/ultrafiltration system ensured that solids (including calcium carbonate) in the overflow stream from the lime softener were removed (suspended solids & turbidity now equal to zero). The overall flow rate of CSG associated water to treat was diminished to 73.58 m<sup>3</sup>/h due to losses associated with backwashing the filtration system.

The H<sup>+</sup>-WAC resin column substantially reduced the solution pH due to the exchange of protons from the resin surface with cations such as sodium, calcium, magnesium, barium, and strontium [Equations 6 & 7; where Alkaline =  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Ba^{2+}$  &  $Sr^{2+}$ ). Correspondingly, the TDS of the solution diminished to 2466 mg/L from 3782 mg/L.

Equation 6: 
$$RCOO^-H^+ + Na^+ \leftrightarrow RCOO^-Na^+ + H^+$$

Equation 7: 
$$2 RCOO^-H^+ + Alkaline^{2+} \leftrightarrow (RCOO^-)_2 Alkaline^{2+} + 2 H^+$$

Decomposition of carbonate and bicarbonate species in the acidic conditions according to Equations 8 & 9 promoted the concentration of dissolved carbon dioxide.

Equation 8: 
$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$$

Equation 9: 
$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O$$

The calculated resin volume was 121,900 L based on a regeneration step once every 48 hours. The amount of HCl required was correspondingly 33790 kg for each regeneration process. The degassing unit operation successfully eliminated dissolved carbon dioxide from the CSG associated water sample and reduced the solution TDS. The subsequent raising of the pH to 10 using sodium hydroxide solution reduced the conductivity and propensity for dissolved silicates to form scale [32]. However, sodium concentration was increased as caustic soda was added.

#### 3.1.2 CSG Associated Water 2

Simulation of the pre-treatment of CSG associated water sample 2 was also investigated, as shown in Table 5. The trends in solution properties after the settling pond were analogous to those reported for CSG associated water sample 2. Namely, an increase in solution pH to 8.61, slightly more carbonate (11.4 to 37.8 mg/L) and total organic carbon (TOC). Concomitantly a reduction in TDS, conductivity, suspended solids, turbidity, total alkalinity, bicarbonate, carbon dioxide, iron, and manganese was observed. The main difference was the lack of barium or calcium removal with CSG associated water sample 2. This situation

presumably occurred due to the significantly lower pH with CSG associated water 2 compared to sample 1 (*c.f.* 8.61 to 9.14).

A lesser amount of lime was required to be added to CSG associated water 2 compared with sample 1 (c.f. 20.11 kg to 52.07 kg) which reflected the reduced buffering capacity of sample 2 (i.e. less bicarbonate/carbonate species present). In the lime softening stage, calcium ions were the only alkaline earth ions removed. It was observed that 87.8 % of calcium ions were removed by the exit of the lime stage with CSG associated water 1; whereas the corresponding reduction for CSG associated water 2 was only 53.0 %. Again, the differences in the total solution alkalinity of CSG associated water 2 after the settling pond compared with sample 1 (c.f. 414.6 compared to 1606 mg/L CaCO<sub>3</sub>), may explain this observation.

The increased TDS of CSG associated water 2 meant that a substantial increase in demand for WAC resin (*c.f.* 324,300 to 121,900 L) and hydrochloric acid for regeneration (*c.f.* 89860 to 33,790 kg) was apparent. Sodium hydroxide in higher amounts was also required do the extra acid generated from the WAC resin bed due to the higher quantity of cations removed from the CSG water sample (*c.f.* 993.6 to 115.8 kg/h). The quality of the water emanating from the pre-treatment stage for CSG associated water 2 was significantly higher in TDS content (8136 mg/L) compared to that for CSG associated water 1 (1865 mg/L). This result highlighted the fact that the composition of the CSG associated water was important and not just the initial salt content (initial ratio of TDS between samples 1 and 2 was 1.94 and after pre-treatment was 4.36).

#### 3.1.3 CSG Associated Water 3

CSG associated water 3 comprised of the largest TDS value of all three water samples evaluated and also the lowest alkalinity content. Consistent with this fact was the minimal demand for lime to adjust the pH of the water from the settling pond to 10 (13.03 kg). In harmony with this calculation was the relatively low removal of calcium ions predicted (32 %). Further softening of the CSG associated water with WAC resin unsurprisingly required the highest amounts of resin and regenerant hydrochloric acid (386,200 L and 107,000 kg, respectively). Moreover, sodium hydroxide demand for final pH adjustment was increased to

Table 5: AqMB simulation of pre-treatment for CSG associated water sample 2

	CSG 2	Exit of Settling Pond	Exit of Lime Softener	Exit of UF	Exit of WAC Resin Column	Degasser then pH adjustment to 10	Units
TDS	8785	8749	8526	8526	6257	8136	mg/L
pH	8.01	8.61	9.73	9.72	1.14	10.0	8/ =
SAR	108.4	108.4	133.3	137.4	155.0	480.7	
Hardness	172	172	114	107	8.35	8.35	
LSI	0.73	1.33	2.05	1.98	0.00	-0.40	
Conductivity	15470	15450	15320	15320	39070	14980	microS/cm
Suspended Solids	154.7	31.0	10		0	0	mg/L
Turbidity	77	15.5	5		0	0	NTU
Total Alkalinity	415.7	414.6	356.1	349.4	0	24.09	mg/L CaCO₃
Flow Rate	100	99.94	90.45	84.12	84.15	84.94	m³/h
Ammonia	1.54	1.54	1.54		1.54	1.54	mg/L (as "N")
Barium	4.89	4.89	4.89	4.89	0.19	0.19	mg/L
Bicarbonate	481	422	126.6	126.6	0.002	0.40	mg/L
Boron	0.17	0.17	0.17	0.17	0.17	0.17	mg/L
Calcium	44	44	20.7	18.0	0.57	0.57	mg/L
Carbonate	11.4	37.8	140.3	136.4	0	0.77	mg/L
Carbon Dioxide	5.44	1.20	0.03	0.03	191.2	0	mg/L
Chloride	4901	4901	4901	4901	4900	4893	mg/L
Fluoride	1.0	1.0	1.0	1.0	1.0	1.0	mg/L
Iron	0.52	0.12	0.005	0.002	0.002	0.002	mg/L
Magnesium	15.2	15.2	15.2	15.2	1.69	1.69	mg/L
Manganese	0.033	0.007	0.000	0	0	0	mg/L
Potassium	16.3	16.3	16.3	16.3	16.3	16.3	mg/L
Silica	14.0	14.0	14.0	14.0	14.0	14.0	mg/L
Sodium	3274	3274	3274	3274	1031	3198	mg/L
Strontium	10.25	10.25	10.25	10.25	1.01	1.01	mg/L
Sulphate	5.0	5.0	5.0	5.0	5.0	5.0	mg/L
Total Organic Carbon	0	0.27	0.26	0.14	0.14	0.14	mg/L
Resin volume					324300		L
HCI Consumption					89860		kg
NaOH Consumption						993.6	kg
Lime Consumption			20.11				kg/h

Table 6: AqMB simulation of pre-treatment for CSG associated water sample 3

	CSG 3	Exit of Settling Pond	Exit of Lime Softener	Exit of UF	Exit of WAC Resin Column	Degasser then pH adjustment to 10	Units
TDS	10080	10070	9872	9872	7309	9782	mg/L
рН	7.95	8.35	9.50	9.47	1.052	10.0	
SAR	80.7	80.7	91.0	92.0	100.0	325.7	
Hardness	401	401	315	308	26.4	26.3	mg/L CaCO₃
SDI/LSI	1.1/0.8	1.5/1.2	2.2/2.0	2.2/1.9	na/na	0.7/0.4	
Conductivity	1800	17990	17860	17850	47300	17860	microS/ cm
Suspended Solids	15.94	3.24	10.0	0	0	0	mg/L
Turbidity	29	1.6	5.0	0	0	0	NTU
Total Alkalinity	228.6	223.2	136.2	129.1	0	27.7	mg/L CaCO₃
Flow Rate	100	100	92.83	86.34	86.35	87.4	m³/h
Ammonia	2.7	2.7	2.7	2.7	2.7	2.7	mg/L (as "N")
Barium	8.92	8.92	8.92	8.92	0.44	0.43	mg/L
Bicarbonate	256	237.3	54.96	54.38	0	0.37	mg/L
Boron	0.17	0.17	0.17	0.17	0.17	0.17	mg/L
Calcium	106	106	71.66	68.83	3.11	3.10	mg/L
Carbonate	8.74	14.5	43.81	40.14	0	0.80	mg/L
Carbon Dioxide	3.24	1.20	0.02	0.02	68.67	0	mg/L
Chloride	5897	5897	5897	5897	5896	5885	mg/L
Fluoride	0.4	0.4	0.4	0.4	0.4	0.4	mg/L
Iron	2.43	0.51	0.02	0.001	0.001	0.001	mg/L
Magnesium	33.1	33.1	33.1	33.1	4.54	4.53	mg/L
Manganese	0.11	0.022	0.000	0.000	0.000	0.000	mg/L
Potassium Silica	20.1 14.0	20.1 14.0	20.1 14.0	20.1 14.0	20.1 14.0	20.1 14.0	mg/L
Sodium	3713	3713	3713	3713	1182	3845	mg/L mg/L
Strontium	18.6	18.6	18.6	18.6	2.22	2.22	mg/L
Sulphate	0	0	0	0	0	0	mg/L
Total Organic Carbon	0	0.27	0.25	0.13	0.13	0.13	mg/L
Resin volume					386200		L
HCl							
Consumption					107000		kg
NaOH Consumption						1254	kg/h
Lime Consumption			13.03				kg/h

1254 kg/h. In summary, there was a correlation between the TDS value of the CSG associated water and the amount of regenerant and pH adjustment chemicals required during the pretreatment stage. In addition, higher amounts of alkalinity buffered the solution with respect to lime softening performance but facilitated attainment of lower TDS solutions prior to the central RO desalination stage.

## 3.2 Simulation of Single & Dual Stage Reverse Osmosis Systems

## 3.2.1 Pre-Treated CSG Associated Water 1

A simulation was performed wherein a single or dual stage RO unit was employed to purify pre-treated CSG associated water 1 [Table 7]. The first RO stage was equipped with 10 vessels which contained 6 DOW BW30-440 membrane modules in each. Whereas the second RO stage had 5 vessels containing 6 DOW BW30-440 membrane modules. Using AqMB the highest water recovery obtained without any error expressions was determined to be 59 % for a single stage RO system. When WAVE was applied to the same water composition the maximum water recovery was predicted to be 60 % (again this was based upon the software indicating no RO design warnings relating to excess flux rates or insufficient brine flow rates). Not only were the water recovery predictions similar for both software packages but also the water recovery predictions were in the suggested range for a 1 stage RO system treating brackish water using 6 elements per stage (40 to 60 % according to DOW [33]). Application of a dual-stage RO system increased the water recovery to 79.5 % when using AqMB to simulate the desalination performance; whereas 80 % water recovery was predicted using WAVE. Again, both simulations estimated a water recovery rate in the range of 70 to 80 % specified by DOW for a 2 stage brackish water RO plant [33]. In terms of operating pressures, AqMB indicated 6.63 bar first stage and 10.0 bar second stage. Whereas, WAVE suggested the corresponding operating pressures were 5.91 and 8.96 bar, respectively (a boost pressure of 5 bar was applied to 2<sup>nd</sup> stage RO unit).

In terms of RO permeate water quality, the pH was in the required range of 6.5 to 8.0, as was the solution conductivity (< 900  $\mu$ S/cm) [20]. SAR values were in excess of recommended values (< 6 to 12 [20]) which meant that small amounts of micronized gypsum would need to be added to the permeate before use for irrigation purposes [19]. Fluoride was also less than the prescribed limit of 2 mg/L [20].

Table 7: Permeate quality for desalination simulation for CSG associated water 1 using single and dual-stage RO units

	Degasser	Permeate	Permeate	Permeate	Permeate	Units
	then pH	1 Stage	1 Stage	2 Stage	2 Stage	
	adjustment	(AqMB)	(WAVE)	(AqMB)	(WAVE)	
	to 10					
TDS	1865	31.84	48.97	63.3	79.79	mg/L
рН	10	9.71	8.23	9.92	8.42	
SAR	462.7	46.5	n.a.	76.5	n.a.	
Hardness	0.46		0.00		0.00	mg/L CaCO₃
LSI	-1.49	-3.82		-3.24		
Conductivity	3635	74.12		143.5		microS/cm
Suspended Solids	0.008	0.011	0.00	0.014	0.00	mg/L
Turbidity	0.004	0.005	0.00	0.007	0.00	NTU
Total Alkalinity	23.6	6.99		9.27		mg/L CaCO₃
Flow Rate	73.89	43.57	44.33	58.71	51.72	m³/h
Ammonia	0.9	1.49	0.00	1.13	0.00	mg/L (as "N")
Barium	0.008	0	0.00	0.0003	0.00	mg/L
Bicarbonate	0.60	0.02	0.06	0.04	0.10	mg/L
Boron	0.35	0.09	0.04	0.36	0.05	mg/L
Calcium	0.036	0.0007	0.00	0.001	0.00	mg/L
Carbonate	0.59	0.005	0.00	0.017	0.00	mg/L
Carbon Dioxide	0.00	0.00	0.00	0.00	0.00	mg/L
Chloride	1111	16.1	29.11	34.8	47.50	mg/L
Fluoride	2.2	0.06	0.10	0.12	0.17	mg/L
Iron	0.005	0.004	0.00	0.006	0.00	mg/L
Magnesium	0.09	0.003	0.00	0.004	0.00	mg/L
Manganese	0.00	0.00	0.00	0.00	0.00	mg/L
Potassium	6.48	0.16	0.30	0.30	0.48	mg/L
Silica	17.9	0.19	0.23	0.41	0.33	mg/L
Sodium	721.6	12.68	18.91	24.22	30.85	mg/L
Strontium	0.04	0.0007	0.00	0.001	0.00	mg/L
Sulphate	0.00	0.00	0.00	0.00	0.00	mg/L
Total Organic Carbon	0.14	0.012	0.00	0.018	0.00	mg/L

Overall water recovery was 58.7 % (based upon AqMB predictions) and 79.4 % for the RO system alone.

## 3.2.2 Pre-Treated CSG Associated Water 2

Again, the RO plant configuration was maintained to be similar to that employed to treat CSG associated water sample 1 [Table 8]. Namely the first RO stage was equipped with 10 vessels each with 6 DOW BW30-440 membrane modules, and the second RO stage had 5 vessels containing 6 DOW SW30XLE-440 membrane modules. Application of AqMB suggested that the highest water recovery obtained without any error expressions was 62 % for a singlestage RO system. When WAVE was applied to the same water composition, the maximum water recovery was calculated to be 60 %. WAVE software indicated that the brine produced was supersaturated with Mg(OH)<sub>2</sub> and recommended that use of anti-scalants may be required. AqMB further identified concerns regarding ferrihydrite formation (0.0016 mol/h). Application of a dual-stage RO system increased the water recovery to 82 % when using AqMB to simulate the desalination performance; whereas only 73 % water recovery was predicted using WAVE. Feed pressures suggested by AqMB were 23.5 bar first stage and 45.8 bar second stage; likewise pressures indicated by WAVE were 17.6 and 26.7 bar, respectively (a boost pressure of 10 bar was applied to second-stage RO unit). The conductivity of the permeate from the RO system was higher than that recorded for CSG associated water 1 (c.f. 550.1 to 143.5  $\mu$ S/cm) but still within prescribed limits [20]. Overall water recovery was 69.9 % (based upon AqMB predictions) and 82.3 % for the RO system alone.

## 3.2.3 Pre-Treated CSG Associated Water 3

In this instance, the RO plant configuration employed in the first RO stage 10 vessels each with DOW SW30XLE-440 membrane modules, and the second RO stage had 5 vessels containing 6 DOW SWHRLE-440 membrane modules [Table 7]. AqMB indicated that the greatest water recovery obtainable was 65 % for a single-stage RO system. When WAVE was applied to the same water composition, the maximum water recovery was calculated to be 66 %. WAVE software again indicated that the brine produced was supersaturated with Mg(OH)<sub>2</sub> and that anti-scalants may be required. In terms of potential for precipitation to occur AqMB also indicated that in the first and second RO stages, a small quantity of ferrihydrite might form (0.00084 mol/h).

Table 8: Permeate quality for desalination simulation for CSG associated water 2 using single and dual stage RO units

	Degasser	Permeate	Permeate	Permeate	Permeate	Units
	then pH	1 Stage	1 Stage	2 Stage	2 Stage	
	adjustment	(AqMB)	(WAVE)	(AqMB)	(WAVE)	
	to 10					
TDS	8136	303.3	317	261.8	295	mg/L
рН	10.0	9.89	8.28	9.77	8.24	
SAR	480.7	81.2	n.a.	73.9	n.a.	
Hardness	8.35		0		0	mg/L CaCO₃
LSI	-0.40	-1.98		-2.27		
Conductivity	14980	636.4		550.1		microS/cm
Suspended Solids	0	0.006	0.00	0.004	0.00	mg/L
Turbidity	0	0.003	0.00	0.002	0.00	NTU
Total Alkalinity	24.09	11.76		8.84		mg/L CaCO₃
Flow Rate	84.94	52.55	50.96	69.94	62.01	m³/h
Ammonia	1.54	2.49	0.01	1.87	0.01	mg/L (as "N")
Barium	0.19	0.007	0.00	0.006	0.00	mg/L
Bicarbonate	0.40	0.04	0.10	0.04	0.08	mg/L
Boron	0.17	0.05	0.02	0.08	0.02	mg/L
Calcium	0.57	0.02	0.00	0.019	0.00	mg/L
Carbonate	0.77	0.02	0.00	0.014	0.00	mg/L
Carbon Dioxide	0.00	0.00	0.00	0.00	0.00	mg/L
Chloride	4893	176.7	191.5	153.0	178.4	mg/L
Fluoride	1.00	0.06	0.07	0.05	0.06	mg/L
Iron	0.002	0.003	0.00	0.003	0.00	mg/L
Magnesium	1.69	0.09	0.00	0.08	0.00	mg/L
Manganese	0.00	0.00	0.00	0.00	0.00	mg/L
Potassium	16.3	0.86	0.77	0.65	0.72	mg/L
Silica	14.0	0.37	0.17	0.42	0.25	mg/L
Sodium	3198	121.0	123.9	104.2	115.5	mg/L
Strontium	1.01	0.04	0.00	0.03	0.00	mg/L
Sulphate	5.0	0.06	0.10	0.05	0.02	mg/L
Total Organic Carbon	0.14	0.011	0.00	0.02	0.00	mg/L

Application of a dual-stage RO system increased the water recovery to 80.6 % when using AqMB to simulate the desalination performance; whereas 79 % water recovery was predicted using WAVE.

Table 9: Permeate quality for desalination simulation for CSG associated water 3 using single and dual-stage RO units

	Degasser then pH adjustment to 10	Permeate 1 Stage (AqMB)	Permeate 1 Stage (WAVE)	Permeate 2 Stage (AqMB)	Permeate 2 Stage (WAVE)	Units
TDS	9782	51.21	56.4	73.93	91.50	mg/L
рН	10.0	7.70	7.44	7.94	7.59	
SAR	325.7	15.4	n.a.	28.9	n.a.	
Hardness	26.3					mg/L CaCO₃
LSI	0.7	-5.77		-5.20		
Conductivity	17860	118.4		163.9		microS/cm
Suspended Solids	0	0.00	0.00	0.00	0.00	mg/L
Turbidity	0	0.00	0.00	0.00	0.00	NTU
Total Alkalinity	27.7	0.36		0.54		mg/L CaCO₃
Flow Rate	87.4	56.63	57.68	70.48	69.05	m³/h
Ammonia	2.7	3.38	0.00	2.82	0.01	mg/L (as "N")
Barium	0.43	0.002	0.00	0.003	0.00	mg/L
Bicarbonate	0.37	0.005	0.00	0.007	0.00	mg/L
Boron	0.17	0.009	0.01	0.04	0.01	mg/L
Calcium	3.10	0.015	0.00	0.022	0.01	mg/L
Carbonate	0.80	0.00	0.00	0.00	0.00	mg/L
Carbon Dioxide	0.00	0.00	0.00	0.00	0.00	mg/L
Chloride	5885	28.64	34.06	42.63	55.27	mg/L
Fluoride	0.4	0.002	0.00	0.005	0.00	mg/L
Iron	0.001	0.0006	0.00	0.003	0.00	mg/L
Magnesium	4.53	0.06	0.02	0.03	0.01	mg/L
Potassium	20.1	0.01	0.13	0.02	0.22	mg/L
Silica	14.0	0.16	0.14	0.24	0.22	mg/L
Sodium	3845	18.92	22.0	28.05	35.69	mg/L
Strontium	2.22	0.01	0.00	0.016	0.00	mg/L
Total Organic Carbon	0.13	0.01		0.016		mg/L

Feed pressures suggested by AqMB were 28.5 bar first stage and 50.6 bar second stage; likewise pressures indicated by WAVE were 32.1 and 40.2 bar, respectively (a boost pressure of 10 bar was applied to second-stage RO unit).

The conductivity of the permeate from the RO system was lower than that estimated for CSG associated water 2 (*c.f.* 163.9 to 550.1  $\mu$ S/cm) and significantly within legislative limits [20].

Overall water recovery was 70.5 % (based upon AqMB predictions) and 80.7 % for the RO system alone.

## 3.3 Economics of CSG Associated Water Treatment using HERO process

The major operational costs for the pre-treatment strategy included electricity consumption, lime, resins, hydrochloric acid for resin regeneration, sodium hydroxide for pH adjustment, UF membrane, and RO membranes [Table 10].

Table 10: Summary of operational costs for CSG associated water treatment

	•	Ch	emic	als and Consun	nables (A\$ pei	annur	n)	
	Lime	WAC R	esin	Hydrochloric	Sodium	l	JF	RO
				Acid	Hydroxide	mem	brane	membrane
CSG 1	135,539	160,6	40	5,488,000	420,112	7,1	L42	11,119
CSG 2	52,342	427,3	64	14,742,656	3,603,804	8,3	385	7,413
CSG 3	33,928	508,9	36	17,554,687	4,546,682	8,3	385	11,119
CSG 1	135,539	1,65	4	12,981	41,995	7,1	L42	11,119
NaCl								
Regen								
				Elect	•			
	Annual P	ower	Annual Power		kWh/m	3		\$/ML
	Consump			Cost				
	(kWh/anı	num)	(,	(A\$/annum)				
CSG 1	3,052,1	.21		457,818	3.735		Į.	522.38
CSG 2	3,418,2	232		512,734	3.901		585.22	
CSG 3	3,502,4	198		525,375	3.995		Į	599.32
CSG 1	972,39	99	145,860		1.110		:	166.43
NaCl								
Regen								

The total operational cost was calculated as A\$7,921, 22,989, and 27,548 per ML of water treated for CSG 1, CSG 2 and CSG 3 samples, respectively. The dominant cost was associated with the demand for HCl to regenerate the WAC resin and sodium hydroxide to raise solution pH to *ca.* 10. This finding was in agreement with Li *et al.* [34] who indicated that ion exchange is amenable to the treatment of brackish water, but there exists a challenge in terms of the economics of resin regeneration. In terms of electricity consumption, air stripping to remove dissolved carbon dioxide present after the passage of the CSG associated water through the acidic WAC resin bed; was the major consumer (*ca.* 70 %). Ghaffour *et al.* [35] reported that

the energy consumption when using a brackish water reverse osmosis (BWRO) system was typically in the range 0.5 to 2.5 kWh/m<sup>3</sup>. This value was in agreement with the predictions of AqMB which were ca. 0.76 kWh/m<sup>3</sup> for the RO units when desalinating CSG associated water types 1 to 3. The operating cost for seawater desalination plants has been intimated to be ca. A\$674 per ML of water treated [36].

## 3.3 Optimization of HERO Process for CSG Associated Water Treatment

Economic analysis has indicated that the use of hydrochloric acid as a regenerant for the WAC ion exchange resin is too expensive. Replacement of HCl with a 10 % sodium chloride solution was thus investigated as this was also a traditional means of regenerating a softening resin [37]. In addition, the air stripper employed to remove dissolved carbon dioxide gas was shown to be the most significant consumer of electricity in the water treatment process. Therefore, a simulation was performed using CSG 1 water sample wherein the changes above were made [Table 11]. The WAC resin removed all traces of alkaline earth ions from the CSG associated water. The most notable difference was that the sodium ion concentration remained substantially higher than (c.f. 1429 mg/L compared to 432.9 mg/L when HCl was employed as the regenerant). The greater salt load on the reverse osmosis modules resulted in a slight rise in total dissolved solids content in the final permeate (c.f. 227.9 mg/L compared to 63.3 mg/L). Nevertheless, the water quality was still suitable for beneficial reuse. Examination of the process economics revealed that the sodium chloride regeneration approach for the resin coupled with no air stripping; remarkably reduced operational costs. The total operational cost was now A\$417 per ML of water treated, which was of similar value to operating costs detailed for other reverse osmosis based plants [36].

Table 11: AqMB simulation of pre-treatment for CSG associated water sample 1 using a sodium chloride regenerant instead of HCl for the WAC resin

	CSG 1	Exit of	Exit of WAC	Permeate 2	Units
		Lime	Resin	Stage	
		Softener	Column	(AqMB)	
TDS	4528	3782	3785	227.9	mg/L
рН	8.37	9.92	9.90	10.19	
Conductivity	6168	5903	5918	432.8	microS/cm
Suspended Solids	112.8	10.0	0	0	mg/L
Turbidity	56.4	5.0	0	0	NTU
Total Alkalinity	1675	1555	1533	116.9	mg/L CaCO₃
Flow Rate	99.98	79.33	73.78	58.62	m³/h
Aluminium	0	0.9	0	0	mg/L
Ammonia	0.9	0.89	0.89	1.13	mg/L (as "N")
Barium	1.12	0.88	0	0	mg/L
Bicarbonate	1897	587.7	605.7	43.8	mg/L
Boron	0.35	0.35	0.35	0.15	mg/L
Calcium	60.8	7.39	0	0	mg/L
Carbonate	70.0	630.5	608.5	40.8	mg/L
Carbon Dioxide	14.3	0.09	0.09	0	mg/L
Chloride	1111	1112	1112	51.1	mg/L
Fluoride	2.2	2.2	2.2	0.18	mg/L
Iron	0.18	0.005	0.005	0.005	mg/L
Magnesium	4.32	4.32	0	0	mg/L
Potassium	6.48	6.48	6.48	0.52	mg/L
Silica	17.9	17.9	17.9	0.61	mg/L
Sodium	1414	1415	1429	86.6	mg/L
Strontium	1.90	1.90	0	0	mg/L
Total Organic Carbon	0.18	0.27	0.14	0.02	mg/L
Resin volume			1255		L
NaCl Consumption			557.5		kg
NaOH Consumption			11.57#		kg/h
Lime Consumption		52.07			kg/h

#dosage of NaOH was made after the IX unit

## 4. Conclusions

The use of computational tools has shown to be essential evaluating preferred process designs for CSG associated water treatment. Rapid evaluation of the influence of variable CSG associated water compositions and the unit operations employed upon treatment performance and cost was achieved. Increasing the TDS of the CSG associated water generally caused an increase in process costs for chemicals and also required the use of larger sized

equipment. AqMB software has indicated that the original HERO concept using a weak acid cation (WAC) resin for softening was only viable if the sodium exchange form was employed. Not only were regenerant costs diminished substantially, but the need for air stripping was negated. As the solution pH was not made acidic the consumption of sodium hydroxide to raise the pH to *ca.* 10 was also lessened. The optimal operational cost of A\$417 per ML of water treated appeared attractive as it of the same magnitude for conventional reverse osmosis processes. The HERO process, therefore, appears potentially suitable to treat GSG associated water. Nevertheless, application of high pH reverse osmosis has not been reported for the treatment of coal seam gas associated water despite the potential benefit of high water recovery rates.

## 5. Acknowledgements

The support of Darren Szczepanski from Salt Water Solutions with regards to AqMB software is appreciated.

## 5. References

- [1] I. Hamawand, T. Yusaf, S.G. Hamawand, Coal seam gas and associated water: A review paper, Renewable and Sustainable Energy Reviews, 22 (2013) 550-560.
- [2] J.J. Sheng, Critical review of field EOR projects in shale and tight reservoirs, Journal of Petroleum Science and Engineering, 159 (2017) 654-665.
- [3] C.A. Rebello, S.J. Couperthwaite, G.J. Millar, L.A. Dawes, Understanding coal seam gas associated water, regulations and strategies for treatment, Journal of Unconventional Oil and Gas Resources, 13 (2016) 32-43.
- [4] G.J. Millar, S.J. Couperthwaite, C.D. Moodliar, Strategies for the management and treatment of coal seam gas associated water, Renewable and Sustainable Energy Reviews, 57 (2016) 669-691.
- [5] M. Stearns, J. Tindall, G. Cronin, M. Friedel, E. Bergquist, Effects of coal-bed methane discharge waters on the vegetation and soil ecosystem in Powder River Basin, Wyoming, Water, Air, & Soil Pollution, 168 (2005) 33-57.
- [6] L.D. Nghiem, T. Ren, N. Aziz, I. Porter, G. Regmi, Treatment of coal seam gas produced water for beneficial use in australia: A review of best practices, Desalination and Water Treatment, 32 (2011) 316-323.
- [7] J.C. Pashin, M.R. McIntyre-Redden, S.D. Mann, D.C. Kopaska-Merkel, M. Varonka, W. Orem, Relationships between water and gas chemistry in mature coalbed methane reservoirs of the Black Warrior Basin, International Journal of Coal Geology, 126 (2014) 92-105.
- [8] G.J. Millar, J. Lin, A. Arshad, S.J. Couperthwaite, Evaluation of electrocoagulation for the pre-treatment of coal seam water, Journal of Water Process Engineering, 4 (2014) 166-178.
- [9] H. Le, Innovative commercial and technical solutions for CSG produced water treatment project, Chemical Engineering World, 52 (2017) 32-40.
- [10] R.S. Dennis, Continuous ion exchange for wyoming CBM produced-water purification: Proven experience, in: SPE E and P Environmental and Safety Conference 2007: Delivering Superior Environmental and Safety Performance, Proceedings, 2007, pp. 321-324.
- [11] G.J. Millar, S.J. Couperthwaite, S. Papworth, Ion exchange of sodium chloride and sodium bicarbonate solutions using strong acid cation resins in relation to coal seam water treatment, Journal of Water Process Engineering, 11 (2016) 60-67.
- [12] Y. Oren, E. Korngold, N. Daltrophe, R. Messalem, Y. Volkman, L. Aronov, M. Weismann, N. Bouriakov, P. Glueckstern, J. Gilron, Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach, Desalination, 261 (2010) 321-330.
- [13] H.C. Duong, A.R. Chivas, B. Nelemans, M. Duke, S. Gray, T.Y. Cath, L.D. Nghiem, Treatment of RO brine from CSG produced water by spiral-wound air gap membrane distillation A pilot study, Desalination, 366 (2015) 121-129.
- [14] P. Zhang, A. Pabstmann, S. Gray, M. Duke, Silica fouling during direct contact membrane distillation of coal seam gas brine with high sodium bicarbonate and low hardness, Desalination, 444 (2018) 107-117.
- [15] H.C. Duong, S. Gray, M. Duke, T.Y. Cath, L.D. Nghiem, Scaling control during membrane distillation of coal seam gas reverse osmosis brine, Journal of Membrane Science, 493 (2015) 673-682.
- [16] J. Rioyo, V. Aravinthan, J. Bundschuh, M. Lynch, A review of strategies for RO brine minimization in inland desalination plants, Desalination and Water Treatment, 90 (2017) 110-123.
- [17] D. Mukhopadhyay Method and apparatus for high efficiency reverse osmosis operation, US6537456B2, (2003).

- [18] K. Moftah, High pH RO for wastewater treatment, Pollution Engineering, 34 (2002) 30-35.
- [19] R. Vedelago, G.J. Millar, Process evaluation of treatment options for high alkalinity coal seam gas associated water, Journal of Water Process Engineering, 23 (2018) 195-206.
- [20] M. Wicks, G.J. Millar, A. Altaee, Process simulation of ion exchange desalination treatment of coal seam gas associated water, Journal of Water Process Engineering, 27 (2019) 89-98.
- [21] C.A. Rebello, S.J. Couperthwaite, G.J. Millar, L.A. Dawes, Coal seam water quality and the impact upon management strategies, Journal of Petroleum Science and Engineering, 150 (2017) 323-333.
- [22] www.aqmb.net, AQMB Simulating Water Solutions.
- [23] <a href="https://water.custhelp.com/app/software/wave">https://water.custhelp.com/app/software/wave</a>, DOW Water & Process Solutions.
- [24] A.J. O'Donnell, D.A. Lytle, S. Harmon, K. Vu, H. Chait, D.D. Dionysiou, Removal of strontium from drinking water by conventional treatment and lime softening in bench-scale studies, Water Research, 103 (2016) 319-333.
- [25] M. Micari, A. Cipollina, A. Tamburini, M. Moser, V. Bertsch, G. Micale, Combined membrane and thermal desalination processes for the treatment of ion exchange resins spent brine, Applied Energy, 254 (2019).
- [26] L. Lipus, D. Dobersek, Influence of magnetic field on the aragonite precipitation, Chemical Engineering Science, 62 (2007) 2089-2095.
- [27] P. Somasundaran, J.O. Amankonah, K. Ananthapadmabhan, Mineral—solution equilibria in sparingly soluble mineral systems, Colloids and Surfaces, 15 (1985) 309-333.
- [28] F. Mohammadesmaeili, M.K. Badr, M. Abbaszadegan, P. Fox, Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment, Water Environment Research, 82 (2010) 342-350.
- [29] A.M. Wachinski, Environmental Ion Exchange: Principles and Design, Second Edition CRC Press, 2016.
- [30] R. Ordóñez, A. Moral, D. Hermosilla, T. Blanco, Combining coagulation, softening and flocculation to dispose reverse osmosis retentates, Journal of Industrial and Engineering Chemistry, 18 (2012) 926-933.
- [31] J. Rioyo, V. Aravinthan, J. Bundschuh, M. Lynch, Research on 'high-pH precipitation treatment' for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility, Desalination, 439 (2018) 168-178.
- [32] P. Sanciolo, N. Milne, K. Taylor, M. Mullet, S. Gray, Silica scale mitigation for high recovery reverse osmosis of groundwater for a mining process, Desalination, 340 (2014) 49-58.
- [33] <a href="https://water.custhelp.com">https://water.custhelp.com</a>, FILMTEC Membranes Steps to Design a Reverse Osmosis System.
- [34] X. Li, D. Hasson, R. Semiat, H. Shemer, Intermediate concentrate demineralization techniques for enhanced brackish water reverse osmosis water recovery A review, Desalination, 466 (2019) 24-35.
- [35] N. Ghaffour, T.M. Missimer, G.L. Amy, Technical review and evaluation of the economics of water desalination: Current and future challenges for better water supply sustainability, Desalination, 309 (2013) 197-207.
- [36] M.P. Shahabi, A. McHugh, M. Anda, G. Ho, Comparative economic and environmental assessments of centralised and decentralised seawater desalination options, Desalination, 376 (2015) 25-34.

[37] A. Hayani, S. Mountadar, S. Tahiri, M. Mountadar, Softening of hard water by ion-exchange with strongly acidic cationic resin. Application to the brackish groundwater of the coastal area of El Jadida province (Morocco), Journal of Materials and Environmental Science, 7 (2016) 3875-3884.