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# Process Simulation of Ion Exchange Desalination Treatment of Coal Seam Gas Associated Water

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The aim of this investigation was to develop an ion exchange process for the remediation of coal seam gas (CSG) associated water to make it suitable for beneficial reuse. The hypothesis was that computational modelling could accelerate the selection of appropriate ion exchange desalination strategies. Hence, we applied AqMB water process engineering software to predict which combination of weak acid cation (WAC), strong acid cation (SAC), weak base anion (WBA) and strong base anion (SBA) resins were most appropriate. Both SAC/WBA and SAC/SBA resin combinations were unable to meet water beneficial reuse standards for conductivity ( $< 950 \mu\text{S}/\text{cm}$ ) due to the presence of bicarbonate species (4973 and 1918  $\mu\text{S}/\text{cm}$ , respectively). Thus, a degasser unit was necessary to remove the large concentrations (*ca.* 1328 mg/L) of dissolved carbon dioxide formed due to decomposition of bicarbonate/carbonate species under acidic conditions in the cation resin stages. pH adjustment of effluent from the preferred SBA resin with acid not only did not meet solution conductivity guidelines but also raised the concentration of chloride or sulphate ions to levels which may be detrimental for crop growth. Addition of a WAC resin allowed production of high quality water (either SAC/SBA/WAC or WAC/SAC/SBA combinations). To comply with sodium adsorption ratio requirements for irrigating soil it was suggested to apply micronized gypsum to the treated water. Economic evaluation suggested the treated water cost was A\$1003 (WAC/SAC/SBA) to A\$1276 (SAC/SBA/WAC) per ML treated which was comparable to estimated costs for a reverse osmosis desalination system.

Keywords: coal bed methane; coal seam gas; desalination; associated water; ion exchange

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## **1. Introduction**

Coal seam gas (CSG) is an unconventional resource which has been exploited in recent years as a substitute for coal and oil [1]. Gas extraction involves decreasing the water pressure which holds the methane in place in the coal cleats [2]. Through this process, significant volumes of associated water are produced [3]. This associated water could be a valuable resource; however, the water composition typically comprises of various salt constituents that make it problematic for beneficial reuse purposes such as irrigation, stock watering, dust suppression, or supplementation of drinking water supplies [4]. Mallants *et al.* [5] demonstrated that irrigation with untreated CSG associated water caused stagnation and a decrease in soil hydraulic conductivity. Similarly, Vance *et al.* [6] recorded detrimental behaviour in plants and soils when saline water was used for irrigation purposes. Consequently, there is a need to implement various water treatment strategies to purify the associated water to comply with regulations and to mitigate environmental risk.

A range of processes have been suggested to be amenable to desalinate CSG associated water which majorly comprises of dissolved sodium chloride and sodium bicarbonate species along with lesser amounts of calcium, magnesium, strontium, barium, boron, potassium and silicate [7]. Ion exchange has been reported to be applicable to the treatment of CSG associated water which is dominated by the presence of sodium bicarbonate [8]. In this instance, a cation resin in the acid form is employed to not only remove cations such as sodium but also to decrease the concentration of bicarbonate ions due to decomposition under the acidic conditions. However, in regions such as Queensland where the CSG associated water comprises of significant concentrations of sodium chloride, compliance with beneficial reuse targets typically requires the implementation of membrane technologies such as reverse osmosis [9] or a combined cation/anion resin demineralization system [10].

A wide range of unit operations are normally required to pre-treat the CSG associated water prior to the central desalination stage [4, 11]. For example, coagulation of CSG associated water has been utilised, albeit performance was inhibited when real samples were compared to simulated solutions [12, 13]. In contrast, electrocoagulation using aluminium electrodes was demonstrated to very effective at removing not only alkaline earth species but also silicates from CSG associated water samples collected from an operating site [14, 15].

Softening of the CSG associated water has also been recommended by Lipnizki *et al.* [11] to protect downstream reverse osmosis membranes from scaling phenomena caused by the presence of alkaline earth ions. Chun *et al.* [16] intimated that forward osmosis could also be employed to protect reverse osmosis membranes from foulants such as calcium, magnesium, dissolved organic carbon and silicates. Whereas, Nghiem *et al.* [17] employed ultrafiltration prior to a reverse osmosis system to inhibit reduction in water recovery due to fouling of the membrane surface.

Due to the inherent complexity of CSG associated water, which can substantially vary in terms of parameters such as salinity, hardness, turbidity, pH, and alkalinity; several treatment plant configurations have been suggested to meet beneficial reuse guidelines. Zhi *et al.* [15] treated CSG associated at pilot scale, which was sourced from Shanxi province in China. The suggested treatment train was comprised of series of manganese greensand, sand, and bag filters followed by the use of ultrafiltration, and anti-scalant addition prior to the central reverse osmosis stage. The presence of the filters was required to primarily reduce the turbidity of the CSG associated water, which was 409 NTU in the as received sample. The final total dissolved solids (TDS) concentration of the treated water was 105 mg/L, which was a substantial reduction when compared to the inlet value of 5466 mg/L. Alternately, Le [18] described a CSG water treatment process which incorporated disc filtration, microfiltration, biocide dosing, two-stage reverse osmosis (RO) and calcium addition to adjust sodium adsorption ratio (SAR) values. QGC have implemented a CSG associated water treatment unit near Chinchilla in Queensland which has lime softening, ultrafiltration, ion exchange and reverse osmosis operations [19]. Pless *et al.* [10] instead designed a dual cation and anion ion exchange (IX) process to remediate CSG associated water.

As can be seen from the previous examination of literature regarding CSG associated water treatment, a pertinent issue is the selection of the most appropriate desalination technology. Due to relatively high energy, operational and maintenance costs associated with reverse osmosis systems, there is interest in exploring where options such as ion exchange may be best employed [20, 21]. Plumlee *et al.* [22] described the applicability of a screening tool they developed for remediation of CSG associated water for USA basins such as the Powder River and San Juan. However, a detailed engineering approach to not only select appropriate

technologies but also to determine process parameters was not provided. Computational design methods would thus appear useful in this context as they are known to accelerate design of water treatment strategies [23]. Vedelago and Millar [23] recently published a study wherein an engineering model was developed using AqMB software to accelerate the selection of appropriate technologies to facilitate beneficial reuse of CSG associated water. Specifically, pH adjustment/chemical amendment and ion exchange using cationic resins were evaluated as treatment options for a range of CSG associated water compositions which were all dominated by the presence of bicarbonate species. A key finding was that both pH adjustment and cation resin remediation of CSG associated water was limited to relatively low total dissolved solids (TDS) content in the original water sample (*ca.* 1000 mg/L). Attempts to treat CSG associated water with higher TDS values resulted in product water which was not compliant with guidelines for successful crop irrigation.

Therefore, the aim of this study was to apply computational methods to develop an optimal ion exchange based water treatment process for a CSG associated water composition which not only had a TDS value in excess of 1000 mg/L but also comprised of a significant concentration of chloride ions. The hypothesis was that use of computational design may facilitate tailoring of ion exchange processes to a broader range of CSG associated water compositions. The research questions which were addressed included: (1) what type of resins are recommended for CSG associated water treatment? (2) what is the impact of CSG associated water composition upon the choice of resins? (3) which ion exchange process configurations are recommended for which water types? (4) what is the techno-economic evaluation of prospective ion exchange options? The approach involved the use of AqMB process simulation software to interrogate various ion exchange process designs, and comparison with previous literature to verify software predictions.

## **2. Materials and Methods**

### **2.1 Coal Seam Gas Associated Water**

A simulated coal seam gas associated water solution was made based upon a typical sample collected from the Surat Basin in Queensland [Table 1].

Table 1: Composition and physical properties of simulated coal seam gas associated water sample

	<b>Original Value</b>	<b>Treatment Target [24]</b>	<b>Units</b>
Flow Rate	10		kL/hour
Total Dissolved Solids	5054		mg/L
Suspended Solids	0		mg/L
Turbidity	0		NTU
Solution pH	8.27	6 to 8.5	
Solution conductivity	6814	< 950	µS/cm
Total Alkalinity	1764		mg/L CaCO <sub>3</sub>
Sodium Adsorption Ratio	70.57	< 6 to 12	
Temperature	20		°C
Sodium	1548		mg/L
Potassium	80.02		mg/L
Calcium	20		mg/L
Sulphate	54	< 400	mg/L
Magnesium	10		mg/L
Barium	0.01		mg/L
Strontium	0.07		mg/L
Chloride	1221		mg/L
Fluoride	7.5	<2	mg/L
Bicarbonate	2049		mg/L
Carbonate	49.95		mg/L
Dissolved carbon dioxide	13.76		mg/L
Dissolved oxygen	9.38		mg/L

The aim of this study was to treat CSG associated water to satisfy quality guidelines for crop irrigation in the state of Queensland, Australia [24]. We note that there is no specific requirement for sulphate levels in the Queensland Government guidelines [24]; however, it

is recommended that sulphate levels do not exceed 400 mg/L to avoid possible inhibition of crop yields and growth [25]. The precise water quality required for plants varies significantly depending upon variety, and their tolerance to growing conditions [26, 27]. However, for this study we will focus on the general guidelines provided in Table 1.

## **2.2 Process Simulation**

Aqueous Mass Balance (AqMB) is a process simulation and concept design software created to streamline process design activities for physico-chemical water treatment applications [28]. AqMB utilises widely accepted theories and models for each individual unit operation to create a model for the overall plant. Model outputs included stream tables of physical properties, precipitated solids, saturation indices, operating costs, concentrations of species in solution, and heat and mass balances.

## **2.3 CSG Water Treatment Unit Operations**

### **2.3.1 Settling Pond**

A settling pond is commonly present to store CSG water from different wells prior to entering the water treatment plant [4]. The settling pond was assumed to have the following physical characteristics: 2.4 ML volume; water temperature 25 °C; zero evaporation rate; average residence time of 240 hours providing sufficient residence time to allow settling of suspended solids and organics increase rate of 10 mg/L per annum.

### **2.3.2 Ultrafiltration**

An ultrafiltration unit was implemented to filter suspended solids in preparation for the ion exchange. Total suspended solids (TSS) must be removed prior to any water demineralisation process in order to prevent clogging and fouling of membranes and resins [29]. A Suez ZW1500-550 pressurized ultrafiltration module was employed. The properties of this module were as follows: 0.02 micron nominal pore diameter; PVDF hollow fibre membrane; outside-in flow path; 51 m<sup>2</sup> of membrane; design flux 60.8 L/m<sup>2</sup>/h; with 3 modules in one train. This system was assumed to operate at a 93 % recovery rate.



### **2.3.3 Ion Exchange Columns & Resins**

Three resin types were evaluated; (1) DOW Marathon C strong acid cation (SAC) resin in the “H<sup>+</sup>” form with 1.2 meq/L cation capacity; (2) DOW MAC-3 weak acid cation (WAC) resin in the “H<sup>+</sup>” form with 1.8 eq/L cation capacity; (3) DOW Marathon A strong base anion (SBA) resin in the ‘OH<sup>-</sup>’ form. Regeneration was conducted using a reverse-flow configuration using 5 % hydrochloric acid for the cation resins and 4 % sodium hydroxide for the anion resins. The regeneration stoichiometric ratio was assumed to be 2 in each instance. The regeneration stoichiometric ratio for an ion exchange resin is defined as shown in Equation 1:

$$\text{Equation 1: } \textit{Regeneration Stoichiometric Ratio} = \frac{\text{Amount regenerant chemical added (eq/L)}}{\text{Resin operating capacity obtained (eq/L)}}$$

The CSG associated water was passed through the columns at a service velocity of 30 m/h.

### **2.3.4 Degasification**

Carbon dioxide degasification was performed by application of a forced draft degasser, which comprised of water being distributed over packing material in a tower, while air was flowed counter-currently through the bed [30]. In this case air at 30 °C and 101.3 kPa pressure was passed through the liquid at a ratio of 5 kg gas/kg liquid.

### **2.3.5 pH Adjustment & Chemical Amendment**

Downstream of the ion exchange process, the water was pumped to a chemical dosing unit at a rate of 100 m<sup>3</sup>/h. To achieve a pH of 7 which was suitable for water discharge for the treated associated, either slaked lime (95 wt %) or sulphuric acid (98 wt %) was used to increase or decrease the pH as required. Use of lime had the added benefit of changing the Sodium Adsorption Ratio (SAR) of the treated water to meet compliance standards. SAR is a ratio of the concentration of sodium ions to the concentration of calcium plus magnesium ions in solution [Equation 2].

$$\text{Equation 2: } \textit{SAR} = \frac{\textit{Na}}{\sqrt{\textit{Mg} + \textit{Ca}}}$$

Where the concentrations of sodium, calcium and magnesium ions are provided in meq/L. Irrigation of soils with water of excessive SAR values can result in soil structural problems and reduced water permeability [31] and cause negative impacts from irrigation [32]. The acceptable SAR level for irrigation varies depending on the crop and type of soil, with most crops having an acceptable level of under 20 [33]; albeit, Queensland guidelines are < 6 to 12 [24]. In the case that the treated water required further chemical amendment to reduce the SAR value, micronized gypsum (calcium sulphate) was dosed to the water [23].

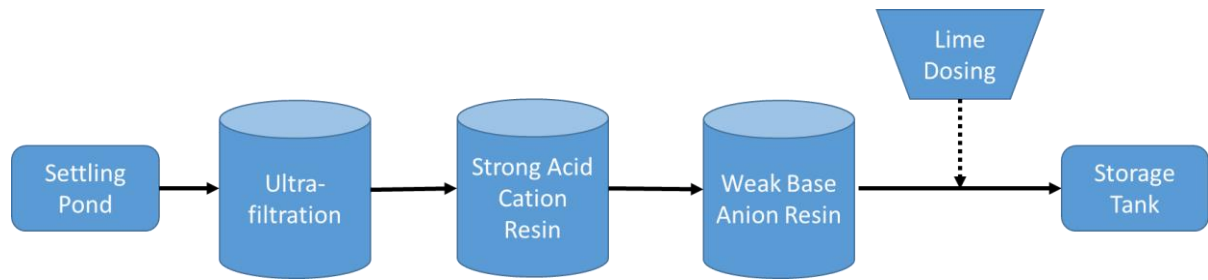
## **2.6 Process Designs**

The fundamental design of the ion exchange water treatment systems involved a pre-treatment stage, ion exchange section, and then a water conditioning stage for pH and SAR adjustment. Four process configurations were selected based upon ion exchange literature [34] and modelled with the AqMB simulation software package [Figure 1].

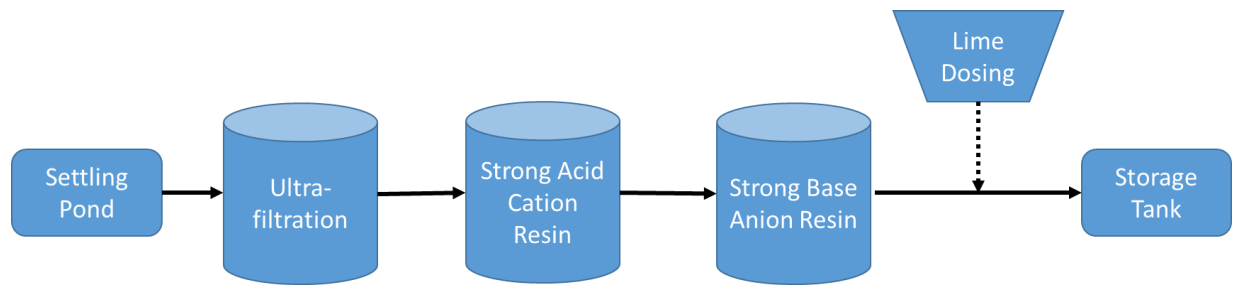
## **2.7 Techno-Economic Evaluation**

The cost of all DOW ion exchange resins was estimated to be A\$5/L and a life span of 3 years was assumed [35]. Electrical consumption for ion exchange considered operation of feed pump, regeneration/displacement pump and backwash pump for each ion exchange stage. For the ultrafiltration pre-treatment power consumption was calculated for feed pump, backwash pump and air scour blower. The degasser unit incorporated a feed pump and air blower, whereas only a feed pump was required to transfer treated water to a storage tank. The cost of sulphuric acid (98 %) was set to A\$300 per tonne and for hydrochloric acid (32 %) to A\$300 per tonne. Sodium hydroxide was supplied as a 32 % solution at a cost of A\$537.60 per tonne. Regeneration occurred on a 48 h basis and the plant had 97 % availability per annum (*ca.* 354 days).

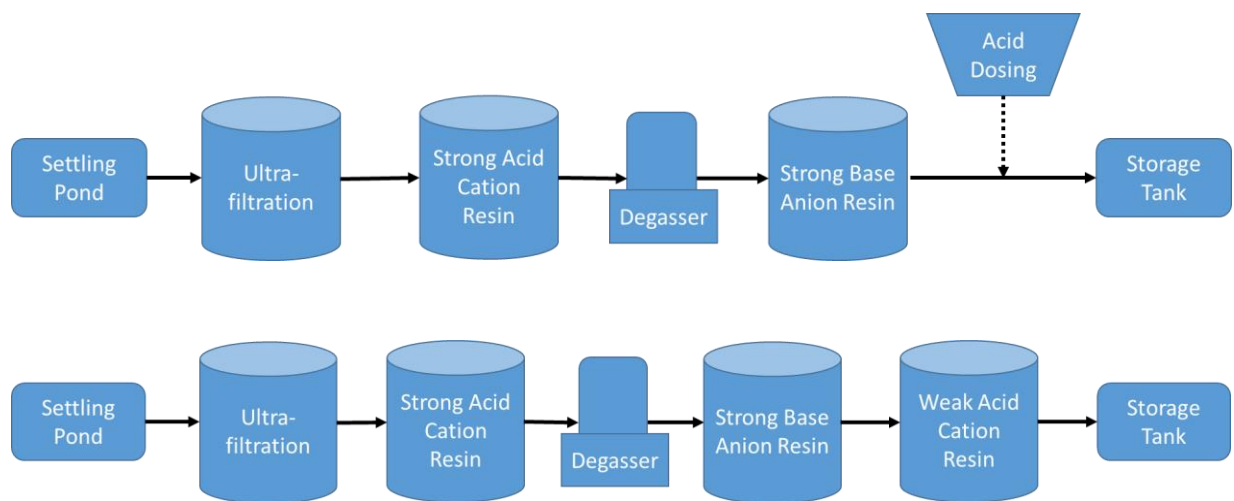
Scenario 1:



Scenario 2:



Scenario 3:



Scenario 4:

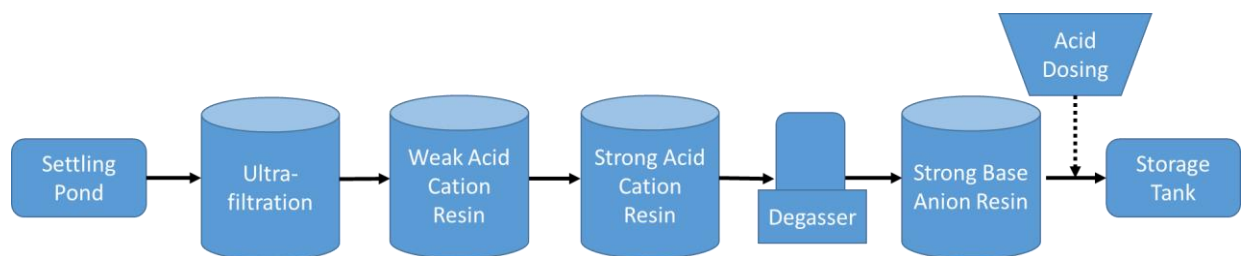


Figure 1: Ion exchange process scenarios simulated by AqMB software

### **3. Results and Discussion**

#### **3.1 Pre-Treatment; Settling Pond and Ultrafiltration Unit Operations**

A common pre-treatment system was implemented to maintain a base-level of water filtration across all evaluated ion exchange process configuration options. Pre-treatment included a settling pond and ultrafiltration process, and simulation results are shown in Table 2.

Table 2. Predicted performance of a settling pond and ultrafiltration process for pre-treatment of CSG associated water

<b>Species</b>	<b>Feed</b>	<b>Settling Pond</b>	<b>Ultrafiltration</b>	<b>Units</b>
Sodium	1548	1548	1548	mg/L
Potassium	80.0	80.0	80.0	mg/L
Calcium	20.0	20.0	7.3	mg/L
Magnesium	10.0	10.0	10.0	mg/L
Barium	0.01	0.01	0.01	mg/L
Strontium	0.07	0.07	0.07	mg/L
Chloride	1221	1221	1221	mg/L
Fluoride	7.5	7.5	7.5	mg/L
Sulphate	54.0	54.0	54.0	mg/L
Bicarbonate	2049	1571	1571	mg/L
Carbonate	49.9	284.6	265.8	mg/L
Dissolved carbon dioxide	13.76	1.39	1.45	mg/L
Dissolved oxygen	9.38	9.38	9.38	mg/L
Solution pH	8.27	9.14	9.13	
Solution conductivity	6061	6054	6034	μS/cm
Total Dissolved Solids (TDS)	5054	4767	4767	mg/L
Total Suspended Solids (TSS)	0	44.4	0	mg/L
Alkalinity	1764	1764	1732	mg/L CaCO <sub>3</sub>
Flow Rate	10.00	10.00	9.30	kL/h
SAR	70.6	70.6	87.4	

Changes noted when the CSG associated water was stored in the pond included an increase in solution pH from 8.27 to 9.14, a reduction in bicarbonate ions from 2049 to 1571 mg/L, concomitant increase in carbonate species (49.9 to 284.6 mg/L), formation of some

suspended solids and a reduction in dissolved carbon dioxide from 13.7 to 1.39 mg/L. AQMB also suggested that the TDS value would slightly decrease and that the level of TSS would change to 44.4 mg/L. It was also predicted that some calcite ( $\text{CaCO}_3$ ) was precipitated due to the changes in solution conditions in the settling pond (3.17 mol/h). Hence, observation of suspended solid formation in the settling pond could be ascribed to the presence of calcium carbonate solids due to the increased alkaline pH value of the CSG associated water. Ranalli and Yager [36] noted that displacement of dissolved carbon dioxide from groundwater exposed to open atmosphere. This process raised the solution pH and consequently the increased carbonate fraction formed as a result of adjustment of bicarbonate/carbonate equilibria was removed by calcite precipitation [37].

Passage of the CSG associated water from the pond through the UF module did not change the water quality markedly as there was no turbidity or suspended solids in the original water sample. The suspended solids that did arise due to the formation of calcium carbonate in the settling pond were removed in the UF system, and accordingly the levels of calcium and carbonate reduced. In harmony, the loss of a portion of the calcium ions present in the CSG water induced a higher SAR value for the water sample. The flow rate also diminished by 7 % to reflect the loss due to backwashing of the membrane system. At this point the pre-treated CSG associated water was characterised by the following corrosion and scaling indices: calcium carbonate precipitation potential = 16.89; Langelier Saturation Index = 1.662; Ryznar Stability Index = 5.803 and Stiff-Davis Index = 1.965.

The Langelier Saturation Index (LSI), Ryznar Stability Index (LSI) and Stiff-David Index (SDI) can be calculated from Equations 3 to 5 [38].

Equation 3:                    Langelier Saturation Index =  $\text{pH} - \text{pH}_s$

Equation 4:                    Ryznar Stability Index =  $2 \text{pH}_s - \text{pH}$

Equation 5:                    Stiff – Davis Index =  $\text{pH} - \text{pH}_s$

Where  $\text{pH}_s$  for the Langelier Saturation Index and Ryznar Stability Index is defined as the calcium carbonate saturation point in solution [Equation 6].

Equation 6: 
$$pH_s = pK_2 - pK_{sp} + pTA + p[Ca^{2+}] + 5pf_m$$

Where:  $K_2$  = second dissociation constant of carbonic acid; TA = total alkalinity; concentration of calcium ions =  $[Ca^{2+}]$ ;  $K_{sp}$  = calcium carbonate solubility product; and  $f_m$  = the activity coefficient of monovalent ions.

For the Stiff-David Index, pHs is defined as in Equation 7:

Equation 7: 
$$pH_s = pCa^{2+} + pAlkalinity + pK$$

Where, pAlkalinity = the negative logarithm of solution alkalinity and pK relates to solution ionic strength and temperature [39]. According to the data provided by Suo *et al.* [38] a RSI value of 5.803 indicates that light to moderate scaling can occur from this solution. Likewise, an LSI value of 1.662 is above “zero” and thus the potential for scale formation is deemed possible [38]. Indeed, Al-Ghamdi [40] viewed a LSI value of 1.6 for a reverse osmosis concentrate as being indicative of high tendency for scale formation. Similarly, the SDI value of 1.965 was positive which suggested that calcium carbonate scaling will occur [39]. Consequently, it may be necessary to add an anti-scalant to the pre-treatment process; however, the fact that the solution pH will become strongly acidic upon passage through the cation resin stages was expected to mitigate any scaling potential the solution had.

### **3.2 Scenario 1: Ion Exchange; Strong Acid Cation Resin & Weak Base Anion Resin**

The first scenario was an ion exchange process, wherein, after the pre-treatment process, the CSG associated water passed through a  $H^+$ -SAC resin bed and then a  $OH^-$ -WBA resin bed [Table 3]. The simulation results show the strong acid cation resin substantially reduced the concentration of sodium (83 %), potassium (89 %), calcium (99 %), magnesium (98 %), barium (100 %), and strontium (100 %). Generically, these processes can be represented as shown in Equations 8 & 9.

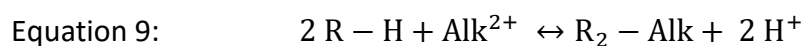
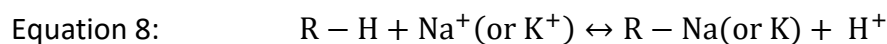


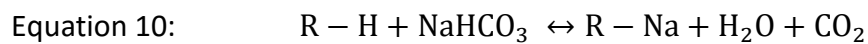
Table 3: Predicted performance of a strong acid cation and weak base anion resin process for desalination of CSG associated water

Species	Exit of UF	Exit of SAC resin	Exit of WBA Resin	Final pH Adjustment with Lime	Units
Sodium	1548	266.5	266.5	266.5	mg/L
Potassium	80.0	8.59	8.59	8.59	mg/L
Calcium	7.3	0.10	0.10	1080	mg/L
Magnesium	10.0	0.18	0.18	0.18	mg/L
Barium	0.01	0.00	0.00	0.00	mg/L
Strontium	0.07	0.00	0.00	0.00	mg/L
Chloride	1221	1220	1216	1216	mg/L
Fluoride	7.5	7.50	7.50	7.50	mg/L
Sulphate	54.0	54.0	24.8	24.8	mg/L
Bicarbonate	1571	0.04	0.04	1572	mg/L
Carbonate	265.8	0.00	0.00	7.78	mg/L
Dissolved carbon dioxide	1.45	1328	1328	188.7	mg/L
Dissolved oxygen	9.38	9.37	9.37	9.38	mg/L
Solution pH	9.13	1.62	1.63	7.00	
Solution conductivity	6034	9192	8985	4973	$\mu\text{S/cm}$
Total Dissolved Solids (TDS)	4767	2914	2880	4233	mg/L
Alkalinity	1732	0.00	0.00	1303	mg/L $\text{CaCO}_3$
Flow Rate	9.30	9.30	9.30	9.30	kL/h
Resin Volume		25560	337.2		L
Regeneration Chemical Used		3728	45.85		kg
pH adjustment (slaked lime)				19.54	kg/h
SAR	87.4			2.23	

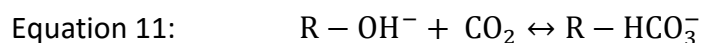
Where  $\text{Alk}^{2+}$  = alkaline earth ions in solution. The percentage removal of alkali and alkaline earth ions by the SAC resin corresponded with the selectivity series presented by Strelow [41] ( $\text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$ ). Millar and co-workers [20, 42-45] examined both sodium and potassium ion uptake on  $\text{H}^+$ -SAC resin and confirmed the greater affinity of SAC resin for potassium ions relative to sodium ions. Interestingly, the kinetic behaviour and loading capacity of the resins were shown to vary according to the solution composition and test conditions. Hayani *et al.* [46] reported that the absolute amount of alkaline earth ions

removed from solution by a SAC resin was reduced if the flow rate was increased and/or the sodium content of the water sample was raised and this is an aspect which should be considered in future studies by investigators. Lazar *et al.* [47] compared the calcium & magnesium removal performance of two different SAC resins and did not find a significant difference between these materials. Thus even though DOW Marathon C was used in the simulation studies it was expected that other SAC resins would provide similar results (AqMB simulation confirmed this deduction, results not shown for sake of brevity).

Hu *et al.* [48] applied a SAC and WBA resin combination to desalinate a simulated seawater solution which only contained sodium chloride species. It was recorded that the solution pH rapidly decreased to *ca.* 3.5 as protons were released from the resin surface exchange sites according to equations 8 & 9. The higher pH in the study of Hu *et al.* [48] compared to the value of 1.62 in Table 4 was due to the fact a mixed cation/anion bed was used in their study which diminished the impact upon solution pH as protons reacted with OH<sup>-</sup> ions to produce water. Bicarbonate and carbonate species were also eliminated from the treated water sample due to the following process [Equation 5].

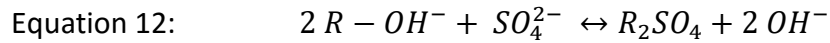


In harmony with the decomposition of the bicarbonate and carbonate species under acidic conditions was the accumulation of dissolved carbon dioxide in the effluent from the SAC column (1328 mg/L). High concentrations of dissolved carbon dioxide are known to inhibit the performance of anion resins due to the formation of bicarbonate groups on the exchange sites [Equation 6] [30].



With regards to the WBA resin, AqMB did not predict significant demineralisation, and the only notable impact this ion exchange incurred was a decrease in sulphate concentration [Equation 12].





As eloquently explained by Sarkar and Sengupta [49] the affinity of sulphate ions relative to chloride ions on basic resins depends on several factors. Of critical importance is the solution normality as when this parameter is relatively low then divalent ions are preferred on the surface sites (as in the case here). In addition, resins with tertiary amine exchange sites (*i.e.* weak base anion resins) have a substantially higher affinity for sulphate ions compared to those with quaternary amine functional groups (*i.e.* strong base anion resins). Hence, the relative ineffectiveness of WBA resin was in agreement with fundamental ion exchange theories.

### **3.3 Scenario 2: Ion Exchange; Strong Acid Cation Resin & Strong Base Anion Resin**

A scenario using a strong base anion (SBA) resin instead of a weak base anion (WBA) resin was modelled to increase the efficiency of chloride removal within the water treatment process. This scenario was simulated using AqMB and the results summarised in Table 4. For ease of comparison with the data for a combined SAC-WBA resin system the treated effluent from the SAC resin described in Table 3 was also shown in Table 4. The main outcome of employing a SBA resin was the reduction in chloride concentration from 1216 (for WBA resin) to 22.9 mg/L. Similarly, the sulphate ions were further removed by the SBA resin to only 0.03 mg/L (*c.f.* 24.8 mg/L for WBA resin). Additionally, fluoride ions were also reduced from 7.50 to 1.29 mg/L which was within the recommended beneficial reuse level [24]. Simultaneously, application of the SBA resin increased the pH of the water from 1.62 to 6.09 in the effluent from the anion resin column. This phenomenon arose due to neutralization of H<sup>+</sup> ions in the CSG associated water feed with hydroxyl ions ejected from the SBA resin during the anion exchange process [Equations 12 - 14].

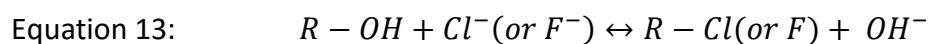


Table 4: Predicted performance of a strong acid cation and strong base anion resin process for desalination of CSG associated water

Species	Exit of SAC resin	Exit of SBA Resin	Final pH Adjustment with slaked lime	Units
Sodium	266.5	266.6	266.6	mg/L
Potassium	8.59	8.60	8.60	mg/L
Calcium	0.10	0.10	285.7	mg/L
Magnesium	0.18	0.18	0.18	mg/L
Barium	0.00	0.00	0.00	mg/L
Strontium	0.00	0.00	0.00	mg/L
Chloride	1220	22.9	22.9	mg/L
Fluoride	7.50	1.29	1.29	mg/L
Sulphate	53.96	0.03	0.03	mg/L
Bicarbonate	0.04	678.5	1541	mg/L
Carbonate	0.00	0.05	3.60	mg/L
Dissolved carbon dioxide	1328	1328	214.5	mg/L
Dissolved oxygen	9.37	9.38	9.38	mg/L
Solution pH	1.62	6.09	7.00	
Solution conductivity	9192	955.2	1918	μS/cm
Total Dissolved Solids (TDS)	2914	1817	2345	mg/L
Alkalinity	0.00	556.6	1270	mg/L CaCO <sub>3</sub>
Flow Rate	9.30	9.30	9.30	kL/h
Resin Volume	25560	26640		L
Regeneration Chemical Used	3728	2131		kg
pH adjustment			5.17	kg/h
SAR	116.5	116.5	4.3	

Alexandratos [50] outlined that SBA resin had a significantly larger affinity for chloride ions relative to fluoride ions. In addition, the concentration of chloride ions was substantially higher than that of fluoride ions. Both these factors highlight the fact that fluoride removal

from CSG associated water was expected to be challenging. The predicted inability of the SBA resin to remove fluoride [Table 4] was therefore in agreement with the prior discussion.

The combined SAC & SBA resin process displayed some negative aspects, namely the solution TDS value was relatively high (1817 mg/L) which made the solution conductivity borderline unacceptable [24]. Moreover, the SAR value was too high at 116.5 compared to irrigation regulations which dictated this parameter should be in the range 6 to 12. The solution pH was also close to the minimum value for beneficial water reuse (pH = 6). Therefore, the addition of calcium ions was required to the effluent from the SBA resin column. One option explored was the addition of slaked lime as this would not only reduce SAR but also increase solution pH [Table 4]. Due to the higher solution pH of the effluent from the SBA resin compared to WBA resin, a diminished amount of chemical dosing was necessary (5.17 kg/h compared to 19.54 kg/h with WBA). As a positive aspect, the SAR value was decreased to 4.3 once pH was raised to 7 and thus compliant with regulations. However, both the solution TDS content and solution conductivity became unacceptably high (2345 mg/L and 1918  $\mu\text{S}/\text{cm}$ , respectively). This behaviour was related to the substantial increase in bicarbonate formation ascribed to reaction of dissolved carbon dioxide with the added lime.

### **3.4 Scenario 3: Ion Exchange; Strong Acid Cation Resin, Strong Base Anion Resin & Degassing Unit**

For scenario 3, a degassing unit was implemented into the same model as Scenario 2, and the results modelled in AqMB [Table 5]. Mechanical de-aeration can be a highly effective at removing a large percentage of the total free  $\text{CO}_2$  dissolved in the water [30]. Application of the degasser unit had the desired effect of substantially reducing the amount of dissolved carbon dioxide present (1328 to 1 mg/L). Consequently, the presence of bicarbonate and carbonate species was virtually eliminated. The lack of bicarbonate/carbonate production resulted in a concomitant decrease in total dissolved solids content to 1589 mg/L. Not only does degassing decrease the level of bicarbonate in the water to acceptable re-use levels, but it also extends the life of the anion bed. Dang *et al.* [30] determined that a high amount of bicarbonate alkalinity present in the water was having a negative effect on anion bed life. Therefore they advocated the removal of free  $\text{CO}_2$  through the addition of a hydrophobic membrane degassing system situated between the cation and anion ion exchange beds [30].

Table 5: Predicted performance of a strong acid cation, CO<sub>2</sub> degasser, and strong base anion resin process for desalination of CSG associated water.

Species	Exit of SAC resin	Exit of CO <sub>2</sub> Degasser	Exit of SBA Resin	pH Adjustment with Sulphuric Acid	pH Adjustment with Hydrochloric Acid	Exit of WAC Resin	Units
Sodium	266.5	266.5	266.8	266.7	266.7	11.2	mg/L
Potassium	8.59	8.60	8.60	8.60	8.60	8.60	mg/L
Calcium	0.10	0.10	0.10	0.10	0.11	0.00	mg/L
Magnesium	0.18	0.18	0.18	0.18	0.18	0.00	mg/L
Barium	0.00	0.00	0.00	0.00	0.00	0.00	mg/L
Strontium	0.00	0.00	0.00	0.00	0.00	0.00	mg/L
Chloride	1220	1221	22.9	22.9	416.7	21.95	mg/L
Fluoride	7.50	7.50	1.29	1.29	1.29	1.29	mg/L
Sulphate	53.96	54.0	0.03	533.6	0.03	0.03	mg/L
Bicarbonate	0.04	0.00	0.01	1.15	1.15	1.17	mg/L
Carbonate	0.00	0.00	1.35	0.00	0.00	0.00	mg/L
Dissolved carbon dioxide	1328	1.00	1.00	0.17	0.18	1.00	mg/L
Dissolved oxygen	9.37	1.30	1.30	1.30	1.30	1.30	mg/L
Solution pH	1.6	1.6	12.1	7.0	7.0	7.0	
Solution conductivity	9192	9192	2390	1182	1405	81.3	µS/cm
Total Dissolved Solids (TDS)	2914	1589	489.6	834.9	695.1	44.52	mg/L
Alkalinity	0.00	0.00	557.2	0.94	0.94	0.96	mg/L CaCO <sub>3</sub>
Flow Rate	9.3	9.3	9.3	9.3	9.3	9.3	kL/h
Resin Volume	25560		26640			27000	L
Regeneration Chemical Used	3728		2131			7482	kg
pH adjustment				1.02	11.8		kg/h
SAR	116.5	116.5	116.5	116.6	116.6		

However, there was a cost to employing the degasser unit as solution pH increased to 12.1 at the exit of the SBA resin column. Therefore, to comply with water reuse regulations, dosing the treated CSG associated water with acid to pH 7 was attempted. When sulphuric acid was employed the sulphate concentration increased in this scenario to 533.6 mg/L. Unfortunately, this sulphate level exceeded the recommended maximum of 400 mg/L for

irrigation purposes [Table 1]. Alternatively, hydrochloric acid was dosed to the effluent from the SBA resin bed. As a consequence, the chloride ion concentration increased to 416.7 mg/L and the solution conductivity was elevated to 1405  $\mu\text{S}/\text{cm}$  (which was in excess of Queensland guidelines of  $< 950 \mu\text{S}/\text{cm}$ ). Acid addition was also ineffective at adjusting the SAR value to meet irrigation standards (SAR 116.6).

Therefore a modified treatment process was evaluated which included an additional weak acid cation resin bed immediately after the SBA column. The rationale for this approach was that  $\text{H}^+$  ions released from the WAC resin would neutralize hydroxyl anions in the effluent from the SBA bed without adding additional anions to the water. Table 5 showed that application of the WAC resin significantly reduced the sodium ion content of the CSG associated water from 266.7 to 11.2 mg/L. Similarly, all trace of alkaline earth ions was eliminated from the treated water. As a result, the TDS in this scenario was reduced significantly to only 44.5 mg/L in the effluent from the WAC unit.

The affinity of WAC resin for alkaline earth ions such as calcium has been investigated by Millar *et al.* [51]. Isotherm profiles were “rectangular” in nature which indicated that the exchange process was almost irreversible; hence, why the removal of alkaline earth ions was shown to be practically complete in Table 5.

The only water quality parameter which was not addressed by incorporation of the WAC resin was the SAR value. Consequently, it was decided to adjust SAR by addition of micronized gypsum [23]. Decreasing the SAR value to 3 required 1 mg/L of calcium ions to be present in the treated CSG associated water. For the flow rate of 9.3 L/h this was equivalent to a dose of 31.6 g gypsum per h.

### **3.5 Scenario 4: Ion Exchange; Weak Acid Cation Resin, Strong Acid Cation Resin, $\text{CO}_2$ Degassing & Strong Base Anion Resin**

A weak acid cation resin can be placed either before a SAC resin bed or after a SBA resin [34]. Therefore, a weak acid cation (WAC) resin column was introduced upstream of the existing SAC and SBA resin columns to determine if this strategy was beneficial or not as the case may be [Table 6].

Table 6: Predicted performance of a strong acid cation and weak base anion resin process for desalination of CSG associated water

Species	Exit of UF	WAC resin	SAC resin	CO <sub>2</sub> Degasser	SBA Resin	pH Adjustment with Sulphuric Acid	Units
Sodium	1548	422.3	63.1	63.2	63.2	63.2	mg/L
Potassium	80.0	80.0	8.60	8.60	8.60	8.60	mg/L
Calcium	7.3	0.14	0.00	0.00	0.00	0.00	mg/L
Magnesium	10.0	0.43	0.00	0.00	0.00	0.00	mg/L
Barium	0.01	0.00	0.00	0.00	0.00	0.00	mg/L
Strontium	0.07	0.00	0.00	0.00	0.00	0.00	mg/L
Chloride	1221	1220	1220	1221	24.74	24.74	mg/L
Fluoride	7.5	7.50	7.50	7.50	1.28	1.28	mg/L
Sulphate	54.0	53.96	53.96	54.02	0.02	105.1	mg/L
Bicarbonate	1571	0.06	0.03	0.00	0.09	1.14	mg/L
Carbonate	265.8	0.00	0.00	0.00	0.00	0.00	mg/L
Dissolved carbon dioxide	1.45	1328	1328	1.00	1.00	0.18	mg/L
Dissolved oxygen	9.38	9.37	9.37	1.30	1.30	1.30	mg/L
Solution pH	9.13	1.81	1.48	1.48	11.36	7.00	
Solution conductivity	6034	8238	13380	13380	554.8	322.3	µS/cm
Total Dissolved Solids (TDS)	4767	3131	2721	1396	136.1	204.4	mg/L
Alkalinity	1732	0.00	0.00	0.00	110.4	0.93	mg/L CaCO <sub>3</sub>
Flow Rate	9.30	9.30	9.30	9.30	9.30	9.30	kL/h
Resin Volume		16980	7613		26600		L
Regeneration Chemical Used		4235	1110		2128		kg
pH adjustment						1.02	kg/h
SAR	87.4	126.2					

The WAC resin majorly removed all four alkaline earth ions from the CSG water (98, 96, 100, & 100 % for Ca, Mg, Ba & Sr, respectively). In contrast, the removal of sodium ions was comparatively less (73 %) and potassium was not predicted to be removed in any notable amount. This data was consistent with the reported selectivity differences between SAC and WAC resins [50]. In mixtures of alkali and alkaline earth ions, WAC resins exhibit significantly higher affinity for alkaline earth ions compared to SAC resins due to their carboxylic acid

functional groups instead of sulphonic acid moieties. Coca *et al.* [52] also demonstrated the superior behaviour of H<sup>+</sup> - WAC resin compared to a SAC resin in column treatment of beet sugar juice to reduce concentrations of calcium ions.

The performance of the SAC resin was promoted by the WAC resin located immediately prior to this bed. Sodium ion concentration was more effectively reduced (63.1 compared to 266.5 mg/L). However, the solution conductivity was extremely high primarily as a result of the lower effluent pH. As before, the degasser removed the majority of dissolved carbon dioxide and the SBA resin the halide and sulphate ions. Due to the lower pH after the SAC resin column the effluent pH of the SBA resin was also diminished (11.36 compared to 12.1 for the SAC/SBA combination). As a consequence, dosing of the treated CSG associated water with sulphuric was possible since the sulphate concentration remained at only 105.1 mg/L (which was within guidelines for irrigation purposes [Table 1]). The solution conductivity was also well within regulations for beneficial water reuse. The effectiveness of the cation resins to remove alkaline earth ions from solution also meant that the SAR value required adjustment. Consequently, reduction of the SAR value to 3 required 33 mg/L of calcium ions to be dosed into the treated CSG associated water. For the flow rate of 9.3 L/h this necessitated the addition of 1042 g gypsum per h. As such the sulphate concentration would also increase from 105.1 to 184.2 mg/L, a figure still within guidelines for water quality.

Overall, implementation of the WAC-SAC resin combination enhanced the removal of cationic species from the CSG associated water. However, as discussed by Bornak [53] this higher performance was offset by increased system complexity, more piping and instrumentation requirements and greater number of vessels. Albeit, operational advantages are evident due to the fact that WAC resin has an inherently higher cation exchange capacity than SAC resins [11, 54]; plus inclusion of a SAC resin with the WAC resin allows operation at all pH ranges (whereas WAC resin alone prefers alkaline solution pH values [4]). The significant increase in the amount of resin required when used a WAC - SAC system compared to the SAC resin needs to be considered. On the plus side is that weak acid cation (WAC) resins are not highly dissociated and exhibit a higher affinity for hydrogen ions than SAC resins and thus can be regenerated more effectively [34].

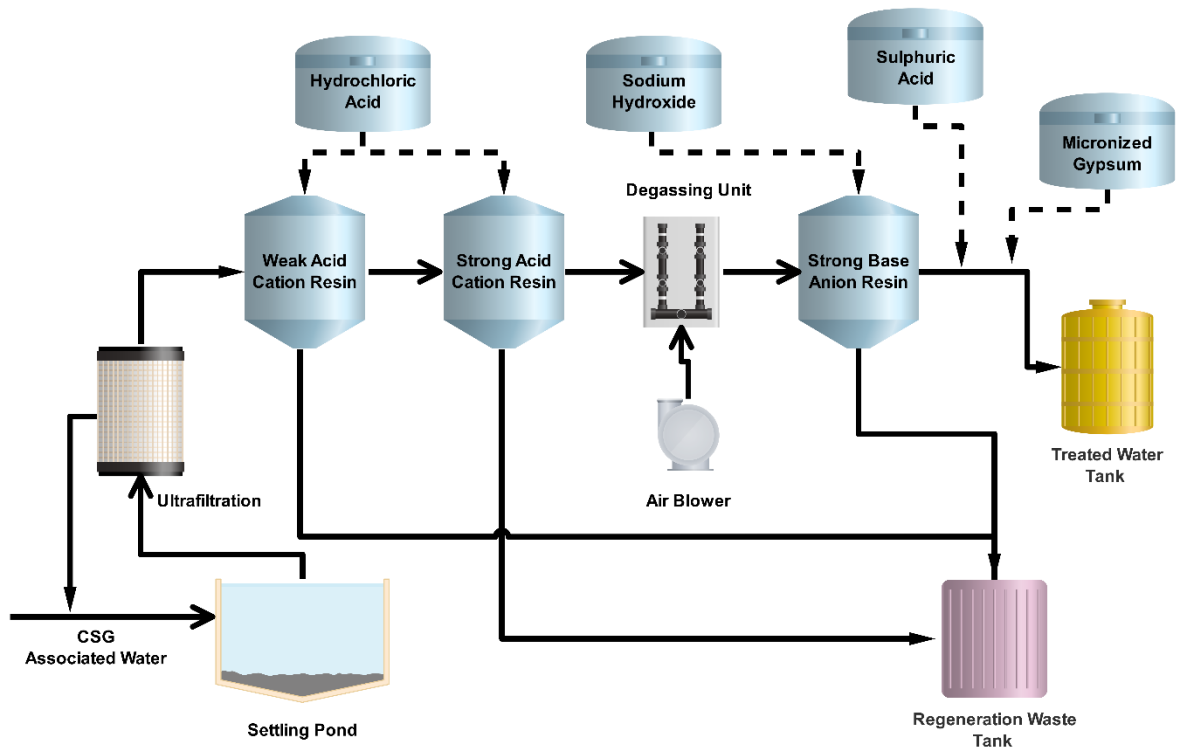
### **3.6 Optimised Process Flow for Ion Exchange Desalination of CSG Associated Water**

Computational analysis has indicated that a water treatment system based upon the implementation of 3 resin types (WAC, SAC & SBA) is potentially an optimal method for desalination of CSG associated water to meet beneficial reuse regulations. Figure 2 illustrates that two process configurations have the most merit; (a) WAC; SAC; SBA resin and (b) SAC; SBA; WAC resin. To decide which process is the best an examination of the techno-economic viability must be made. A major cost in ion exchange is the requirement for regeneration chemicals as the resins become exhausted. For this investigation, the cation resins were regenerated with 5 % hydrochloric acid instead of the less expensive sulphuric acid. It is also noted that if the CSG associated water had a significant concentration of species such as dissolved iron, then a higher concentration of hydrochloric acid may be required [55]. The CSG industry would prefer sulphuric acid as it is readily available in the remote areas where the gas fields are located [23]. However, use of sulphuric acid in the presence of alkaline earth ions can result in formation of insoluble sulphate materials which block resin beds and decrease operational efficiency [56]. Anion resins were regenerated with a sodium hydroxide solution as per accepted practice [57].

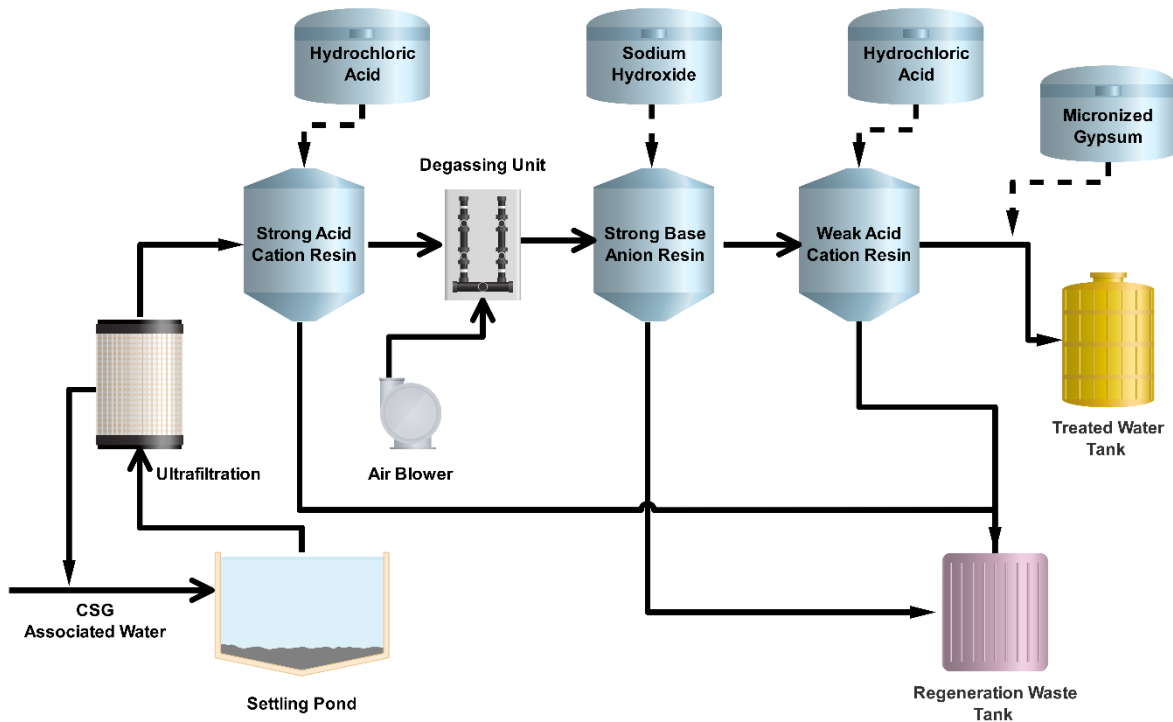
For scenario (a) in Figure 2, the consumption of regeneration chemicals was estimated as 5345 kg of hydrochloric acid @A\$300 per 1000 kg (32 % basis) = A\$1603.50 and 2128 kg of sodium hydroxide @A\$537.60 per 1000 kg (32 % basis) = A\$1144.01 per 48 hour regeneration cycle. The power consumption was estimated at 3.47 kWh/m<sup>3</sup> (A\$346.79 per ML) based upon an electricity price of A\$0.1 per kWh. pH adjustment with 98 % sulphuric acid required 9072 kg per annum which equated to A\$2722 per annum (assuming A\$300 per tonne of 98 % H<sub>2</sub>SO<sub>4</sub>). The annualized cost of resin was A\$22,376 for WAC resin; A\$35,093 for SBA resin; A\$10,032 for SAC resin; and, A\$932 for UF membrane.

For scenario (b) in Figure 2, the consumption of regeneration chemicals was estimated as 11210 kg of hydrochloric acid @A\$300 per 1000 kg (32 % basis) = A\$3363 and 2131 kg of sodium hydroxide @A\$537.60 per 1000 kg (32 % basis) = A\$1145.63 per 48 hour regeneration cycle. The power consumption was estimated at 3.554 kWh/m<sup>3</sup> (A\$213.25 per ML) based upon an electricity price of A\$0.1 per kWh. The annualized cost of resin was A\$35,581 for WAC resin; A\$35,133 for SBA resin; A\$33,683 for SAC resin; and, A\$932 for UF membrane.





(a) WAC; SAC; SBA resin



(b) SAC; SBA; WAC resin

Figure 2: Proposed optimal desalination processes based upon ion exchange treatment of CSG associated water: (a) WAC; SAC; SBA resin and (b) SAC; SBA; WAC resin

Assuming 97 % plant availability, 177 regeneration steps per annum and a total volume treated per annum of 850 ML the initial techno-economic evaluation suggested that the operating cost for a WAC, SAC & SBA resin combination was A\$1002.63 per ML and for the SAC, SBA & WAC combination A\$1276.03 per ML. We note that the regeneration stoichiometric ratio was set to 2 which could be potentially reduced based upon subsequent testing and refinement of the process selected.

To put the estimated costs for ion exchange treatment in context, reverse osmosis desalination systems are said to cost in the range of US\$660 to US\$1320/ML (A\$898 to 1796 at an exchange rate of A\$1 = US\$0.735) [58]. Hence, ion exchange appears to be attractive as an option to treat CSG associated water.

#### **4. Conclusions**

In general, the robustness of the simulation process was demonstrated as predicted data agreed with previous literature regarding demineralization of saline solutions. Application of computational methods accelerated the assessment of water treatment strategies and highlighted the challenge in meeting water quality guidelines when remediating CSG associated water for beneficial reuse.

Simple combinations of SAC and WBA or SBA resins were not satisfactory due to the inhibiting presence of bicarbonate/carbonate species inherent to CSG associated water. Hence a degassing stage was required to reduce the concentration of dissolved carbon dioxide.

Satisfying discharge regulations relating to pH, conductivity, and SAR required a creative approach to water treatment plant design. Acid or alkali dosing could aid the attainment of discharge pH conditions but these chemicals not only detrimentally impacted solution conductivity but also did not reduce SAR to acceptable values.

Introduction of a WAC resin was considered; one configuration involved the WAC resin to be situated before the SAC resin and the second involved a WAC resin after the SBA resin. In both cases the quality of the treated CSG associated water was suitable for irrigation purposes (once micronized gypsum was added to adjust SAR).

With regards to the aim of this study which was to develop an optimised water treatment process design for CSG associated water, a WAC, SAC, degasser, SBA & pH adjustment system was concluded to be most prospective based upon economic consideration. Albeit, the SAC, degasser, SBA & WAC configuration produced water of higher quality but at a slightly higher cost per ML of water treated. Notably, this configuration has not been employed in the CSG industry to the best of our knowledge.

Future studies should focus on expanding the simulations to a variety of coal seam gas associated water compositions to determine whether one process design is suitable or that customization is required. It is also recommended that bench and pilot scale testing of resin performance is conducted using both simulated and actual CSG associated water samples as more detailed process engineering information is required to facilitate creation of a more comprehensive economic model.

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