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Process evaluation of treatment options for high alkalinity coal seam gas associated water



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ABSTRACT

Both chemical amendment and ion exchange with cation resins were investigated in regards to remediation of coal seam gas (CSG) associated water characterized by relatively high concentrations of bicarbonate species. The aim of this study was to develop process engineering models using AqMB software which would accelerate selection of appropriate technologies to facilitate beneficial water reuse. Chemical amendment of CSG associated water was best conducted using sulphuric acid addition instead of hydrochloric acid due to cost considerations. However, the sulphate or chloride added to the CSG associated water restricted amendment processes to water samples comprising of < 1000 mg/L bicarbonate ions. Use of weak acid cation (WAC) and strong acid cation (SAC) resin effectively remediated low salinity water samples (conductivity < 650 µS/cm). For CSG associated water of higher salinity, SAC resin produced better water quality; albeit, less volume of WAC resin was required and this material is inherently easier to regenerate. Ion exchange was preferred to chemical amendment as acid addition detrimentally increased the amount of anions present in solution (sulphate or chloride) and thus limited the irrigation potential for the treated water. Regardless of the remediation strategy, dosing with a source of calcium was required to manipulate sodium adsorption ratio to meet regulatory guidelines. Future studies should consider cation/anion resin systems and also membrane based methods for CSG associated water treatment.

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1. Introduction

Coal seam gas (CSG) or coal bed methane (CBM) is being developed as a solution to meet increasing global energy demands, while enabling the transition from oil and coal to lower greenhouse gas emitting resources [1,2]. Coal seam gas is found in the pores within coal, and is extracted by reducing the pressure; causing the gas to be brought to the surface, accompanied by associated water [3]. CSG associated water is typically brackish in character, and the volume of water produced can be significant with for example 44 GL per annum generated in the Queensland gas industry alone [4]. The composition of CSG associated water varies depending on the location of the well [5], with typical samples majorly comprised of sodium, bicarbonate and chloride ions in addition to lesser concentrations of potassium, magnesium, iron, aluminium, barium, silica, strontium and calcium [6-9]. In Queensland and China, the concentration of total dissolved solids (TDS) mainly varies from 1500-10,000 mg/L [6,10,11], whereas, in the USA the salinity of CSG associated water can range from a few hundred mg/L to 42,700 mg/L [12,13].

Due to these water characteristics, the associated water is often not

suitable for direct application for beneficial use options such as irrigation, livestock watering and dust suppression [14]. Increased salinity levels can accumulate in the soil thus inhibiting water and nutrient uptake; which may lead to decreased plant growth and yields [15]. To be suitable for irrigation, water should have a conductivity content of less than $650 \,\mu\text{S/cm}$ for sensitive crops, with tolerant crops able to accommodate levels up to 8100 µS/cm [16]. Crops also exhibit a specific tolerance for each individual mineral present in the irrigation water [16]. Sodic soils occur when greater than 15% of the cation exchange sites are occupied by sodium, and this phenomenon is mainly due to the irrigation of crops with water characterized by a high sodium adsorption ratio (SAR) [16,17]. The SAR value for a particular CSG associated water can be calculated as shown in Eq. (1) [18].

$$SAR = \frac{Na}{\sqrt{0.5(Ca + Mg)}} \tag{1}$$

Irrigation of soils with water of excessive SAR values can result in soil structural problems and reduced water permeability [19]. In the case of sodium sensitive crops, negative impacts from irrigation with

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high SAR water can occur even before the soil is classified as sodic [17]. 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 [16].

Several different methods are currently being used to treat CSG associated water including either chemical amendment or desalination methods such as reverse osmosis and ion exchange [2,20]. Selection of which technology to use depends upon the water composition to be treated. The simplest approach is to employ pH adjustment which involves dosing of the CSG associated water with an acid that reacts with bicarbonate ions, producing carbon dioxide and water [21]. The object of the pH adjustment is to lessen the probability of calcium carbonate precipitation in the soil [22]. This outlined method can potentially be cost effective at reducing the bicarbonate concentration of the associated water, but on its own may not reduce the TDS of the water [23]. As this method does not inherently reduce SAR levels, chemical amendment with materials such as calcite (CaCO₃) or gypsum (CaSO₄) is used to adjust the treated water composition to prevent the sodification of soils. Species such as gypsum add calcium to the soil which displaces and prevents sodium occupying soil exchange sites [24].

Remediation of CSG associated water can also be achieved by use of ion exchange (IX) which has been reported to be effective for the demineralisation of CSG associated water [25–28]. To decompose bicarbonate ions in solution, either a strong acid cation or weak acid cation is used [7,29]. Dennis [25] described the use of cation resins as part of Higgins Loop continuous ion exchange technology to treat CSG associated water from the Powder River Basin in USA. It was claimed that sodium ion concentrations could be reduced to < 10 mg/L and that SAR values could be modified by addition of calcium carbonate post the IX process. Regeneration of the resins was achieved by application of either dilute hydrochloric or sulphuric acid solutions.

If CSG associated water comprises of relatively high TDS values and/or significant concentrations of chloride ions then membrane based desalination technologies such as reverse osmosis (RO) may be required [30]. Although reverse osmosis is a well proven desalination method it requires extensive pre-treatment of feed water to prevent fouling/scaling of equipment and membranes thus resulting in decreased water recovery rates [31–35]. Moreover, due to the use of high pressure to promote the membrane desalination process the cost of electricity consumption can be significant [36].

Despite the demonstrated applicability of the aforementioned methods for CSG associated water treatment, the case for selecting one technology over another has not been clarified yet. Plumlee et al. [37] developed a software screening tool which suggested technology options to remediate CSG associated water of various compositions and with several beneficial reuse options offered. After screening technology options, process engineering information is required to implement the treatment strategy. In particular, information to allow simulation and optimization of technologies would be helpful for the demineralization of CSG associated water characterized by not only high bicarbonate concentrations but also relatively low TDS values (< 3500 mg/L). These types of CSG associated water may be more amenable to application of simpler technical solutions such as pH adjustment, chemical amendment or ion exchange; rather than the current situation in Queensland wherein reverse osmosis is universally applied [38]

Therefore, the aim of this study was to develop process models for the treatment of a range of high alkalinity CSG associated water samples and to confirm predictions using appropriate experimental methods. The approach taken was novel in that a process engineering evaluation of CSG associated water treatment options has not been published as yet. The hypothesis was that the remediation of high alkalinity CSG water can be optimized by understanding in greater detail the factors responsible for process performance. The critical aspect to support this hypothesis was the development of a software tool which could rapidly identify benefits and limitations of suggested CSG
 Table 1

 Water characteristics of high bicarbonate CSG associated water samples.

	CSG 1 [39]	CSG 2 [22]	CSG 3 [40]	Units
TDS	776	1294	3463	mg/L
pН	7.8	8.3	8.2	
SAR	31.62	24.19	33.58	
Barium	0.00	0.00	1.40	mg/L
Bicarbonate	520	853	2416	mg/L
Boron	2.50	0.00	0.20	mg/L
Calcium	6.00	8.90	28.00	mg/L
Carbon Dioxide	36.80	0.00	18.90	mg/L
Carbonate	1.72	61.50	0.00	mg/L
Chloride	143.70	12.80	28.40	mg/L
Fluoride	0.79	0.94	1.00	mg/L
Iron	0.00	0.00	0.00	mg/L
Magnesium	0.90	3.90	14.60	mg/L
Potassium	3.00	3.10	35.20	mg/L
Silica	10.70	0.00	15.00	mg/L
Sodium	314.1	344.0	880.0	mg/L
Strontium	0.00	0.00	0.90	mg/L
Sulphate	0.70	0.00	1.00	mg/L

associated water treatment plants. Specific research questions addressed included: (1) which is the most appropriate acid to employ for pH adjustment? (2) what constraints exist regarding the type of CSG associated water which can be pH adjusted and chemically amended? (3) what is the impact of water composition upon cation resin effectiveness? (4) should a weak or strong acid cation resin be employed? (5) which strategy is more appropriate for coal seam gas associated water treatment, pH adjustment & chemical amendment or cation exchange? To answer the aforementioned questions AqMB water process engineering software was applied to create models of pH adjustment, chemical amendment, and cation exchange processes. Bench trials of ion exchange columns were conducted using simulated CSG associated.

2. Materials and methods

2.1. CSG associated water composition

A range of coal seam gas associated water compositions were selected from published literature [Table 1]. All CSG associated water types were comprised of bicarbonate ions as the most prevalent anion in solution and represented a range of bicarbonate concentrations from 520 to 2416 mg/L.

2.2. CSG associated water treatment target values

To be suitable for irrigation purposes, water must have an appropriate conductivity relating to the sensitivity of the crop involved. Table 2 displays the tolerance of the crop to conductivity and SAR [16].

In addition, the presence of major ions such as bicarbonate, chloride and sodium in irrigation water is regulated [16]. Table 3 shows the general tolerance of plants to major ions in irrigation waters.

Table 2	2
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Recommended irrigation water conductivity by plant suitability.

Salinity rating	Plant suitability	Conductivity (µS/ cm)	Recommended SAR Range
Very low	Sensitive	650	2–8
Low	Moderately Sensitive	650–1300	8–18
Medium	Moderately Tolerant	1300–2900	18–46
High	Tolerant	2900-5200	46–102
Very High	Very Tolerant	5200-8100	
Extreme	Generally too saline	> 8100	

Table 3

Irrigation wate	r standards	for major ions.
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	Tolerance	(mg/L)		
Contaminant	Sensitive	Moderately Sensitive	Moderately tolerant	Tolerant
Bicarbonate	< 76	76–91	91-122	122-152
Chloride	< 175	175-350	350-700	> 700
Sodium	< 115	115-230	230-460	> 460
	Long Term	n Trigger Value	Short Term Trig	ger Value
Aluminium	5		20	
Boron	0.5		0.5–15 ^a	
Fluoride	1		2	
Iron	0.2		10	

^a Dependent on crop type.

Australian standards have no specific guideline for the concentration of sulphates in irrigation water. Nevertheless, high concentrations of sulphates may have adverse effects on crop yields and growth, as well as having a significant effect on the conductivity of the water. Due to this situation, the recommended range of sulphates in irrigation water is less than 400 mg/L [41].

We note that the tolerance of plants to irrigation water properties such as salinity, dissolved salt composition, and conductivity is somewhat complex [23]. However, for the purposes of demonstrating the usefulness of the process modelling approach developed in this investigation, the values reported in Tables 2 and 3 have been used. In practice, practitioners should make decisions relating to suitability of irrigation water based upon their specific plants and conditions.

2.3. AqMB software

AqMB process engineering software was used to simulate the treatment of coal seam gas associated water and various unit operations were included to compare processing options. AqMB utilises widely accepted theories and models for each individual unit operation to create a model for the overall plant [42]. This software produced a comprehensive analysis of the treatment plant, including: equipment parameters; stream compositions; material balances; predictions of precipitate formation; and operating costs.

2.4. Process designs for CSG associated water treatment

2.4.1. pH adjustment and chemical amendment

The first stage was to allow the CSG associated water to reside in a settling pond for an average period of 10 days [Fig. 1 (a)]. The water was subsequently pumped at a rate of $100 \text{ m}^3/\text{h}$ (2.4 ML/day) to a chemical dosing unit that adjusted the pH of the CSG associated water as required. For the dealkalization of CSG associated waters, suitable acids included hydrochloric and sulphuric acid [Eqs. (2) and (3)].

$$2HCO_3^- + H_2SO_4 \rightarrow 2CO_2 + 2H_2O + SO_4^{2-}$$
 (2)

$$HCO_3^- + HCl \rightarrow CO_2 + H_2O + Cl^-$$
(3)

A degassing unit was added to remove the carbon dioxide from the associated water, which resulted from the pH adjustment. Carbon dioxide removal from process water is often achieved by use of forced draft degasifiers wherein a tower is employed which contains packing material and water is distributed over the packed bed while air is flowed counter currently through the bed [43]. From the degassing unit, the treated CSG associated water was fed into a final storage tank.

2.4.2. Ion exchange

As with the pH adjustment & chemical amendment process, the first stage of the ion exchange system was to allow the CSG associated water to reside in a settling pond for an average period of 10 days [Fig. 1(b)].

Similarly, the water was pumped at a rate of $100 \text{ m}^3/\text{hr}$ (2.4 ML/day); albeit, in this instance the next unit operation was an ultrafiltration unit which was employed to remove any suspended solids before passing through the ion exchange column. Resin in the acid exchanged form was located in the ion exchange column and reverse flow regeneration using 5% hydrochloric acid was simulated. The regeneration stoichiometric equivalent ratio was 1.8. A linear velocity of 30 m/s was assumed for the feed solution passing through the resin bed. A forced draft degassing unit was then used to remove carbon dioxide that was present in the associated water. If required, the associated water was dosed with lime to increase the pH and SAR values to satisfy water reuse regulations, before entering a final storage tank.

2.5. Chemicals and resins

Concentrated sulphuric acid (98%) and hydrochloric acid (32%) were used in the pH adjustment simulations, and were estimated to cost A\$300/tonne and A\$297/tonne [42], respectively. Slaked lime (95 wt %) was used to neutralize CSG associated water samples which were acidic. The strong acidic cation resin chosen was Dow Marathon C in the acid exchanged form. The cost of DOW Marathon C was estimated to be \$5/L and a life span of 5 years was assumed. The working capacity of the strong acid cation resin was assumed to be 1.2 eq/L. The weak acidic cation resin selected was Dow MAC-3 in acid exchanged form. MAC-3 costs approximately \$5/L and has a life span of 5 years. The working capacity of the weak acid cation resin was assumed to be 1.8 eq/L.

2.6. Column ion exchange trials

Strong acid cation resin (DOW Marathon C) in the acid form was loaded into a 0.0254 m diameter u-PVC column until the bed height was 0.783 m; which corresponded to a bed volume (BV) of 0.397 L. The column diameter was chosen to minimize the possibility of the feedwater by-passing the resin bed due to factors such as wall effects [44]. A flow rate of 16.2 L/h was employed which was equivalent to 40.8 BV/h which was in harmony with previous ion exchange studies relating to water treatment [45]. The linear velocity of the feed stream was 32.0 m/h. Sampling of the feed and effluent streams was regularly conducted and collected solutions immediately stored in sealed containers.

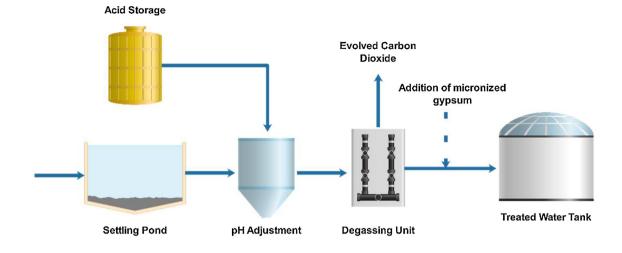
2.7. Solution analysis

2.7.1. Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

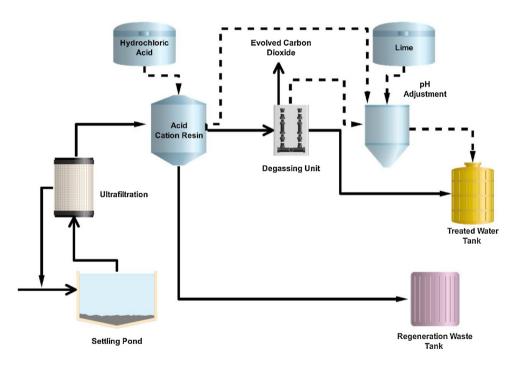
A Perkin Elmer Optima 8300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with integration times of 0.15 s and 10 replications was used to analyse solutions resultant from the ion exchange column tests. Samples were diluted to a concentration between 1 and 1000 mg/L using a Hamilton auto-dilutor equipped with 10 and 1 mL syringes. A certified standard from Australian Chemical Reagents (ACR) was diluted to form multi-level calibration curves. An external reference was used to monitor instrument drift and accuracy of the results.

2.7.2. pH and conductivity

Conductivity and pH were measured by means of a smartCHEM-Lab analyser equipped with suitable probes (TPS Pty Ltd). The conductivity sensor used a k constant of 10 and was calibrated appropriately to 2.76 mS/cm. Calibration of the pH probe was completed using buffer solutions with a pH of 4 and 7.



(a) pH Adjustment & Chemical Amendment of CSG Associated Water



(b) Ion Exchange of CSG Associated Water

Fig. 1. Process Flow Diagram (PFD) for (a) pH adjustment & chemical amendment and (b) ion exchange of CSG associated water.

3. Results and discussion

3.1. Chemical amendment

3.1.1. Sulphuric acid addition to CSG associated water

Table 4 shows the AQMB simulation data when sulphuric acid was dosed into CSG associated water sample 1, to create a range of effluent pH values (after both pH adjustment and degasification).

According to the model, the bicarbonate concentration was not reduced to a level tolerated by sensitive plants (< 76 mg/L) until the solution pH was adjusted to 5.5. Correspondingly, sulphuric acid addition to pH 5.5 resulted in an increase in the conductivity from 1237 to 1402 mg/L. The initial water sample was suitable for use with

moderately sensitive crops (< 1300 μ S/cm), but as a result of acid addition increased to approximately 1404 μ S/cm which was amenable only to moderately tolerant crops. The dosing of sulphuric acid resulted in a sulphate concentration of 360.9 mg/L at pH 5.5 which was within the recommended limit of 400 mg/L [41]. Further reduction of the solution pH to 4.5 [Table 4] did not appear justified as the sulphate concentration was now above 400 mg/L and the solution conductivity also remained above 1300 μ S/cm which indicated the treated water was still unsuitable for moderately sensitive crops. Similarly, simply dosing the CSG associated water to pH 6.5 was not sufficient to diminish the bicarbonate concentration to satisfy requirements for even tolerant plant varieties. Bern et al. [46] investigated deep subsurface drip irrigation (SDI) of either hay or alfalfa crops using coal seam gas associated

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Stage	CSG Associated Water	Target pH – 6.5 for acid add	addition	Target pH - 5.5 for acid addition	lition	Target pH – 4.5 for acid addition	lition
	COLINDOSITION IN FORM	CSG Associated Water Composition After Acid Dosing Stage	CSG Associated Water Composition After Degassing Stage	CSG Associated Water Composition After Acid Dosing Stage	CSG Associated Water Composition After Degassing Stage	CSG Associated Water Composition After Acid Dosing Stage	CSG Associated Water Composition After Degassing Stage
CSG Associated Water 1							
Hd	8.71	6.5	8.80	5.5	7.74	4.5	6.41
TDS (mg/L)	952.6	1071	926.4	1191	877.1	1222	865.9
Conductivity (µS/cm)	1237	1319	1319	1404	1402	1436	1423
Total Alkalinity (mg CaCO ₃ /L)	429.4	247.8	247.8	54.02	54.03	4.00	4.00
Bicarbonate (mg/L)	482.3	301.9	295.6	66.1	64.7	7.5	4.9
Carbon Dioxide (mg/L)	1.38	144.5	0.97	314.6	0.97	356.9	0.97
Carbonate (mg/L)	17.86	0.07	2.53	0.001	0.25	0	0
Sulphate (mg/L)	0.7	175		360.9		408.8	
Amount of Acid Used (kg/h)	0	17.78		37.28		42.51	
CSG Associated Water 2							
Hd	8.95	6.5	8.161	5.5	7.974	4.5	6.71
TDS (mg/L)	1305	1538	1276	1758	1185	1815	1164
Conductivity (µS/cm)	1438	1409	1409	1719	1718	1765	1752
Total Alkalinity (mg CaCO ₃ /L)	802.3	456.2	456.3	100.7	100.8	9.028	9.032
Bicarbonate (mg/L)	855.4	555.9	543.5	123.1	121	14.03	11.02
Carbon Dioxide (mg/L)	1.383	261.2	0.972	573.3	0.981	652	0.984
Carbonate (mg/L)	60.07	0.138	6.224	0.003	0.902	0	0.004
Sulphate (mg/L)	0	332		673.2		761.2	
Amount of Acid Used (kg/h)	0	34.05		69.71		79.26	

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Stage	CSG Associated Water	Target pH – 6.5 for acid addition	ion	Target pH – 5.5 for acid addition	ion	Target pH – 4.5 for acid addition	lon
	Composition in Pond	CSG Associated Water Composition After Chemical Dosing	CSG Associated Water Composition After Degassing	CSG Associated Water Composition After Chemical Dosing	CSG Associated Water Composition After Degassing	CSG Associated Water Composition After Chemical Dosing	CSG Associated Water Composition After Degassing
CSG Associated Water 1							
Hd	8.75	6.5	8.06	5.5	7.75	4.5	6.52
TDS (mg/L)	981.6	1021	882.2	1092	783.5	1112	758.8
Conductivity (µS/cm)	1239	1349	1348	1469	1467	1512	1499
Total Alkalinity (mg CaCO ₃ /L)	474.5	251.0	251.0	55.93	55.95	4.637	4.639
Bicarbonate (mg/L)	474.5	305.8	299.0	68.4	66.9	7.81	5.63
Carbon Dioxide (mg/L)	1.20	138.4	0.85	309.6	0.85	353.3	0.85
Carbonate (mg/L)	21.33	0.08	2.74	0.00	0.3	0.00	0.00
Chloride (mg/L)	143.7	270.1		270.1		408.1	
Amount of Acid Used (kg/h)	0	40.62		85.02		96.7	
CSG Associated Water 2							
ЬН	8.95	6.5	8.131	5.5	8.00	4.5	6.85
TDS (mg/L)	1305	1441	1190	1572	1010	1607	964.2
Conductivity (µS/cm)	1438	1649	1648	1867	1866	1936	1923
Total Alkalinity (mg CaCO ₃ /L)	802.3	460.0	460.1	103.4	103.5	10.06	10.07
Bicarbonate (mg/L)	855.4	560.5	547.3	126.3	123.9	14.44	12.26
Carbon Dioxide (mg/L)	1.383	249.8	0.85	562.9	0.86	643.5	0.86
Carbonate (mg/L)	60.07	0.16	6.66	0.00	1.07	0.00	0.00
Chloride (mg/L)	12.8	255.1		507.5		573.9	
Amount of Acid Used (kg/h)	0	77.89		159.1		180.3	

water which had initially been pre-treated with sulphuric acid. These authors recommended pH adjustment to 6.0; albeit, only chloride concentrations were reported in the CSG associated water sample (7-10 mg/L). A companion study by Bern et al. [18] provided greater detail regarding the composition of the coal seam gas associated water used in SDI studies. The initial CSG associated water was characterized by a solution conductivity of $2100 \,\mu\text{S/cm}$, pH of 8.0, sulphate < 0.06 mg/L, sodium equal to 529 mg/L and total alkalinity of 1240 mg CaCO₃/L. Following sulphuric acid addition the relevant water quality parameters were: a solution conductivity of 2600 µS/cm; pH of 5.9; sulphate 972 mg/L; sodium equal to 568 mg/L and total alkalinity of 223 mg CaCO₃/L. Although the data was consistent with the water quality simulations in this study it was noted that the sulphate concentration was significantly in excess of recommended values of less than 400 mg/L [41]. However, as described by Bern et al. [18,46] the SDI approach was developed to allow soils and plants to cope better with use of saline water for irrigation and emphasis was placed upon disposing of the CSG associated water as much as irrigating plants. Placement of drip tubing at 92 cm depth inhibited the rise of sodium ions from the CSG associated water to the surface and thus limited the detrimental impact of poor soil drainage. The drawback of the deep SDI system was the fact that only deep rooted plants such as grasses and alfalfa could access the water at the outlined depth.

As expected, the degassing unit reduced the amount of carbon dioxide that was present in the treated water; hence, raising the solution pH to 7.74 for the preferred dosing strategy of sulphuric acid addition to pH 5.5. Notably, a pH value of 7.74 was compliant with irrigation recommendations. As for the SAR value of 31.62 for the treated CSG associated water sample 1, this was in the range stated to be acceptable for moderately tolerant crops (18-46) [Table 2]. Nevertheless, care would have to be taken with this level of SAR as the type of soil is also important not just the crop to be irrigated. For example, the Queensland government recommends a maximum SAR value of 12 for light soils [47]. Addition of micronized gypsum could be performed if the SAR value was required to be lowered further [24]. Furthermore, the studies of Johnston et al. [22] have shown that optimal infiltration rates were achieved when irrigating with CSG associated water when the water was not only pH adjusted with acid but also when gypsum and sulphur were added as amendments.

CSG associated water sample 2 differed from sample 1 mainly in terms of comprising of a higher bicarbonate concentration, lower chloride concentration, higher solution pH and lower SAR value [Table 1]. pH adjustment with sulphuric acid was again simulated and results displayed in Table 4. Reduction of the pH to 5.5 only decreased the bicarbonate concentration to 123 mg/L, which meant the treated water was only potentially compatible with moderately tolerant or tolerant crops [Table 3]. However, dosing the acid until the CSG associated water attained a pH of 5.5 raised the concentration of sulphate ions to 673.2 mg/L which was substantially in excess of the recommended limit of 400 mg/L [41]. To make the level of sulphate ions compliant in the treated sample, acid dosing to pH 6.5 was necessary. However, this situation resulted in excessive concentrations of bicarbonate ions in solution which were not compatible with even tolerant plant species [Table 3]. To make use of this pH adjusted water may require consideration of innovative irrigation practices such as deep subsurface drip irrigation [18,46]; albeit, in the Queensland context this approach has not yet been demonstrated. Instead, overhead-irrigation to the foliage of both Rhodes grass and Leucaena with CSG associated has been described [48]. For both outlined plant species the application of CSG associated water had negative impacts such as necrotic leaf tips and chlorotic leaves. However, the extent of the detrimental effects upon plant health were dependent upon several factors such as plant species, water quality, and growing conditions. Rhodes grass appeared particularly resilient and its known capacity as a halophyte (wherein it can accumulate excess salt in the soil in its leaves) makes it worthy of further consideration in relation to the current study

of potential CSG associated water pH adjustment & chemical amendment practices.

From the data in Tables 4 and 5 it was apparent that greater amounts of bicarbonate species in the CSG associated water would require increasing quantities of sulphuric acid to be dosed. Hence, it was evident that for CSG associated water sample 3 which comprised of 2416 mg/L bicarbonate species; that the sulphate concentration would be above the recommended limit of 400 mg/L in all cases where the pH was adjusted to 6.5 or less. Indeed, calculations indicated sulphate values of 873.1, 1657 and 1866 mg/L mg/L for CSG associated water sample 3 after pH adjustment to 6.5, 5.5 and 4.5, respectively (detailed results of these simulations were not shown for sake of brevity). What can be concluded is that when applying sulphuric acid for pH adjustment perhaps only CSG associated water with less than approximately 1000 mg/L bicarbonate ions was generally amenable to providing water which is usable for irrigation purposes. We emphasise that the value of 1000 mg/L bicarbonate ions is only a guideline and is dependent upon plant species.

In practice, the addition of sulphuric acid to bicarbonate containing solutions such as CSG associated water should take into account the rate of reaction between these outlined species. For Eq. (2), the rate law can be described as shown in Eq. (4) [21] and the Arrhenius form as illustrated in Eq. (5) [21].

$$\frac{d_{CO_2}}{dt} = k \left(C_{NaHCO_3}^0 - C_{CO_2} \right)^{1.5} \left(C_{H_2SO_4}^0 - 0.5C_{CO_2} \right)^{3.2}$$
(4)

$$k(T) = 3.13x10^{34} e^{-\frac{27061}{T}} (mol^{-3.7}xL^{3.7}xsec^{-1})$$
(5)

Where: t = time; $C^{o} = initial$ concentration; T = temperature;

Consequently, the rate of reaction was predicted to increase from 0.049 mol^{-3.7}xL^{3.7}xsec⁻¹ at 15 °C to 2.782 mol^{-3.7}xL^{3.7}xsec⁻¹ at 30 °C [21] (a temperature range approximating that encountered in the gas fields in Queensland).

3.1.2. Hydrochloric acid addition to CSG associated water

From the analysis in Section 3.1.1 it was apparent that a critical restriction in use of treated coal seam gas associated water was the presence of sulphate ions in excess of recommended values for irrigation use. Hence, the addition of hydrochloric acid to CSG associated water samples 1 & 2 was evaluated [Table 5] as the tolerance of crops to chloride ions was broadly higher than that compared to sulphate ions [Table 3]. As a general observation, the mass of acid required was greater when using hydrochloric acid compared to sulphuric acid. This result reflected the higher concentration of sulphuric acid (98%) relative to hydrochloric acid (32%). In addition, the trends in alkalinity, TDS, bicarbonate, carbon dioxide, and carbonate were similar to the case with sulphuric acid addition to the same sample [Table 4]. In terms of chloride concentration, by pH 5.5 after HCl addition, this was already in excess of 400 mg/L which indicated that this treated CSG associated water was only suitable for moderately tolerant pant species. Similarly, the amendment of CSG associated water sample 2 was also examined [Table 5].

Due to the higher alkalinity of sample 2 the quantity of HCl required was greater compared to the situation with sample 1. At a pH of 6.5 the bicarbonate level was not compatible with irrigation use, but upon adjusting the pH to 5.5 the treated CSG associated water was potentially suitable for application to moderately tolerant and tolerant plants. Further decrease in solution pH made the treated water suitable for plants sensitive to bicarbonate ions but the chloride concentration of 574 mg/L was only recommended for moderately tolerant plants. Hence, it was not considered feasible to reduce the pH of CSG associated water sample 2 to less than *ca.* 5.5.

pH adjustment of CSG associated water sample 3 with hydrochloric acid resulted in bicarbonate concentrations (17 mg/L) suitable for irrigation of sensitive crops at a pH of 4.5. However, the conductivity of the water increased from 3319 to $4152 \,\mu$ S/cm giving it a high salinity

rating. The hydrochloric acid dosing resulted in the chloride concentration increasing from 336.1 to 759.2 mg/L after pH adjustment to 6.5 which was above recommended levels for even salt tolerant crops (results not shown in depth for sake of brevity).

Further pH adjustment of CSG associated water sample 3 to 5.5 and 4.5 exasperated the problem of excessive chloride levels (1165 and 1270 mg/L, respectively). Addition of hydrochloric acid to CSG associated water sample 3 was potentially interesting as not only did this solution have the greatest initial concentration of bicarbonate ions (1759 mg/L) but also a relatively low chloride concentration (28.4 mg/L). Nevertheless, in this case after pH adjustment the chloride concentrations were 675.1, 1252 and 1402 mg/L at final pH values of 6.5, 5.5 and 4.5, respectively. Only at pH 6.5 was the chloride ion concentration acceptable for tolerant plants albeit it was noted that the bicarbonate concentration of 1284 mg/L was not suitable for irrigation. Again, for the sake of brevity we have not shown all the data which was simulated.

It was clear from the aforementioned results and discussion that application of pH adjustment approaches to make CSG associated water more acceptable for irrigation use has constraints. The question arises as to how this practice may be implemented more widely, such as the application of deep SDI [18,46]. Interestingly, Poudyal et al. [49] conducted irrigation trials of dill using CSG associated water. Key findings included that shorter irrigation times with CSG associated water may be viable in terms of maintaining acceptable soil quality and retaining essential oil production in the plant itself. Similarly, Sintim et al. [50] examined the impact of both CSG associated water and CSG associated water diluted with fresh water upon Camelina growth. Use of 100% CSG associated water was found to be problematic in terms of Camelina cultivation and soil quality. However, addition of tap water to make a 50:50 mixture inhibited any negative impacts upon Camelina growth apart from a slightly later emergence (which may have been due to surface crusting). Thus dilution of CSG associated water with conventional water resources may be viable, albeit it is noted that Sintim et al. [50] expressed concern about long term use of CSG associated water due to sodium accumulation in the soil. A similar study by Zheljazkov et al. [51] regarding irrigation of spearmint and peppermint concluded that using 100% CSG associated water or a sample wherein 25% of the associated water was replaced with tap water; resulted in inhibition of both crop and oil yields. In addition, potential stress to the plant was evident as the total phenol and flavonoid content increased. Again, a 50:50 mixture of associated water and tap water was found to be acceptable in terms of plant yield. Li and Harold [52] also advocated dilution of CSG associated water to minimize the impact of excess chloride ions when used for irrigation. Hence, there may be scope to use acid amended CSG associated water as a supplement to conventional fresh water sources. For instance, as discussed by Monckton et al. [53] CSG associated water is typically offered at minimal cost to farmers and indeed it was proposed that the majority of farmers in Queensland who have access to this unconventional resource would use it if possible.

3.1.3. Chemical usage and cost

The estimated annual acid usage and its associated cost is shown in Table 6. Each model was assumed to treat 876.6 ML on an annual basis.

Table 6

Predicted annual chemical consumption and cost.

Universally, a larger volume of hydrochloric acid than sulphuric acid was required to treat the same sample as outlined previously. As the assumed costs for hydrochloric and sulphuric acid were similar (297 and 300 \$/tonne, respectively) this situation resulted in hydrochloric acid to be over double the cost than that of sulphuric acid. In addition to the chemical costs, electricity costs were also applicable with the degassing unit which would be essentially the same value regardless of acid type used.

In relation to the discussion in Section 3.1.2 regarding the financial attractiveness of using CSG associated water for irrigation purposes, the acid cost and accompanying capital expenditure required for a chemical dosing system must be considered.

3.2. Ion exchange of coal seam gas associated water

3.2.1. Weak acid cation (WAC) resin

The predicted ability of weak acid cation resin (H⁺-WAC) to demineralize the various CSG associated water samples is shown in Table 7. The results indicated that there was a significant decrease in the concentrations of bicarbonate, calcium, carbon dioxide, carbonate, magnesium, and sodium. The affinity for calcium and magnesium ions by weak acid cation resins is well known. For example, Pesavento et al. [54] investigated the uptake of both calcium and magnesium ions on Amberlite CG-50 resin which had carboxylic acid functional groups. Above a solution pH of *ca*. 5.5 the uptake of both alkaline earths was favoured, which was consistent with the data in Table 7 wherein the initial solution pH was alkaline in character. The significantly lesser affinity of WAC resin for sodium ions compared to alkaline earth ions was also evident in Table 7 [55].

For example, for CSG associated water 1 the removal efficiencies for calcium, magnesium, and sodium ions were 99.5, 99.1, and 70.9%, respectively. The relevant exchange processes are shown in Eqs. (6)-(8).

$$2R - COOH + Ca^{2+} \leftrightarrow R_2 - COOCa + 2H^+ \tag{6}$$

$$2R - COOH + Mg^{2+} \leftrightarrow R_2 - COOMg + 2H^+ \tag{7}$$

$$R - COOH + Na^{+} \leftrightarrow R - COONa + H^{+}$$
(8)

Dealkalization of solutions comprising of sodium bicarbonate by weak acid cation resins is described by Eqs. (9) and (10) [56]:

$$R - COOH + NaHCO_3 \leftrightarrow R - COONa + H^+ + HCO_3^-$$
(9)

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O \tag{10}$$

Hence, the observed almost complete reduction in bicarbonate concentration and concomitant presence of dissolved carbon dioxide in significant levels was in harmony with reported resin chemistry.

As a result of the exchange process, with sample one, the conductivity decreased from 1239 to $656.5 \,\mu$ S/cm. Notably, the effluent from the ion exchange was pH 3.30, therefore dosing with lime (1.99 kg/h) was necessary to increase the pH to 7 to make this solution suitable for beneficial reuse. A benefit of the pH adjustment was the reduction in SAR to 6.78 which was compliant with irrigation of sensitive crops [Table 2]. Indeed, all parameters recorded in Table 7 for

Final pH	CSG Associate	d Water Sample 1			CSG Associated	d Water Sample 2		
	HCl		H_2SO_4		HCl		H_2SO_4	
	Mass (t)	Cost (\$)	Mass (t)	Cost (\$)	Mass (t)	Cost (\$)	Mass (t)	Cost (\$)
6.5	356.1	105,761	155.9	46,670	682.6	202,742	298.5	89,545
5.5	745.3	221,336	326.8	98,048	1394.6	414,189	611.1	183,329
4.5	847.8	251,763	372.6	111,787	1,580.8	469,511	694.8 208,446	

Table 7

Ion exchange of CSG associated water using weak acid cation resin.

Sample CSG associated water 1				CSG associated water 2			CSG associated water 3					
Stage	Pond	WAC Column	Degasser	Lime Dosed (after degasser)	Pond	WAC Column	Degasser	Lime Dosed (after WAC Column)	Pond	WAC Column	Degasser	Lime Dosed (after WAC Column)
pН	8.75	3.30	3.30	7.00	8.99	5.88	8.16	7.00	9.26	6.01	8.16	7.00
TDS (mg/L)	948.2	603.0	244.8	255.6	1294	836.5	356.1	1154	2953	1972	1014	2596
Conductivity (µS/cm)	1239	656.5	656.1	506.5	1441	407.9	408.7	1119	3294	1106	1108	2365
Total Alkalinity (mg CaCO ₃ /L)	429.4	0	0	0.89	802.3	197.3	197.4	626.2	1966	555.3	555.8	1399
SAR	28.32	108.4	108.4	6.78	25.2	130.3	130.3	2.06	34.69	168.3	168.4	3.85
Bicarbonate (mg/L)	474.5	0.48	0.00	0.98	833.9	240.6	236.3	760	1670	677.0	662.5	1695
Calcium (mg/L)	6.0	0.03	0.03	11.04	8.9	0.02	0.02	171.7	21.37	0.03	0.03	337.7
Carbon Dioxide (mg/ L)	1.205	359.0	0.85	0.15	1.204	480.7	0.85	104.9	1.204	957.4	0.87	219.9
Carbonate (mg/L)	21.33	0	0	0	70.59	0.01	2.07	1.69	352.7	0.05	7.00	5.14
Magnesium (mg/L)	0.9	0.008	0.008	0.008	3.9	0.014	0.014	0.014	14.6	0.089	0.089	0.089
Sodium (mg/L)	281.4	81.8	81.8	81.8	358.6	98.2	98.2	98.2	849.3	256.9	257.1	256.9

CSG associated water sample 1 after WAC resin treatment and final pH adjustment were suitable for using this water to irrigate sensitive plant types.

In contrast, for CSG associated water samples 2 and 3, the effluent pH from the WAC resin column was significantly higher (ca. 5–6) than found for CSG associated water sample 1 (3.3). This behaviour was consistent with the greater presence of alkalinity remaining in the effluent after the ion exchange column. A subsequent degassing stage was sufficient to reduce the TDS/conductivity of the solutions and concomitantly raise pH to approximately 8.00 \pm 0.16. However, the SAR values were 130.3, and 168.4 for CSG associated water samples 2 and 3, respectively; which meant that this treated water was unsuitable for crop irrigation [Table 2]. Consequently, addition of lime to raise the pH of the effluent water from the WAC resin column to 7.00 was evaluated [Table 7] without a degassing stage. This strategy was successful in reducing SAR to less than 4 for CSG associated water samples 2 & 3. However, the lack of a degassing stage allowed the formation of bicarbonate species as the lime was dosed, and in turn the solution conductivity and total dissolved solids content were invariably too high for irrigation purposes [Tables 2 and 3]. Hence, using lime to adjust solution pH post a WAC resin column without the presence of a degassing unit was not recommended.

Instead, adjustment of SAR values using micronized gypsum addition following degasser treatment of CSG associated water samples 2 & 3 appeared a more practical choice. If the aim was to reduce SAR to less than 8 [Table 2], then calcium content would equate to 11.4 and 66.2 mg/L for CSG associated water samples 2 & 3, respectively. Strontium tracer studies have proven that this calcium in the gypsum is indeed plant available when added in conjunction with CSG associated irrigation water [24]. In terms of added sulphate the recorded values corresponded to 27.3 & 158.7 mg/L for CSG associated water samples 2 & 3, respectively. The estimated levels of sulphate were less than 400 mg/L and thus potentially compatible with irrigation practices.

For CSG associated water sample 3, it was estimated that calcium fluoride would precipitate after pH adjustment to 7.0 using lime (7.56 mol/h). This prediction was in accord with the fact that sample 3 had the greatest fluoride concentration when compared to CSG associated water samples 1 & 2 [Table 1]. No other precipitates were determined to form under the treatment conditions described using the WAC resin for all four CSG associated water samples studied. This prediction may indicate that a fluoride control technology is also necessary and as the fluoride concentration is < 20 mg/L, a sorption process could be viable. For example, chelating resins exchanged with aluminium ions have been shown to be effective at removing fluoride from solution [57]. Alternatively, activated alumina was demonstrated to reduce the concentration of fluoride ions in high alkalinity groundwater to less than the discharge limit of 2 mg/L [58].

With increasing TDS of the CSG associated water the amount of resin required was correspondingly increased (31250, 40570, and 95130 L, for CSG associated water samples 1, 2 & 3, respectively).

3.2.2. Strong acid cation (SAC) resin

The predicted ability of strong acid cation resin (H^+ -SAC) to demineralize the various CSG associated water samples is shown in Table 8.

As with the WAC resin, the SAC resin generally decreased the concentration of bicarbonate, calcium, carbon dioxide, carbonate, magnesium and sodium in the CSG associated water according to Eqs. (11)-(13).

$$2R - H + Ca^{2+} \leftrightarrow R_2 - Ca + 2H^+ \tag{11}$$

Table 8	
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Ion Exchange with SAC Resin Results.

Sample	CSG associated water 1				CSG associated water 2			CSG associated water 3		
	Pond	SAC Column	Degasser	Lime Dosed	Pond	SAC Column	Degasser	Pond	SAC Column	Degasser
pH	8.75	2.68	2.68	7.00	8.99	5.55	8.10	9.26	5.72	8.15
TDS (mg/L)	948.2	567.3	209.1	252.1	1294	762.9	203.1	2953	1786	638.8
Conductivity (µS/cm)	1239	1147	1147	515.8	1441	245.4	245.0	3294	716.6	717.2
Total Alkalinity (mg CaCO ₃ /L)	429.4	0	0	0.90	802.3	106.7	106.7	1966	338.7	339.0
SAR	28.32	112.5	112.5	1.94	25.22	105.2	105.2	34.69	132.5	132.5
Bicarbonate (mg/L)	474.5	0.12	0	0.98	833.9	130.2	128.2	1670	413.0	404.8
Calcium (mg/L)	6.0	0.01	0.01	44.9	8.9	0.01	0.01	21.37	0.016	0.016
Carbon Dioxide (mg/L)	1.205	359	0.85	0.14	1.204	560.4	0.86	1.204	1148	0.87
Carbonate (mg/L)	21.33	0	0	0	70.59	0.003	0.90	352.7	0.015	3.84
Magnesium (mg/L)	0.9	0.002	0.002	0.002	3.9	0.008	0.008	14.6	0.071	0.071
Sodium (mg/L)	281.4	47.1	47.1	47.1	358.6	58.2	58.2	849.3	175.6	175.7

$$2R - H + Mg^{2+} \leftrightarrow R_2 - Mg + 2H^+ \tag{12}$$

$$R - H + Na^+ \leftrightarrow R - Na + H^+ \tag{13}$$

Strelow [59] determined the selectivity of SAC resins to be in the order $H^+ < Na^+ < Mg^{2+} < Ca^{2+}$, hence why greater removal efficiencies were noted in Table 8 for alkaline earth ions relative to sodium ions for all water types examined. Column studies of sodium exchanged SAC resin by Snoeyink et al. [60] also confirmed the stronger affinity of the resin for calcium ions compared to magnesium ions.

Dealkalization of solutions comprising of sodium bicarbonate by strong acid cation resin is summarized in Eq. (14):

$$R - H + NaHCO_3 \leftrightarrow R - Na + H_2O + CO_2 \tag{14}$$

The trend in removal effectiveness of the SAC resins was similar to that of the WAC resins in that increasing alkalinity and TDS of the CSG associated water resulted in effluent from the resin bed comprising of correspondingly greater concentrations of bicarbonate and sodium ions. Therefore, for sample 2 the bicarbonate concentration after the degassing stage (128.2 mg/L) was suitable for only tolerant plant species and for sample 3 this same parameter was in excess of recommended values for irrigation of any plants (404.8 mg/L).

As a result of the ion exchange process, a significant increase in the SAR value was evident, with all samples exhibiting unacceptably high SAR values after the ion exchange stage. Sample one was dosed with lime (8.125 kg/h) following the degasser unit, to increase the pH to 7 and this approach reduced SAR to 1.94 which meant the water was now suitable for irrigation purposes. The presence of calcium in the treated water (44.9 mg/L) was not perceived as problematic as the water was classified as "soft" and the negligible amount of bicarbonate present in the treated CSG associated water meant that there was minimal chance of precipitation of calcium carbonate when added to the soil [52]. Due to the fact that the degassing process elevated the pH levels to above 8 for CSG associated water samples 2 & 3, it was not feasible to further dose with lime as the resultant final pH would not be suitable for irrigation water (unless post-modified by acid addition).

Similar to the situation with WAC resin, increasing TDS of the CSG associated water enhanced the amount of resin required (46860, 60240 and 140100 L, for CSG associated water samples 1, 2 & 3, respectively).

Comparing the performance of the weak and strong acid cation resins we can infer the following. For CSG associated water sample 1 the composition of the final treated water after the lime dosing stage was remarkably similar for both resins types. The main predicted difference was the reduced amount of resin required when using the weak acid cation resin (31,250 L) compared to the strong acid cation resin (46,860 L). Given that the price for weak acid and strong acid cation resins is usually similar (ca. A\$5 per L) then use of weak acid cation resin may be favoured when treating CSG associated water with relatively low alkalinity. Moreover, regeneration of weak acid cation resin is generally easier than for strong acid cation resin due to the enhanced affinity of weak acid cation resin for acid. For samples 2 & 3, the most notable difference between the performance of the resins was the lower alkalinity after the resin bed when strong acid cation resin was employed. Whether this outcome was sufficient to negate the extra volume of resin required was not certain and requires further investigation of process economics which was outside the scope of the current investigation.

3.2.3. Ion exchange of CSG associated water

Bench trials were performed using the SAC resin, Marathon C, and CSG associated water [Fig. 2]. The bench scale results showed that the SAC resin in a column was more effective at removing the sodium ions than predicted with the AqMB simulation.

The reason for the enhanced removal of sodium ions from the CSG associated water can be attributed to the influence of the co-presence of bicarbonate ions in solution [Eq. (14)].

Notably, sodium ions associated with bicarbonate species were

more thermodynamically preferred by the resin due to the subsequent bicarbonate decomposition process under acidic conditions which produced carbon dioxide and water [29]. Detailed equilibrium isotherm studies of sodium ion exchange with strong acid cation resin from sodium chloride solution compared to those from sodium bicarbonate solutions, revealed that the Langmuir equilibrium coefficient was indeed significantly greater in the presence of bicarbonate ions [29]. In accord with the discussion regarding the promoting effect of bicarbonate species upon sodium ion exchange, the effluent pH was approximately 2.00 in the bench trials which was less than the calculate value of 2.49. The greater the degree of exchange of cations with protons on the resin the lower the effluent pH would be. For strong acid cation resins the effluent pH should be in the range 2-3 which was in agreement with this study [61]. It was also noted that the concentration of sodium ions in the effluent eventually attained a value which was actually higher than the incoming feed solution. This observation was consistent with the fact that once all the exchange sites were occupied on the resin the more preferred ions (such as calcium and magnesium) would now displace the less preferred sodium ions.

3.3. Comparison of pH adjustment with ion exchange using a cation resin

Inspection of the data for pH adjustment of CSG associated water sample 1 with the cationic resins revealed that the total dissolved solids content was greater when acid was simply added (877.1 mg/L for sulphuric acid and 255.6 & 252.1 mg/L for WAC & SAC resins, respectively). In turn, the solution conductivity was higher for the pH adjusted CSG associated water sample (c.f. 1402 µS/cm for sulphuric acid addition to sample 1, compared to 506.5 and 515.8 $\mu S/cm$ for WAC & SAC resins, respectively). A major reason for the observed increase in TDS and conductivity was the presence of extra anions inherently present when acid was added. In harmony with the given explanation, as the salinity of the CSG associated water increased the disparity in TDS and conductivity values for the treated solutions from pH adjustment and ion exchange became greater (as the amount of anions added in the chemical amendment process was enhanced). For example, the TDS of CSG associated water after remediation with sulphuric acid was 1276 mg/L which was substantially higher than the corresponding values for the cation resins (356.1 and 203.1 mg/L for WAC & SAC resins, respectively).

Nevertheless, despite the apparent superiority of the ion exchange process, in certain situations pH adjustment would be preferred due to operational simplicity. Likewise, ion exchange using a single cation resin also has been demonstrated to potentially not be applicable to all CSG associated water compositions. Indeed, alternate process configurations involving cation and anion resin combinations [62] or membrane based technologies such as reverse osmosis [63] may need to be considered as being optimal. Albeit, the suggested approaches are more expensive in terms of capital expenditure and operational costs. In such instances, the application of software modelling as demonstrated in this investigation can aid in appropriate technology selection.

4. Conclusions

The aim of this study was to provide a foundation for rapid selection of appropriate treatment methods for high alkalinity coal seam gas associated water. From the aforementioned analysis of acid adjustment and ion exchange using cationic resins the following aspects were deduced.

Acid adjustment of CSG associated water appeared to be restricted to water compositions which comprised of less than approximately 1000 mg/L bicarbonate species and thus cannot be universally used in the gas industry to remediate produced water. If cost was the main factor then sulphuric acid was the preferred acid to employ for acid adjustment purposes as it was significantly less expensive than hydrochloric acid. However, other considerations such as environmental

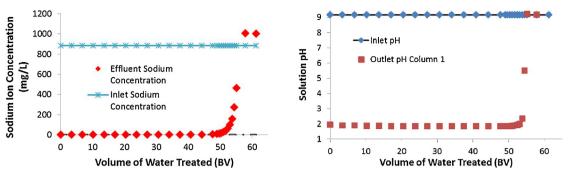


Fig. 2. Inlet and effluent sodium concentration and pH when treating CSG associated water sample 3 with strong acid cation resin.

aspects, regulatory conditions, ease of handling/storage should also be considered. To broaden the beneficial reuse of acid adjusted CSG associated water for irrigation purposes, strategies may include selection of salt tolerant plant species, addition of micronized gypsum and sulphur, dilution of acid adjusted CSG associated water with freshwater and limited application periods.

Ion exchange with either weak or strong acid cation resins was effective for desalination of coal seam gas water according to the modelling software. When the TDS value of the CSG associated water was less than 1000 mg/L the water quality produced after solution degassing and lime addition was acceptable for beneficial reuse options. As the TDS increased for the CSG associated water, the final conductivity of the treated water could be reduced to target levels (< 650 μ S/cm) (particularly with strong acid cation resin). Selection of the appropriate resin to use depended upon reduced resin volume and ease of regeneration advantages of WAC resin relative to improved water quality of SAC resin.

Comparison of calculated resin performance against actual resin performance in the laboratory indicated that the software was conservative in its estimation of water quality. The presence and decomposition under acidic conditions of bicarbonate species provided a thermodynamic driving force to further improve demineralization.

pH adjustment was more limited in its scope of application than ion exchange with cation resin, due to the increased solution TDS and conductivity values related to addition of anionic species to the treated CSG associated water. However, the pH adjustment process was simpler to operate than ion exchange and thus could be employed in select opportunities.

Overall, the application of AqMB software has been demonstrated to provide a firm basis for further development of water process solutions in the coal seam gas industry. The use of this software package allowed rapid evaluation of process options and narrowed the scope of potential solutions for the wide range of water compositions which occur in the industry. Future studies should not only address coal seam gas associated water samples which contain significant chloride concentrations but also expand the range of treatment technologies to include anionic resins and membrane methods such as reverse osmosis.

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R. Vedelago, G.J. Millar

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