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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.

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 µS/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].

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

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 ($CaCO_3$) or gypsum ($CaSO_4$) 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 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.

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
pH	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

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
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	