PILOT PLANT STUDIES OF ION EXCHANGE FOR DESALINATION OF COAL SEAM GAS PRODUCED WATER

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ABSTRACT

This paper reports a study of ion exchange (IX) as an alternative CSG water treatment to the widely used reverse osmosis (RO) desalination process. An IX pilot plant facility has been constructed and operated using both synthetic and real CSG water samples. Application of appropriate synthetic resin technology has proved the effectiveness of IX processes.

INTRODUCTION

Australia, and in particular Queensland, is experiencing a boom in the development of CSG production (Hamawand, Yusaf et al. 2013). The extraction of CSG releases significant volumes of groundwater that is typically saline and sodic in character with total dissolved solids content of 2,000 to 10,000 mg/L. The major species present are sodium chloride and sodium bicarbonate with traces of other ions such as calcium, magnesium, and potassium (Nghiem, Ren et al. 2011). Reverse osmosis (RO) has become the conventional means for desalination of CSG water (Averina, Rasul et al. 2008) as it has proved to be a reliable way of achieving the industry’s high environmental standards for the beneficial reuse of treated water. However, RO is an inherently costly technology due to the requirement for extensive pre-treatment of the CSG water prior to the RO membrane stage and the use of energy-intensive high pressure systems (Greenlee, Lawler et al. 2009). Membrane biofouling and scaling are common operational issues found with all applications of membrane desalination including CSG water treatment. While these challenges do not impact the reliability of the RO process, preventing these problems does incur significant extra operational costs. Ion exchange (IX) provides the opportunity to avoid these process issues and achieve operational cost savings and treatment efficiencies. Ion exchange has been used extensively in the USA for treatment of CSG water, both for desalination and also softening of CSG water as part of a pre-treatment strategy for RO (Dennis 2007). However, CSG water in the USA is typically composed of primarily sodium bicarbonate which means that only a single cation resin column is required to exchange sodium from the water and decompose the bicarbonate ions by exposure to acidic conditions. In the Queensland context, a system comprised of a strong acid cation (SAC) and weak base anion (WBA) resin (for chloride removal) combination is envisaged as a minimum requirement for IX desalination treatment.

The main aim of the IX process is to desalinate the CSG water with primary process performance targets being to minimize chemical costs, reduce the volume of brine produced and to be resilient to process shocks such as sudden feed concentration change and composition fluctuation. To achieve the latter goals, it is necessary to test different resin types, various resin bed configurations and examine the impact of flow rate, feed composition and resin regeneration conditions. Consequently, this paper presents data from both pilot plant and bench top studies of: the application of a weak acid cation (WAC) resin bed prior to the SAC resin stage; effect of CSG water composition; desalination performance; and the use of various regenerants and process conditions.

![Figure 1: Ion Exchange Pilot Plant](image)

EXPERIMENTAL

To conduct pilot plant studies a custom designed IX plant was constructed by Integra Water Treatment Solutions and located at the Banyo Pilot Plant Precinct operated by Queensland University of Technology [Figure 1].
The pilot plant consisted of a pre-treatment stage comprising of one glass bead and two activated carbon filters which were present to remove particulate matter and organic impurities. Four IX columns made of fibreglass reinforced plastic (FRP) were employed for the desalination step. Normally, 100 L of synthetic resin was deployed in the form of a wet slurry to ensure even packing of the bed. Pilot plant performance was evaluated on-line by means of in situ solution pH and electrical conductivity measurements and also by grab samples for laboratory analysis. The nominal pilot plant water treatment capacity was 100 kL per day and as such 45 tonnes capacity of industrial grade storage tanks were used to store feed water, 45 tonnes capacity for treated water and 22.5 tonnes capacity for regenerant water, flush water and rinse water.

A typical experiment involved four stages. Stage one was the loading cycle wherein CSG water was fed through the resin columns at a fixed rate (expressed as bed volumes per hour) until breakthrough was observed. Stage two involved backflushing of the resin bed with pure water to remove particulate matter and to redistribute the resin beads. Regeneration of the spent resins occurred in stage three, with 5 wt% hydrochloric acid solution used to replenish the cation resins and 5 wt% sodium hydroxide for the anion resin bed. Finally, a rinse cycle was applied in stage four to remove traces of the regenerant solution.

Comparative tests were also conducted using a bench scale IX system supplied by Miontec Gmbh, which had the same four column configuration of the pilot plant [Figure 2]. Bench studies were more convenient in terms of evaluating optimum conditions for pilot plant operation.

![Image](image_url)

**Figure 2: Bench Scale Ion Exchange Testing Unit**

The bench scale facilities could operate at the same velocities as the pilot plant system. Wall effects were minimized by using column diameters in excess of 5 cm and the columns themselves were made of transparent uPVC in order to allow observation of any changes in resin bed structure. During desalination tests the IX unit was normally pressurized to avoid evolution of carbon dioxide from solution. Resin volumes were typically less than 1 L in bench scale tests.

Real CSG water samples were supplied by Santos GLNG from the Surat Basin. Analysis of the water was conducted using ICP-OES (Perkin Elmer), pH and electrical conductivity. Synthetic CSG water samples were made using addition of appropriate soluble salts to either deionized water at bench scale or potable water at pilot plant level. Composition of “Low total dissolved solids (TDS)” and “High TDS” CSG water samples prepared in this study are shown in Table 1 & 2.

<table>
<thead>
<tr>
<th>Species</th>
<th>“Low TDS”</th>
<th>“High TDS”</th>
<th>“Real” CSG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>1050</td>
<td>2100</td>
<td>870</td>
</tr>
<tr>
<td>Potassium</td>
<td>36</td>
<td>72</td>
<td>54</td>
</tr>
<tr>
<td>Calcium</td>
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<td>18</td>
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</tr>
<tr>
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<tr>
<td>Iron</td>
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</tr>
<tr>
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<td>0.02</td>
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<tr>
<td>Carbonate</td>
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<td>215</td>
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<tr>
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<tr>
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<td>Phosphate</td>
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<tr>
<td>Boron</td>
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<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>20</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

Resins used in this study were supplied by Lanxess Gmbh and Purolite. For the synthetic CSG water tests, the WAC resin (Lanxess CNP-80) was supplied in the sodium exchanged form. Consequently, prior to use it was treated with a solution of hydrochloric acid to change it to the acid form. The SAC resin (Lanxess S108 H) was supplied in the proton exchanged form and used as received. A WBA resin (Lanxess MP68) was converted from the chloride form to the “OH” form by treatment with a sodium hydroxide solution. In the “Real” CSG water tests the WAC resin used was Purolite C104+ and the other resins remained unchanged.
RESULTS AND DISCUSSION

“Low TDS” Synthetic CSG Water

The first set of pilot plant trials were designed to examine the performance of a WAC, SAC & WBA resin bed configuration [Figure 3] for desalination of “Low TDS” synthetic CSG water sample characterized by a low TDS content (Table 1). The flow rate used was equivalent to 86.4 bed volumes (BV) per hour for the WAC bed and 21.6 BV per hour for both the SAC and WBA resin beds. In each case the linear velocity was 16.7 m/h.

Figure 3: Resin Bed Configuration for Pilot Plant Studies

![Resin Bed Configuration](image)

The flow rate used was equivalent to 86.4 bed volumes (BV) per hour for the WAC bed and 21.6 BV per hour for both the SAC and WBA resin beds. In each case the linear velocity was 16.7 m/h.

Figure 4: Performance of Weak Acid Cation Resin Bed for Sodium Removal from “Low TDS” CSG Water

![Sodium Concentration](image)

Figure 4 shows that only the portion of the sodium ions associated with the bicarbonate ions in solution were removed by the WAC resin. This confirms results of previous laboratory studies of equilibrium behaviour of sodium chloride and sodium bicarbonate species with WAC resin where sodium ions in a sodium chloride solution had practically no affinity for WAC resin surface sites. In contrast, sodium ions from sodium bicarbonate solution readily exchanged with a WAC resin and this process was accompanied by evolution of carbon dioxide due to decomposition of the bicarbonate species. The SAC resin bed subsequently removed the majority of sodium ions remaining in solution [Figure 5].

Practically, the easiest means to monitor the IX progress was found to be recording the solution electrical conductivity on-line. Figure 6 shows the large increase in solution electrical conductivity due to release of highly conductive protons as sodium ions were concomitantly removed from solution using a SAC resin.

![Solution Conductivity](image)

Figure 6: Change in Solution Electrical Conductivity during Desalination Step with Strong Acid Cation Resin Bed for Sodium Removal from “Low TDS” CSG Water

The removal of chloride from the “Low TDS” CSG water was shown to be excellent as may be expected since acidic species such as “HCl” have a strong affinity for WBA resin exchange [Figure 7].

Figure 5: Performance of Strong Acid Cation Resin Bed for Sodium Removal from “Low TDS” CSG Water

![Chloride Concentration](image)

Figure 7: Performance of Weak Base Anion Resin Bed for Chloride Removal from “Low TDS” CSG Water

The breakthrough of chloride ions occurred at a smaller number of bed volumes relative to the SAC resin system and this reflected the lower

Figure 6: Change in Solution Electrical Conductivity during Desalination Step with Strong Acid Cation Resin Bed for Sodium Removal from “Low TDS” CSG Water
stated exchange capacity for WBA resin (1.3 eq/L) compared to SAC resin (2.0 eq/L). This observation has importance in terms of design of commercial IX units where there may be good capacity for cation uptake in the WAC and SAC resin beds but limited capacity for anion exchange in the corresponding anion resins. Consequently, it may be prudent to examine the use of anion resins with greater exchange capacity.

“High TDS” Synthetic CSG Water

The general performance trends observed in the treatment of “High TDS” CSG water were similar to those recorded for the “Low TDS” CSG water [c.f. Figures 4 & 8]. The main difference was the time to breakthrough of the sodium ions. With the “Low TDS” CSG water the breakthrough occurred after ca. 40 BV of water was passed through the SAC resin bed [Figure 5], whereas with the “High TDS” water sample the breakthrough time was reduced to ca. 20 BV [Figure 9]. This latter behaviour is in harmony with the inverse relationship between dissolved cation concentration and loading time for the resin.

“Real” CSG Water

Extensive tests were conducted with a “Real” CSG water which had a composition similar to the “Low TDS” sample illustrated above (Table 1). The amount of WAC resin loaded was increased to 75 L compared to the case for synthetic water where the resin volume was only 25 L. The increase in WAC resin quantity was in order to ensure that minimum bed depth of resin was present which in turn would improve IX performance. As a result the flow rates were 28.8 BV/h for the WAC resin and 21.6 BV/h for the SAC and WBA resins.

Notably, the resin bed configuration employed was still able to reduce the sodium ion concentration to <5 mg/L in the effluent water. Consequently, the resistance of the resin performance to system shocks such as increased feed concentration has been demonstrated.

Figure 10: Performance of Weak Acid Cation Resin Bed for Sodium Removal from “Real” CSG Water

The deeper WAC resin bed appeared to operate better than previously observed with shallower bed depths. Nevertheless, only sodium ions associated with bicarbonate were removed from solution [Figure 10]. Further exchange of residual sodium ions with the SAC resin reduced the sodium concentration to <5 mg/L, similar to the case with synthetic CSG water [Figure 11]. As expected from the lower concentration of sodium ions present compared to the “Low TDS” synthetic water sample, the breakthrough of sodium was extended to ca. 50 to 55 BV. Further information about the nature of the exchange process can be determined from Figures 12 & 13. Figure 12 shows that the potassium ions were also substantially removed using the sequential WAC & SAC resin beds. Furthermore, the potassium ions were completely removed at the point the sodium ions were breaking through into the effluent solution. This latter behaviour suggested that the selectivity for potassium ions was greater for these resins compared to sodium ions.
Similarly, the exchange of calcium using the cation resin beds was seen to be highly effective [Figure 13]. It was evident that calcium was strongly bound to the resin surface as ca. 0 mg/L eluted from the SAC column even when the sodium ions began breaking through. This observation was in accord with the general rule that multiple charged ions are preferentially exchanged rather than singly charged ions.

Again, examination of the solution electrical conductivity profile for the inlet and outlet streams of the SAC resin bed revealed an excellent correspondence to the degree of IX and ultimate loading time for the resin.

Notably, the experimental data suggested minimal difference between the behaviour of synthetic and “Real” CSG water samples. In practice, CSG water samples can contain algae, dissolved organic and particulate matter which may ultimately foul IX resins. However, during our studies the filtration and backflushing strategies used appeared sufficient to protect the resin media.

Regeneration of Resin Beds

Options are available for regeneration of the spent resin beds because of the use of a series of WAC and SAC resin beds in the pilot plant. Of particular interest is the sequential regeneration of cation resin beds by passing concentrated acid solution through the SAC resin bed and then passing the dilute effluent acid through the WAC resin bed in order to maximize efficiency [Figure 15].

Normally, SAC resin beds require flushing with excess acid to achieve effective levels of regeneration. The high affinity of the WAC resin for acidenables this resin to be regenerated with dilute acid effluent from the regenerating SAC resin beds. The sequential regeneration of SAC and WAC beds minimizes production of brine, overall acid consumption and IX operating costs.
Another issue with regeneration of cation resin beds is the choice of acid. In outback Queensland sulphuric acid is by far more cost effective acid regenerant compared to hydrochloric acid. However, sulphuric acid is known to cause problems in IX treatment processes due to the precipitation of calcium sulphate during regeneration processes, thus care needs to be taken to optimise sulphuric acid cation resin regeneration.

An experiment was conducted at bench scale to investigate calcium sulphate precipitation. A series of WAC & SAC resin beds was initially loaded with a synthetic “Low TDS” CSG water solution. Subsequently, the resin beds were concurrently regenerated with a 3 wt% solution of sulphuric acid and the contents of the regenerant solution analyzed as a function of volume used.

Figure 16 indicates that up to 20,000 mg/L sodium ions were present in the eluent of the SAC resin column regenerated with dilute sulphuric acid solution. Notably, while the acid regenerant was being consumed the solution electrical conductivity was low [Figure 17] and this parameter rapidly increased when regeneration was nearing completion excess acid exited the SAC resin column.

Passage of the regenerant solution from the exit of the SAC resin column to the WAC resin bed resulted in a further increase in the sodium ion concentration [Figure 18]. Consequently it could be deduced that the excess acid from the SAC column acted as an efficient regenerant of the WAC.

A sharp breakthrough of acid was observed at the end of the regeneration stage as evidenced in Figure 19 by the rapid increase in solution electrical conductivity.
CONCLUSION

A major driver for the CSG industry is to minimise CSG water treatment costs and the volume of brine produced. Ion exchange is potentially more efficient and cost-effective than standard RO treatment processes for CSG water up to 5000 mg/L TDS. The key operating cost driver of IX systems is chemical usage. Consequently, the use of a WAC resin bed prior to the SAC resin vessel appears to have merit as the capacity of the WAC resin is inherently higher than a SAC resin. Notably, the WAC resin also reduced the acid consumption required in the regeneration stage. Hence, both brine volume and chemical costs will be reduced when using a WAC-SAC-WBA resin bed combination compared to a SAC-WBA system.

ACKNOWLEDGMENT

Santos GLNG Sustainability provided financial support, supplied CSG water for research purposes and afforded QUT understanding of the CSG industry and its water treatment challenges. The support of the Institute for Future Environments at QUT has also been outstanding and we cannot thank enough all those whose hard work made the construction and operation of the IX plant possible. Lastly, we are grateful for the support we have had from the major global resin suppliers Lanxess and Purolite who have provided excellent advice and guidance to us.

REFERENCES


