



Final Report

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Prepared by: Paul Jensen
University of Queensland
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Evaluation of a Midell Water (now Arris Pty Ltd) Sodium Absorption Ratio Reduction System

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Executive Summary

This is the final report for project P.PIP.0330: Evaluation of a Midell Water (now Arris Pty Ltd) Sodium Absorption Ratio Reduction System. The project focused on reducing the SAR in the wastewater that is generated from the rendering process and fleshers and associated cleaning.

The final SAR reduction process included 3 steps: pre-treatment consisting of settling and filtration to remove organics from the wastewater; ion exchange using a Zeolite filter; and a separate regeneration process. The pilot facility contained 2 process trains, each consisting of a 22,000 L concrete tank operated as an up-flow filter. The 2 process trains operated in parallel with a common settling tank, pre-filter and 10,000 L regeneration tank.

The SAR reduction process was designed to operate with a 4 day service cycle and a 2 day regeneration cycle. While SAR was initially close to the target value of 7, the performance deteriorated rapidly during the service cycle, with SAR exceeding 15-20 within 24 hours after regeneration (approximately 6 BV flow). There was little evidence that sodium was removed in the ion exchange process and results indicated that any reductions in SAR were due to calcium and magnesium leaching out of the media bed after regeneration.

There were several factors contributing to poor performance of the full-scale process. Experimental analysis determined exchange capacity for the zeolite media in the process was much lower than the suppliers' literature indicated (approximately 50% of capacity specified). Competition for cation exchange sites from calcium and magnesium strongly reduces the practical capacity of the Zeolite column media for sodium removal. Therefore it was concluded that Zeolite-2 media is not likely to be effective at removing sodium from cattle hide processing wastewater and should not be used in this application. Strong acid cation resins, such as Amberlite AR-120 resin are much more effective at cation exchange for this application. However, treated effluent from this style of resin column is acidic due to the H⁺ being displaced from the resin media and requires post-treatment prior to discharge.

Biofouling was identified as a potential cause of poor sodium absorption and poor performance of the SAR reduction process. Cleaning trials in the laboratory and on-site failed were effective at removing organic material from the medium, but did not improve the ion exchange ability of the filter and therefore it was concluded that the organic matter in the wastewater was having little effect on the sodium removal.

Though the Zetos filter technology seemed promising for SAR reduction, particularly for coal seam gas wastewater, this project demonstrates that the technology is not appropriate for treatment of cattle hide processing wastewater and alternate technologies should be investigated.

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Glossary

| | |
|--------|--|
| Anion | A negatively charged molecule |
| AMPC | Australian Meat Processor Corporation |
| BOD | Biological Oxygen Demand |
| BSD | Balancing Storage Dam |
| BV | Bed Volume, the volume occupied by a media bed, including interstitial spaces |
| Ca | Calcium |
| Cation | A positively charged molecule |
| CBA | Cost Benefit Analysis |
| DEHP | Department of Environment and Heritage Protection |
| DERM | Department of Environment and Resource Management |
| ECEC | Effective Cation Exchange Capacity |
| ERA | Environmentally Relevant Activity |
| HRT | Hydraulic Residence Time |
| Mg | Magnesium |
| MLA | Meat and Livestock Australia |
| Na | Sodium |
| PP | polishing pond |
| SAC | Strong Acid Cation |
| SAR | Sodium Absorption Ratio |
| TEP | Transitional Environmental Program |
| TSS | Total Suspended Solids |
| VRWS | represents a volcanic vock filter medium |
| XRF | X-ray Fluorescence |
| YBR | represents a filter medium |
| Zetos | proprietary name for a cation exchange column designed and built by Arris Water and utilising volcanic rock as media |

1 Introduction

1.1 Background

Sodium adsorption ratio (SAR) is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water. In general, a higher SAR is less suitable for irrigation and long term irrigation using water with high SAR can result in the sodium in the water displacing calcium and magnesium in the soil. This may decrease the ability of the soil to form stable aggregates and cause a loss of soil structure and tilth. There are also risks of reduced soil permeability and problems with crop production. The formula for calculating sodium adsorption ratio is:

$$SAR = \frac{Na^+}{\sqrt{0.5(Ca^{2+} + Mg^{2+})}}$$

Where:

Na⁺ is sodium in meq/L;

Ca²⁺ is calcium in meq/L;

Mg²⁺ is magnesium in meq/L.

Traditionally chemical treatment methods have been used to adjust the SAR value of a wastewater. These include adding lime (calcium hydroxide), gypsum (calcium sulphate) or calcium chloride to reduce the SAR value. However, all of these treatments are based on increasing the levels of calcium to mask the effect of the sodium and do nothing to reduce the amount of sodium being irrigated to the pasture. Long term irrigation with high levels of sodium can damage soils therefore SAR reduction technologies that reduce sodium are required.

Volcanic rocks, such as zeolite and scoria, have been used for decades as ion exchange and ion adsorption filtration media in the water industry. Traditionally volcanic rock filtration media have been used for either water softening or nitrogen reduction. However, it is well established that certain volcanic rocks such as zeolites can exchange certain cations out of water. In terms of SAR reduction, an ion exchange process could reduce sodium in the wastewater by absorbing the cations onto a filter medium, at the same time calcium and magnesium in the filter medium could desorb into the water stream. This process would reduce SAR in 2 ways, first by reducing sodium concentration, second by increasing calcium and magnesium to mask the effect of any residual sodium.

1.2 SAR technology

The system proposed by Midell Water was designed to remove sodium from the wastewater via ionic exchange rather than mask the effects of sodium, and is therefore designed to address the key issue within the wastewater quality. The Midell Water system has been used successfully in many different industries within Australia for SAR reduction including the Coal Seam Gas industry.

Reported advantages of the Midell Water approach over other chemical treatments are as follows:

- Sodium is removed giving a much more environmentally desirable outcome with long term sustainability for irrigation of the wastewater by reducing the level of chlorides.
- The filters have the flexibility to handle fluctuating sodium levels in the waste steam, which is difficult with chemical addition systems.
- The approach is beneficial in complying with objectives of the TEP and will reduce the need to add agricultural lime/gypsum to the soils to control SAR.
- The system does not require large quantities of chemical to be added on a daily basis hence reducing ongoing operational costs.

1.3 Project Objectives

- Demonstrate the ability of the Midell Water system to remove the Sodium ions from the wastewater.
- Demonstrate the benefits of the system in particular achieving compliance with the Environmental Licence conditions and in turn the ability to irrigate higher volumes of water.
- Demonstrate the reduced ongoing operation costs with this technology.
- Demonstrate by chemical analysis the sustained removal of sodium ions and replacement with Calcium and Magnesium ions.
- Cost-benefit analysis of adopting the Midell Water system at plant level.

2 Overall Process Design

2.1 Existing Treatment Train

The up-stream wastewater treatment train at the time of the project is summarised in Figure 1. Wastewater from the hide processing plant is first treated in an aerobic lagoon to stabilise organic contaminants. Solids are then separated from the treated wastewater using a clarifier, the solids stream is separated and thickened further in a secondary clarifier; the thickened solids are then dewatered in a belt press and are added to a mixed compost stream. Clarified water is transferred to the polishing pond (PP) and then on to the balancing storage dam (BSD). In this project, the SAR reduction process would be applied to water exiting the polishing pond.

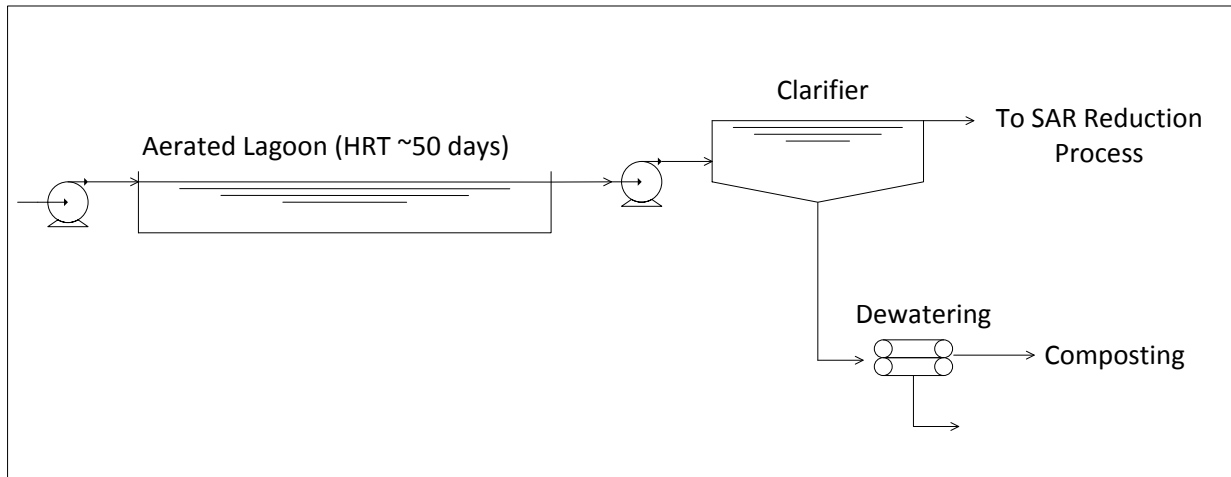


Figure 1: Process flow diagram of upstream wastewater treatment process at SAR demonstration site

2.2 Design Summary

The SAR reduction process was designed around a single stage Zeolite filter, with a separate regeneration process. The pilot facility contained 2 process trains, each consisting of a 22,000 L concrete tank operated as an up-flow filter. The 2 process trains operated in parallel with a common 10,000 L re-generation tank, as shown in Figure 2. The plant was designed to treat approximately 60,000 L of wastewater per day, therefore the treatment volume through each tank was approximately 30,000 L per day and was equal is approximately 6 bed volumes (volume of media filter bed).

The operational cycle was four days of service flow followed by a regeneration cycle. Regeneration involved draining the bed, filling with a concentrated calcium and magnesium chloride solution, left standing for the weekend and draining of the spent regeneration solution. After this, service flow was resumed.

The plant was installed in May 2012 (Figure 3) to treat wastewater after removal of organic contaminants in an aerobic lagoon and subsequent sludge removal in a clarifier. Treated effluent from the SAR reduction process was discharged to a holding lagoon prior to irrigation.

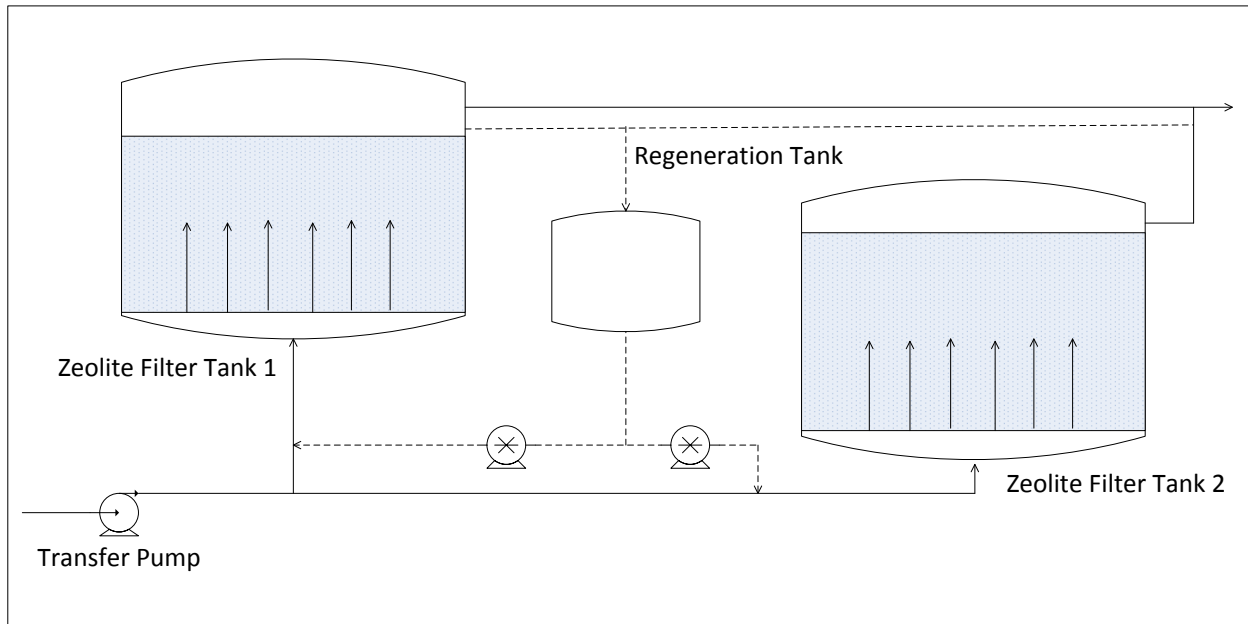


Figure 2: Process flow diagram of SAR pilot plant installed at an Australian Meat Processing Facility



Figure 3: SAR Process installed on site in 2012

2.3 Filter Media Selection

Filter media selection focused on natural zeolites that have a cation exchange affinity for sodium and which in turn reduce SAR. Previous work by Midell Water has reported a number of volcanic filtration media to be effective at reducing the SAR in coal seam gas wastewater, as shown in Figure 4; in these trials the best performing volcanic media

reduced the SAR of raw coal seam gas wastewater from approximately 100 down to approximately 6. Subsequent research by Midell Water demonstrated that a combination of volcanic media has a cumulative treatment benefit and reduces the SAR even further, shown in Figure 5. In Figure 5 wastewater was treated using VRWS, followed by a VRWS-YBS media blend, this media combination was able to reduce the SAR from approximately 200 down to approximately 4.

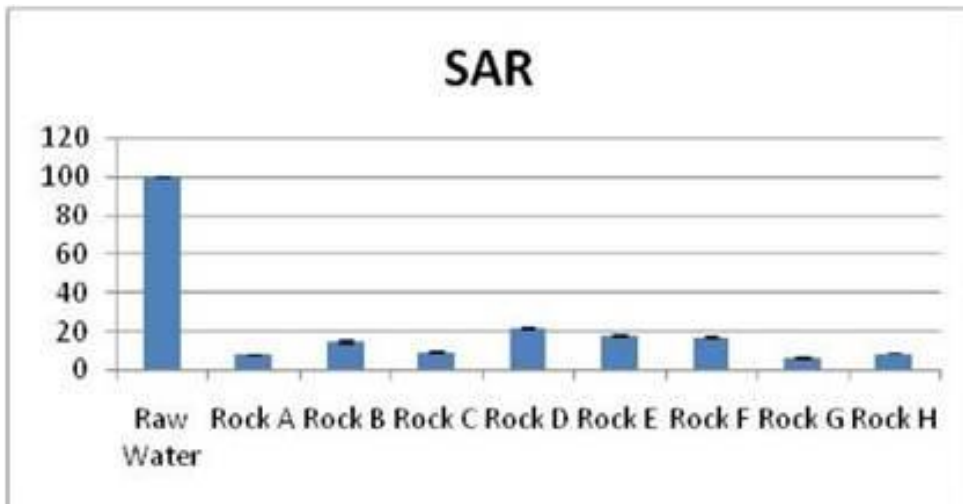


Figure 4: Single volcanic media SAR reduction

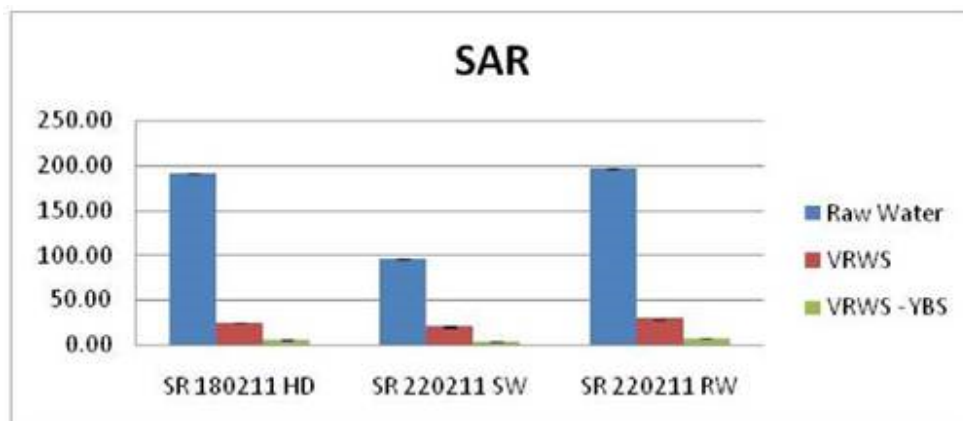


Figure 5: Multiple volcanic media SAR reduction

Volcanic media reduces the SAR by cation exchange. During the cation exchange, sodium ions in the raw wastewater are replaced by calcium and magnesium ions from within the media. The reduction in sodium concentration and the increase in calcium and magnesium concentrations levels have the combined effect of significantly decreasing SAR. Volcanic media was selected for this project as a cost effective and sustainable technique for reducing SAR, this was based on demonstrated performance treating coal seam gas water and the recommendations of Midell Water and Central Queensland University.

2.4 Zeolite Filter Tanks

Installation of the tanks and filter media was completed by Midell Water. Each Zetos filter tank consisted of a 22,000 L concrete tank, configured as an up-flow filter. Each tank contained approximately 18 tonnes of filter media in 3 layers (Scoria, Zeolite-1 and Zeolite-2). Each filter tank contained internal PVC pipework to improve distribution of

wastewater throughout the filter media. The internal pipe-work shown in Figure 6 and Figure 7 consisted of a grid arrangement on the tank base and contained numerous holes drilled into the PVC. Once the filter media was in place, the pipe-work was connected and the media flushed with clean water. During operation, the tanks filled from the bottom with wastewater and overflowed from the top. During regeneration, concentrated regeneration media could be added through both the top and bottom of the tank.

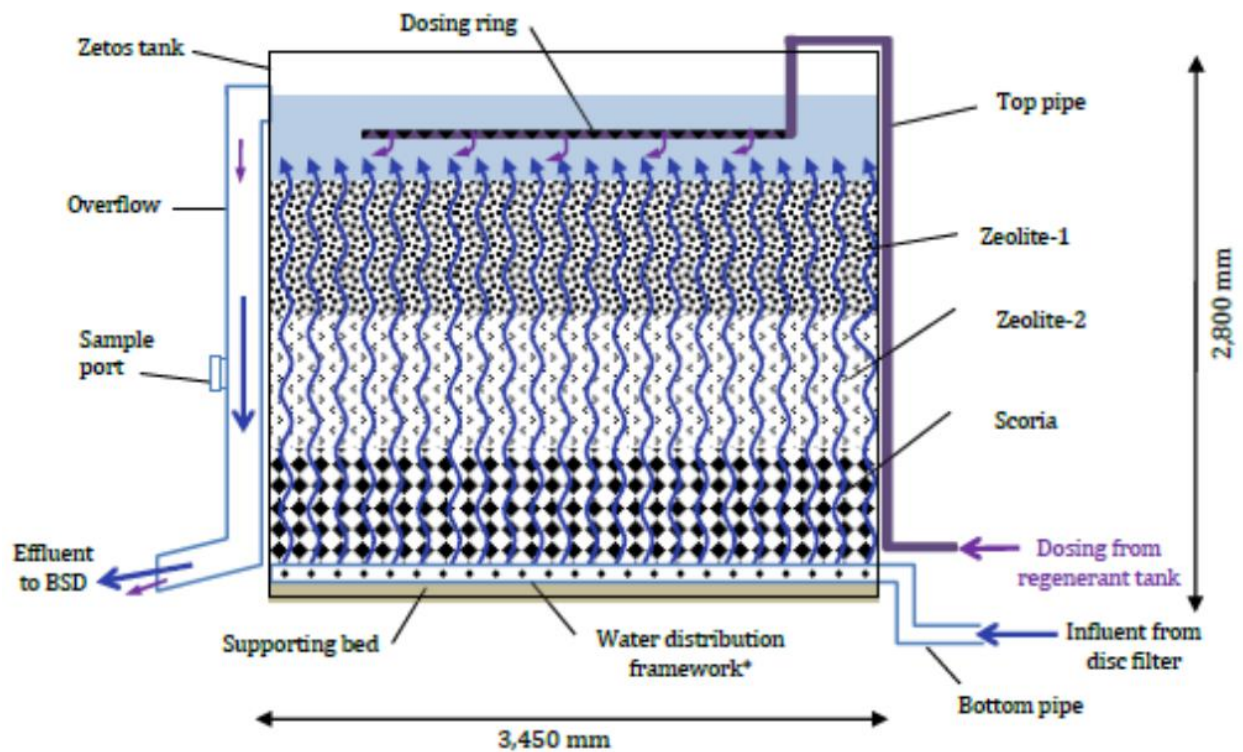


Figure 6: Design of Zeolite filter tanks installed as part of SAR reduction process, tanks included 3 filter media and internal pipework to distribute wastewater flow (Kodel 2013)



Figure 7: Internal arrangement of distribution pipe-work

2.5 Regeneration Tanks

A 10,000 L tank was installed and operated as a regeneration tank for the zeolite filter media (Figure 8). The Zeolite media is designed to reduce SAR by ion exchange, where the media accumulates sodium ions, at the same time calcium and magnesium ions are depleted. Regeneration is used to replenish calcium and magnesium ions in the zeolite media and is achieved by draining the filter tanks and filling them with a solution of concentrated calcium and magnesium compounds. During the regeneration cycle, the ion exchange process works in 'reverse'.

The regeneration compounds, concentrations, intervals and duration are design variables that will be investigated during the project. The effects of the organic loading on the filter material and ion exchange rate will also be subject to ongoing research during the project duration.



Figure 8: Filter Tanks with Regeneration tank in foreground

3 Processing Performance

3.1 Collection of Baseline Data

The composition of wastewater entering the holding lagoon was measured for a period of 18 months prior to installation of the SAR reduction plant to establish a baseline wastewater composition and benchmark performance of the SAR reduction process. The water quality parameters measured included total nitrogen, total phosphorus, biochemical oxygen demand (BOD), total suspended solids, key cations and sodium adsorption ratio (SAR). A summary of cation concentrations and SAR is shown in Figure 9, additional composition data is included in Appendix 1. Prior to collection, this wastewater was treated in an aerated lagoon to remove organic contaminants and a clarifier to reduce TSS.

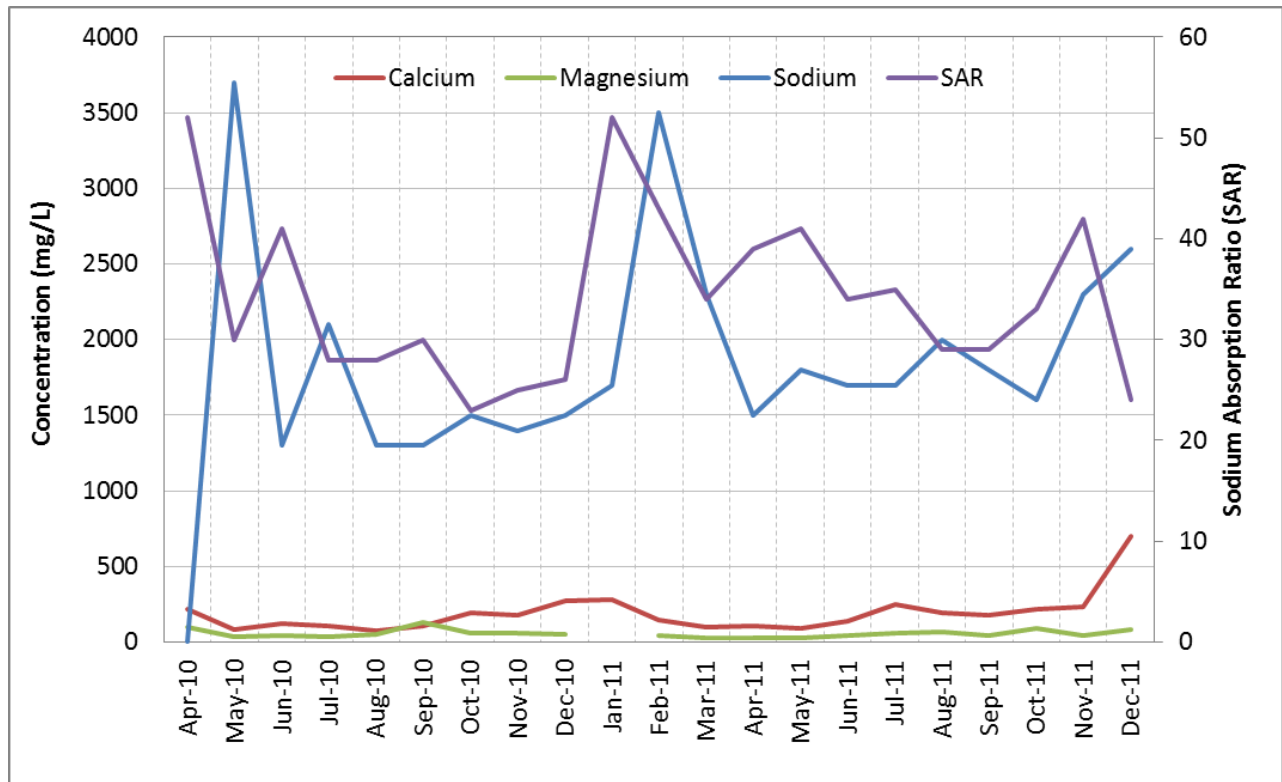


Figure 9: Baseline wastewater concentration prior to installation of the SAR reduction process

3.2 Plant Performance

3.2.1 Sodium Absorption Ratio Reduction

The standard operational cycle for the filter tanks was four days of service flow followed by a regeneration cycle. Regeneration involved draining the bed and filling with a concentrated calcium and magnesium chloride solution which was left standing for 2 days (typically over the weekend). After regeneration was complete, the spent regeneration solution was drained and normal service resumed.

Figure 10 and Figure 11 show example data from operation of the Zetos filters over 4 day service cycles. The results show that, while SAR was initially close to target value of 7, the performance deteriorated rapidly during the service cycle. In October 2012, the SAR exceeded 18 within 1 hour after regeneration and exceeded 25 within 24 hours after regeneration (approximately 6 BV flow). Between October 2012 and February the SAR reduction plant received several major upgrades including a pre-settling tank and pre-filter screens for organic solids removal (described in Section 4.1), however process performance was still below expectations. In February 2013, the SAR exceeded 10 within hours after regeneration and exceeded 15 within 24 hours after regeneration.

In October 2012, there was no significant reduction in sodium ions through the Zetos filters. In February 2013, there was a minor reduction of approximately 5 meq/L (115 mg/L) during the first three days, however the sodium concentration increased in the later stages of the service cycle. Most importantly, calcium and magnesium concentrations in the effluent were significantly higher than baseline concentrations, particularly in the first 3 days of the service cycle and this indicates that SAR reduction was influenced by calcium

and magnesium leaching out of the media bed after regeneration, and not removal of sodium ions.

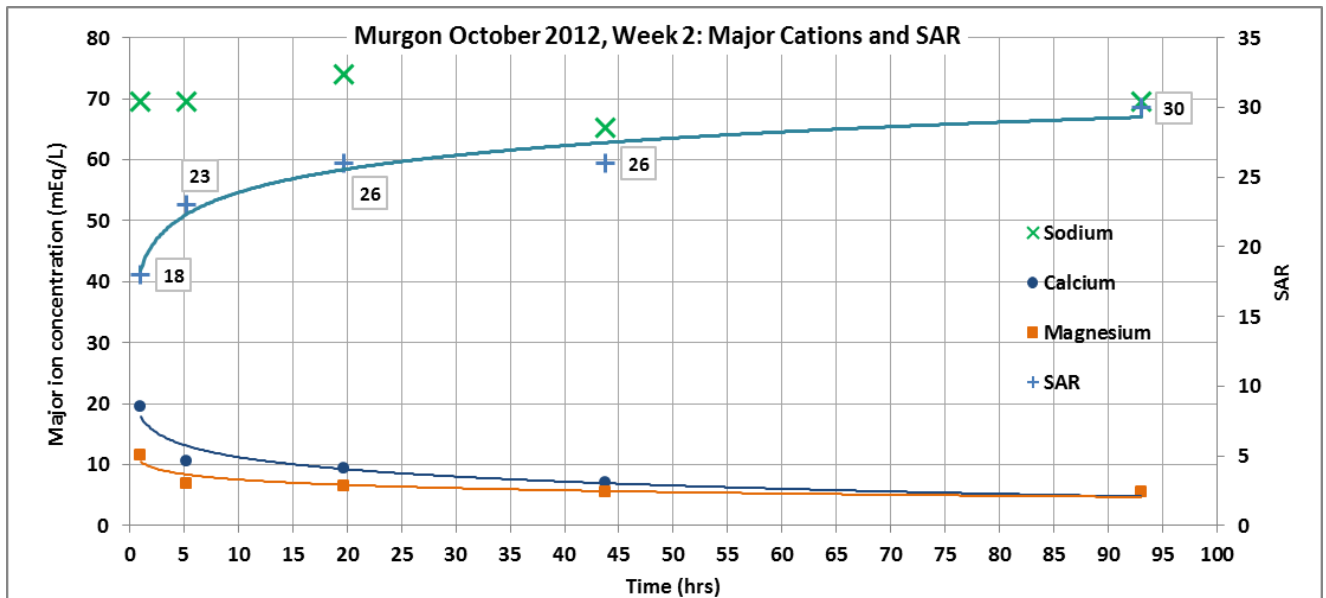


Figure 10: Major cations and SAR measured in the effluent from the Zetos filters in October 2012.

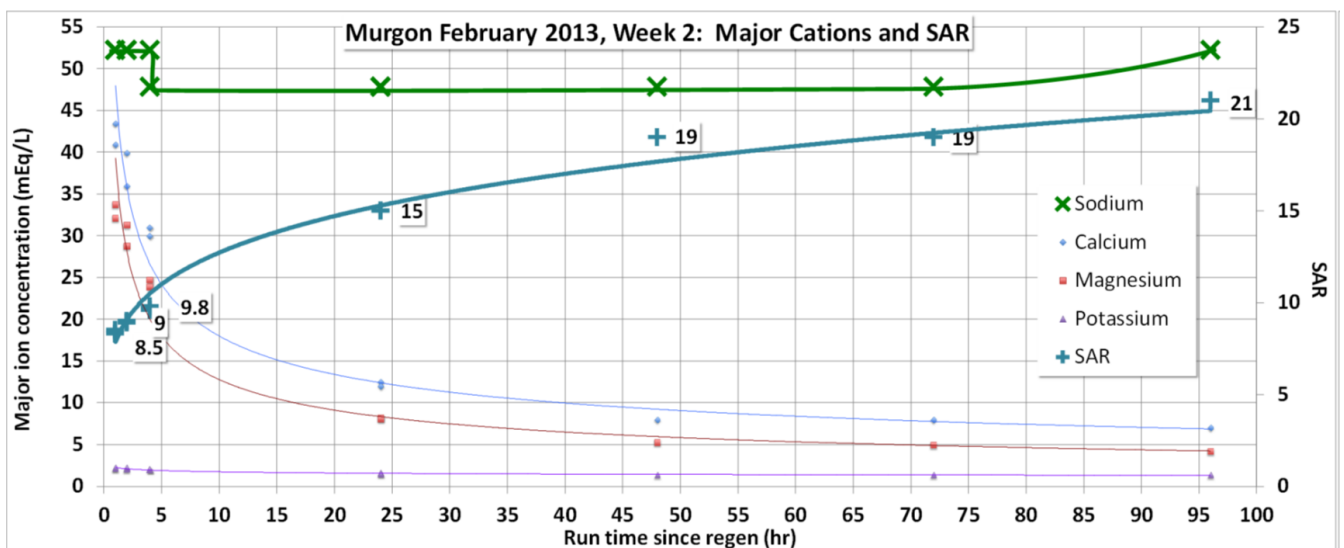


Figure 11: Major cations and SAR measured in the effluent from the Zetos filters in February 2013.

Comparisons of Figure 10 and Figure 11 demonstrate minor improvements in 2013 compared to 2012, however the process was not achieving performance targets (SAR target is approximately 7); and comprehensive testing of the wastewater before and after the filter did not identify any chemical components of the wastewater that were being regularly removed in the Zetos tank. Proposed explanations for the poor performance included:

- Limited forward exchange capacity,
- Poor regeneration,
- Biofilm accumulation,
- Biofouling (iron sulphide deposition) and
- Inorganic fouling (carbonate precipitation).

3.2.2 Ion exchange capacity.

The effective cation exchange capacity (ECEC) of a medium is defined as the total sum of exchangeable cations that it can adsorb under specific conditions (such as pH). In terms of the SAR reduction process, the ECEC is an important parameter represents the capacity of the Zetos media to absorb sodium and exchange for calcium and/or magnesium. The ECEC of each component of the filter tank media was determined by ammonium desorption, the results are presented in Figure 12.

The results are from a multifactorial experiment comparing granular and powdered media and flask or bottle agitation. The powdered media had a higher ECEC in all cases, however, the porosity of the rocks meant that there was only a small increase. Of the granular media, Zeolite-2 had the highest ECEC at 60 meq/100g. Granular Zeolite-1 had the largest cation exchange capacity not already utilised by sodium at 41 meq/100g. Most significantly, the experimental determined exchange capacity for the zeolites was much lower than the suppliers' literature indicated (approximately 50% of capacity specified), this limited exchange capacity likely contributed to poor performance of the Zetos filters:

- Zeolite-1 (powder): Experiment = 63 meq/100g, Supplier literature = 120 meq/100g.
- Zeolite-2 (powder): Experiment = 85 meq/100g, Supplier literature = 148 meq/100g.

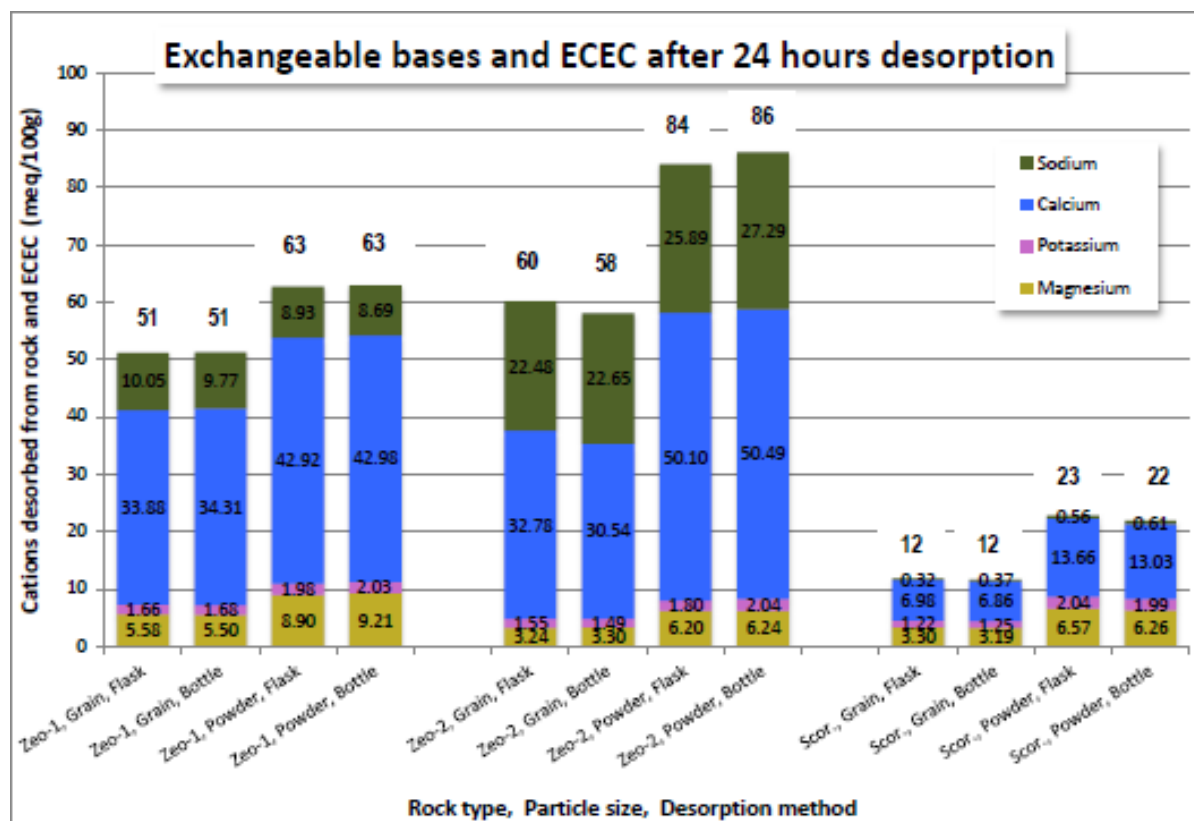


Figure 12: Effective cation exchange capacity (ECEC) and exchangeable cations as determined by 24 h desorption in ammonium chloride solution.

3.2.3 Regeneration Effectiveness

The Zetos filters were subjected to a weekly regeneration cycle using a strong calcium and magnesium salt solution, which was added to the filter tanks and allowed to stand for 2-3 days. The aim of regeneration was to displace sodium absorbed on the filter media during the service period in exchange for calcium and magnesium from the regenerant solution. The level of regeneration could be estimated by the change in sodium concentration in the spent regenerant solution. Several regeneration solutions were trialled throughout the project, including:

- 150 kg calcium chloride and 50 kg magnesium chloride;
- 225 kg calcium chloride and 75 kg magnesium chloride, pH 3;
- 300 kg calcium chloride, pH 3;
- 300 kg magnesium chloride, pH 3;

Figure 13 represents an averaged result from regeneration cycles between October 2012 and March 2013. The effect of mixing with residual service water was included in the analysis. During regeneration, the following changes were observed in the regenerant solution:

- Calcium reduced by 165 meq/L;
- Magnesium reduced by 59 meq/L;
- Sodium increased by 77 meq/L.

The results show that calcium and magnesium consumed by regeneration was significantly higher than sodium released. When examining earlier regeneration cycles from September 2012, less calcium and magnesium was consumed, however the amount of sodium stripped from the media did not change (Figure 14). This suggests that the forward exchange process is only permitting a small concentration of sodium to be trapped on the media each service cycle, therefore the forward exchange capacity was identified for troubleshooting and research into process improvement.

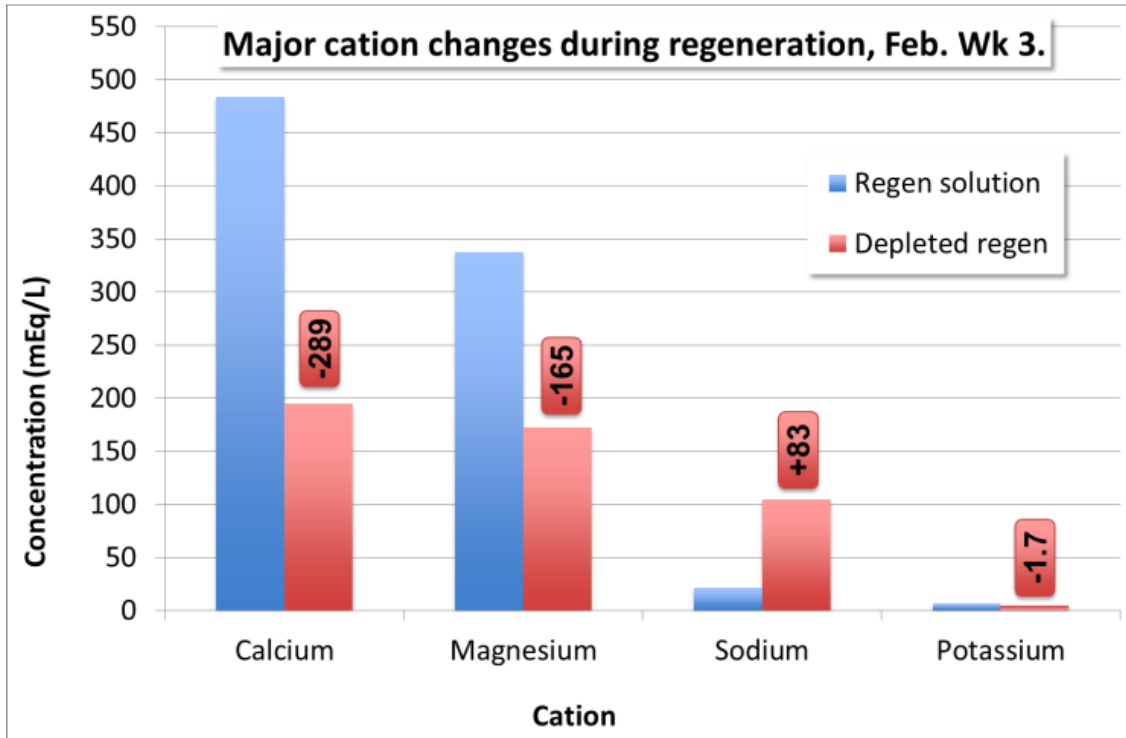


Figure 13: The major cation concentrations are shown for the virgin regenerant solution (blue) and the spent solution (red). The label above the red columns shows the change in concentration of each cation. Calcium and magnesium were depleted in the solution by 454 meq/L. However, only enough sodium was desorbed into solution to raise the concentration by 83 meq/L.

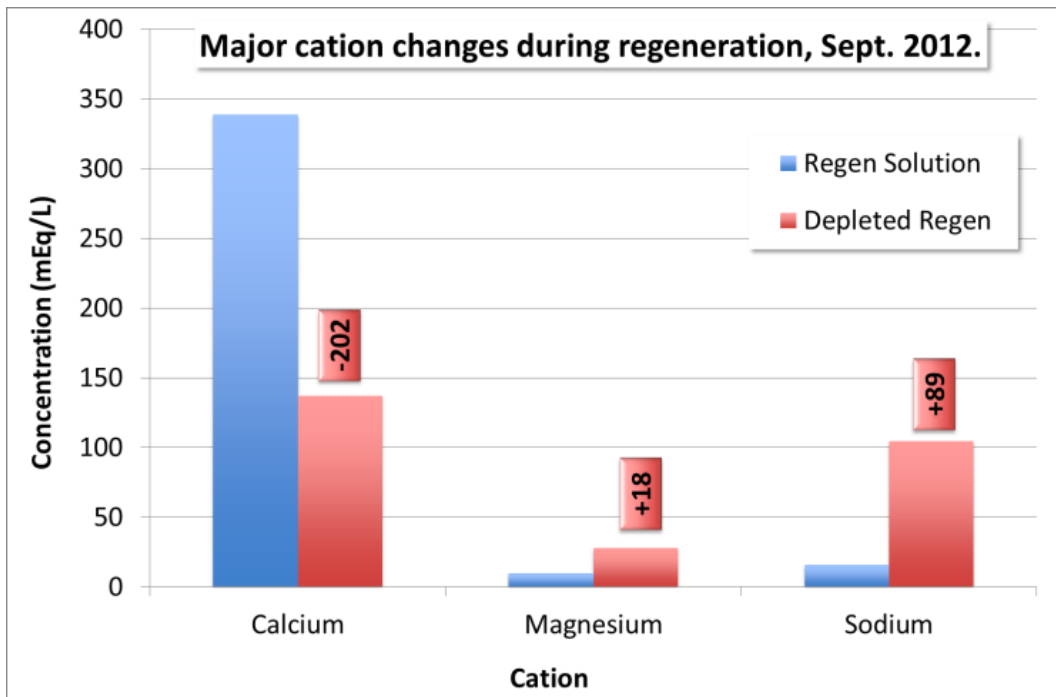


Figure 14: The earliest Zetos filter regeneration cycle for which samples were taken. Note that the concentration of the regenerant calcium at the start of the cycle was much lower than the calcium and magnesium concentration later cycles.

3.2.4 Biofouling

During operation there were significant variations in flow rates that were believed to be caused by the build-up of organic material from the wastewater depositing on the filter media and restricting flow. Core sampling of the media through its complete depth confirmed that there were considerable amounts organic material held within the filter, and not released during regeneration

Examination of Zetos media collected from the process showed evidence of black fouling (Figure 15), chemical and x-ray fluorescence (XRF) examination of the black fouling deposit indicated that the fouling contains iron sulphide. Individual grains were split and revealed that the biofouling has impregnated into the rock (Figure 15). Under the conditions in the Zetos filters, sulphate reduction by bacteria is the only mechanism that can cause iron sulphide deposition, therefore fouling must have been the result of anaerobic microbial activity.

Table 1: Selected results of surface XRF analysis of Zetos media.

| Element | Units | Virgin Media | Bio-fouled Media |
|---------|-------|--------------|------------------|
| Si | mg/kg | 49,300 | - |
| Al | mg/kg | 2,617 | 689 |
| Fe | mg/kg | 6,165 | 7,632 |
| S | mg/kg | 1 | 191 |



Figure 15: Iron sulphide deposition on media obtained from the Zetos filters.

A lab-scale column experiment was set up to replicate similar conditions of the full-scale process and study bio-fouling, the lab-scale experiment contained molasses as an additional carbon source. Microscopic examination of biofilm from this lab-scale column is shown in Figure 16. The morphology of the bacteria was consistent with *Desulfovibrio* sp. which is within a known sulphate reducing genus. Investigations into biofouling indicate that this is a possible cause for poor sodium absorption and poor performance of the SAR reduction process. However, cleaning trials in the laboratory and on site failed to improve the ion exchange ability of the media.

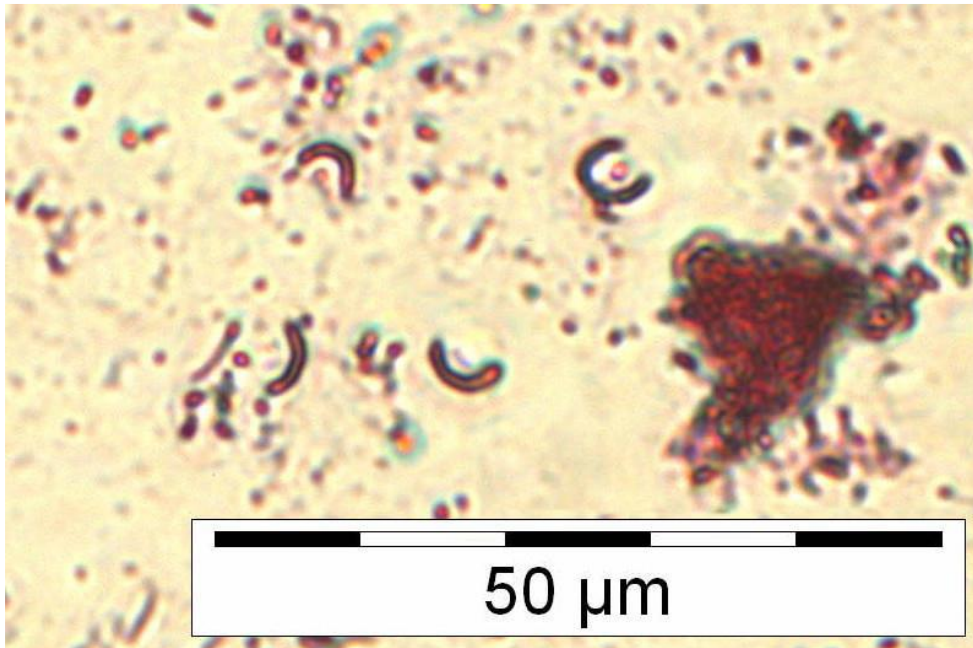


Figure 16: Composite photomicrograph of biofilm taken from an experimental column. The column was fed with PP water which was fortified with molasses as a carbon source. Morphologically, the bacteria are consistent with *Desulfovibrio* sp. which is within a known sulphate reducing genus.

4 Process Troubleshooting and Optimization

4.1 Volumetric Flowrate

The SAR process was originally operated with a single pump to transfer material through the filters and into the storage lagoon. However, from June 2012 to September 2012 there were significant operational issues with maintaining consistent flow rates through the two Zetos filter tanks. Specifically, flow through each tank was not equal and was variable. Variations in flow rates were believed to be caused by the build-up of organic material from the wastewater depositing on the filter media and restricting flow. As there was only a single pump feeding both tanks, restrictions from the build-up of organic material caused differential flow rates between the tanks. The organic matter is also believed to have created preferential flow pathways through the media; this short circuiting effect further reduced poor performance for removal of SAR.

4.1.1 Compressed Air

Compressed air was installed to blast each tank on a regular basis to remove any accumulated organic matter and therefore minimise flow restrictions and/or blockages. Although this was successful for short periods of time (approximately 1 hour), this was not a long term solution.

4.1.2 Installation of Settling Tank, Pre-filter and Flow Control Valves

A coarse screen filter (Figure 17) was installed in the feed line prior to the Zetos tanks in November 2012; this screen system was designed to remove larger suspended solids prior to entering the filter tanks. Again, the coarse screen was initially effective however flow rates declined and flow variability increased over time. Laboratory testing on wastewater before and after Zetos filter tanks confirmed that suspended solids were still being removed by the filter media. A finer mesh screen was trialled; however the fine mesh blocked rapidly and required manual cleaning multiple times per day. The operator input to maintain the fine mesh was not manageable; therefore a coarser mesh was reinstalled.

A settling tank (Figure 17) was installed prior to the Zetos tanks to remove as much as possible of the suspended solids prior to treatment. During installation of the settling tank, the Zetos feed system was changed and an independent pump and filter installed for each Zetos tank (Figure 18). Control of flowrates was significantly improved after installation of the filters and independent pumps. However no improvement on SAR performance was observed. Subsequent laboratory trials demonstrated that the rate of ionic exchange on the resin is not impacted until the flow rate exceeds 150,000 L per tank per day, which is double the design specification.



Figure 17: Pre-filter, Flow Control Valves and Power Control Systems installed November 2012



Figure 18: Settling Tank installed January 2013

4.2 Filter Media Cleaning

Analysis of filter media from the Zetos filters showed that the resin contained biofouling and a relatively high iron content, which may have been contributing to poor performance. Two media washing methods, using either hydrochloric acid or hydrogen peroxide were trialled as a technique to clean the medium and improve performance. The washing procedure is described in Appendix 2.

The impact of washing with hydrochloric acid at different concentrations is shown in Figure 19. Based on visual inspections, the media retained some fouling, even at high acidity, pH values of 0 – 1. There was also a characteristic odour of H_2S that remained after the rinsing, regeneration and sodium adsorption steps. Odour was strongest for the more acidic treatments and this suggests that FeS was being consumed in the reaction. However, it should also be noted that the level of acidity used in the more concentrated cleaning trials (1 N and 0.5 N) was much higher than would likely be used at full-scale. At full-scale, the cleaning protocol would likely use 0.001N HCl for treatment, and would be ineffective based on the lab-scale trials.

The impact of washing with hydrogen peroxide at different concentrations is shown in Figure 20. Based on visual inspections, cleaning was effective at 5% H_2O_2 , the lowest concentration tested. Therefore follow up analysis at lower concentrations (1–5%) would be recommended to determine the most cost effective and safest concentration to use. Cleaning with hydrogen peroxide will release O_2 during to decomposition reactions in the cleaning process. The quantity of O_2 gas released may create problems from expansion of the media bed. However, it may be possible to mitigate this risk by disrupting the media (e.g. with air blasts) to release the O_2 or by minimising the hydrogen peroxide dose. Minimising the hydrogen peroxide dose would have additional benefits such as reducing chemical consumption costs.

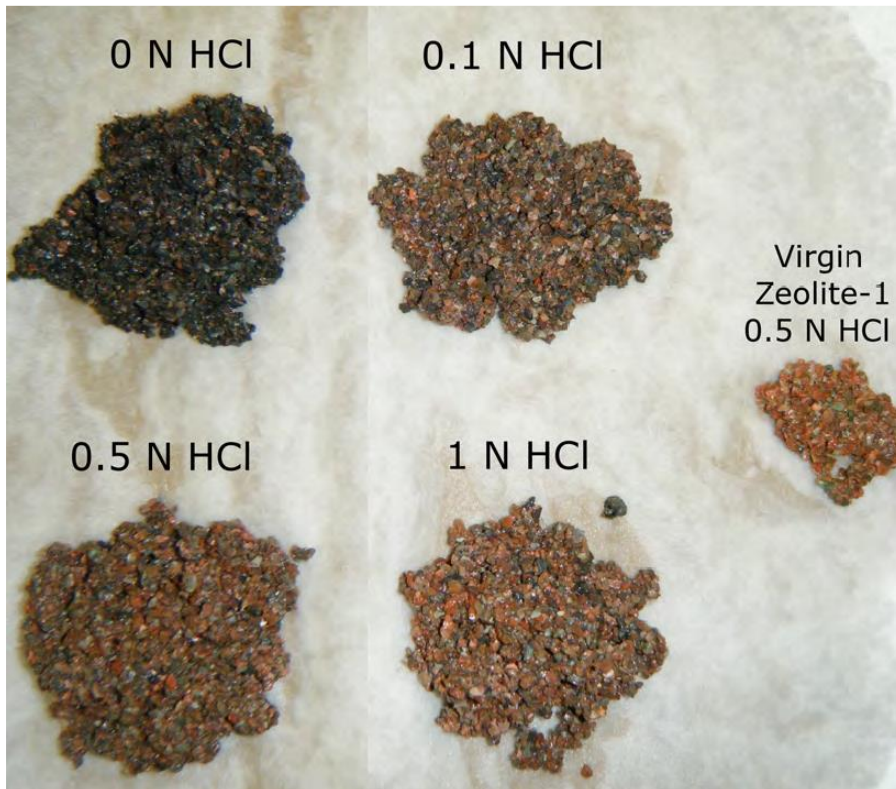


Figure 19: Results from washing fouled media from the Zetos filter tanks with HCl

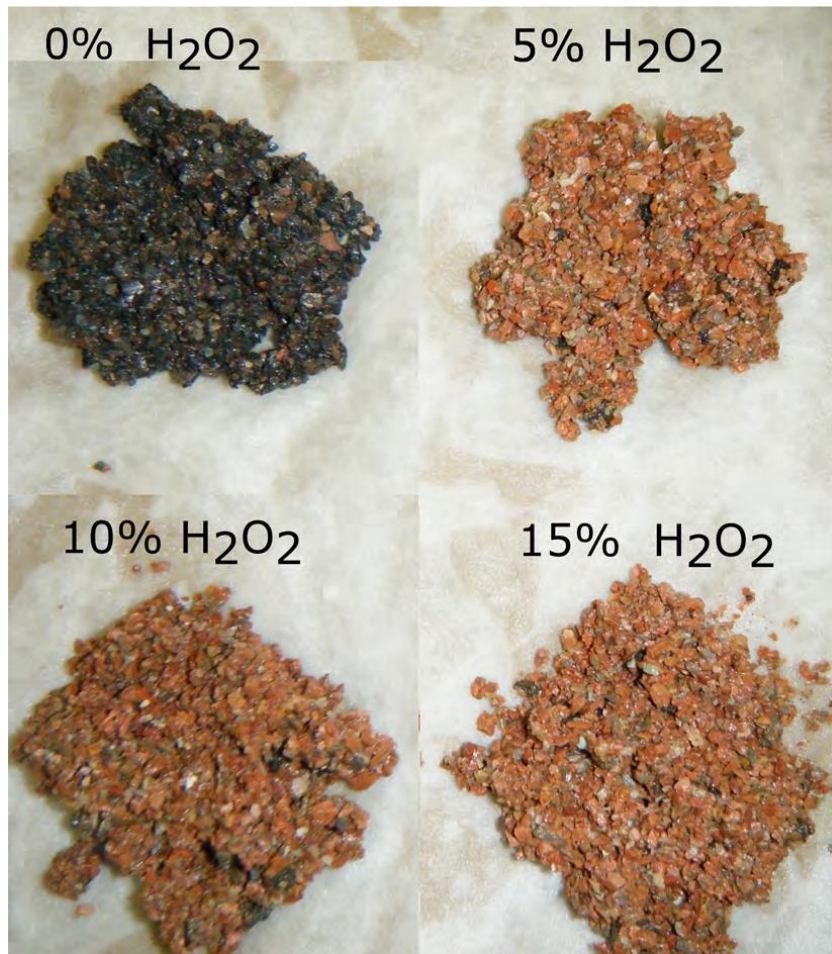


Figure 20: Results from washing fouled media from the Zetos filter tanks with H₂O₂

Based on the results above, hydrogen peroxide was identified as the more effective method of cleaning the filter media. The cleaning method was applied to one filter tank at full-scale however there was very little change in performance between the dirty and clean filter. Therefore, there remains no clear evidence if biofouling was a key issue that was reducing filter performance.

4.3 Chemical Dosing

The full-scale SAR reduction process was not operating effectively and the performance was not significantly improved by troubleshooting methods described in Section 4. Therefore, SAR was reduced via chemical dosing. Chemical dosing involved addition of magnesium sulphate to the discharge stream from the Zetos filter, however this method reduced SAR by increasing magnesium, not by removing sodium; and based on agronomist advice, this method is short term solution only, due to the adverse long term effect on the pasture of the magnesium sulphate added to the irrigation water.

5 Laboratory Experiments for Process Optimisation

The results in Section 3 and Section 4 of this report clearly demonstrate that the full-scale SAR reduction process, using zetos filter medium, did not meet performance expectations.

Therefore, a pilot plant was set up at Central Queensland University to mimic the Zetos plant, assess if the poor performance was repeatable, identify the reasons for poor performance and examine strategies to improve the plant.

5.1 Impact of Organic Contaminants

Acid wash of the filter media resulted in a high removal of organic matter and a short term improvement in SAR reduction performance, this suggested organic material may be reduced filter performance. To test this theory, a synthetic solution was made which contained the same level of cations as the actual process wastewater but without the organic contaminants. The rate of sodium removal did not change when compared to process wastewater containing the organic matter. Therefore it was concluded that the organic matter in the wastewater is having little effect on the sodium removal.

5.2 Age of Filter Media

Virgin Resins, with no prior usage, were compared with the used resins from the Zetos filters installed in the SAR reduction process. The comparison used process wastewater and a similar sodium removal pattern was found for both the virgin and used resins. This suggested that the used filter resin has not become fouled during operation or that the fouling did not impact media performance. The rate of sodium removal by the virgin resin was much lower than the expected rate based on manufacturer specifications for the resin. This was also observed for the used resins as demonstrated in Section 3.2.2.

5.3 Impact of Major Cation Ratios in Wastewater

The impact of major cation concentration in the wastewater on sodium removal was investigated using an array of column experiments. Figure 21 shows experiments using a fixed concentration of Ca and Mg (15 meq/L and typical of the BSD water). The influent sodium concentration was varied between experiments, from 25 to 100 meq/L. As expected, sodium sorption increased as sodium concentration increased.

Figure 22 shows experiments using a fixed sodium concentration (80 meq/L and typical of the BSD water). The influent concentration of Ca and Mg was varied between experiments, from 0 and 25 meq/L. The results show that at 0 meq/L (i.e. no competing calcium or magnesium) sodium sorption rate continued to be high up to 25 BV. However, at any concentration of calcium and magnesium (i.e. 2, 15 or 25 meq/L), sodium sorption was limited. These results demonstrate that competition for exchange sites from calcium and magnesium reduces the practical capacity of the column media for sodium. Most cation exchangers have a low affinity for sodium. As such, other competing cations like potassium or ammonium will most likely also inhibit sodium uptake. Based on these results, Zeolite 2 media is not likely to be effective at removing sodium from cattle hide processing wastewater and should not be used in this application.

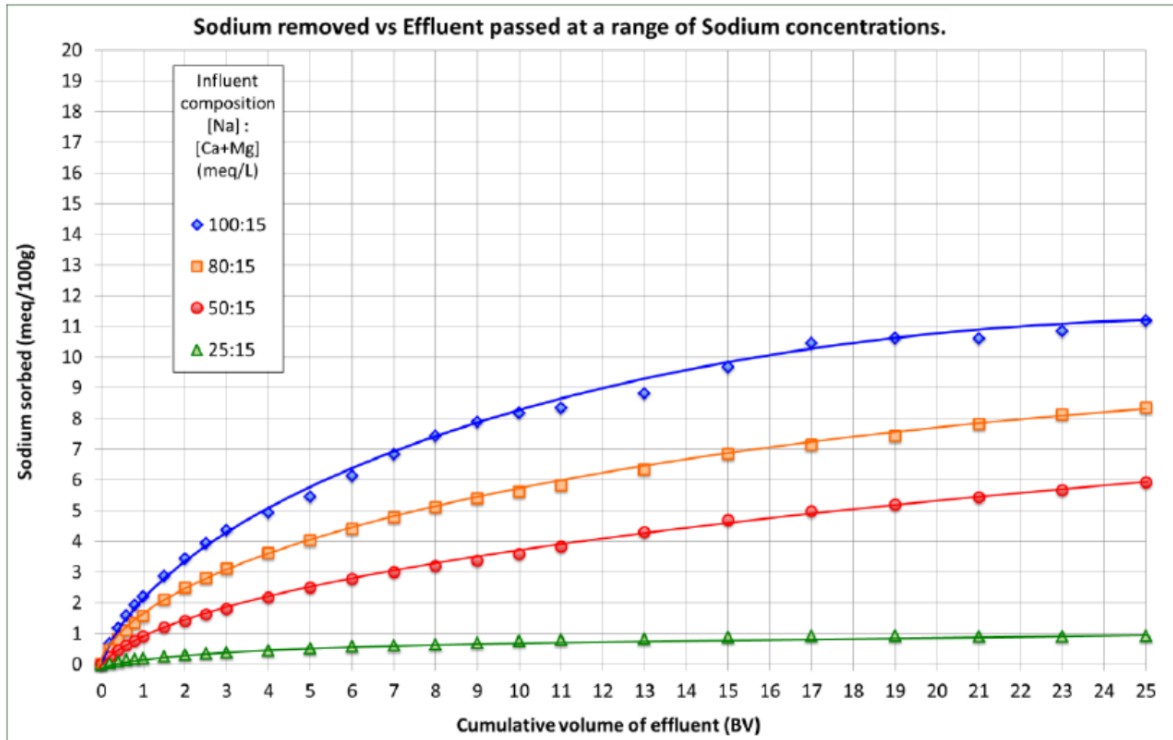


Figure 21: Sodium removal by Zeolite 2 in column experiments. Each column had the same calcium + magnesium concentration (15 meq/L which is typical of the BSD water). The influent sodium concentration was varied, between treatments, from 25 to 100 meq/L. As expected, sodium sorption increases as sodium concentration increases.

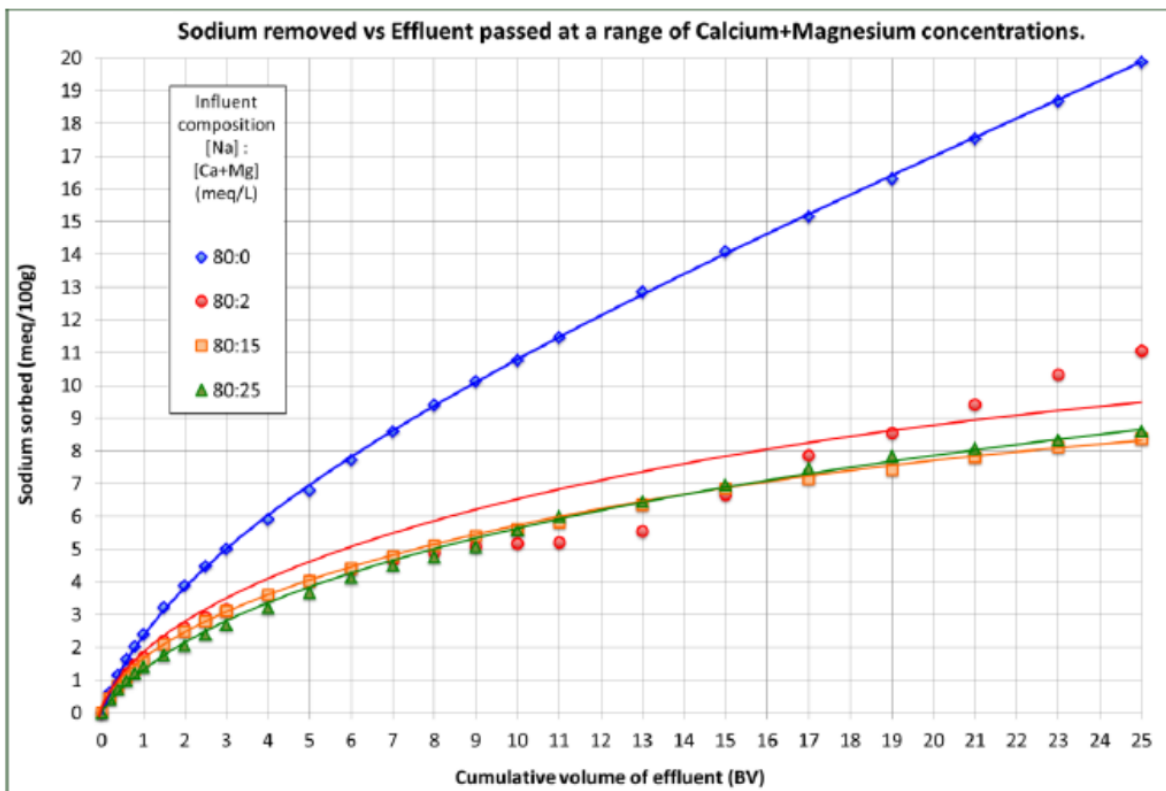


Figure 22: Sodium removed by Zeolite 2 in column experiments. Each column had an influent sodium concentration of 80 meq/L which was typical of the BSD water. The calcium + magnesium influent concentration was varied between 0 and 25 meq/L. At any concentration of calcium + magnesium (i.e. 2, 15 or 25 meq/L), sodium sorption was limited. However, at 0 meq/L (i.e. no competing calcium or magnesium) sodium sorption rate continued to be high up to 25 BV.

5.4 Impact of Filter Media – Zeolite-2 Compared to Amberlite IR-120 Resin

Based on the findings in Section 5.3 the project investigated an alternative type of resin; one that was acidic and contained hydrogen ions for the exchange process. The hydrogen ions are much more readily exchangeable with the sodium ion than the calcium and magnesium ions in the Zetos resins. However it is expected that this type of resin will be less selective and remove all major cations Calcium, Magnesium, Potassium and Sodium and therefore the overall impact on SAR required investigation.

Investigations were conducted using a lab-scale small column apparatus, shown in Figure 23. Zeolite-2 was the commercial resin used to represent the Zetos process; because of the experimental scale, a finer grain zeolite (355 – 600 μm) was used. Amberlite IR-120 was selected for comparison because it is a well characterised strong acid cation (SAC) resin available in H^+ form. Both media were pre-treated by flushing the column with hydrochloric acid and then rinsing with deionised water. The column was left saturated with rinse water. Columns were then operated in down-flow mode, at 2BV/h with synthetic BSD water influent. Effluent samples were collected for 25 BV and analysed for major cations.

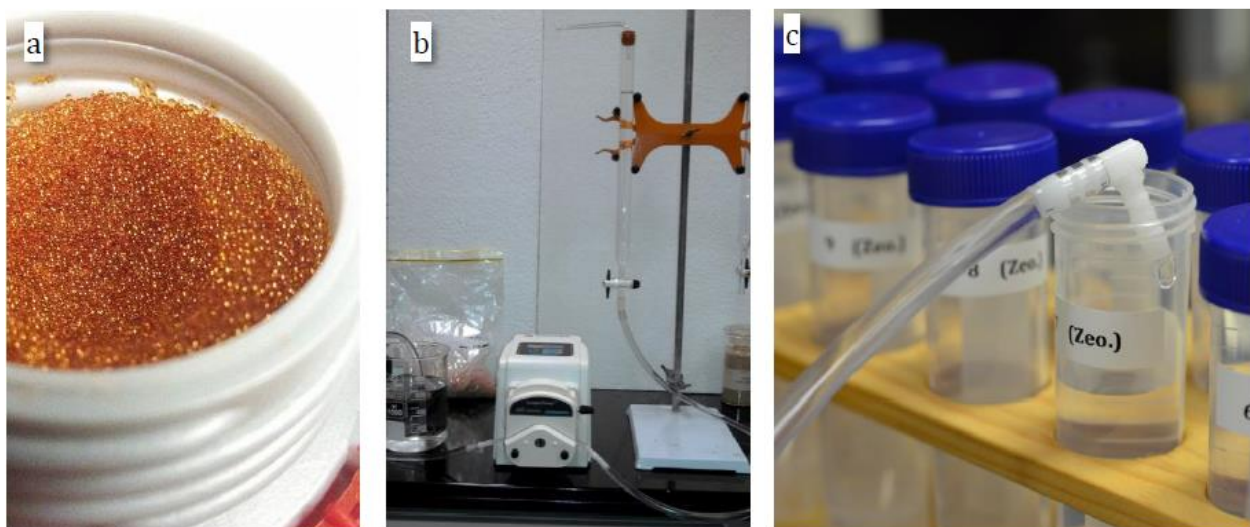


Figure 23: Apparatus for small column experiment. a) Amberlite IR-120 resin. b) Peristaltic pump beside glass column. c) Effluent sample collection.

The results of the Zeolite-2 experiment are shown in Figure 24 and performance seems to be improved in this experiment, compared to both full-scale performance and previous lab-scale testing. This is most likely due to acid pre-treatment (H^+ is monovalent and more readily exchanged for monovalent Na^+) and smaller grain sizes permitting faster exchange rates.

However, excessive acid treatment of the zeolite will result in degradation of the minerals responsible for the cation exchange process. Evidence of this was the high measurements of aluminium (data not shown) in the zeolite column effluent.

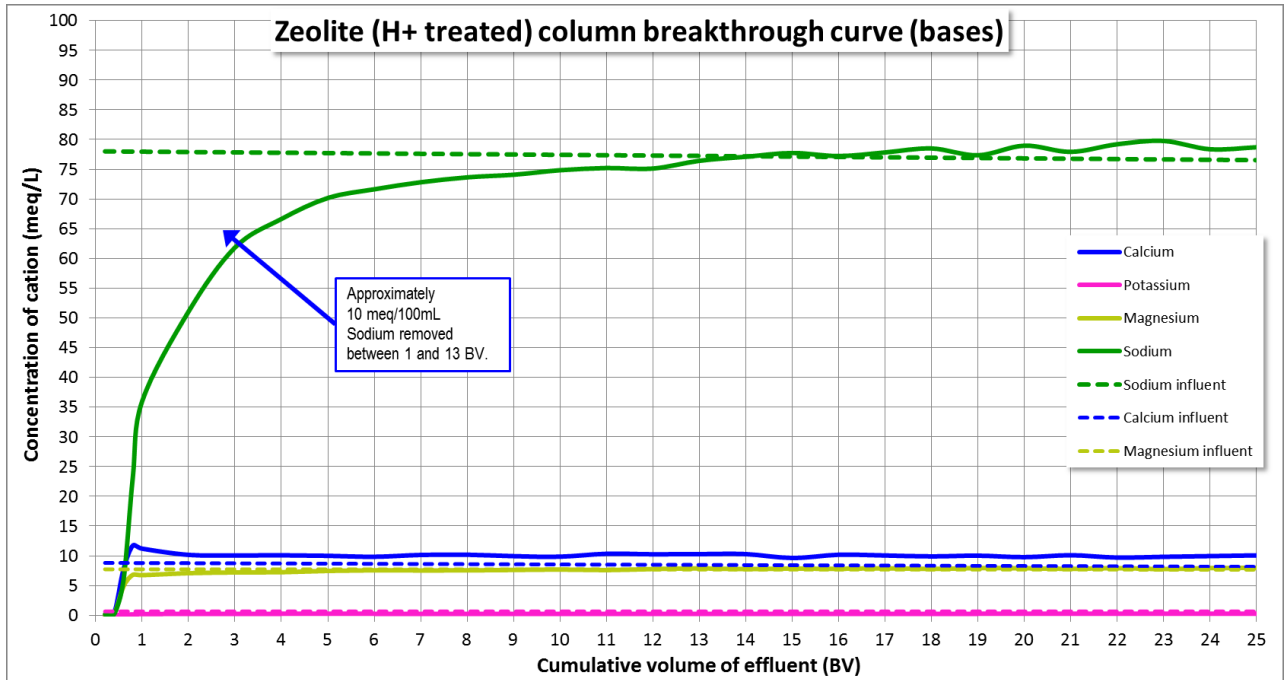


Figure 24: Breakthrough curves for major cations in Zeolite 2 packed column. Sodium curve shows a typical zeolite breakthrough profile. Sodium removal is incomplete, lasts for approximately 12 BV. There is a practical capacity of about 10 meq/100mL. Between 0 and 1 BV, the concentration of the effluent is dominated by the rinse water which was still being displaced by the influent.

The results of the Amberlite resin in Figure 25 and performance was consistent with the manufacturer listed cation exchange capacity of 180 meq/100mL. However, the effluent of the resin column was acidic due to the H⁺ being displaced from the resin media into the solution and would require post-treatment prior to discharge.

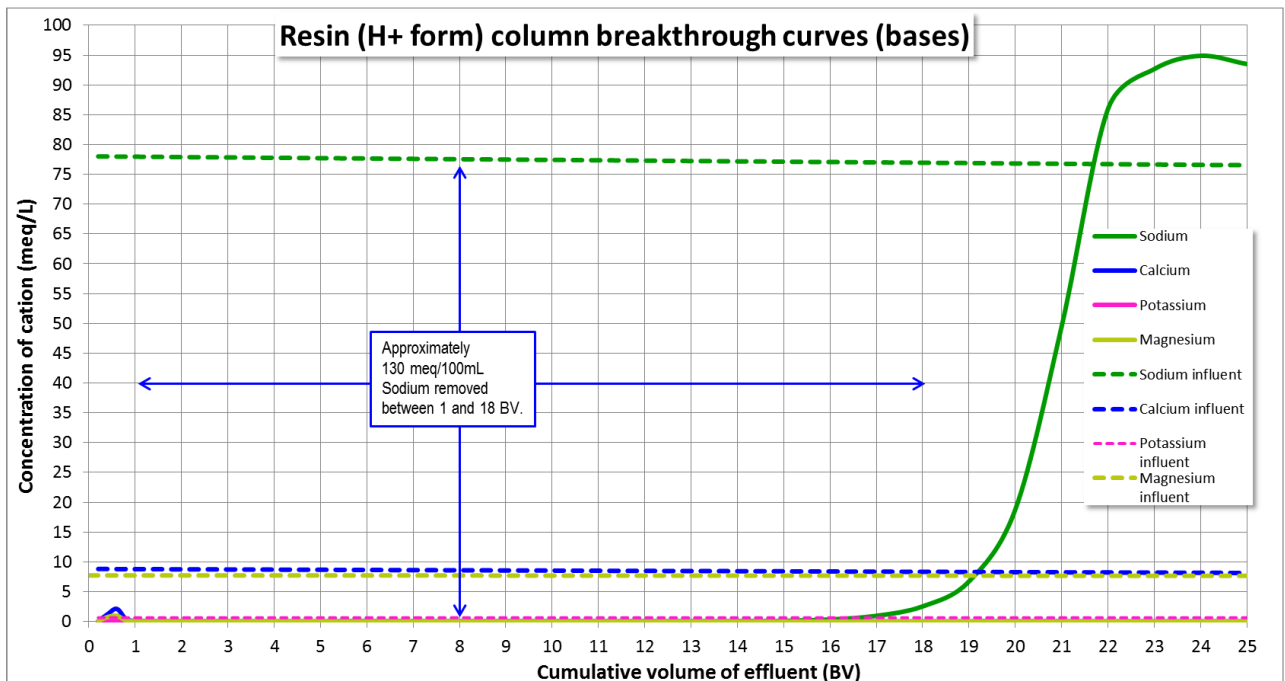


Figure 25: Breakthrough curves for major cations in Amberlite IR-120 resin packed column. Sodium curve shows a typical resin breakthrough profile. Sodium removal is complete and lasts for approximately 17 BV. There is a practical capacity of about 130 meq/100mL. Between 0 and 1 BV, the concentration of the effluent is dominated by the rinse water which was still being displaced by the

influent. Beyond 22 BV, a strong chromatographic peak is seen, where sodium is being displaced from the media while calcium, magnesium and potassium are still being adsorbed.

5.5 Summary

Results from pilot scale investigations at Central Queensland University are summarised as follows:

- It was concluded that the organic matter in the wastewater is having little effect on the sodium removal.
- The rate of sodium removal by the virgin resin was similar to the rates for used resins in the full-scale plant. Therefore, it was concluded that resin age was having little effect on sodium removal.
- Competition for exchange sites from calcium and magnesium strongly reduces the practical capacity of the Zeolite column media for sodium removal. It was concluded that Zeolite-2 media is not likely to be effective at removing sodium from cattle hide processing wastewater and should not be used in this application.
- Acid washing of Zeolite-2 media results in a minor improvement in performance, however excessive acid treatment of the zeolite will result in degradation of the minerals responsible for the cation exchange process.
- Amberlite resin is a well characterised strong acid cation resin and is much more effective at cation exchange for cattle hide processing wastewater. However, the resin is not specific to sodium and the effluent of the resin column was acidic due to the H⁺ being displaced from the resin media into the solution and would require post-treatment prior to discharge.

6 Revised Configuration for SAR Process

Investigations confirm the current SAR reduction process trialled at full-scale is not effective. This section outlines a revised process configuration for an ion-exchange process that incorporates information from both full-scale trials and lab-scale analysis. The quantities used are based on the results of a single experiment and will require further investigation and optimisation. However, other advanced water treatment technologies are available and based on project outcomes, ion exchange is not recommended.

Pre-treatment

Wastewater on site (e.g. polishing pond or balancing storage dam) is high in solids and BOD. These factors must be reduced or eliminated to increase the efficacy and life of the ion exchange resin. A recommended pre-treatment chain is:

1. Disc filter (or similar) to remove large suspended solids.
2. Trickling filter to reduce BOD. Alternatively, aggressive oxidation with hydrogen peroxide or ozone.
3. Sand filter to remove excess sludge from trickling filter effluent.

4. Optional use of ozone to polish the effluent prior to ion exchange. Note that many resins are intolerant to excess oxidising agents.

This pre-treatment protocol needs to be validated using small scale experiments. A small reverse osmosis unit will be a useful addition; however an ion exchange demineralising process would also be effective for rinse water and regenerant production.

Ion Exchange

Using acid treated resin will reduce dissolved salt cations and replace them with hydrogen cations in the effluent solution. When the media becomes exhausted, the pH will rise and sodium will be eluted at a higher concentration than influent. Thus, it is important to not over run the service part of the cycle.

1. Service flow. Approximately 18 BV of pre-treated wastewater fed in down flow mode. 18 BV based on concentration of 100 meq/L (approximately 10 mS/cm). Flow rate at 5 – 40 BV/h. Ion exchange service effluent is directed to a calcite filter for post-treatment. Some service effluent may be directed to an anion exchange process for demineralised water production.
2. Stop flow.
3. Rinse with demineralised water (e.g. rain or reverse osmosis water) for at least 1 BV. Rinse water can be recycled to source (e.g. polishing pond) or disposed with plant effluent.
4. Counter-flow regeneration flush 1: 1 BV of roughing regenerant (predominantly 8% hydrochloric acid). The regeneration flow rate should be lower than service flow (i.e. approximately 1 – 2 BV/h).
5. Counter-flow regeneration flush 2: 1 BV of fining regenerant (8% hydrochloric acid). Fining regenerant effluent is stored for use as the next roughing regenerant. The acidity of this stored solution will need to be adjusted back down to pH 1 due to dilution and H⁺ exchanging out of solution.
6. Rinse in down flow with demineralised water for at least 1 BV. Excessive rinsing should not cause a problem.
7. Resume service flow (Step 1).

Post-treatment

Assuming complete exchange occurs (and is insignificant H⁺ or carbonate in the influent), the concentration of H⁺ in the effluent will be the same equivalent concentration of total cations in the influent (e.g. Na⁺, Ca²⁺, NH⁴⁺, Sr²⁺). Cations in the influent solution total 100 meq/L, therefore, the H⁺ concentration in the effluent is expected to be 0.1 N and requires post-treatment to neutralise the acidity.

The simplest solution to neutralise acidity in the effluent is treatment using a calcium carbonate filter (e.g. calcite or limestone). This media will be consumed in the reaction and need to be replaced. The replacement rate will be approximately 50 kg of calcite per 10 kL of 0.1 N HCl effluent. The additional benefit of this neutralisation method is that the H⁺ is replaced with Ca²⁺. Increased Ca²⁺ in the post-treated effluent will further reduce

SAR, this may present an opportunity for a portion of BSD wastewater to bypass treatment while still achieving SAR of 8 or less.

7 Preliminary Cost-Benefit Analysis

A cost-benefit analysis (CBA) of adopting the Midell Water SAR reduction system at full-scale plant level was originally planned as part of the project. However, the technology did not successfully reduce SAR during the project and the technology was not considered suitable for full scale implementation. Therefore CBA is not required.

8 Summary and Recommendations

The SAR reduction process was designed to operate with a 4 day service cycle and a 2 day regeneration cycle. While SAR was initially close to the target value of 7, the performance deteriorated rapidly during the service cycle, with SAR exceeding 15-20 within 24 hours after regeneration (approximately 6 BV flow). There was little evidence that sodium was removed in the ion exchange process. Results indicated that any reductions in SAR were due to calcium and magnesium leaching out of the media bed after regeneration.

There were several factors contributing to poor performance of the full-scale process. Experimental analysis determined exchange capacity for the zeolite media in the process was much lower than the suppliers' literature indicated (approximately 50% of capacity specified). This limited SAR reduction during the service cycle. Poor sodium removal was confirmed during analysis of the regeneration cycle. Significant biofouling was observed on the surface and penetrating into the core of the zeolite media particles. Biofouling was identified as a potential cause of poor sodium absorption and poor performance of the SAR reduction process. However, cleaning trials in the laboratory and on-site failed to improve the ion exchange ability of the media.

Pilot-scale investigations were conducted at Central Queensland University in an attempt to identify the reasons for poor process performance and strategies for process optimisation, the pilot scale results are summarised as follows:

- It was concluded that the organic matter in the wastewater is having little effect on the sodium removal.
- The rate of sodium removal by the virgin resin was similar to the rates for used resins in the full-scale plant. Therefore, it was concluded that resin age was having little effect on sodium removal.
- Competition for exchange sites from calcium and magnesium strongly reduces the practical capacity of the Zeolite column media for sodium removal. It was concluded that Zeolite-2 media is not likely to be effective at removing sodium from cattle hide processing wastewater and should not be used in this application.
- Acid washing of Zeolite-2 media results in a minor improvement in performance, however excessive acid treatment of the zeolite will result in degradation of the minerals responsible for the cation exchange process.

- Amberlite resin is a well characterised strong acid cation resin and is much more effective at cation exchange for cattle hide processing wastewater. However, the resin is not specific to sodium and the effluent of the resin column was acidic due to the H⁺ being displaced from the resin media into the solution and would require post-treatment prior to discharge.

Though the Zetos filter technology seemed promising for SAR reduction, particularly for coal seam gas wastewater, this project demonstrates that the technology is not appropriate for treatment of cattle hide processing wastewater and alternate technologies should be investigated.

Appendix 1

Table 2: Chemical analysis of wastewater feed to establish process baseline

| Parameter | Conc. | Literature | Jul-10 | Aug-10 | Sep-10 | Oct-10 | Nov-10 | Dec-10 | Jan-11 | Feb-11 | Mar-11 | Apr-11 | May-11 | Jun-11 | Jul-11 | Aug-11 | Sep-11 | Oct-11 | Nov-11 | Dec-11 | Av. |
|------------------|-------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------------|
| BOD | mg/L | 60-85 | 74 | 78 | 88 | 190 | 81 | 100 | 43 | 57 | 70 | 17 | 35 | 170 | 140 | 73 | 50 | 46 | 31 | 23 | 72.8 |
| Suspended Solids | mg/L | 100-300 | 160 | 130 | 350 | 200 | 100 | 430 | 36 | 110 | 190 | 51 | 130 | 280 | 220 | 170 | 150 | 150 | 180 | 69 | 157.2 |
| Chromium Total | mg/L | 0.1-0.3 | 0.04 | 0.19 | 0.35 | 0.22 | 0.07 | 1.3 | 0.09 | 0.31 | 0.18 | 0.04 | 0.2 | 0 | 0.1 | 0.1 | 0.04 | 0.03 | 0.06 | 0.07 | 0.2 |
| Nitrogen | mg/L | 10-20 | 8.3 | 6.9 | 31 | 22 | 21 | 35 | 20 | 16 | 25 | 4.6 | 7.4 | 11 | 17 | 19 | 1.2 | 15 | 14 | 8 | 15.6 |
| Calcium | mg/L | 180-220 | 110 | 77 | 110 | 190 | 180 | 270 | 280 | 150 | 97 | 110 | 87 | 140 | 250 | 190 | 180 | 220 | 230 | 700 | 190.1 |
| Magnesium | mg/L | 40-80 | 35 | 51 | 130 | 59 | 60 | 48 | | 44 | 28 | 31 | 27 | 42 | 60 | 66 | 42 | 87 | 43 | 83 | 55.6 |
| Sodium | mg/L | 1500-2300 | 1300 | 1300 | 1500 | 1400 | 1500 | 1700 | 3500 | 2300 | 1500 | 1800 | 1700 | 1700 | 2000 | 1800 | 1600 | 2300 | 2600 | 2500 | 1957 |
| SAR | mg/L | N/A | 28 | 28 | 30 | 23 | 25 | 26 | 52 | 43 | 34 | 39 | 41 | 34 | 35 | 29 | 29 | 33 | 42 | 24 | 34.2 |
| Sulphate Total | mg/L | 300-900 | 390 | 630 | 900 | 760 | 730 | 650 | 370 | 400 | 200 | 200 | 220 | 490 | 560 | 650 | 480 | 870 | 590 | 780 | 584.3 |
| Phosphorus | mg/L | 0.3-1.8 | 0.19 | 0.61 | 1.1 | 1 | 0.31 | 1.8 | 0.24 | 0.32 | 0.98 | 0.11 | 1.3 | 5 | 5.3 | 3.2 | 1.2 | 0.9 | 1.2 | 0.53 | 1.2 |
| Phosphate | mg/L | 0.3-1.5 | 0.02 | 0.02 | 1 | 0.31 | 1.5 | 0.13 | 0.09 | 0.27 | 1.2 | 0.02 | 0.03 | 14 | 9.5 | 5.5 | 0.07 | 0.03 | 0.37 | 0.02 | 1.6 |
| Chloride Nitrate | mg/L | 2000-3200 | 2200 | 2100 | 2100 | 1800 | 1900 | 1600 | 3200 | 2800 | 2100 | 2200 | 2300 | 2300 | 2500 | 2700 | 2500 | 2800 | 3200 | 4700 | 2629 |
| Nitrogen | mg/L | 0.2-2.0 | 0.1 | 0.24 | 1.4 | 0.15 | 0.04 | 0.07 | 11 | 0.02 | 0.13 | 0.03 | 0.01 | 0 | 0.11 | 0 | 0.01 | 0.02 | 0.05 | 0.11 | 0.7 |
| Potassium | mg/L | 30-50 | 35 | 29 | 50 | 46 | 11 | 71 | 30 | 41 | 32 | 28 | 39 | 36 | 44 | 54 | 47 | 51 | 52 | 60 | 42.3 |
| Carbonate | mg/L | 5.0-30 | 1.8 | 0.67 | 0.55 | 4.6 | 5 | 4.3 | 29 | 3.4 | 2.9 | 11 | 2.4 | 4 | 53 | 31 | 4.8 | 26 | 2.6 | 8.2 | 13.0 |
| Bi-Carbonate | mg/L | 200-650 | 280 | 210 | 200 | 430 | 370 | 460 | 510 | 370 | 350 | 510 | 400 | 370 | 410 | 440 | 510 | 630 | 340 | 450 | 416.2 |

Appendix 2 – Washing Method used to Clean Zetos Filter Media

Aim:

To test the efficacy of both hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) at cleaning bio-fouled media from the Zetos filters at Murgon.

Method

Will attempt to replicate what can be done on site and minimise cleaning of the media by air exposure, abrasion or heating:

1. 25 – 30 mL quantities of fouled media (F) and virgin washed media (V) were placed in centrifuge tubes.
2. Each media type (F and V) were subjected to 48 hr contact with H₂O₂ at 0%, 5%, 10% and 15%; or HCl at 0N, 0.1N, 0.5N and 1.0N.
3. The treatment solutions were drained and the media rinsed 5 Times with RO water.
4. The media were contacted with 0.2 M CaCl₂ (8,000 mg/L) solution for 72 hr.
5. The media were drained and rinsed until Cl⁻ was not detected by reaction with AgNO₃ solution. This was 6 batch rinses in most cases.
6. 10 mL samples of each media type/treatment were dried on paper (Figures) and packed into clean tubes.
7. 10 mL media samples were contacted with 10 mL of 0.1M NaCl solution (2,300 mg/L) for 1 hr and 12 hr.
8. Samples are to be analysed for Na and Ca to determine effects of treatment on cation exchange behaviour.