

# SODIUM REMOVAL FROM MARAMARUA COAL SEAM GAS WATERS USING NGAKURU ZEOLITES

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## ABSTRACT

Coal seam gas (CSG) waters are a by-product of natural gas extraction from underground coal seams. The main issue with these waters is their elevated sodium content, which in conjunction with their low calcium and magnesium concentrations can generate soil infiltration problems in the long run, as well as short term toxicity effects in plants due to the sodium ion itself.

Zeolites are minerals having a porous structure, crystalline characteristics, and an aluminosilicate configuration resulting in an overall negative charge which is balanced by loosely held cations. In New Zealand, Ngakuru zeolites have been mined for commercial use in wastewater treatment applications, cosmetics, and pet litter.

This research focuses on assessing the capacity of Ngakuru zeolites to reduce sodium concentrations of CSG waters from Maramarua. Batch and column test (flow through) experiments revealed that Ngakuru zeolites are capable of sorbing sodium cations from concentrated solutions of sodium. In batch tests, the sodium adsorption capacity ranged from 5.0 to 34.3 meq/100g depending on the solution concentration and on the number of times the zeolite had been regenerated. Regeneration with  $\text{CaCl}_2$  was found to be effective. The calculated sodium adsorption capacity of Ngakuru zeolites under flow-through conditions ranged from 11 to 42 meq/100g depending on the strength of the solution being treated and on whether the zeolites had been previously regenerated. The slow kinetics and low cost of the zeolites, coupled with potentially remote sites for gas extraction, could make semi-batch operational processes without regeneration more favourable than in more industrial ion exchange situations.

## KEYWORDS

**Adsorption, batch test, Coal Seam Gas, column test, flow-through test, ion exchange, Ngakuru, sodium, separation factor, wastewater treatment, zeolites.**

## 1 INTRODUCTION

Zeolites are excellent minerals to use in cation exchange applications because their aluminosilicate configuration results in an overall negative charge which is balanced by loosely held cations. In addition, zeolites can also function as ionic sieves capable of selectively absorbing certain ions, depending on the size of the cavities forming the porous structure and on the size of the ions entering the zeolite structure (Coombs, 1959). Other properties of importance include a high degree of hydration/dehydration, low density, good crystal stability when dehydrated, and their ability to adsorb ions in gaseous form (Christie et al., 2002). Common zeolite applications include their use as pet litter, oil/chemical and odour absorbents, wastewater treatment, and their use as slow release fertilisers (NZ Natural Zeolite, 2006).

Zeolites in New Zealand occur mainly in the Taupo Volcanic Zone, Northland, Auckland, and Southland (Christie et al., 2002). Ngakuru zeolites are found in the Taupo Volcanic Zone about 20 km south of Rotorua. These zeolites are hydrothermally altered and occur in lake sediment beds of Quaternary age up to 45 m deep (Mowatt, 2000). The main type of zeolites in Ngakuru is mordenite (40-80%) (Mowatt, 2000). Bolan and Mowatt (2000) have successfully used these zeolites in trials to remove ammonium cations in wastewaters from tannery operations. Previous New Zealand studies by Nguyen and Tanner (1998) focused on removing

ammonium cations from dairy farm effluent and piggeries using clinoptilolite and mordenite obtained from different sites.

Coal seam gas (CSG) waters are a new type of wastewater which could become fairly common on the New Zealand landscape and waterways. These groundwaters are a by-product of natural gas extraction from underground coal seams. Their production rate sometimes can be as high as 40m<sup>3</sup>/day per well with thousands of wells in areas like the Powder River Basin (USA) or the Surat and Bowen Basins (Australia). CSG waters tend to exhibit similar quality in terms of salinity and major ion composition. Their specific conductance varies depending on their travel time within the coal aquifer which accounts for different degrees of mineralisation. Their major ions are sodium, bicarbonate, and sometimes chloride. Overall, these waters tend to be fairly alkaline with low calcium, magnesium, and sulphate concentrations (Van Voast, 2003). The main issue with these waters is their elevated sodium content, which in conjunction with their low calcium and magnesium concentrations, can generate soil infiltration problems in the long run, as well as short term toxicity effects in plants due to the sodium ion itself.

CSG is still under exploration in New Zealand, but its development is imminent within the next few years. CSG water samples taken from a CSG pilot scale operation in Maramarua have high sodium and low calcium and magnesium concentrations (Taulis and Milke, 2007). The environmental effects due to CSG water disposal could extend to receiving environments both on the land and on surface waters. In some instances, CSG waters could damage valuable agricultural soils or riparian vegetation on protected ecosystems so restrictions on their disposal will be stringent. One way of reducing sodium concentrations of CSG waters might be by using New Zealand natural zeolites as exchange materials. Treating CSG waters in this way could not only make CSG waters comply with local regulations, but it could also transform CSG waters into a useable water resource. There is a direct economic benefit from using Ngakuru zeolites instead of commercial ion exchange resins. Ngakuru zeolites are easy to mine and readily available – their price ranges from about NZ \$75/tonne to \$350/tonne depending on their quality, whereas the price of synthetic zeolites can be as high as NZ \$ 69/kg (Christie et al., 2002). Hence, the objective of this research is to study the feasibility of New Zealand natural zeolites for CSG water treatment.

## 2 MATERIALS AND METHODS

Ngakuru zeolite samples were obtained from NZ Natural Zeolite, a subsidiary of Resource Refineries Ltd. These samples were sieved and grouped into 0.15-0.3 mm, 0.3-0.6mm, and 0.6-1.180mm particle size ranges. The moisture content for these samples ranged between 3.4% and 4.5% with a specific density of about 1.5 g/cm<sup>3</sup>. X-ray diffraction analyses were carried out on these samples at the Geological Sciences Department (University of Canterbury) using an X-ray diffractometer for mineral identification. These analyses revealed that the main crystalline materials present in these zeolites were 70-75% mordenite and 25-30% sanidine. Previous studies by Mowatt (2000) had revealed that their CEC ranged from 40 to 110 meq/100 g, while their surface area ranged from 34 to 138 m<sup>2</sup>/g.

Synthetic solutions of NaCl, NaOH, HCl, CaCl<sub>2</sub>, and KCl in various concentrations (ranging from 0.01M to 1M) were prepared for batch testing and preliminary flow-through testing. These solutions were characterised by measuring their pH and specific conductance according to APHA (1999) methods. For the final flow-through study, actual Maramarua CSG water samples were used to assess the sodium removal capacity of Ngakuru zeolites. These samples had been collected between August and October, 2004, and April and June, 2005, and stored below 4°C. The samples were combined and then filtered through a 1.2 µm glass filter, making up about 4.5 litres of CSG water. The chemical analyses results for this composite sample are presented in Table 1.

Table 1: Chemical analyses results for composite CSG samples

	Unit	Composite sample analysis 23/03/2006
pH <sup>(1)</sup>	pH units	8.57
Specific conductance <sup>(1)</sup>	µS/cm	1264
Total alkalinity <sup>(2)</sup>	mg/l as CaCO <sub>3</sub>	488
Sodium Adsorption Ratio (SAR)		29.6
Bicarbonate <sup>(3)</sup>	mg/l	564
Sodium <sup>(2)</sup>	mg/l	304
Chloride <sup>(2)</sup>	mg/l	147
Total Organic Carbon <sup>(2)</sup>	mg/l	29.2
Carbonate <sup>(3)</sup>	mg/l	14.8
Dis. carbon dioxide <sup>(3)</sup>	mg/l	5
Reactive silica <sup>(2)</sup>	mg/l	10.4
Total calcium <sup>(2)</sup>	mg/l	6
Total potassium <sup>(2)</sup>	mg/l	4
Total magnesium <sup>(2)</sup>	mg/l	1.2
Sulphate <sup>(2)</sup>	mg/l	2.9
Total boron <sup>(2)</sup>	mg/l	2.5
Fluoride <sup>(2)</sup>	mg/l	1.10
Dissolved iron <sup>(2)</sup>	mg/l	0.09
Total iron <sup>(2)</sup>	mg/l	<0.4
Dissolved manganese <sup>(2)</sup>	mg/l	0.03
Total manganese <sup>(2)</sup>	mg/l	0.04
Total aluminium <sup>(2)</sup>	mg/l	<0.06
Total cobalt <sup>(2)</sup>	mg/l	<0.004
Total chromium <sup>(2)</sup>	mg/l	<0.01
Total nitrogen	mg/l NH <sub>4</sub> -N	0.07
Total nickel <sup>(2)</sup>	mg/l	<0.01
Total zinc <sup>(2)</sup>	mg/l	0.12

<sup>(1)</sup> Measured at the Environmental Engineering Laboratory, University of Canterbury

<sup>(2)</sup> Sample analysed through Hill Laboratories, Hamilton, New Zealand

<sup>(3)</sup> Calculated using from carbonate chemistry using alkalinity and pH values

<sup>(4)</sup> Sample analysed by CRL Energy Ltd Laboratory, Wellington, NZ

Photograph 1: Flask shaker used in batch testing of Ngakuru zeolites and NaCl solutions



### 3 BATCH TESTS USING CONCENTRATED SOLUTIONS

Four types of batch tests were carried out as preliminary experiments to determine the feasibility of using Ngakuru zeolites for the removal of sodium cations from solution:

- **PHASE I.** The first batch tests focused on assessing the sodium removal capacity of Ngakuru zeolites while evaluating the effects of particle size using 1 M NaCl solutions.
- **PHASE II.** A second type of batch-testing experiment was carried out to determine whether there was any dissolution taking place along with the sorption.
- **PHASE III.** This third type of batch test experiment was carried out to determine the effect of different concentrations on zeolite ion exchange reactions.
- **PHASE IV.** The objective of this last type of batch testing was to determine whether it was possible to regenerate Ngakuru zeolites after they had absorbed sodium cations. This also helped assess how rigid or prone to mechanical breakdown were the zeolites, and to determine a maximum sodium exchange capacity (useful for preliminary sizing calculations in the flow-through experiments).

#### 3.1 METHODS

In these experiments, zeolites were rinsed with deionised water and then dried in an oven at 100°C. Zeolites were then placed in conical flasks along with concentrated NaCl solutions. The flasks were then shut closed with a plastic stopper and placed in a flask shaker (Photograph 1), which was activated for a predetermined amount of time. Once the shaking had finished, the zeolite solution was filtered through a 1.2 µm glass filter and analysed for calcium, hardness, pH, and specific conductance according to APHA (1999) methods. In some of these experiments, the zeolite solution was analysed for sodium using a calibrated Cole-Parmer sodium ion electrode. In PHASE IV, different service/regeneration cycles were carried out using concentrated sodium solutions for service along with various calcium, potassium, and acid solutions for regeneration. In this batch test experiment the service/regeneration cycle was repeated five times with different solutions of varying concentrations while analysing the final solutions resulting from each shaking period. Some of the samples in PHASE IV were analysed for potassium at the Department of Chemistry (University of Canterbury) using atomic absorption, and two of the samples were analysed for chloride and sulphate using HACH methods 8225 and 8051 (Hach Company, 2003). A more detailed description of these methods is provided in Taulis (2007).

#### 3.2 RESULTS

##### 3.2.1 PHASE I

In general, particle size did not pose a major influence in ion exchange processes. Different particle sizes produced zeolitic solutions having approximately the same hardness and calcium concentrations. However, a minor trend was noticed where exchanged cations seemed to increase slightly with fine particle size (passing and retained on the 150 µm sieve) and with coarser sizes (1180 µm and 2360 µm). This can be observed by analysing the plots of calcium concentrations vs. particle size in Figure 1. This figure also shows that shaking time does have an influence on reaction kinetics as the zeolitic solutions that were shaken for 8 hours have more calcium ions than the solutions that had been shaken for just 1 hour and 45 minutes. There was no pattern in pH changes for the different shaking times and particle sizes being tested (pH 4.5-5.7). Based on these results it was decided to work with high-grade zeolites with a medium ranged particle size (300 or 600 µm).

Figure 1: Calcium concentrations after vigorous shaking

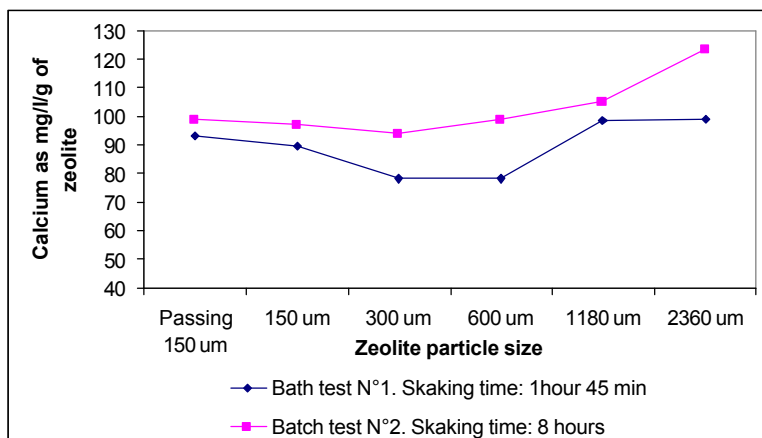
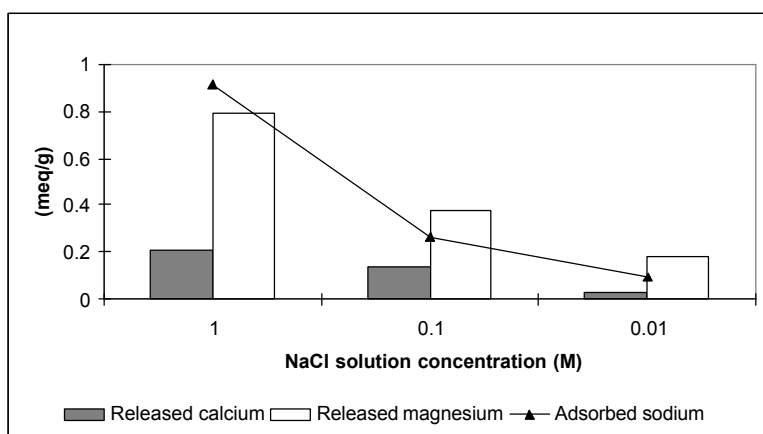


Figure 2: Effect of NaCl concentration on zeolite ion exchange processes



### 3.2.2 PHASE II

Shaking for 9.5 hours with low concentration NaCl solution (0.005 M) revealed that there was little or no change in specific conductance (from 538 to 546  $\mu\text{S}/\text{cm}$ ), and some calcium (8 mg/l) and hardness (32 mg/l as  $\text{CaCO}_3$ ) were detected at the end of the shaking time. In addition, pH decreased from 6.2 to 5.5, which suggests that hydrogen ions were being exchanged for sodium. When using deionised water, results indicated very small amounts of calcium (3.2 mg/l) and hardness (4.2 mg/l as  $\text{CaCO}_3$ ) being released, and a slight increase in specific conductance (from 1.9 to 41.8  $\mu\text{S}/\text{cm}$ ). These results suggest that some dissolution could have been taking place.

### 3.2.3 PHASE III

The results of batch testing Ngakuru zeolites using different types of concentrated solutions are plotted in Figure 2. These results show that more sodium cations are absorbed while more hardness cations (calcium & magnesium) are released from the zeolites at higher NaCl concentrations. In addition, the type of solution itself can play an important role in the exchange process. For example, results showed that the 0.01 M NaOH adsorbs almost as much sodium as the more-concentrated-0.1 M NaCl solution, but with practically no calcium and magnesium being released. In all of these experiments the pH decreased by about 1 pH unit after shaking, which shows that hydrogen ions are being released as part of the exchange/dissolution process.

### 3.2.4 PHASE IV

In this phase, a series of five experiments were conducted. Full details can be found in Taulis (2007).

### 3.3 DISCUSSION

Batch tests (PHASES I, III, and IV) revealed that Ngakuru zeolites were capable of sorbing sodium cations from concentrated solutions of sodium. This was accompanied by the release of cations, originally contained within the zeolites, and some loss of zeolite mass. Particle size posed no significant effects on the overall process (PHASE I). The process by which sodium ions were sorbed into the zeolites can be described as an ion exchange process, and the additional release of ions from the zeolite structure is mainly a dissolution process (PHASE II).

In these experiments, sodium was the only cation available for zeolite adsorption as calcium, magnesium, potassium, and hydrogen were being released from the zeolites. In theory, if these were the only intervening ions, then their net charge difference would be zero as a consequence of ion exchange. If this value is not zero, then this means there is a cation contribution not being accounted for, which could be explained by zeolite dissolution. The charge balance was zero for numerous runs in Phase IV; therefore, for these runs, the ions involved in the exchange were sodium (in solution) and magnesium, calcium, and hydrogen (originally in the zeolites). Since the difference in charge balance was nil, then there were no cations being released as a consequence of zeolite dissolution. However, the charge balance difference was not always nil throughout these experiments, which suggests some zeolite dissolution.

There was a large mass loss (about 85%) between the first and the last experimental runs, especially during regeneration trials. This should have produced a significant ion charge imbalance, particularly during the first experimental runs where dissolution was the highest (i.e. 36% after the first service run). However, cation differences (charge balance) remained low and similar experiments revealed no anion dissolution (sulphate or chloride). What could have happened was mechanical breakup of the zeolite material. That is, a given 1180  $\mu\text{m}$  particle could have been broken into smaller pieces due to collisions with other particles during shaking. These particles could have kept disintegrating with increasing shaking, but adsorbed cations could have still remained trapped by these smaller zeolite particles. Indeed, with increasing shaking the zeolitic solution appeared brownish in colour due to this mechanical breakup. Later, flow-through experiments (carried out without mechanical shaking) showed that, as sodium loaded solutions percolated through the zeolite column, some dissolution did take place at the beginning of each experiment (brownish colour). However, after the first couple of aliquots had been collected, the solution became clear in colour, which shows that dissolution had stopped soon after the first aliquots had gone through. Therefore, the loss of mass in batch tests is mainly due to mechanical shaking.

Batch experiments with deionised water and a low-concentration NaCl solution suggested that the dissolution process is highly dependent on the ionic strength of the solution being treated. Therefore, it is possible that dissolution is enhanced when the zeolites are exposed to strong alkali or acid solutions, as observed in some runs in PHASE IV.

Batch testing showed that it is possible to regenerate Ngakuru zeolites for further use with different types of solution. However, repeated cycles of service/regeneration resulted in significant loss of mass, which could have practical implications for zeolite reutilisation. For example, one experiment yielded good results with concentrated solutions of HCl,  $\text{CaCl}_2$ , and KCl, but after 11 cycles the zeolite mass was reduced by about 15%.

With NaOH, sodium sorption during service runs increased from 10.8 meq/100g (no previous regeneration) to 13.1 and 21.2 meq/100g after regenerating with 0.1M HCl and 1M HCl respectively. This exchange increase is due to the regenerant displacing sodium and other occluded salts, thus making more sites available for the exchange during the service run. Also, an increase in regenerant concentration forces more sites to become available due to a more extensive exchange during the regeneration phase. For instance, after regenerating with  $\text{CaCl}_2$  sodium sorption decreased to 5 and 8 meq/100g, however after regenerating with KCl this value increased to 16.6 meq/100g. This suggests that higher valence cations (for example  $\text{Ca}^{2+}$ ) are more difficult to remove from the zeolite lattice than cations having the same balance ( $\text{K}^+$  or  $\text{H}^+$ ) as the cation to be exchanged in solution (in this case  $\text{Na}^+$ ).

Throughout batch tests, the total cations being exchanged were calculated by analysing the differences in concentration between the initial solution and the final (treated) solution. Thus, for the sodium ion this capacity ranged from 5.0 to 34.3 meq/100g depending on the solution concentration and the number of times the zeolites had been regenerated. These results were later used in flow-through experiments as initial estimates of total

zeolite capacity. This was useful in the design of experiments so that enough volume of sodium solutions was available to carry out these experiments. In addition, flow-through tests were designed to address the issues arising from batch test experimental results. For example, flow-tests were designed so that their results gave a good indication of the kinetics of the ion exchange process as well as an adequate quantification of the dissolution taking place.

## 4 FLOW-THROUGH TESTS

The objective of column tests, or flow-through tests, was to determine the sodium exchange capacity of Ngakuru zeolites in laboratory experiments resembling field-operating conditions. This also helped to determine the efficiency of the process and the optimal operating mode.

### 4.1 METHODS

Flow-through tests involved the use of a zeolite-packed column with feed solution running through it. Table 2 summarises the different experiments and provides relevant details. The column used in these experiments was specially designed and manufactured at the University of Canterbury, and it consisted of a 3 mm glass tube of about 75 cm in length, with a funnel attached to one of its openings. In addition, this column had a sintered glass filter at the funnel, and two taps for controlling flow in and out of the column (Photograph 2). Most of the experiments with the ion exchanged column used about 240 g of zeolite material, but about 180 g were used in Experiment N°7.

Operation in downflow mode led to channelling and preferential flow, so experiments were conducted in upflow mode where the feed solution was supplied through a 10mm plastic tube attached to the bottom tap. The average retention time was about 14 minutes.

Typical operation mode included service, backwash, regeneration, and rinse. Backwash was carried out with deionised water at a high flow rate (as high as 180 cm<sup>3</sup>/min) and always in upflow mode. Regeneration was carried out in the same direction of flow and same rate as in service mode using 1 litre KCl (1 M) and CaCl<sub>2</sub> (0.044 M) solutions. The next step was the rinsing step, which was necessary to remove any excess regenerant prior to service. This step was carried out with deionised water in upflow mode and at two different flow rates – a slow rate (as slow as the regeneration rate) to displace excess regenerant from the zeolite bed, and a fast rate (about twice as fast) to remove any residual solution from the zeolites. After rinsing, the bottom tap of the column was opened to drain any remaining liquid from the column. In addition, one of these experiments was carried out with a warmed feed solution (~40°C) to determine if efficiency improved significantly with higher temperatures.

During experiment n°4, the feed solution was heated to 100°C, but it cooled down while being pumped into the column, entering it at a temperature of approximately 40°C. The original NaCl concentration was 0.1M, but this could have increased because of water evaporation from the heated beaker. In addition, the zeolites were washed with deionised water inside the column before the experiment started. This was done to keep the zeolite bed moist in order to promote saturated flow at the start of the test.

In experiments n° 1, 2, 4, and 5 (Table 2) zeolites were prewashed with deionised water before each service run. Experiments n° 3 and 6 tested regenerated zeolites that had previously been used in experiments n° 2 and 5 respectively, so no pre-washing was carried out (except for the rinsing after the regeneration cycle). Experiment n°7 was carried out without any pre-washing and with no previous regeneration.

In each of these experiments, 100 ml aliquots were collected during service runs either from the top tap (upflow mode) or bottom tap (downflow mode). These aliquots were stored in sample bottles and analysed after the service run had finalised. Before analysis, samples were filtered using 1.2 µm glass filters. Basic analyses carried out at the Environmental Engineering Laboratory (EEL, University of Canterbury) included pH, specific conductance, calcium, and hardness, which were carried out according to the methods outlined in APHA (1999). Also, sodium concentrations were determined using a calibrated Cole-Parmer sodium ion electrode. For experiments n° 6 and 7 (Table 2) samples were analysed for pH and specific conductance at the EEL, and then sent to Hill Laboratories for a complete analysis.

Data from flow-through experiments was used to generate breakthrough curves showing the sodium adsorption capacity of Ngakuru zeolites. This allowed for the calculation of the total number of exchanged sodium cations for a given mass of zeolites, while taking into account the interaction of other ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ). Further interpretation of data included calculating and plotting adsorption isotherms, and comparing these to other isotherms from known equilibrium relationships. In addition, it was possible to calculate the separation factor,  $r$ , for the whole isotherm (or  $R$  for a section of the isotherm) to determine the type of reaction taking place in relation to adsorption kinetics.

## 4.2 RESULTS

Experiments n°1 and n°2. These experiments were early trials and are not reported further here (for further details see Taulis (2007)).

Experiment n°3. This experiment was carried out in upflow mode with KCl-regenerated zeolites from experiment n°2. In this experiment, 1780 ml of 0.1 M NaCl were run through the column. The total sodium exchange taking place throughout this experiment was at least 40.9 meq/100g.

Experiment n°4. Sodium concentrations in the collected samples increased in logarithmic form ( $R^2=0.99$ ) until reaching the original sodium concentration (after 1400 ml of feed solution had gone through the column). The total sodium sorption by Ngakuru zeolites was 19.3 meq/100g. Samples in experiment n°4 had pH values in the 4.07-5.38 range which is consistently lower than the original pH value of 5.85.

Experiment n°5. The total sodium sorption that took place throughout this experiment was 15.9 meq/100g. The maximum sodium sorption took place at the beginning of the experiment - sodium concentrations increased almost linearly until about 700 ml of feed solution had flowed through the column. From then onwards, sodium concentrations increased logarithmically until reaching a final value of 38.4 meq/l.

Calcium concentrations tended to increase linearly at first and finishing at 12.8 meq/l (sample n°5). Later, calcium concentrations decreased in inverse logarithmic form until reaching a final value of 4.8 meq/l. Similarly, magnesium concentrations increased to 14.3 meq/l and then decreased to 1.1 meq/l.

Throughout this experiment, pH values stayed fairly low and within the 4.45-4.79 pH range. This is almost 2 pH units below the original pH (6.35), and it shows that hydrogen ions are also taking part in the cation exchange. Specific conductance of the outflow remained fairly constant throughout this experiment.

Experiment n°6. This experiment was carried out with regenerated zeolites (using  $\text{CaCl}_2$ ) from experiment n°5. Results for this experiment are presented in Figure 3. The total sodium sorption that took place throughout this experiment was approximately 16.7 meq/100g. The maximum sodium sorption was initially at 75% removal. The sodium concentration in the effluent slowly increased to 35.8 meq/l. As shown in Figure 3, the zeolites studied did not exhibit a sharp breakthrough front.

Calcium concentrations decreased throughout this experiment. Calcium concentrations at the start of the experiment are as high as 27.2 meq/l, but at the end of this experiment calcium concentrations reached a low value of 4.9 meq/l. Magnesium concentrations at the start of the experiment were about 0.58 meq/l, and decreased to around 0.11 meq/l by the end. Potassium concentrations in aliquots were fairly constant throughout this experiment averaging 2.8 meq/l.

Throughout this experiment, pH values stayed below the original pH value of 5.85. The first sample had the highest pH value (5.25), and subsequent pH values stayed below the 5.0 mark. Specific conductance remained constant throughout this experiment.

The breakthrough curve in this experiment can be standardised by calculating its adimensional isotherm, which represents the relative change in concentration of the outflow solution in relation to the relative change in sodium content within the zeolite. The isotherm for experiment n°6 is presented in Figure 4, and it shows the sodium exchange process until the experiment reaches the end of the experiment (35.1 meq/l in this case); the liquid phase is the change in sodium concentration in the outflow solution divided by the maximum outflow concentration minus the initial outflow concentration. Similarly, the solid phase is the relative change in sodium



absorbance, within the zeolites, as the experiment approaches 'breakthrough'. The resulting isotherm is linear (Equation 1), with an  $R^2$  value of 0.99. In addition, the separation factor ( $R$ ) was calculated for each step of this experiment, and this value ranged from 0.92 to 1.51 with an average of 1.2 ( $\sigma = 0.2$ ).

Experiment n°7. This experiment was carried out with actual CSG water from Maramarua (Table 1). The same cations analysed in the previous experiments, were also analysed in experiment n°7, but in this case a more thorough analysis was carried out in 4 of the samples to compare these against the original feed solution. Major cation exchange results and properties for aliquots throughout this experiment are presented in Figure 5, and detailed analyses for selected samples are presented in Table 3.

Throughout this experiment, the total sodium sorption that took place was approximately 11.3 meq/100g. The first two aliquots presented higher sodium concentrations than the third one, which was the sample with the lowest sodium concentration. From sample n°3 onwards, sodium concentrations in aliquots increased in a quasi logarithmic fashion reaching a limit of approximately 10.0 meq/l (76% of original concentration). Discarding these first two samples, an isotherm is presented in Figure 6, and it has a linear trendline with an  $R^2$  value of 0.95. Equation 2 presents the linear relationship for this isotherm, and its calculation procedure. In this case, the separation factor ( $R$ ) ranged from 0.28 to 4.7 for each of the aliquots throughout this experiment with an average of 1.5 ( $\sigma = 0.93$ ).

Magnesium and calcium cations tended to decrease in a quasi-logarithmic manner. Potassium concentrations throughout this experiment were lower than 1.2 meq/l. Also, pH values increased logarithmically starting at 6.45 and finishing at 8.36 after 4.5 litres of treated feed solution. For the first 200 ml of treated feed solution, specific conductance values were higher than in subsequent samples and higher than in the original feed solution. After the first sample, specific conductance values decreased linearly from 2.10 dS/m to 1.15 dS/m (sample n°5), and then gradually increased to a value just higher than the original specific conductance value (1.26 dS/m).

Thorough analyses for selected samples (Table 3) indicate increased concentrations for some of the original sample constituents in the first sample (sample n°1), but not for the remaining samples (n°7, n°19, and n°36). Throughout this experiment, reactive silica concentrations increased to an average of 26.3 mg/l from 10.4 mg/l. In addition, aluminium concentrations showed a marked increase.

Table 4 shows the theoretical sodium adsorption values (from breakthrough trendline) calculated for experiments n°3-7. In general, differences between the theoretical value and the value calculated directly from sample analyses were low.

Photograph 2: Glass column used in flow-through experiments

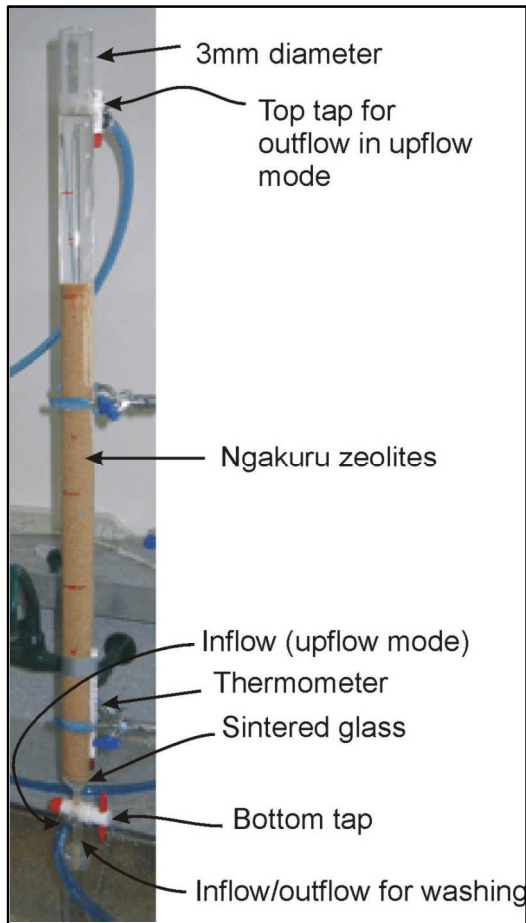


Table 2: Summary of flow-through experiments

N°	Experiment type	Feed Solution	Direction of flow	Flow Rate cm <sup>3</sup> /min	Feed volume litres	Zeolites size (µm)	Zeolites Mass grams	Retention Time min
1	No prior regeneration	0.01 M NaCl	Downflow	21-26	10.1	1180	269.7	13.2
2	No prior regeneration	0.1 M NaCl	Downflow	33	1.8	600	240.0	8.4
3	Prior regeneration with 1M KCl (1litre) and zeolites from experiment n° 2	0.1 M NaCl	Upflow	13-19	1.83	600	240.0	17.4
4	No regeneration but feed solution was heated to ~40°C	0.1M NaCl	Upflow	13-19	1.5	300	240.1	17.1
5	No prior regeneration	0.044M NaCl	Upflow	12-21	2.7	600	240.1	16.1
6	Prior regeneration with 0.044M CaCl <sub>2</sub> (1 litre) and zeolites from experiment n° 5	0.044 M NaCl	Upflow	14-20	2.7	600	240.1	15.6
7	No prior regeneration	Maramarua CSG water <sup>(1)</sup>	Upflow	15-17	4.53	600	180.0	11.3

(1) Equivalent to a 0.013M NaCl concentration as per the composite sample in Table 1 ([Na] = 304 mg/l).

Figure 3: Experiment n°6 Results

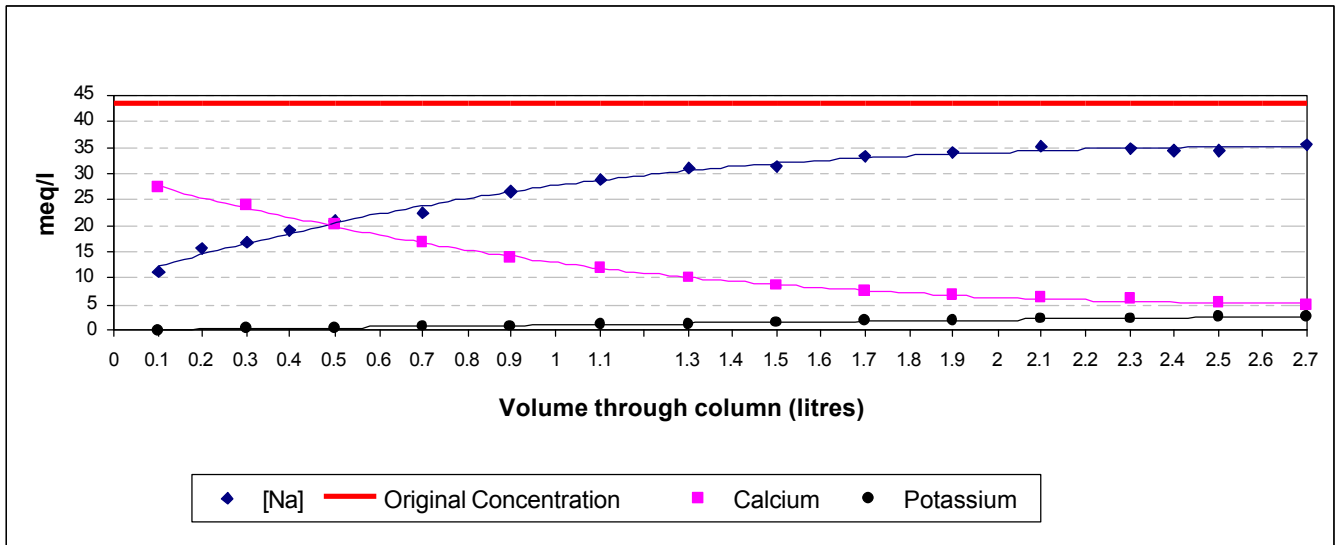
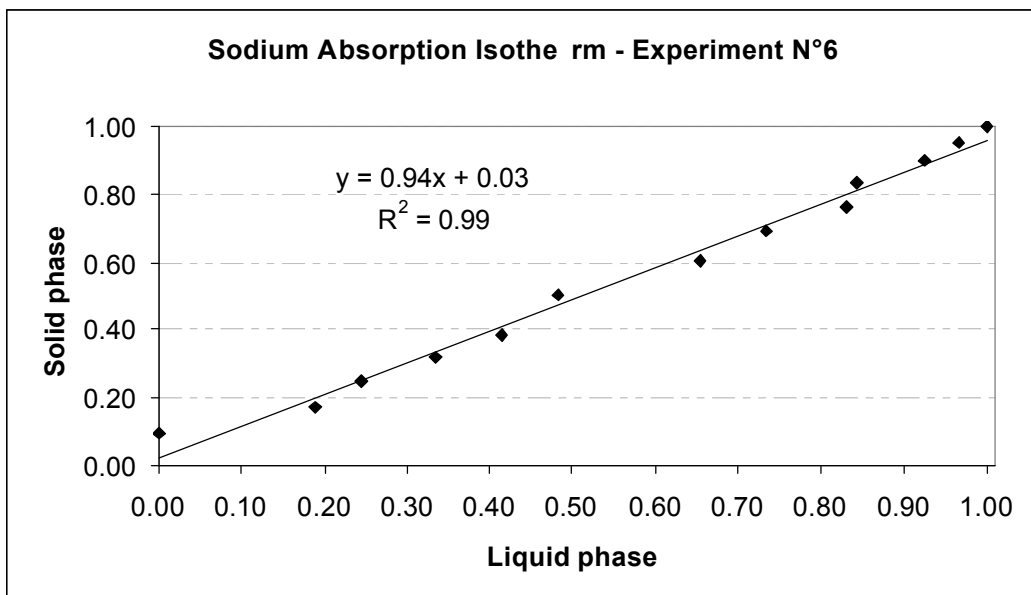


Figure 4: Fractional solid-concentration isotherm for experiment n°6



Equation 1

$$Q = 0.94 \times C + 0.03$$

Where,

$$C = \frac{c - c'}{c'' - c'}$$

$$Q = \frac{q - q'}{q'' - q'}$$

$c$  = outflow concentration

$c'$  = minimum outflow concentration (first sample, 11.1 meq/l)

$c''$  = maximum outflow concentration (breakthrough, 35.1 meq/l)

$q$  = sodium ion in zeolite

$q'$  = initial zeolite sodium adsorption (3.2 meq)

$q''$  = total zeolite adsorption (at breakthrough, 35.0 meq)

### 4.3 DISCUSSION

#### 4.3.1 OPERATIONAL ISSUES IN EXPERIMENTATION

Throughout flow-through tests, a number of operational issues were observed while carrying out these experiments. For instance, in experiments n°1 and n°2 preferential flow or channelling was observed as the feed solution dripped in downflow mode into the ion exchange column. This translated into an inefficient use

of the packed zeolite column, so subsequent experiments were conducted in upflow mode instead. These inefficiencies were fairly noticeable as even minor variations in flow impacted on experimental outcomes.

When particle size was small (<300  $\mu\text{m}$ ) and service rates were high enough (>15  $\text{cm}^3/\text{min}$ ), the zeolitic material inside the column became buoyant and the material exhibited fluid behaviour. This was observed in pre-trials and at the top of the ion exchange column in experiment n° 4. Mobility of zeolite material inside the column generates operational problems because, when this takes place, zeolites are carried out of the ion exchange column with the treated solution. In addition, this could reduce the contact time between the feed solution and the zeolite material generating lower exchange rates. Therefore, small particle sizes were avoided and service flow rates were kept as low as was practical given the equipment available.

Other sources of experimental errors were the first 100ml aliquots collected at the start of the experiments which had previously undergone rinsing with deionised water. These initial samples had been “contaminated” with deionised water as they contained little or no sodium, calcium, and magnesium cations. Experiments n° 3 and 4 experienced these types of problems, so the first 100 ml aliquots resulting from these experiments were discarded from further analyses. In addition, in experiment n°4 the original NaCl concentration was 0.1M, but this value could have increased due to water evaporation from the heated beaker. This possibility is supported by the last two outflow samples resulting from the column test experiment which present higher concentrations than the one corresponding to the original feed solution.

*Table 3: Full analyses for selected samples (experiment n°7)*

	Unit	Samples <sup>(1)</sup>			
		n°1	n°7	n°19	n°36
Total alkalinity	mg/l as CaCO <sub>3</sub>	278	428	468	498
Bicarbonate	mg/l	339 <sup>(2)</sup>	519 <sup>(2)</sup>	561 <sup>(2)</sup>	590 <sup>(2)</sup>
Chloride	mg/l	164	151	147	149
Total Organic Carbon	mg/l	216	<0.5	27.7	30.7
Carbonate	mg/l	0.1 <sup>(2)</sup>	1.5 <sup>(2)</sup>	4.6 <sup>(2)</sup>	8.2 <sup>(2)</sup>
Dis. carbon dioxide	mg/l	390 <sup>(2)</sup>	41 <sup>(2)</sup>	16 <sup>(2)</sup>	10 <sup>(2)</sup>
Reactive silica	mg/l	25.1	27.6	27.1	25.5
Sulphate	mg/l	28.0	3.3	2.9	2.9
Total boron	mg/l	67.4	2.8	2.6	2.0
Fluoride	mg/l	0.23	0.94	1.68	1.28
Dissolved iron	mg/l	<0.02	<0.02	0.02	0.03
Total iron	mg/l	<0.4	<0.4	<0.4	<0.4
Dissolved manganese	mg/l	1.96	0.33	0.07	0.0121
Total manganese	mg/l	1.89	0.33	0.07	0.02
Total aluminium	mg/l	<0.06	<0.06	0.09	0.15
Total cobalt	mg/l	0.005	<0.004	<0.004	<0.004
Total chromium	mg/l	<0.01	<0.01	<0.01	<0.01
Total nickel	mg/l	0.02	<0.01	<0.01	<0.01
Total nitrogen	mg/l NH <sub>4</sub> -N	0.03	NA	NA	NA
Total zinc	mg/l	0.74	0.05	0.03	<0.02

Notes:

<sup>(1)</sup> Samples analysed through Hill Laboratories, Hamilton, New Zealand

<sup>(2)</sup> Calculated using from carbonate chemistry using alkalinity and pH values

Figure 5: Sorption results for experiment n°7

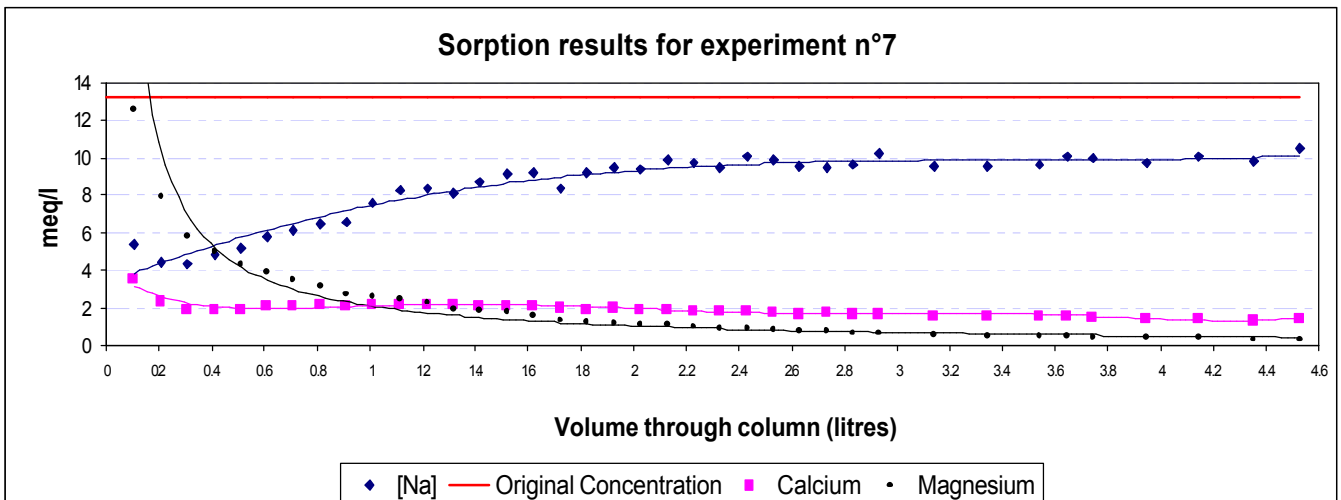
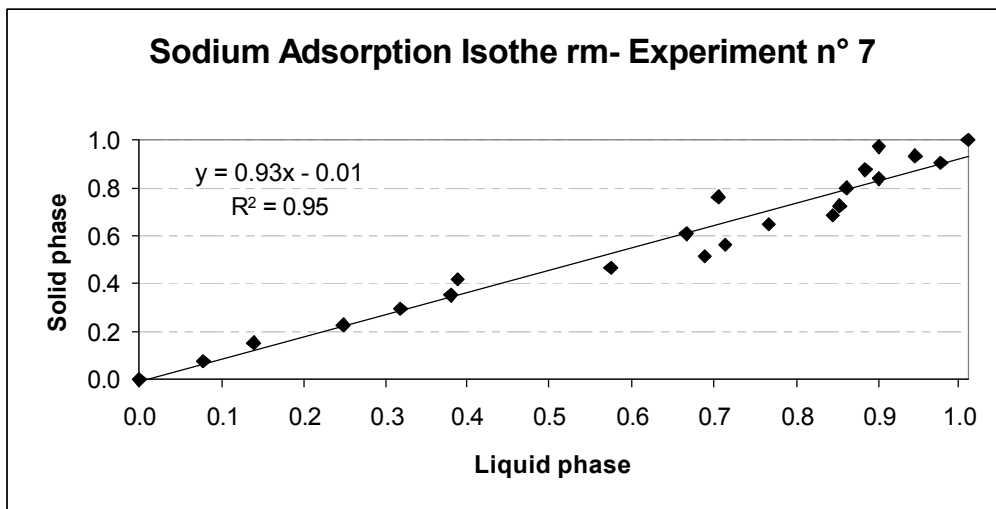


Figure 6: Fractional solid-concentration isotherm for experiment n°7.



Equation 2

$$Q = 0.93 \times C - 0.01$$

Where,

$$C = \frac{c - c'}{c'' - c'}$$

$$Q = \frac{q - q'}{q'' - q'}$$

$c$  = outflow concentration

$c'$  = minimum outflow concentration (first sample, 4.4 meq/l)

$c''$  = maximum outflow concentration (breakthrough, 10.0 meq/l)

$q$  = sodium ion in zeolite

$q'$  = initial zeolite sodium adsorption (2.5 meq)

$q''$  = total zeolite adsorption (at breakthrough, 13.1 meq)

Table 4: Total sodium adsorption throughout column test experiments

Experiment n°	Solution concentration	total sodium adsorption <sup>(1)</sup> meq/100g	theoretical sodium adsorption <sup>(2)</sup> meq/100g
3	0.1 M NaCl 600 µm	40.9	42.8
4	0.1 M NaCl 300 µm	19.3	21.5
5	0.044 M NaCl 600 µm	15.9	15.0
6	0.044 M NaCl 600 µm	16.7	15.9
7	Maramarua CSG water <sup>(3)</sup>	11.3	11.7

Notes:

- (1) Total sodium adsorption calculated from remaining sodium concentrations in collected samples
- (2) Theoretical sodium adsorption was calculated by integrating trendline equations and subtracting from the total original concentration over the studied range
- (3) Equivalent to 0.013 M NaCl

### 4.3.2 ANALYTICAL ISSUES

Charge balance results from experiments n°6 and n°7 are presented in Figures 7 and 8. Except for the first samples (sample n°1 in experiment n°6 and samples n°1 and n°2 in experiment n°7), charge balance results are fairly low and almost within the  $\pm 1$  meq/l range. These low charge balance results in recovered aliquots indicate that the main exchange processes taking place solely involve sodium, calcium, magnesium, and potassium. Hydrogen ions are also being exchanged, but their concentrations were too low to pose a significant impact in the final charge balance results. Differences in charge balance are likely to be a product of minor zeolite dissolution throughout these experiments. This was especially noticeable with sample n°1 in experiment n°6 and samples n°1 & 2 in experiment n°7, which presented an increased net charge balance concentration for the cations being analysed. In addition, there was a Specific Conductance increase detected in samples n°1 & 2 in experiment n°7, and this would have been mainly a consequence of an increased concentration of TOC, sulphate, and boron (Table 3).

Differences within the  $\pm 1$  meq/l range could have also been attributed to the accuracy of the analytical method used in the laboratory. However, the method used by Hill Laboratory was APHA 3125-B (Inductively Coupled Plasma) with very low detection limits ( $<0.05$  mg/l) and very good accuracy, so charge balance differences are not likely attributable to the accuracy of the measuring procedure.

High potassium, calcium, and magnesium concentrations at the start of this experiment suggest dissolution of these cations along with the exchange process. Sodium could have also dissolved from the zeolites at the beginning of the experiment, and this could have generated the unusually high sodium concentrations detected in the first two 100 ml aliquots. In addition, other elements like chloride, manganese, cobalt, and nickel (Table 3) would have contributed with low quantities of additional ions, dissolving from the zeolites, as the feed solution passed through the ion exchange column. In experiment n°7, after 200 ml of feed solution had passed through the column, one concludes that the dissolution processes stopped almost completely as seen by a reduction in specific conductance to values nearing the original value. In addition, TOC, sulphate, boron, chloride, manganese, cobalt, and nickel concentrations were reduced to about the same ion concentrations as the ones for the original (untreated) sample (samples n° 7, 19, and 36 in Table 3). However, reactive silica concentrations for these samples remained higher than the original sample's concentration, which suggests that the dissolution process had not completely stopped. Fluoride and aluminium concentrations also showed some increase at the end of this experiment.

Figure 7: Charge balance results for selected samples in experiment n°6

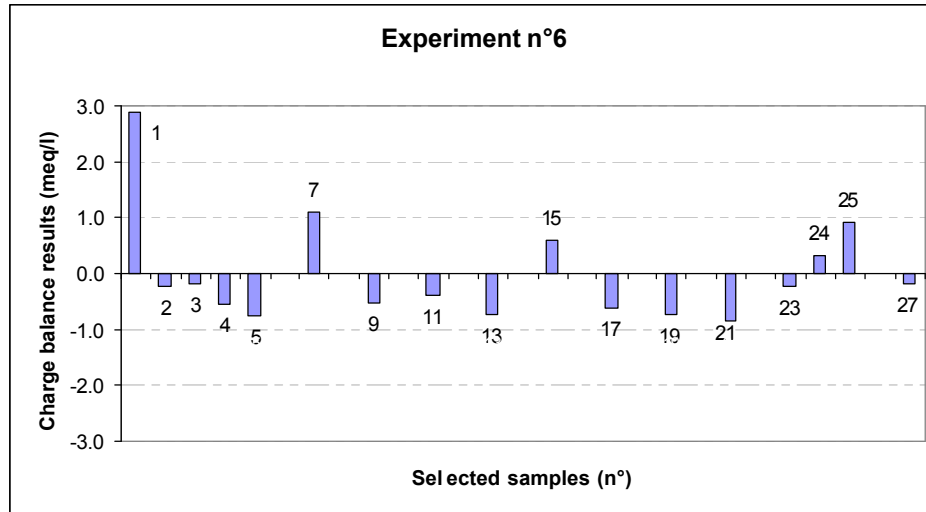
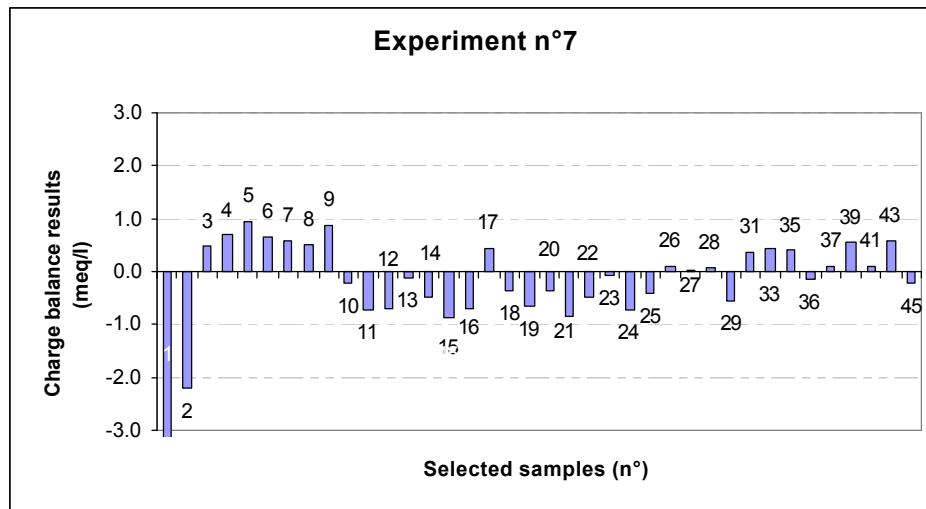


Figure 8: Charge balance results for selected samples in experiment n°7. Sample n°1 is off the chart with a net difference of -8.9 meq/l.



### 4.3.3 SODIUM ADSORPTION CAPACITY

Sodium adsorption from feed solutions throughout these experiments decreased almost logarithmically, with the highest sodium adsorption taking place at the start of each experiment, and the lowest taking place at the very end. These breakthrough curves represent the total sodium adsorbed by the zeolites, which can be expressed in terms of the zeolite mass being used, to give an indication of the total sodium adsorption capacity (Table 4) per 100g of zeolites (meq/100g). Sodium adsorption values were generally lower than the CEC values reported by Mowatt (2000) (40-110 meq/100g), which is logical because in CEC determinations zeolite samples would typically be leached with 1M solutions of ammonium acetate and sodium chloride (Blakemore et al., 1987). As discussed in the batch adsorption experiments section, the cation exchange process is highly influenced by the concentration of the leaching solution – the higher the concentration, the more extensive the cation exchange process. Since, the concentration of the feed solutions used in flow experiments n°1-7 was lower than or equal to 0.1M NaCl, the cation exchange processes would have not been as extensive as the one in a typical CEC determination. Therefore, the total sodium adsorption capacity reported in these experiments is lower than reported CEC values.

The highest sodium exchange was obtained in experiment n°3 (40.9 meq/100g) which took place under a 0.1M NaCl feed solution and with prior 1M KCl regeneration. In the rest of the column test experiments, sodium adsorption was in the 11-20 meq/100g range, but none of the zeolites in these experiments had undergone such a strong regeneration (i.e. 1M KCl) process. The second highest sodium adsorption rate was obtained in experiment n°4, which was carried out with a heated (40°C) 0.1M NaCl solution, however the total sodium

adsorption obtained in this experiment was quite similar to the one obtained in experiment n°2, which was identical to n°4 except it was conducted in downflow mode and without heating the feed solution. This is not surprising because the kinetics of ion exchange processes are highly dependent on diffusion within the zeolite, which is temperature dependent in exponential form – a 30°C temperature increase would enhance diffusion by only 10% (Slater, 1991). Since in this experiment the temperature was increased only by about 20°C, the effects of this increase were not significant in the overall ion exchange process.

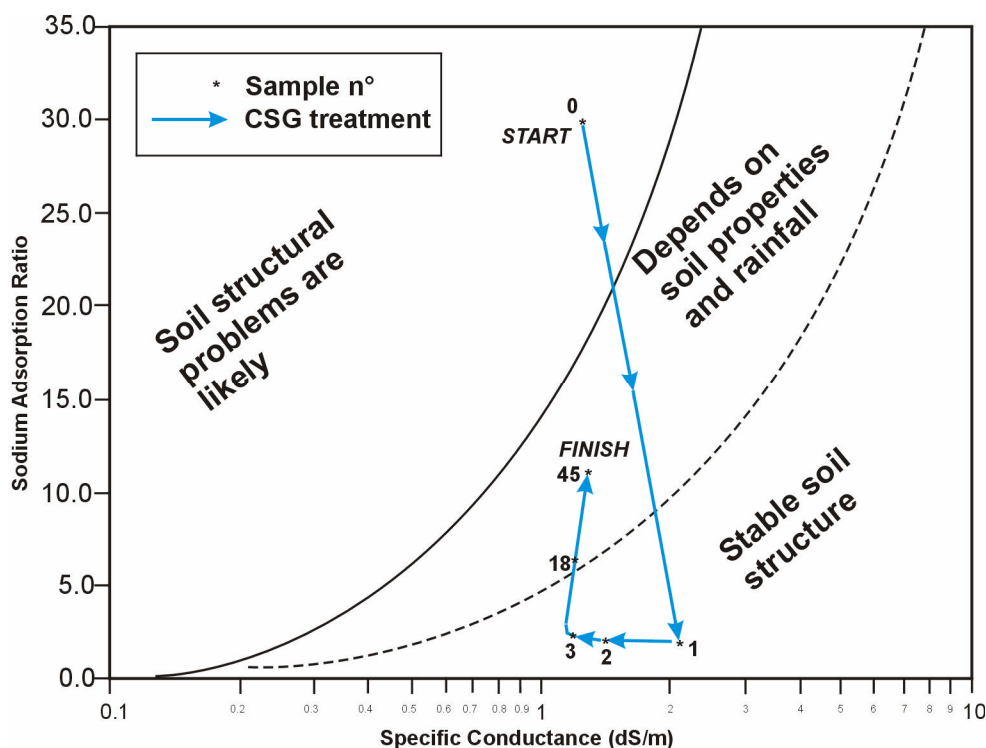
According to results of experiments n°5 and n°6, regeneration with a weak alkali solution (0.044 M CaCl<sub>2</sub>) increased the sodium adsorption capacity of Ngakuru zeolites by only 5%. Although the zeolite's adsorption capacity did not improve significantly, the regeneration process did restore their initial sodium adsorption potential for reuse.

The lowest sodium adsorption was recorded with experiments n°1 and n°7, but the feed solutions in these experiments had the lowest sodium concentration although the flow rates were different. The service flow rate in experiment n°1 was the highest service flow rate used in these experiments (78 cm<sup>3</sup>/min), but the service flow rate in experiment n°7 was one of the lowest, therefore service flow rate does not seem to pose major implications for the studied range. This suggests that overall sodium adsorption is highly dependent on feed solution concentration, and this could also influence the efficiency of the regeneration process (i.e. sodium adsorption capacity could be significantly enhanced if regenerating with a highly concentrated solution).

For both batch tests and flow-through experiments the total sodium adsorption capacity is a function of the time of exposure (shaking time or flow rate), solution concentration, and type of solution being used (strong acid or alkali solution). However, it is possible to make some comparisons. For example, for the 0.013 – 0.044 M NaCl range, the total sodium adsorption capacity ranged from 11.3 to 15.9 meq/100g (Table 4) for flow-through tests with no regeneration, whereas for batch tests, sodium adsorption ranged from 9.6 to 16.7 meq/100g for similar concentrations (0.01M NaCl). These two ranges of values are quite similar for both types of experiments, which shows how batch tests can be accurate in determining total adsorption values before conducting a flow-through experiment.

Experiment, n°7 showed that Ngakuru zeolites are able to remove sodium cations from CSG waters when operating in flow-through mode. The effectiveness of the CSG water treatment process can be evaluated by determining whether the outcome of the treatment process fits the requirements prescribed in guidelines for assessing sodicity effects.

Figure 9: Effectiveness of zeolite treatment system for experiment n°7



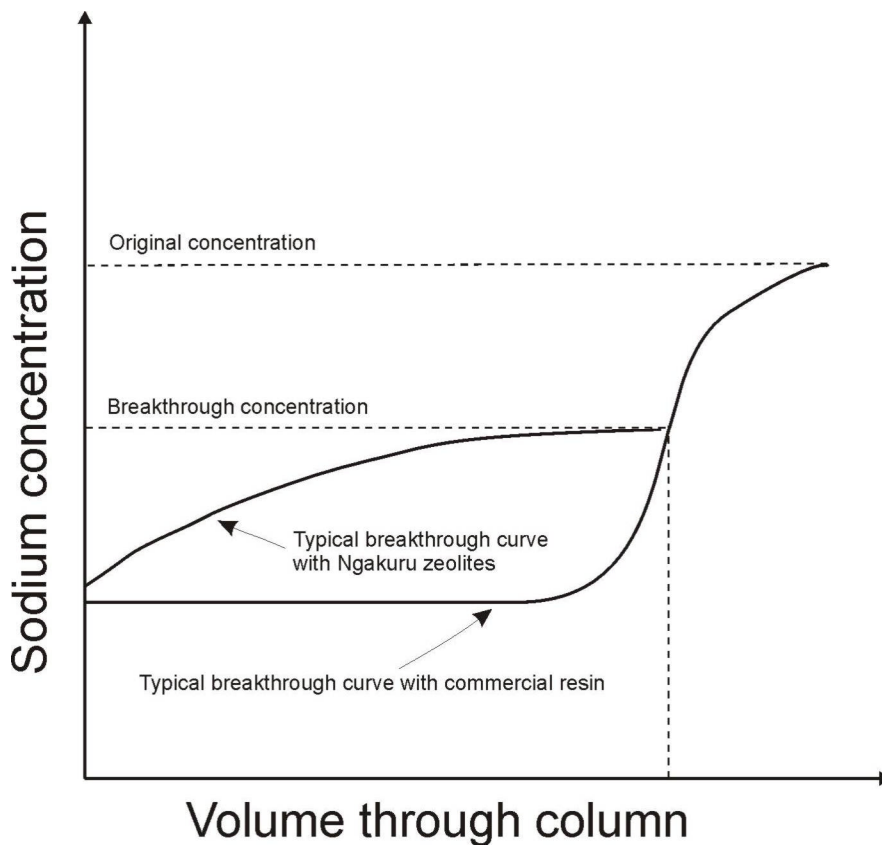


The effectiveness of the zeolite treatment system to reduce infiltration problems (due to high SAR) can be assessed using the ANZECC guidelines. For this purpose, a plot of the treated effluent aliquots is presented in *Figure 9*. This plot shows that the initial value (sample n°0) is in the zone where “soils structural problems are likely”, but the zeolite treatment system effectively shifts this position into the stable soil structure zone and into an intermediate zone where soil properties and rainfall play a more important role. *Figure 9* shows that for the first 17 treated aliquots (n°1-17) the zeolite treatment system is effective in completely eliminating potential soil infiltration problems, however for the last 28 aliquots (n°18-45) the system starts to lose its effectiveness because the treated CSG water falls in the zone where infiltration problems “depend on soil properties and rainfall”.

#### 4.3.4 KINETICS OF ADSORPTION

Throughout these experiments, sodium breakthrough curves followed a logarithmic trendline; *Figure 10* shows the shape of the breakthrough curves obtained with Ngakuru zeolites compared against a typical breakthrough curve using commercial resins (Wachinski and Etzel, 1997). In this figure, the breakthrough curve for Ngakuru zeolites reaches an asymptote which is not necessarily the original feed solution concentration. This hints that, at some stage, the efficiency of the exchange decreases but it is still taking place albeit at a lesser rate. This could be due to main exchange sites within the zeolite becoming depleted, and only secluded secondary sites being available for the exchange. In addition, it was not possible to obtain a breakthrough curve for pH in experiments n°1-6, but these values were always below the initial pH, which shows that hydrogen ions also form part of the exchange process, and the final breakthrough limit has not yet been reached. However, in experiment n°7, the pH breakthrough curve (not shown) follows the same logarithmic trendline as the sodium breakthrough curve, marking the end of the experiment. The same holds true for calcium, magnesium, and potassium cations released from the zeolites (*Figure 5*). This shows that, as the availability of sites decreases, the exchange process slows down to a minimum, with less calcium, magnesium, potassium, and hydrogen ions in the zeolite being exchanged for less sodium ions in solution.

*Figure 10: Comparison between Ngakuru zeolites and typical commercial resin breakthrough curves. Adapted from Wachinski (1997)*



In general, the separation factor ( $R$ ) for experiments n°6 and n°7 was greater than 1 but less than 2 and, for most of the aliquots, closer to one. According to the classification of Isothermal Breakthrough Cases presented in Perry et al. (1973), this case corresponds to an *unfavourable equilibrium* ( $R>1$ ), but very close to *linear equilibrium* ( $R=1$ ). This description explains the raw breakthrough curves (meq/l vs. litres through column) obtained throughout these experiments and described in Figure 10 – Ngakuru zeolites are not as efficient as commercial resins for ion exchange applications involving sodium removal.

#### 4.3.5 IMPLEMENTATION ISSUES

These flow-through experiments show encouraging results for the potential treatment of CSG waters with natural zeolites. However, implementing this treatment system on site could be complicated operationally (constant monitoring, specialised laboratory equipment for measuring breakthrough, and trained personnel). On the other hand, batch treatment could be simpler to implement. A batch treatment process would still need extensive experiments to determine adequate retention times and volume of zeolite material. Therefore, a combination of these two systems could be highly effective for simplicity and ease of implementation (semi-batch operational mode). Consequently, a proposed methodology for carrying out CSG water treatment using Ngakuru zeolites is the following:

- 1) Select a zeolite particle size which fits operational requirements. The recommended particle size range is 600-2360  $\mu\text{m}$ . Smaller particle size would prove difficult to work with, but it is possible to work with sizes larger than 2360  $\mu\text{m}$ , though the slower kinetics could lead to larger volumes of zeolites required
- 2) A laboratory batch test is carried out to determine the maximum sodium adsorption capacity. This results in a rough estimate of the sodium adsorption capacity, which is used to design the experimental setup in step 3.
- 3) A flow-through experiment is carried out under laboratory conditions. This results in a more accurate determination of the sodium adsorption capacity of the zeolites, while making it possible to calculate the retention time to be used with a given flow rate, mass, and zeolite volume. Steps 2 and 3 would have to be carried out every time zeolite quality is thought to have changed (i.e. zeolites from a different quarry) and for each new well having a different CSG water quality.
- 4) Scale up. Zeolite mass is calculated according to a given volume of water to be treated using the calculated retention time. This can be implemented on site by digging holes in the ground, which can be lined with concrete, asphalt, or an impermeable liner. The holes are then filled with a pre-calculated amount of zeolite material (zeolite pits).
- 5) CSG water treatment: the calculated volume of CSG water is fed into the zeolite pits. Even though this is not a columnar application, it is recommended to introduce the CSG water into the zeolite pits in upflow mode, mainly to provide adequate mixing throughout.
- 6) Once the CSG water has been mixed and has remained in contact with the zeolites for the prescribed amount of time, the treated water can be removed from the pits either by gravity drainage (if the site topography permits it) or by using a capable pump. This water could temporarily be stored in ponds to manage its disposal. The treated water can then be used for irrigation applications or safely disposed on land, or selected rivers or streams.
- 7) The next step is to regenerate the zeolites, and this can be accomplished with concentrated calcium solutions following the same procedure as in steps 2-6. Alternatively, the used zeolites can be completely discarded and a fresh batch of zeolite material can be used instead. If regeneration is selected, then the concentrated wastewater resulting from this process would be of low volume, and it could be hauled to a water treatment facility or evaporated on site.

This methodology is just a framework as the ultimate treatment solution would depend on factors like CSG water quality and quantity, location, topography, regulatory requirements, and stakeholder involvement.

## 5 CONCLUSIONS

This research has chosen to examine, in a broad overview, the potential for natural New Zealand zeolites to aid in the treatment of New Zealand CSG waters. The results from these preliminary experiments indicate that Ngakuru zeolites show promise in removing sodium cations from sodium-loaded solutions and Maramarua CSG waters, though it is not clear yet that they will provide a practical treatment option. Whether operating in batch or columnar mode, Ngakuru zeolites were able to absorb sodium cations from feed solutions while releasing calcium, magnesium, some potassium, and at a lesser extent hydrogen.

Treating CSG waters with Ngakuru zeolites has the potential to transform a potential wastewater into a valuable resource. These materials are readily available in New Zealand at less than 0.5% of the cost of synthetic materials. If operated in semi-batch mode, this treatment system can be implemented with ease and with little or no specialised on site equipment if preliminary studies have previously been carried out (i.e. in a laboratory). The footprint left by this treatment system could be larger than with commercial resins, but the same facility can be used to treat CSG waters from different wells. The main advantage of treating CSG waters using natural zeolites is the reduction of SAR levels in these waters, thus making them suitable for irrigation applications.

The exhausted zeolite bed can be regenerated for reuse using alkali solutions (i.e.  $\text{CaCl}_2$ ); if strong concentrations are used this can even result in enhancement of the treatment system. On the other hand, the zeolites could be used only once and then discarded (without being regenerated) or used in another application. For example, the sodium-loaded zeolite could be used in water softening or stock feed applications.

In sum, zeolites can be regenerated, re-used in reverse ion exchange treatment solutions, or used in agricultural applications. However, the ultimate way in which zeolite treatment solutions are implemented will depend on water quality, local regulations, and stakeholder involvement.

## ACKNOWLEDGEMENTS

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