

Regeneration of zeolites used for ammonium removal from anaerobic groundwater



Yvonne Mikkers

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Yvonne Mikkers

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Committee:

Prof.ir. J.C. van Dijk

Dr.ir. S.G.J. Heijman

Ir. W.W.J.M. de Vet

Dr. J. Gascon

Delft University of Technology
Dept. of Sanitary Engineering
Delft University of Technology
Dept. of Sanitary Engineering
Oasen Drinking water company
Delft University of Technology
Depts. of Sanitary Engineering and Biotechnology
Delft University of Technology
Dept. of Catalysis Engineering

Sanitary Engineering Section, Department of Water Management
Faculty of Civil Engineering and Geosciences
Delft University of Technology, Delft

Summary

Research performed of the last decades in the waste water treatment field has shown the ability of zeolites to adsorb ammonium via ion-exchange. Recent research has proven that zeolites might also be capable to remove the lower concentrations of ammonium present in groundwater to the for drinking water required standards. This makes it a promising technique as replacement for the traditional biological treatment. Still there is not much known about the effect of multiple regenerations with the different types of regenerant on the adsorption capacity and the durability of the zeolites.

This research focuses on the chemical regeneration of zeolites which have been used to remove ammonium from anaerobic groundwater. The main goals hereby have been:

- The determination of the effect of multiple regeneration on the ion-exchange capacity of the zeolites
- The testing of the effectiveness of two types of regenerant: NaOH and NaCl
- To see whether it is possible to reduce the amount of chemicals used for regeneration by reusing the regenerant.

Because the adsorption experiments have been done with anaerobic water, an extra objective has been to investigate whether ammonium adsorption is hindered by the presence of Fe^{2+} .

A 4 column set-up has been designed in which two types of zeolite, clinoptilolite and aqualite, have been used. At a drinking water treatment plant a side stream of the influent of their rapid sand filters was used as influent for the columns. Two columns (one of each material) have been regenerated with 0,1 M NaOH, the other two with 1,8 M NaCl that was being recirculated.

By monitoring the influent and effluent concentration of both ammonia and Fe^{2+} , breakthrough curves could be determined. By comparing these, the impact of the regenerations on the adsorption capacity could be established. Extensive analyses of the used regenerant showed which ions were affected by regeneration and how much regenerant was actually used per regeneration.

In the end the zeolites have been loaded and regenerated 11 times. The NaCl also has been used 11 times.

Hereby it has been determined that the zeolites do lose some of their ion-exchange capacity by regeneration. This loss is the biggest after the first regeneration. After that the adsorption capacity fluctuates around 80% (NaOH) and 70% (reused NaCl) of its original capacity. The fluctuations are caused by changing lengths of the adsorption phase while the regeneration period stays constant. The reused NaCl shows a higher loss in capacity than the NaOH in combination with a higher chemical usage. From an economical point of view NaOH is more feasible. The effect of the extreme pH on the zeolites has not been investigated though.

It has been possible to reuse the regenerant and still obtain reasonable results. Whether that really is a reduction of the used chemicals, is not completely clear because no comparative study with single use NaCl has been performed.

There has been no evidence that the presence of Fe^{2+} in the source water interferes with the ammonium adsorption. The positive effect that was found is that the iron is removed by the zeolites to great extent as well.

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1. Introduction

1.1. Traditional Groundwater treatment

In 2007 approximately 55% of the Dutch drinking water was prepared from groundwater (VEWIN, 2008).

Water extracted from the deeper layers in the ground usually is more or less anaerobic. As a result of that the water can contain methane, hydrogen sulphide, manganese, dissolved iron and especially ammonium.

When anoxic groundwater is treated, standard procedure is to aerate and filter the water. For deep anaerobic ground water, this process may have to be repeated before the water is ready to be distributed. The general treatment process of anaerobic ground water is shown in Figure 1-1.

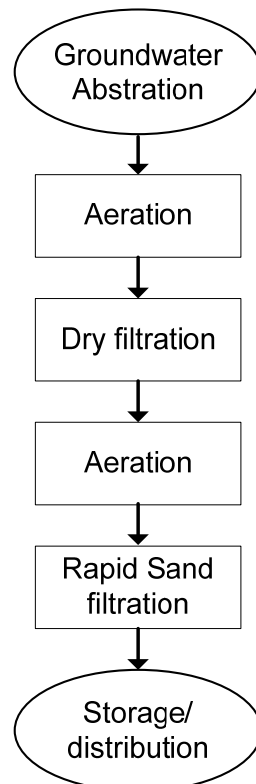


Figure 1-1: General treatment process deep anaerobic groundwater

During filtration solids are removed from the water but some other processes take place as well. Methane and hydrogen sulphide are stripped, manganese, iron and ammonium are oxidized. The oxidation processes are partly bacteriological and have proven their efficiency over the years. Researchers also showed that using biological treatment would reduce the biofilm formation potential in the distribution network (Persson et al., 2006). Nevertheless, other research has proven that counter effects of bacteriological treatment, such as discolouration, change in odour and even the

reformation of pathogens in the distribution system, can not be ruled out completely (e.g. (Hallam et al., 2001) and (Thomas et al., 2008)). Therefore it is useful to investigate non-microbial treatment methods for the removal of for example ammonium.

1.2. Alternative

Research done over the last thirty years has shown that, at least when ammonium removal is concerned, there is an alternative. It has turned out that certain zeolites (see also section 2.2) can be used as ion-exchange medium with a high selectivity for ammonium. If the ion-exchange process, which will be explained in section 2.3 can be made feasible, the biological ammonium conversion inside the rapid sand filters is not necessary anymore.

The main reasons why these filters still haven't been implemented on large scale is that either the cost of chemical regeneration is too high (between 60 and 80% of the total costs) or regeneration is performed biologically.

Chemical regeneration of the zeolite is carried out by flushing the filter with a concentrated NaCl solution. Although this solution can be used multiple times, hereby reducing the costs of used chemicals, it is still a big load that has to be stored somewhere. When the regenerant is worn out, the solution will still have a relatively high salinity and of course ammonium concentrations will be high as well. Some of the literature found does propose several solutions, but they have never been tested on large scale yet.

The costs are made up by the expenses for the large amount of chemicals used in the regenerant and the costs for treatment and disposal of the waste stream (a strong brine solution with high ammonium concentration). In order to deal with the money problem it means that the two major problems regarding regeneration, which are 'need for space' and 'what to do with the waste stream', have to be solved.

Noteworthy is that the majority of research carried out so far, has been done on waste water. The ammonium levels in waste water however are much higher than the levels in groundwater. The other important difference between waste water treatment and drinking water treatment is the required ammonium level in the effluent. Obviously, the maximum concentration allowed in drinking water is much lower than the allowable concentration of treated waste water. This means that the preferred system has to function at low ammonium levels, but it also must have a high performance.

The research carried out for drinking water purposes all has been performed with aerobe water. This means that dissolved gases such as methane and hydrogen sulphide are already stripped from the water and there is no dissolved iron present either. Nevertheless, the research performed (for example (Abrahamse et al., 2007)), does show that zeolites perform still up to standard when it

comes to low ammonium concentrations in the influent and extremely low effluent concentrations. It can be concluded, therefore, that if the regeneration process and the re-use of regenerant can be optimized, zeolites can, against slightly higher costs, replace rapid sand filters as a mean to remove ammonium from drinking water.

2. Literature Review

2.1. Introduction

Using zeolites as ion-exchange system has proven to be a suitable and robust alternative to the use of biological sand filters. Over the years a lot of research has been done on zeolite systems, mainly within the waste water field. A very thorough literature review on ammonium removal with zeolites has been published (Hedström, 2001). This paper will serve as steppingstone for the literature review.

The purpose of this literature review is to find out more about the properties of different types of zeolites, gain a better understanding of the ion-exchange process and factors that might be of influence and investigate the possibilities for regeneration of zeolites.

2.2. Zeolites

A zeolite is a mineral built up from hydrated aluminosilicates.

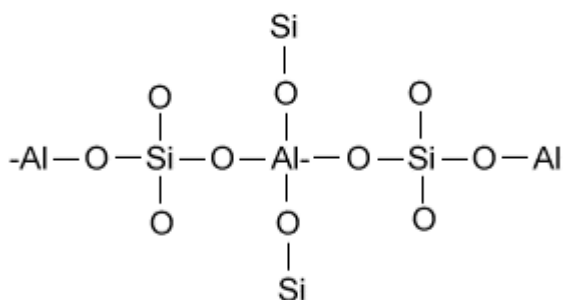


Figure 2-1: Basic chemical structure of zeolite molecules (Source: (Page, 2008))

As can be seen in figure 2-1 the basic structure is very regular. Consequently, the small pores in the mineral essentially all have the same size and provide a large surface area.

The large amount of regular pores makes zeolite a very useful molecular sieve. Only molecules smaller in size than the pores will pass through, the rest will be rejected.

Besides being a molecular sieve, zeolites can function as an ion-exchange medium. The aluminium silicates are strongly negatively charged, so cations are needed to form a neutral mineral. The most commonly encountered cations attached to zeolites are sodium, potassium and calcium.

Research done over the last 30 years has proven that zeolites not only have a high cation-exchange capacity, they also have a special affinity for ammonium (Jorgensen, 1975; Jorgensen et al., 1976; Semmens et al., 1977). This affinity is a quality rarely found in other ion-exchange media.

Zeolites come in many types and are roughly classified by their silicon / aluminium ratio. The most commonly named natural zeolite type in literature on ammonium removal is clinoptilolite (e.g. (Belar-

Baykal and Cinar-Engin, 2007, Blokland Visser et al., 2006, Hlavay et al., 1982, Semmens et al., 1977)), but chabazite (Green et al., 1996) and mordenite (Miladinovic and Weatherley, 2008) are frequently mentioned as well. Besides the natural types there are also about 150 types of synthetic zeolites, which are not widely tested in the field of water treatment.

Clinoptilolite appears to be the zeolite most suitable for the use in water treatment because there is an appropriate ratio between its ammonium affinity and its durability (Blokland Visser et al., 2006). It must be taken into account however that the origin of the zeolite very much influence its suitability (Hedström, 2001).

Zeolites are products of nature and therefore they are not always created under the same circumstances. Structural imperfections but also the amount of different cations in the structure might influence the ion-exchange capacity. In addition the mineral found does not always have the same purity. Experiments have been done on zeolites with a purity of 40-50% but also on zeolites with a purity up to 90% (Jorgensen et al., 1979). As a result of this, it can only be concluded that the exact ion-exchange capacity of a natural zeolite can be established by experiments on that specific zeolite and that values found in literature might under but also overestimate the ion-exchange capacity of a certain type of zeolite.

2.3. Ion-Exchange

Ion-Exchange can be described as a reversible chemical reaction between a relatively insoluble substance and a solution. During the reaction ions attached to the substance are substituted by ions dissolved in the solution. The exchanged ions will all have the same electric charge. With cationic exchange, positively charged ions are substituted. With anionic exchange the negatively charged ions are exchanged.

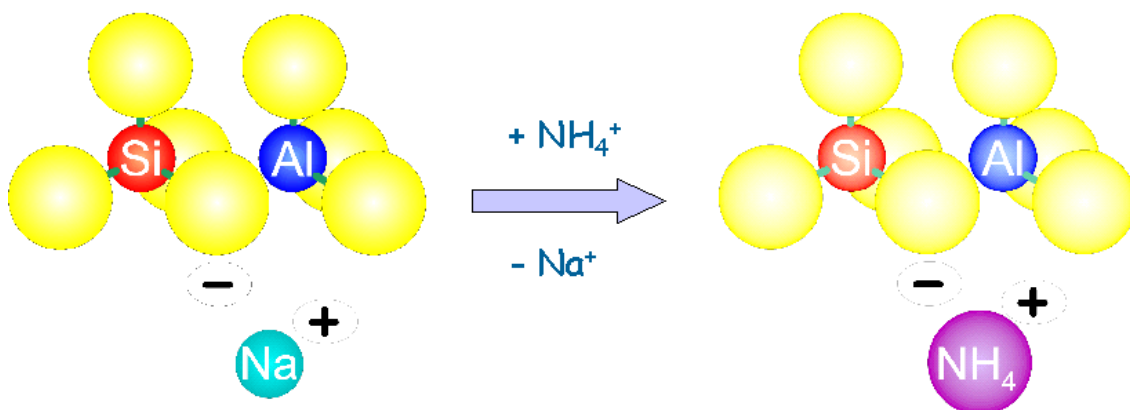


Figure 2-2: Ion-Exchange on a zeolite (Source: (Schmidt, 2008))

Figure 2-2 schematizes the ion-exchange on natural zeolites. Ammonium (NH_4^+) is dissolved in water until it comes into contact with the zeolites. The sodium (Na^+), which was attached to the zeolite, dissolves in the water and the ammonium takes its place on the zeolite.

Usually, different types of ion-exchangers have a different affinity for certain types of ions. Besides sodium, cations such as calcium and magnesium are also found on natural zeolites. The presence of these ions influences the ion-exchange capacity of the zeolite.

2.3.1. Ion-exchange mechanisms

Although they are not completely similar, ion-exchange and adsorption have some basic characteristics that are very much the same. Both systems remove specific substances from an aqueous solution by means of a porous substance. Where adsorption only removes material from a solution, ion-exchange also introduces new substances into the liquid. An other difference between the two systems is that with adsorption neutral substances can be removed, while with ion-exchange the substance needs to have an electrical charge, hence the substance needs to be ionised to be removed.

The general similarity between both systems means that some kinetic principals are also fundamentally the same.

The main mechanism that helps the removal is diffusion. Diffusion is described as the transport of molecules or ions from a region with higher concentration to one of lower concentration by random molecular movement. In case of ion-exchange, or adsorption, this mechanism can be divided into three steps.

- 1) Transport of the specific substance from the bulk liquid to the outer surface of the adsorbent material by molecular diffusion. Although there is no real film present, this mechanism is called film diffusion. A layer of ions forms resistance to the mass transfer at the surface of the particles. The concentration gradient in this layer or film forms the driving force for this type of diffusion.
- 2) The second step is the transport of ions from the particle surface into interior site by diffusion within the pore filling liquid. This is called internal or intra-particle diffusion.
- 3) The third step is the adsorption of ions on the active sites of the interior surface of the pores. Because this is a very quick process and therefore it can not be rate determining (Faust and Aly, 1998).

If step 3 is not rate controlling, then step 1 or 2 must be. This is depended on several factors.

These factors are described as follows (Inglezakis and Pouloupoulos, 2006) :

- The concentration in the liquid phase (higher concentration means higher driving force in the film layer)
- The ion-exchange capacity of the material (higher capacity means higher driving force in the exchanger)
- Particle size (smaller particle size means short mass transfer distances in the pores)
- The openness of the ion-exchanger's structure (larger pores means less obstructions, easier access)
- Amount of agitation of the liquid (agitation of the liquid means easier mixing of ions around particles)
- Selectivity of the exchanger (high selectivity quickens adsorption of certain ions)

2.3.2. Interruption test

Based on the above stated factors an educated guess can be made about which mechanism is the rate controlling one. To be sure though, an interruption test can be performed. This test starts with a normal loading period, after which the ion-exchange medium and the bulk liquid are separated for a while. During this period the concentration gradients within the particles disappear.

When the ion-exchange medium is submerged again in the bulk liquid, the ion-exchange process will of course continue. Since the ion-exchange rate is monitored, it can be determined whether there is a difference in between the rate before and after the interruption.

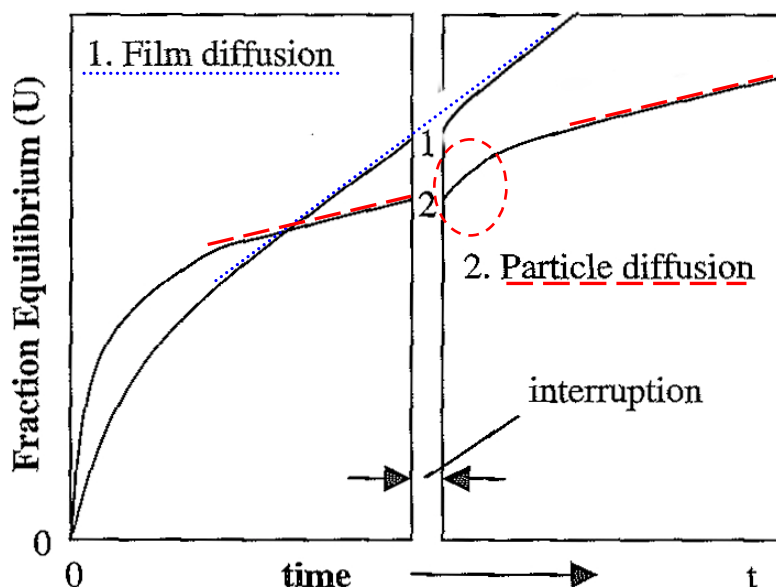


Figure 2-3: Interruption test with film diffusion control and particle diffusion control¹

¹ Adapted from: INGLEZAKIS, V. J. & POULOPOULOS, S. G. (2006) *Adsorption, Ion-exchange and Catalysis Design of operations and environmental applications*, Amsterdam, Elsevier B.V., p. 292

If there is a difference, like line 2 shows in Figure 2-3, the rate determining mechanism is particle diffusion. If there is no significant difference, the dominating mechanism is film diffusion. The variation in exchange rate with particle diffusion is caused by the continuation of ion-exchange in the pores while the ion-exchange medium and the bulk solution are separated. Once the interruption ends, a new equilibrium has established within the pores. The higher concentration of the specific ion in the bulk load disturbs this equilibrium and increases the driving force until the 'old' equilibrium has established itself again.

With film diffusion the disruption of the concentration gradient is not that big, therefore the effect is not that apparent.

2.4. Ammonium-Ammonia equilibrium

Ammonium (NH_4^+) is the conjugated acid of the weak base ammonia (NH_3 (g)). When ammonia is dissolved in water it reacts with the water molecules to form ammonium according to the reaction presented in equation (2.1).



The K_b , which is the base constant of this reaction, is $1,8 \cdot 10^{-5}$ mol/L at a water temperature of 298 K. It equals equation (2.2).

$$K_b = \frac{[NH_4^+] \cdot [OH^-]}{[NH_3]} = 1,8 \cdot 10^{-5} \quad (2.2)^2$$

When the acid-base equilibrium (see equation (2.3)) and the rules $pH = -\log[H_3O^+]$ and $pOH = -\log[OH^-]$ are taken into account, the relative ammonium and ammonia concentration in water of a certain pH can be calculated.

$$K_w = [H_3O^+] \cdot [OH^-] = 1 \cdot 10^{-14} \quad (2.3)$$

² From: VERKERK, G., BROENS, J. B., BOUWENS, R. E. A., GROOT, P. A. M. D., KRANENDONK, W., VOGELZANG, M. J., WESTRA, J. J. & WEVERS-PRIJS, I. M. (2004) *BINAS havo/vwo*, Groningen, Wolters-Noordhoff bv.; Tabel 49

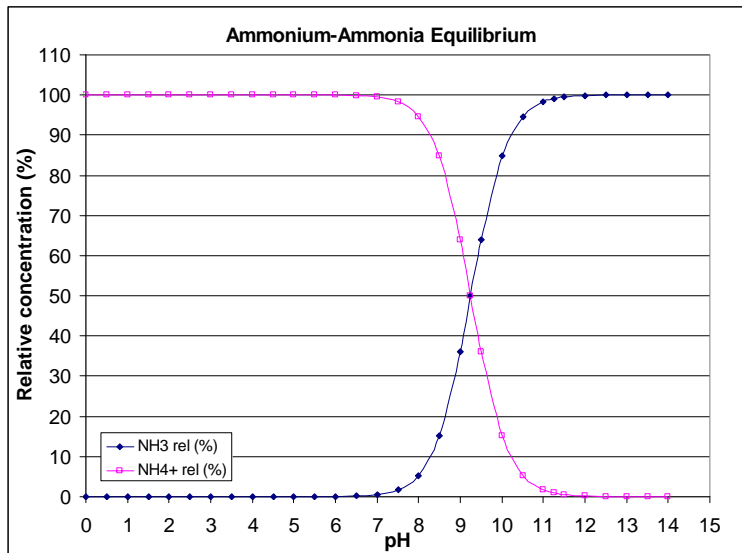


Figure 2-4: Relative ammonium (NH_4^+) and ammonia (NH_3) concentrations based on the pH of water

This leads to the graph shown in figure 2-4. In the graph it can be seen that at a pH of 9.25 the ammonium and ammonia concentration are equal. At a pH lower than 7 there is barely any ammonia left in the solution and above pH 11 almost all ammonium is converted to ammonia.

2.5. Aspects that influence the ion-exchange of ammonium on zeolites

2.5.1. Type of zeolite

As described above, zeolites come in many different types. Because soil layers throughout the world vary a lot and zeolites were created within these layers, there is a large diversity within the types as well. Although not every type of zeolite has the same affinity for ammonium, research has made clear that zeolites take up ammonium best when they contain sodium (Hlavay et al., 1982). Hedström (Hedström, 2001) summarizes that the best form of zeolite is the homo-ionic form with only sodium ions bound to the aluminosilicate skeleton. Chemical pre-treatment might aid the ion-exchange capacity, this however might not be necessary when the zeolite is regenerated with a sodium solution. Other studies showed that zeolites performed better and better after the first few regeneration cycles (Jorgensen et al., 1976).

2.5.2. Grain size

When using filter beds, the grain size of the filter material always influences the productivity. In the case of zeolites used as ion-exchange medium this is not only valid when head loss is concerned, but also when ion-exchange capacity is regarded.

Small filter material means fine pores which leads to more friction and therefore a higher head loss. Smaller zeolite grains and a small grain size distribution also lead to a higher ion-exchange capacity

((Hlavay et al., 1982) and (Hedström, 2001)). Using grain sizes > 1,0 mm decreases the ion-exchange capacity of zeolites. This probably is due to a decrease of specific surface area. It is also stated that the decrease of ion-exchange capacity for larger grain sizes only matters in case of higher surface loadings.

2.5.3. Ammonium concentration

As previously explained, ion-exchange only takes place when the medium has an affinity for the specific ion. Besides the affinity, concentrations turn out to have a major influence as well. It was concluded that a higher ammonium concentration in the feed water results in a quicker breakthrough of the filter (Hedström, 2001). It was also found that higher influent concentrations led to higher uptake of ammonium on the zeolite (Jorgensen et al., 1979). This of course has to do with the diffusion mechanism discussed in section 2.3.1.

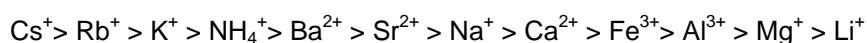
2.5.4. Filtration velocity and hydraulic retention time

From the literature it can be concluded that a low hydraulic retention time can be used to achieve a desired effluent quality, since ammonium adsorption is a relatively fast process (Hedström, 2001). The hydraulic retention time does however influence the filter runtime. With a retention time smaller than 3 - 5 min, breakthrough occurs too fast. The same results were found by (Beler-Baykal and Cinar-Engin, 2007).

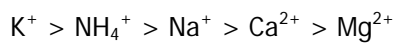
Besides the hydraulic retention time filtration velocity influences the effluent quality as well. Low velocities increase the contact time, but it also means that a layer of water is formed around the zeolites. This layer with a lower ammonium concentration acts as a shield between the higher concentrated water and the zeolites. During some regeneration experiments this effect was encountered in a strong form (Dimova et al., 1999). The water layer around the zeolites is fully saturated, but is not disturbed enough by the surrounding water flow to mix properly. The mechanisms behind this effect are explained in 2.3.1.

2.5.5. Competition

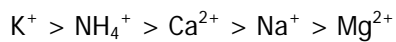
Zeolites have a specific affinity for ammonium adsorption. This does not mean however, that other cations will not be adsorbed. Every cation that is adsorbed on a zeolite takes a place where one or more (depended on the valance of the adsorbed ion) ammonium ion could have bonded. This means that every cation could be potential competition. Not every cation is adsorbed that easily. Research done in the 1960's show that the selectivity of a variety of cations on clinoptilolite is as follows (Langwaldt, 2008):



During selectivity studies a similar sequence was found at 0,01 N (Dryden and Weatherley, 1987), namely:



This is slightly different from the sequence they reported from literature based on a study at 0,1 N. Here the sequence was found to be:



Compared to ammonium clinoptilolite shows less affinity for all cations present in groundwater but potassium. This seems a positive sign, since potassium is present in much lower concentrations than ammonium or calcium.

The influence of other cations present in groundwater can not be ignored though.

Early literature on ammonium adsorption by zeolites report that a cation concentration of 0,01 mol/L significantly decrease the zeolites ability to adsorb ammonium (Hedström, 2001). Experiments where adsorption tests were performed with distilled water and tap water showed that the adsorption capacity of ammonium in tap water was significantly lower than when distilled water was used. (Belar-Baykal and Cinar-Engin, 2007) ran a series of tests in order to determine the effect of the hardness (in this case calcium concentration) of the water and concluded that calcium might form a serious competition. In some cases over 50% of the bonding places were taken by competing cations (mainly calcium). These results show that competition is a aspect to take into account when designing ion-exchange columns to remove ammonium from water.

The main cation to be concerned of regarding competition when treating groundwater is expected to be calcium, since this ion is present in the water in relatively high concentrations (see also paragraph 4.5).

2.5.6. pH

Ammonia (NH_3 (g)) is a strong base. Ammonium (NH_4^+ (aq)) can only exist at neutral or lower pH. This implies that changing the pH of an ammonium solution means varying the ammonium concentration as well. The literature (Hedström, 2001) found on the topic of pH showed that the optimum pH for ion-exchange of ammonium on zeolites is 6 - 7. This is supported by other research (for example (Langwaldt, 2008)). At lower pH H^+ forms a serious competition for the bonding places on the zeolites. At higher pH, ammonium will convert to ammonia which is not an ion, so can not be removed by ion-exchange.

2.5.7. Temperature

Biological nitrification is a temperature sensitive process. When water temperatures drop below 4 °C bacteria go into hibernation and the process comes to a halt. Not much is written about the influence temperature changes have on ion-exchange kinetics. It is only stated that assumptions about temperature not having any influence at all, seem to be correct (Hedström, 2001).

2.5.8. Scale

Most experiments performed on ammonium removal by zeolites, were done at very small scale (bench or lab scale). Literature about experiments done in pilot-plant size systems has not been found. The only comments found on differences in results when using different sizes of systems are from (Hlavay et al., 1982). Results on small systems are significantly more positive than the results found on the system which was a 100 times bigger. So lab-scale results may say something about the possibilities but up-scaling seems to have a negative influence on the results.

2.6. Regeneration

Once the effluent quality reaches the maximum allowable ammonium concentration, an equilibrium has established between the ammonium concentration in the feed water and on the zeolite. The zeolites will not adsorb more ammonium. In order to restore the zeolites' ion-exchange capacity they have to be regenerated.

Regeneration can be done in several ways:

- Chemical regeneration
- Biological regeneration
- Bio - Chemical regeneration

2.6.1. Chemical Regeneration

The goal of chemical regenerations is to make the bonding places on the zeolite available again. This is done by using a chemical solution to desorb the ammonium and other ions. Since the homo-ionic sodium form of zeolites is most suitable one for ammonium adsorption, the regeneration solution should contain a relatively high amount of sodium. Different studies (Liberti et al., 1981), (Ashrafizadeh et al., 2008) and (López-Vigil et al., 2006) all applied different concentrations (0,6 - 1,0M) of NaCl. Other researches (Jorgensen et al., 1976) used NaOH or a mixture of NaCl and NaOH as regenerant. This can be especially useful when air stripping is used to remove NH₃-gas after regeneration. Counter effect is that high pH might damage the zeolite. A second disadvantage of using a high pH regenerant is the possibility of calcium precipitation on the zeolite or in the pores. Calcium ions are slightly too big for the pores in the zeolite and might get stuck, hereby blocking the

pores permanently. Increase of pH does result in less bed volumes of regenerant needed to restore the zeolite, though. At a pH of 11,5 20 BV of 1,2% brine were needed, as for a pH of 12,5 only 10 BV were needed to regenerate the zeolites properly (Hedström, 2001).

It was also concluded that when medium high flow velocities (10 - 20 BV/h) are used, the performance of the regeneration is independent of the flow velocity (Hedström, 2001).

Low velocities (< 5 BV/h) have a very negative effect on the regeneration time. It takes significantly more time to regenerate the same amount of zeolite. (Dimova et al., 1999) concluded the same.

The bottom line is that the time needed to regenerate the zeolite is depended on the concentration of the regenerant and the pH of the solution.

2.6.2. Biological regeneration

Biological regeneration uses the principle of nitrification to turn ammonium into nitrate (see equation (2.4)).



Bacteria are added to the process to eliminate the use of chemicals. The bacteria attach themselves to the zeolites waiting to start the ammonium conversion.

When a bulk load of ammonium flushes through the filter, bacteria start converting the ammonium but of course they can't keep up with the high load. Zeolites will adsorb the ammonium overdose.

When the ammonium concentration in the solution around the zeolites drops, ammonium redissolves in the water and will be converted by the bacteria.

Because the biological process needs a lot of oxygen, extra air has to be brought into the columns to keep the bacteria going.

The negative side-effect of the bio-film layer is that, according to (Lahav and Green, 2000), the layer decreases the ion-exchange capacity with approximately 30%.

2.6.3. Bio-Chemical regeneration

With bio - chemical regeneration a regenerant is used to remove the ammonium from the zeolites.

After biological treatment of the regenerant in (a separate vessel) the regenerant can be reused. The two major issues that have to be taken into account with this type of regeneration are the brine concentration when reusing the treated brine and whether the bacteria can handle the brine concentration. Additionally, bacteria can't handle extreme pH-ranges and they do need lots of oxygen to keep the nitrification going (Miladinovic and Weatherley, 2008).

When the bio-chemical regeneration takes place in the filter column, a regenerant is used (in up-flow) to desorb the ammonium from the zeolite. Bacteria will convert the ammonium into nitrate. By

recirculating the regenerant, all the ammonium will eventually be transformed and the regenerant can be reused.

If the biological conversion takes place in a separate vessel, an extra medium is necessary to be used as carrier for the bacteria. Apart from that, the principle is just the same as with the nitrification in the filter bed.

The big advantage of the separate nitrification is that the biological activity is placed outside the production process. The risk of bio fouling of the zeolite and biomass carry-over can be limited this way, making the system more suitable for drinking water treatment purposes.

When using a buffer tank to store the ammonium saturated regenerant before it will be nitrified, there will be a second advantage compared with the bio regeneration in the filter. According to (Hedström, 2001) the regeneration time is much lower in case of the separate nitrification.

During biological regeneration H_3O^+ is formed, this means pH adjustments need to be made in order to maintain a stable environment for the bacteria and keep optimum conditions for desorption of ammonium. Na_2CO_3 can be used as a pH-buffer. An advantage of this addition is that it will replenish the sodium lost to the zeolite while adjusting the pH. A side effect of this addition might be the precipitation of calcium carbonate. This can be a positive effect because it removes the calcium ions from the regenerant. It can also be a negative effect if the substance precipitates at unwanted places.

2.7. Influence of chemical regeneration on ion-exchange capacity

During chemical regeneration a loss of adsorption capacity might occur. (López-Vigil et al., 2006) performed several batch experiments to test whether chemical regeneration might influence the ion-exchange capacity of homo-ionic clinoptilolite. It was found that there was no significant loss of ion-exchange capacity between zero and ten regeneration cycles. (Beler-Baykal and Guven, 1997) on the other hand, found that there was a loss in capacity between the virgin zeolite and the same zeolite regenerated ten times.

2.8. Gases in water

Many gases can be dissolved in water. The actual concentrations are depended on the solubility of the gas (defined by Henry's law), the partial pressure of the gas in the atmosphere, the temperature and the concentration of impurities in the water (for example the salinity).

The saturation concentration (concentration at which the amount of gas dissolved in the liquid is in equilibrium with the concentration of that same gas in the air) is a function of the type of gas and the partial pressure of the gas in contact with the liquid.

Henry's law is written in many ways. One of these ways describes the relationship between the mole fraction of the gas in the atmosphere above the liquid and the mole fraction of that same gas in the liquid as:

$$c_a = \frac{H}{P_T} c_w \quad (2.5)^3$$

where:

- c_a = mole fraction of the gas in air [-]
- H = Henry's law constant for the specific gas [atm]
- P_T = Total pressure [atm]
- c_w = mole fraction of gas in water [-] (mole gas/mole water and water)

an other form of expressing Henry's law is in a unitless way.

$$\frac{C_g}{C_s} = H_u \quad (2.6)$$

where:

- C_g = concentration of constituent in gas phase [mg/l]
- C_s = saturation concentration of constituents in liquid [mg/l]
- H_u = Henry's law constant [-]

The dependence of the temperature is shown in the relation:

$$H_u = \frac{H}{RT} \quad (2.7)$$

where:

- H_u = Henry's law constant [-]
- H = Henry's law constant [atm.m³/mole]
- R = Universal gas law constant [atm.m³/mol.K] (=82,057.10⁻³)
- T = Temperature [K]

³ From: METCALF & EDDY, I. (2003) *Wastewater engineering, Treatment and reuse*, McGraw-Hill.

Gas Stripping

The idea of gas stripping is that gas dissolved in a liquid is transferred to a gas. This is done by adding a gas that does not contain the specific substance to the liquid. The reaction that follows this disturbance of the equilibrium between the gases in the liquid and the gas above the liquid forces the specific gas out of the liquid, into the gas.

Since the solubility of gases in water is varying with the type of gas, the amount of 'force' that needs to be applied varies as well.

Based on Henry's law constant (see equation (2.5)) an analysis can be made about how much effort is needed to remove a substance from a liquid.

According to (Metcalf & Eddy, 2003) substances with a constant higher than 500 atm are readily strippable. Substances with a constant of around 0,75 to at least 38 atm are badly strippable and substances with a constant lower than 0,1 atm are practically not strippable at all.

Ammonium has a constant of 0,75 atm and is therefore not easily removed from a liquid.

The first requirement of course is that the ammonium is present in the gas phase. As is explained in section 2.4 this can be done by raising the pH. If the pH is higher than 9,25 the majority of the substance is present as gas. The higher the pH becomes, the more gas is present and the stripping will become easier.

Beside the concentration in and above the liquid and the temperature, the size of the liquid surface area in contact with the gas phase is also very important. This is expressed in the air-to-liquid ratio that is needed to achieve the removal of a certain gas. In the waste water industry the recommended air-to-liquid ratio to remove ammonium efficiently is 2.000-6.000 to 1. Compared to the ratio of 20-60 to 1 recommended for removal of VOC's this is huge. The stripping of ammonium will be very difficult.

2.9. Conclusions

In the introduction of this chapter it was stated that a lot of research regarding ammonium removal with zeolites has been done in the field of waste water treatment. Only a very small part of the literature found is based on experiments for the purpose of drinking water treatment.

The adsorption of ammonium on zeolites is a relatively simple process. Critical note hereby must be that most of the research has been done in bench- or lab-scale systems and the one research where a small and a larger system are compared showed a decrease of effectiveness with an increase of system size. It can be expected that a full scale system shows even more reduced results. The three effects that can influence the ammonium removal the most are grain size of the zeolite, pH and competition of other cations (potassium and calcium being the biggest threats).

Regeneration is quite a different matter. Although there are multiple methods to regenerate the zeolite, all of them are either complex or costly. By nitrifying the regenerant, costs are saved, but the nitrification process still is fragile.

The two studies on the effect of regeneration on the adsorption capacity are in conflict with each other. One says there is no apparent loss of capacity in 10 regenerations, the other one claims the loss in that period is significant enough to be mentioned. Still all data is about only 10 regeneration cycles, which is not that much considered the expected life span of the zeolites. Re-use of regenerant might be a cost-effective and waste reducing improvement. This is only feasible if ammonium can be removed from the regenerant. Although expected to be difficult, one way might be gas stripping. This does require a very high air-to-liquid ratio.

3. Problem analysis

3.1. Problem description

Research has shown that ion-exchange by zeolites can be a suitable alternative to the traditional form of ammonium removal in drinking water treatment. Still there are several reasons why this method has not been implemented on large scale yet. One might be unfamiliarity. Because the system has not been used widely yet, not much experience has been gained, which is why people are hesitant to use it.

Then there is the aspect of regeneration. Chemical regeneration is costly because a lot of regenerant is needed during regeneration, disposing of used regenerant is complex and not much is known yet about the long term effects of regeneration on the zeolites and their ion-exchange capacity. These are issues that might be dealt with by doing research.

3.2. Research Objectives

The focus of this research is the chemical regeneration of zeolites, after they have been used to remove ammonium from groundwater.

Main goals hereby are to:

- determine the effect of multiple regenerations on the ion-exchange capacity of the zeolites
- test the effectiveness of two types of regenerant: NaOH and NaCl
- find out whether it is possible to reduce the usage of chemicals by reusing the regenerant

While the regeneration is the main objective, an extra objective can be expressed: To investigate whether removal of ammonium from anaerobic water is possible or that the Fe^{2+} present will interfere with the ion-exchange process.

3.3. Research questions

In order to achieve the goals set, several questions need to be answered.

- Can the zeolites be regenerated to their full potential?
- How much regenerant is needed to achieve that?
- Is there a difference in performance between the zeolites regenerated with NaOH or NaCl?
- Can the amount of chemicals needed for regeneration be reduced by stripping ammonium from the regenerant and re-circulate the left-over stream?
- What is the composition of the regenerant at the time it can not be used anymore and can it be disposed of easily?
- What is the effect of Fe^{2+} on the removal of ammonium from groundwater?

3.4. Plan of approach

In order to answer the questions and thus realize the objectives, a zeolite containing system in which it is possible to monitor ammonium and iron concentrations has to be designed and built.

Once the set-up is running, breakthrough curves for ammonium and iron have to be established.

Since two types of regenerant are used, comparison of the respective breakthrough curves will give insight in the performance of the regenerants.

The re-use of regenerant is tested by re-using 20 L of NaCl over and over again. By adding nitrogen gas to the regenerant while the pH is raised will test whether it is possible to strip the NH_4^+ from the regenerant. Concentrations of competing ions in the re-used regenerant will be determined and mass balances can be made.

4. Materials and methods

4.1. Set-up

As explained in the plan of approach, two main methods of chemical regeneration will be tested. The first one will be the use of NaOH as a regenerant, the second will be the use of NaCl.

Per type of regenerant two types of zeolite will be tested, namely natural clinoptilolite and aqualite.

This means a four-column set-up needs to be designed in which it is possible to regenerate with the earlier mentioned chemicals without damaging the set-up. Besides that, it must be possible to reuse the NaCl solution.

Other necessities for the set-up are:

- The possibility to rinse the columns with demi water or tap water
- The possibility to blow nitrogen into the columns
- The possibility to operate the columns both in up-flow and down-flow conditions
- The possibility to monitor ion concentrations, pH value and redox potential of the columns' effluent
- The possibility to drain the columns

These demand led to the design presented in Figure 4-1. The full page version can be found in Appendix A.

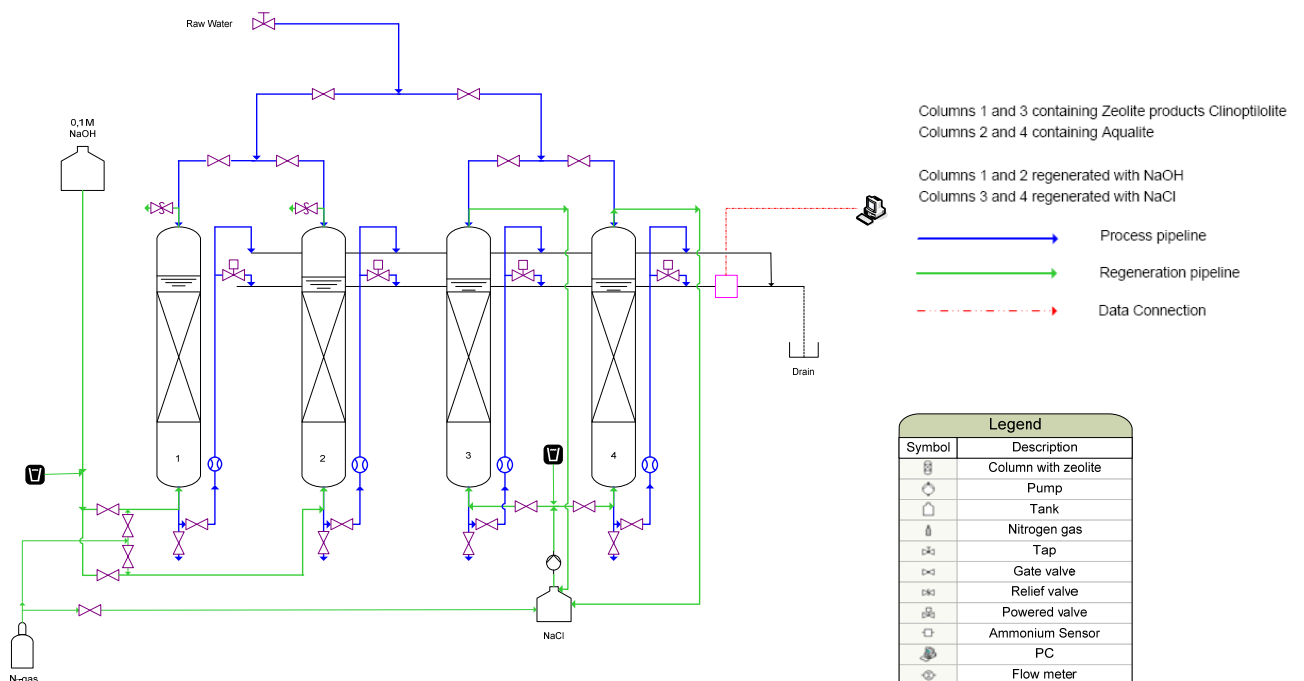


Figure 4-1: Schematic overview of set-up

Besides the fixed parameters, there are still a number of variables.

- Empty Bed Contact Time (EBCT)
- NaCl concentration
- Regeneration duration
- pH of NaCl solution

The four columns are made of transparent pvc and they have an inner diameter of 34 mm and a height of 1200 mm. The zeolites are contained within the column by placing filter plates at the top and bottom of the columns. In the plates holes are drilled with a diameter of 0,4 mm. Their total surface area of 12,57 mm² is the same as the surface area of the tubing connected to the columns. The tubes, valves and connections used are all from Festo's PUN/QS system. This is a push-in system that is originally designed for gas distribution systems, but adapted for wet conditions. The suitability for gas guarantees anaerobic conditions.

A Watson-Marlow 505Du pump is used for the distribution of NaCl regenerant. The NaOH is fed to the columns by gravity. A 25 litre tank is used as container for the 0,1 M NaOH solution, a 100 litre tank with a diameter of 38 cm as container for the NaCl regenerant

4.2. Zeolites

Two types of zeolites are used as ion-exchangers. Natural clinoptilolite was kindly provided by Zeolite Products. Aqualite is a relatively new type of zeolite, provided by the Dutch distributor of Josab International.

The chosen particle size range is 1,0 – 2,5 mm. A sieve analysis is performed to establish the size distribution.

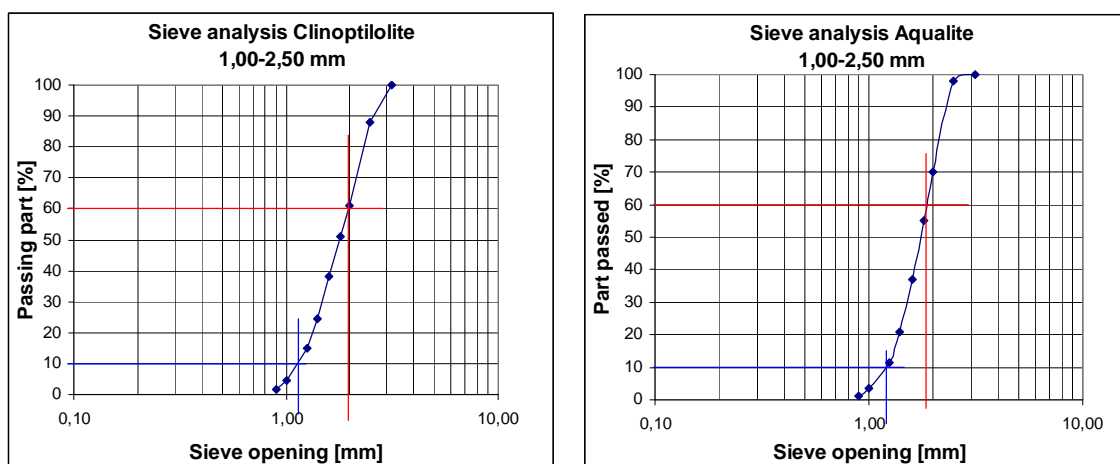


Figure 4-2: Sieve analysis Clinoptilolite (left) and Aqualite (right)

From the sieve analyses in Figure 4-2 the uniformity coefficient U can be determined for the filter material.

$$U = \frac{d_{60}}{d_{10}} \quad (4.1)$$

U = uniformity coefficient [-]

d_{10} = size of sieves that let pass 10% of the sand mixture [mm]

d_{60} = size of sieves that let pass 60% of the sand mixture [mm]

This coefficient reflects the variety of grain sizes in a batch of filter material. If the coefficient is 1, the material is very uniform. This means there is hardly any variety in grain size. To avoid stratification of the filterbed during regeneration a uniformity coefficient of 1,3 to 1,5 is recommended for rapid sand filters.

Based on equation (4.1) and Figure 4-2 it can be said that the uniformity coefficient of the clinoptilolite used is 1,8 and for Aqualite 1,6.

4.3. Chemicals

All chemicals used are made of analytical grade. For the ammonium analyses a photospectrometer kit from Merck is used (type 1.14752). Because the colour reagent in this analytical kit is temperature dependant, the official reaction time of 5 minutes was lengthened to 7 minutes while storing the vials inside a coat pocket. This to compensate for the water temperature, which was maximum 15 °C and the environmental temperature which was approximately 15 °C as well.

Iron analyses were also performed using a Merck photospectrometric kit (1.14549). For these analyses the official method found in the manual were followed.

The chemical analyses of the regenerant are performed by the Vitens Drinkingwater Laboratories. They are board certified according to NEN-EN-ISO/IEC 17025 regulations. The ammonium analyses are performed by raising the pH in the sample to 12,4. After that the ammonia concentration is measured by photospectroanalysis and the result is presented in concentration NH_4^+ .

4.4. Column Experiments

The impact of the variables mentioned in section 4.1 will be tested in two sets of experiments.

Experiment 1: Adsorption - Regeneration cycles with anaerobic groundwater EBCT = 6 min

Based on the results from the column tests reported in (Blokland Visser et al., 2006) and the wish to run a regeneration cycle every day, a bed height of approximately 70 cm was chosen in combination with a flow velocity of 6,5 m/h. The average NH_4^+ concentration in the groundwater is 6,5 mg/l (0,36 mmol/l).

When the columns are filled up to 70 cm, a volume of 0,64 l is used. This is in accordance with approximately 650 grams of zeolite. To make the columns comparable, the amount of zeolite used, was set at 650 grams. Since the zeolites are delivered in packages containing only the desired grain size range, no pre-treatment has been carried out.

Experiment 2: Adsorption - Regeneration cycles with anaerobic groundwater EBCT = 17 min

Although ion-exchange is a quick process, an Empty Bed Contact Time of 6 minutes turned out to be too short to use the zeolites up to their full capacity. The zeolites were replaced by new ones and the columns are filled up to 110 cm. Since the first experiments showed a lot of stratification in the filter beds, the zeolites were sieved through a 2,5 mm mesh and a 1,0 mm mesh first. This reduced the amount of small particles significantly.

The flow rate of the raw water passing through the filter bed was lowered to approximately 3,5 m/h resulting in an EBCT of 17 min.

4.5. Raw water quality parameters

The experiments all have been conducted at Oasen's water treatment plant ZS Lekkerkerk in Lekkerkerk. The water treatment plant has two well fields. The set-up was continuously fed with water from well field Tiendweg. The average water quality parameters for the period 2003 – 2006 are presented in Table 4-1.

Table 4-1: Water quality parameters well field Tiendweg, ZS Lekkerkerk

Well field Tiendweg 2003-2006		Median	Average	Median	Average
		mg/l	mg/l	mmol/l	mmol/l
Ammonium	N	4,3	4,4	0,31	0,31
Ammonium	NH ₄	5,6	5,7	0,31	0,32
Calcium	Ca	81,6	81,5	2,04	2,03
Chloride	Cl	127	121,8	3,58	3,44
Iron	Fe	5,4	5,6	0,10	0,10
Potassium	K	2,7	2,7	0,07	0,07
Magnesium	Mg	10,8	10,7	0,44	0,44
Manganese	Mn	0,58	0,61	0,01	0,01
Methane	CH ₄	0,722	1,075	0,05	0,07
Sodium	Na	61,8	61,5	2,67	2,67
Sulphate	SO ₄	46,3	45,7	0,48	0,48
Hydrogen carbonate	HCO ₃	225	228	3,69	3,74
Acidity (pH) at 20°C		7,2	7,22		
Temperature [°C]			13		

4.6. Important values drinking water law and sewage regulations

In the Netherlands Drinking Water Companies have to make sure their product complies with the regulations set in the 'Drinkwaterwet' and the 'Waterleidingbesluit'.

A sewage treatment plant can only dispose of its treated water onto surface water if the water quality is in accordance with 'Lozingsbesluit WVO stedelijk afvalwater'.

In the research questions in paragraph 3.3 a number of substances have been mentioned. Table 4-2 provides an overview of the allowable concentrations in the drinking water.

Table 4-2: Maximum allowable values in drinking water according to (Drinkwaterbesluit, 2009)

	Drinkwaterbesluit	
Ammonium (NH₄⁺)	mg/l	0,20
Calcium (Ca)	mmol/l	1 <(Mg ²⁺ + Ca ²⁺) <2,5
Iron (Fe)	µg/l	200
Magnesium (Mg)	mmol/l	1 <(Mg ²⁺ + Ca ²⁺) <2,5
Manganese (Mn)	µg/l	50
Potassium (K)		N/A
Sodium (Na)	mg/l	150

The only substance of interest for this research that has been regulated in waste water is ammonium in the form of total nitrogen. The maximum allowable concentration is 10 mg/l for large Waste Water Treatment Plants and 15 mg/l for smaller ones. Substances present in the waste stream of ion-exchange reactors can harm the waste water treatment process though.

Since every wastewater treatment plant has a specific loading and capacity there are no standard rules or regulations about disposing of industrial waste water. Nonetheless, industrial waste water can not be discharged onto the municipal sewer systems straight away. In order to do so the sewer manager and the wastewater treatment plant to which the sewer is connected have to be contacted first. After it is established what the composition of the waste water is and how much is going to be disposed of per period of time, the cost will be determined.

5. Key results and conclusions

The main goal of this research has been the chemical regeneration of zeolites which were used to remove ammonium from groundwater. Focus points hereby have been the effect of multiple regenerations on the adsorption capacity, the differences between two types of regenerant and the reduction of necessary chemicals.

The second objective is to find out whether the presence of Fe^{2+} in anaerobic groundwater might interfere with the removal of ammonium by means of ion-exchange.

In this chapter the key results found during Experiment 1 and Experiment 2 will be discussed.

For a drinking water company the primary goal is to produce good quality drinking water. Since this goal is not pursued at any cost, an equilibrium needs to be established between quality and costs. A mass balance helps finding that equilibrium by determining the efficiency. It can also provide a better insight in why certain operations gained better results than others. Naturally the ammonium concentrations in the columns' effluent will be presented as well.

Experiment 1 had an EBCT of roughly 6 minutes. This turned out to be too short to achieve a desirable effluent quality, but the experiments did give some useful insights in the process. These will be discussed.

Experiment 2 had an EBCT of approximately 17 minutes. This resulted in a better water quality. Extensive analyses have been performed on the used regenerant. With these results a better understanding of the regeneration process and the type of competition for adsorption sites could be gained. This will be discussed later in this chapter.

A complete list of results can be found in the measuring reported in Appendix B.

5.1. Experiment 1

5.1.1. General performance of the columns

The general performance of the columns is determined by analysing the effluent quality after every regeneration. For each column the effluent quality is compared per regeneration but the performance per column is also compared with the performance of the other columns.

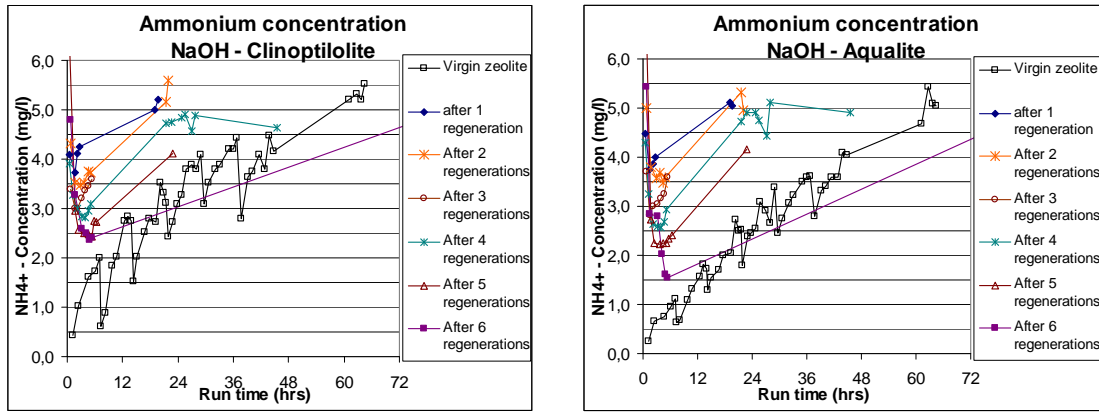


Figure 5-1: Ammonium concentrations in the effluent of Clinoptilolite (left) and Aqualite (right) before and after the six regeneration cycles with NaOH

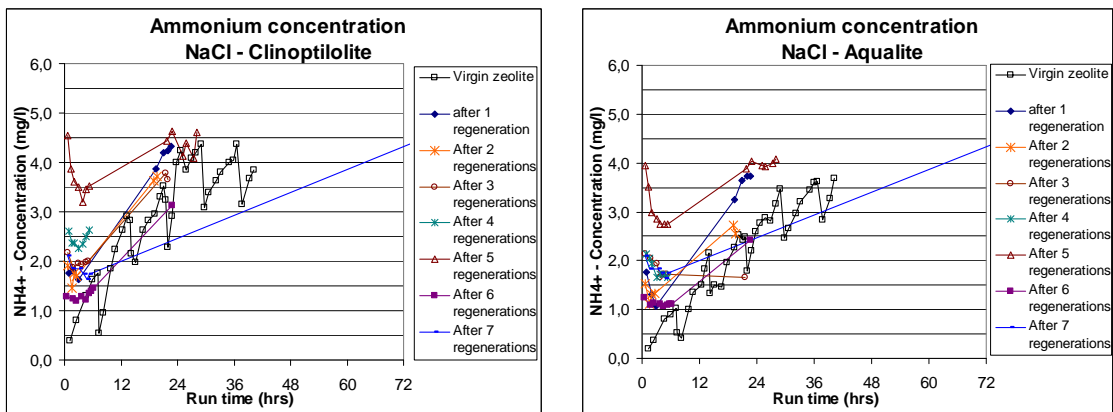


Figure 5-2: Ammonium concentrations in the effluent of Clinoptilolite (left) and Aqualite (right) before and after the seven regeneration cycles with NaCl

Figure 5-1 and Figure 5-2 give an overview of the ammonium concentrations in the effluent of the columns. If the Clinoptilolite graphs (left) are compared with the Aqualite ones (right) it can be seen that regardless of which type of regeneration is applied, filtration with Aqualite always gives lower ammonium concentrations.

If regeneration with NaOH (Figure 5-1) is compared to regeneration with NaCl (Figure 5-2), it shows that the performance of the NaOH columns is getting better by the regeneration, while the effluent of the NaCl columns is deteriorating until the regenerant is refreshed after the fifth regeneration. The improvement in regeneration efficiency with NaOH is probably due to improvements in regeneration method and the use of more regenerant each time. A complete overview of how the columns were regenerated can be found in Appendix B.

One fact that can be noticed with all four columns is that the effluent quality deteriorates quickly throughout a cycle. The lowest ammonium concentration is only achieved a very short while, after which the concentration rises again. Although there are big gaps between measurements taken, the trend seems to be that once the rising in concentration starts it rises fast. This indicates that the time the water and the zeolites are in contact with each other is not long enough.

This theory is supported by results from experiments done by (Dimova et al., 1999). They found that to achieve a minimum concentration of 0,5 - 1,0 mg/l NH_4^+ in water with an influent concentration of 10 to 25 mg/l NH_4^+ and a flow rate between 5 and 7 m/h a minimum contact time of 4 to 6 minutes was necessary. With lower influent concentrations, the ion-exchange rate would slow down which means a longer contact time is needed.

With a flow velocity of approximately 6,6 m/h and a maximum NH_4^+ concentration of 7 mg/l a contact time of 6 minutes is not high enough to achieve effluent concentrations that approach the maximum, allowable ammonium concentrations in drinking water (see paragraph 4.6).

5.1.2. Interruption test

During the first days of the experiment, the columns were shut down overnight. This had the effect of an interruption test (see also paragraph 2.3.2).

As explained, this test can help to determine the main adsorption mechanism. The rate at which adsorption continues after an ion-exchanger is separated from the solution and then re-immersed reveals which mechanism is rate limiting. If film diffusion is the key mechanism, the rate after continuation will not be very different from the adsorption rate before interruption. If particle diffusion is the key mechanism adsorption will continue with a higher rate than before, but it will level itself once the equilibrium inside the particles has established itself again.

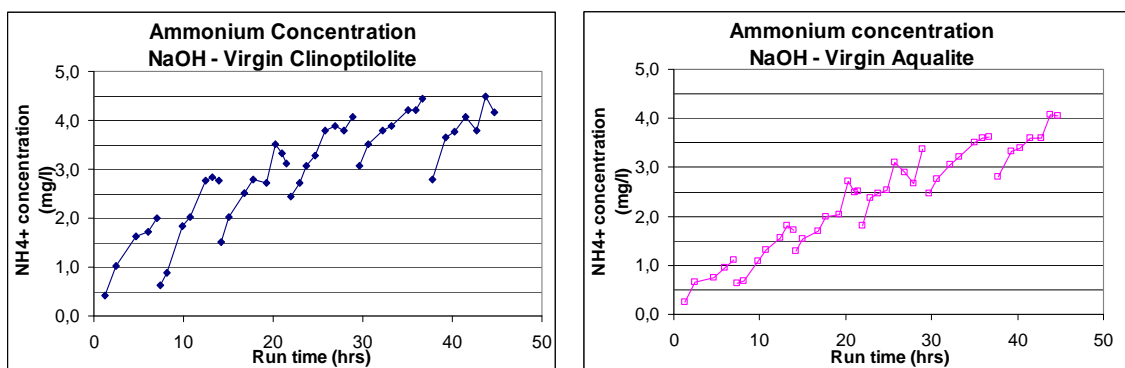


Figure 5-3: Ammonium concentrations in effluent column 1 (left) and column 2 (right) after interruption

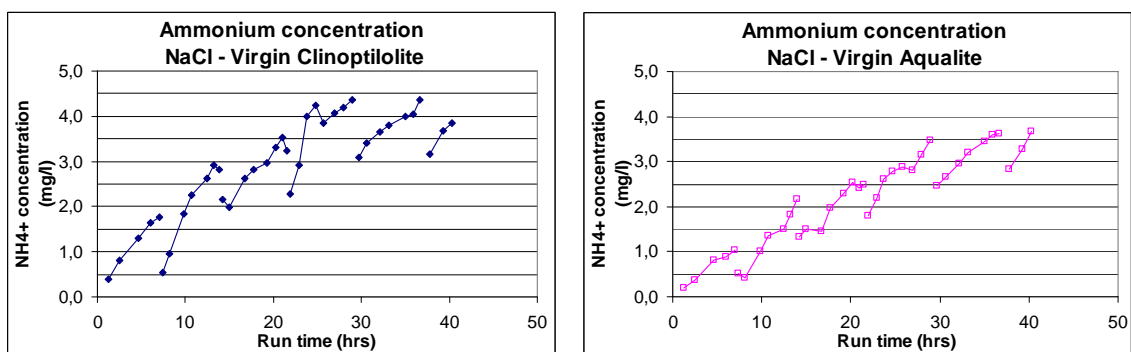


Figure 5-4: Ammonium concentrations in effluent column 3 (left) and column 4 (right) after interruption

Figure 5-3 and Figure 5-4 show the ammonium concentrations before and after interruption. All four graphs show that the ammonium uptake has not been very constant throughout the intervals. A lot of peaks and dips can be recognised. Despite these inconsistencies a general trend in ammonium uptake rate can be recognised in most intervals. Since the rate in most of these intervals is relatively the same and very little changes can be seen between the beginning of a new interval and the rest, it might be concluded that film diffusion is the rate limiting mechanism. To be absolutely sure though, the tests would have to be done again while trying to keep the flow rates as constant as possible.

After an interruption the effluent concentration always is much lower than right before the interruption. Since the influent concentration and the adsorption do not change significantly it is expected that the effluent concentration would just continue at the same level as where it was before interruption. Since this is obviously not the case, it can be concluded that an equilibrium between the ammonium in the feed water and on the zeolite has not been established.

5.1.3. Effectiveness regeneration

Two columns have been regenerated multiple times with the same 20 l of NaCl. As discussed in paragraph 5.1.1 the regenerations were getting less and less successful each time. Figure 5-5 shows that after the fourth regeneration the performance of the zeolites gets worse with a big step.

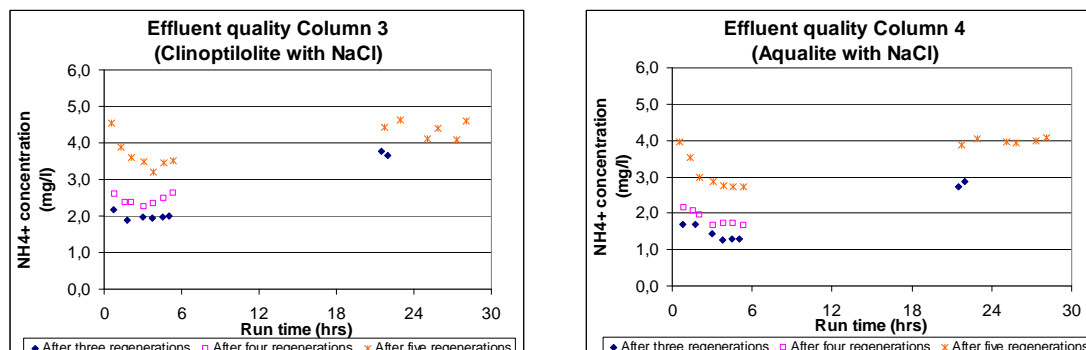


Figure 5-5: Ammonium concentration in effluent column 3 (left) and column 4 (right) after 3 (♦), 4(□) and 5(*) regenerations

Refreshing the regenerant improves the performance of the zeolites, as can be seen in Figure 5-6.

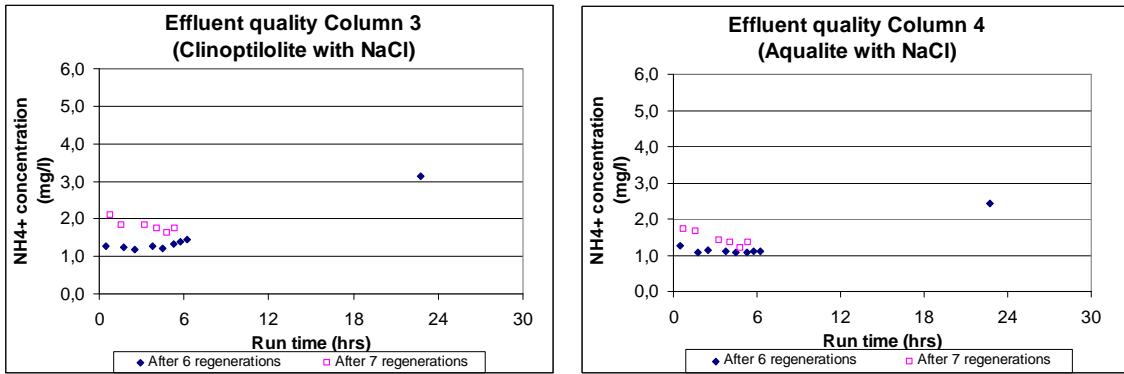


Figure 5-6: Ammonium concentrations in effluent of column 3 (left) and column 4 (right) after 6 (♦) and 7 (□) regenerations

This indicates that the regenerant has worn out. Whether that is due to high amounts of ammonium or competing ions in the regenerant or low sodium concentrations can not be told though.

5.1.4. Rinsing after regeneration

After every regeneration all four columns were back-washed with tap water for 10 minutes at a rate of approximately 60 l/h to remove left-over regenerant. After this the columns were flushed 5 minutes with raw water, also with a velocity of approximately 60 l/h. The high speed at which the anaerobic water entered the aerobe columns helped prevent clogging. The moment reduced iron comes into contact with more aerobe conditions it oxidises and starts forming iron-oxide flocs which will precipitate on the zeolites. The shear stress provided by the high velocity prohibited precipitation. After those five minutes, the columns were closed of to insure the anaerobic conditions and the flow direction was reversed again.

In total the columns were rinsed 15 minutes before a new cycle would be initiated. It was expected that this would be enough to clear the zeolites from residual regenerant. Unfortunately, measurements showed differently.

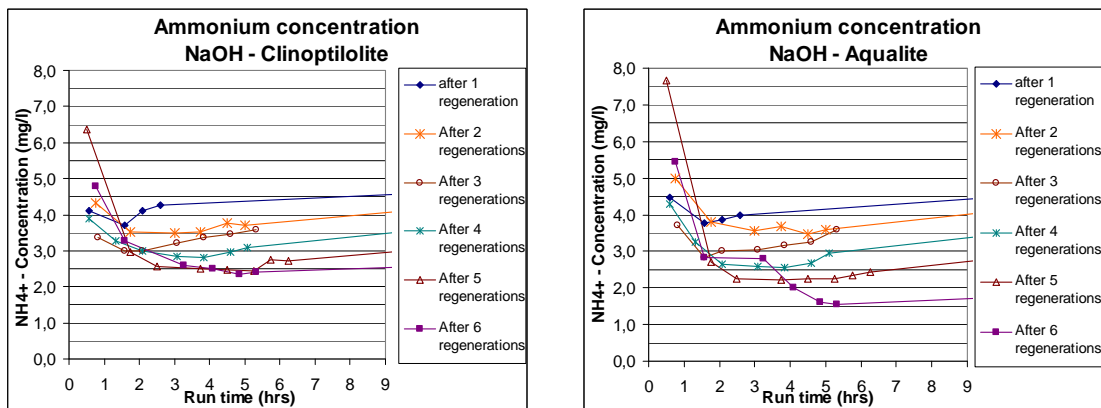


Figure 5-7: Ammonium concentration during the first hours after regeneration with NaOH (left: Clinoptilolite; right: Aqualite)

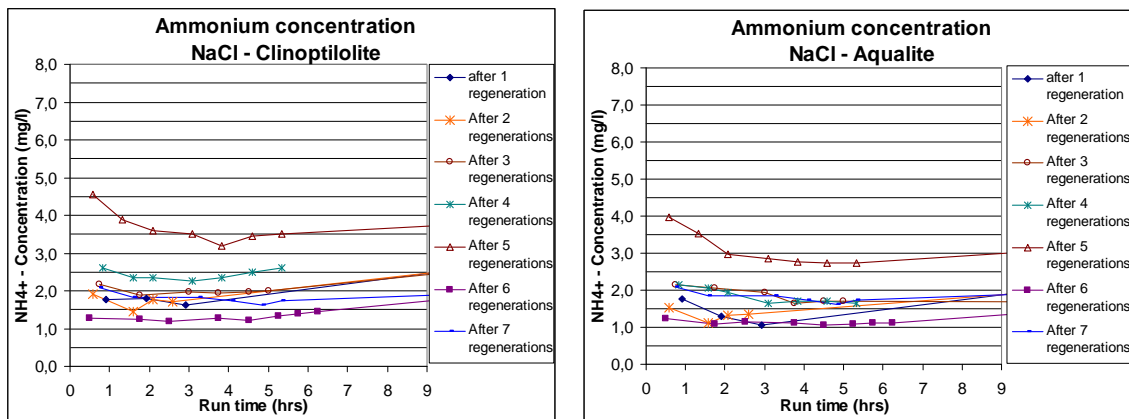


Figure 5-8: Ammonium concentration during the first hours after regeneration with NaCl (left: Clinoptilolite; right: Aqualite)

Figure 5-7 and Figure 5-8 show the ammonium concentrations in the effluent during the first 9 hours after regeneration. They clearly show high concentrations during the first two hours. After approximately five hours the ammonium concentrations have dropped and levelled out at a certain base line.

If the performances of the columns are compared with each other per regenerant, not much difference is found in the course of the curves between the two materials. If the two regeneration types are compared though, it can be seen that the columns regenerated with NaOH have much higher ammonium concentrations during the first two hours than the columns regenerated with NaCl. This implies that the rinsing of the columns regenerated with NaCl is much more effective than the rinsing of the NaOH-columns. It is very likely that this has to do with the amount of regenerant used. Because so many more litres of regenerant pas columns 3 and 4 during their regeneration all possibly exchangeable ions have been exchanged already. This makes the rinsing part easier. Columns 1 and 2 are regenerated with only one twentieth of the amount of regenerant used for the other two columns. Still the results are not that much worse. The plots in Figure 5-8 do bring to mind that the regeneration is incomplete and the rinsing is not complete either. The drop in ammonium concentrations during the first two to four hours is simply too big. With all four columns it takes too long before the minimum level is reached. Ideally the minimum level is found right after the moment an equilibrium is reached within the column. This way maximum quality can always be guaranteed and less production time and water is wasted.

5.1.5. General conclusions after Experiment 1

Based on the results found during this experiment it can be said that the Empty Bed Contact Time of roughly 6 minutes is not long enough to have a full removal of ammonium from the raw water. Although that is not the main goal of this research, it is important to know because the research parameters should be as close to reality as possible to get reliable results. Furthermore, the

improvement in removal efficiency of the columns regenerated with NaOH show that the minimum amount of regenerant necessary to regenerate zeolites properly has not been added yet.

The regenerations with NaCl that is being reused show that it is possible to regenerate multiple times with the same regenerant. Since the regenerant was completely worn out after four regenerations, there are still some limiting factors to deal with. To tackle those factors, it first needs to be determined which they are.

5.2. Experiment 2

5.2.1. General performance of the columns

During Experiment 2 it was noticed that not every regeneration cycle is as effective. In the case of NaCl as regenerant, this of course partly has to do with the reuse of regenerant. However, every new regeneration of column 3 and 4 should be a little less effective than the one before. Figure 5-9 shows that that is not the case. The efficiency is calculated by dividing the total amount of ammonium removed at that time by the total amount of ammonium that has entered the column at that same time. Although the removal efficiency does decrease over a number of regenerations, there are cycles that worse than others. If a cycle is doing worse, like cycle number 3, it is doing worse in all four columns, which can also be seen in Figure 5-10. This must have a reason.

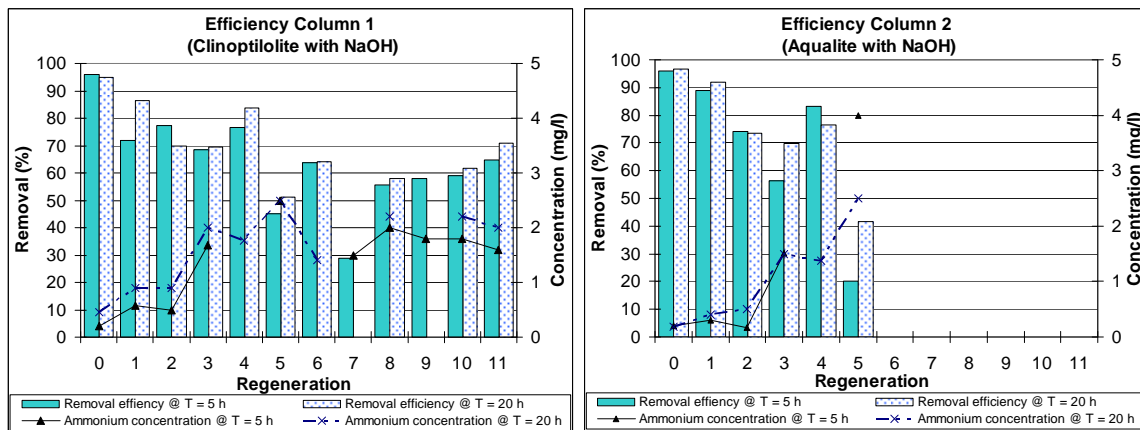


Figure 5-9: Performance of Column 1 (left) and 2 (right) after 5 hours of loading

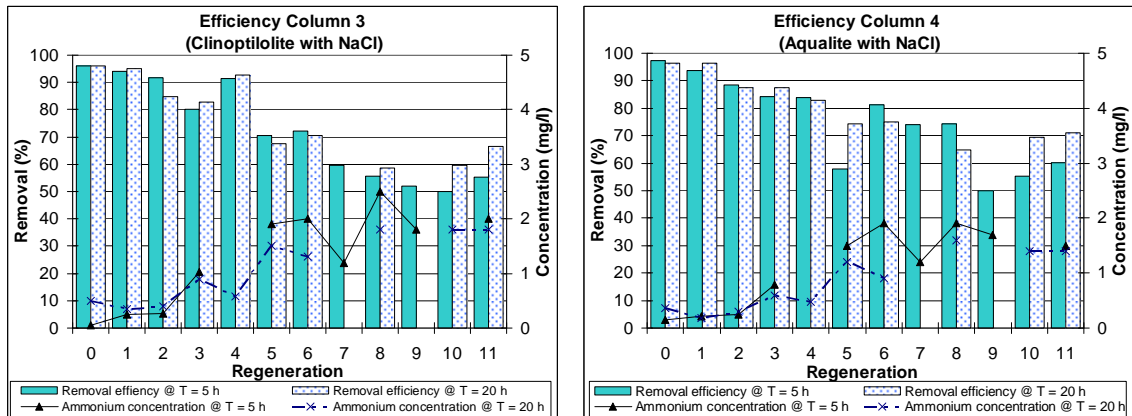


Figure 5-10: Performance of Column 3 (left) and 4 (right) after 5 hours of loading

The cycles after regeneration 2, 4, 7 and 9 all had a run-time for approximately 100 hours, while the rest only lasted a maximum of 45 hours. As a result regeneration 3, 5, 8 and 10 had to remove many more ions than the other regenerations. In the figures it can be seen that at a run-time of 5 hours (hatched columns) all four columns had a lower efficiency after a long cycle than after shorter cycles. After 20 hours (dotted columns) this effect is not as strong.

This implies that the regenerations after a long run have not been complete. The zeolites were not cleaned completely, therefore they are saturated quicker.

So in order to maintain an equal performance between cycles with varying lengths, it is necessary to adjust the regeneration length as well.

Besides the removal efficiency Figure 5-9 and Figure 5-10 also show the ammonium concentration in the effluent at 5 (▲) and 20 (x) hours after starting a new cycle. In the lines the cycles after a long run can be recognised again. The effluent concentration is higher in most cases than in the cycle before or after.

The striking thing where these values are concerned is that for column 2, 3 and 4 the effluent quality at 20 hours is equal to or even lower than at 5 hours. This leads to think that besides the fact that regenerations have not been complete, the columns also have not been rinsed properly. Regenerant containing higher amounts of ammonia is leaking from the pores during the first hours after regeneration, but it probably also prevents ammonium in the feed water from attaching to the zeolite. So this mechanism has a double effect on the total removal during the first hours of a new run.

Although it is clear that the effectiveness of a regeneration is influenced by the length of the loading run before the regeneration and the thoroughness of the rinsing afterwards, these definitely are not the only factors of influence. This will be discussed in the following sections.

5.2.2. Analyses of the used regenerant and mass balances

To assess the effectiveness of the regenerations properly, it first needs to be established whether there are big differences between the loadings of the columns over time. If the loadings during the various runs are similar enough, it can be said that there is a relation between them. This would make them comparable, which is what is needed to create proper mass balances. In Table 5-1 to Table 5-4 an overview is given of the total amount of ammonium (in mg) that has entered the respective columns.

Table 5-1: Total amount of ammonium entered [mg] in column 1 after T hours per run

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Average	St. Dev
20 hrs	399	361	415	371	384	411	416	398	385	429	426	433	402,3	23,34
48 hrs			995		906			956		1043			975,0	58,2
96 hrs			1990		1786			1912		2096			1946,0	130,6

Table 5-2: Total amount of ammonium entered [mg] in column 2 after T hours per run

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Average	St. Dev
20 hrs	425	366	429	390	178	421							368,2	96,3
48 hrs			1030		675	1032							912,3	486,1
96 hrs			2061		1535	1930							1842,0	947,8

Table 5-3: Total amount of ammonium entered [mg] in column 3 after T hours per run

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Average	St. Dev
20 hrs	416	400	379	358	235	365	350	392	404	433	330	433	374,6	54,6
48 hrs			908		753			950		1056			916,5	126,1
96 hrs			1818		1632			1906		2126			1871,0	205,1

Table 5-4: Total amount of ammonium entered [mg] in column 4 after T hours per run

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Average	St. Dev
20 hrs	460	398	364	365	292	362	366	380	376	365	400	423	379,3	40,4
48 hrs			879		802			904		881			866,5	44,8
96 hrs			1762		1669			1802		1766			1749,8	56,8

All columns have had runs that lasted for at least 20 hours. For each run the loading during that time has been determined and based on those values the average and standard deviation have been calculated. For all four columns the average loading at 20 hours lies between 360 and 405 mg. The spread in loading per run is varying over the columns though. As a result, the standard deviation for

column 1 is only a little over 5%, for column 2 the standard deviation is 26,2%! During the fifth run, there were some problems with the flow rate of column 2. This resulted in a much lower loading. If this run is left out of the calculations, the average becomes 406,2 mg, with a standard deviation of 27,3. This is only 6,7% of the average. As can be seen in Table 5-3 and Table 5-4, column 3 and 4 also suffered from some problems during the fifth run. Since these values are so far of the average, the fifth run has also been left out of the analysis in these runs. The corrected average for column 3 is now 387,3 mg with a standard deviation of 32,4 mg. Column 4's corrected average becomes 387,2 mg with a standard deviation of 29,6 mg.

So although there are differences between the runs, they are considered small enough to say that the different runs are comparable.

Now that it is established that there is a relation between the various runs, the analyses can continue. The next step is to see how much ammonium each run removed compared to the first run, which is the run that performed the best. So if the removal of that run is set at 100%, how well did the other runs do? This assessment is made for the first 24 hours only, since most of the runs lasted at least that long.

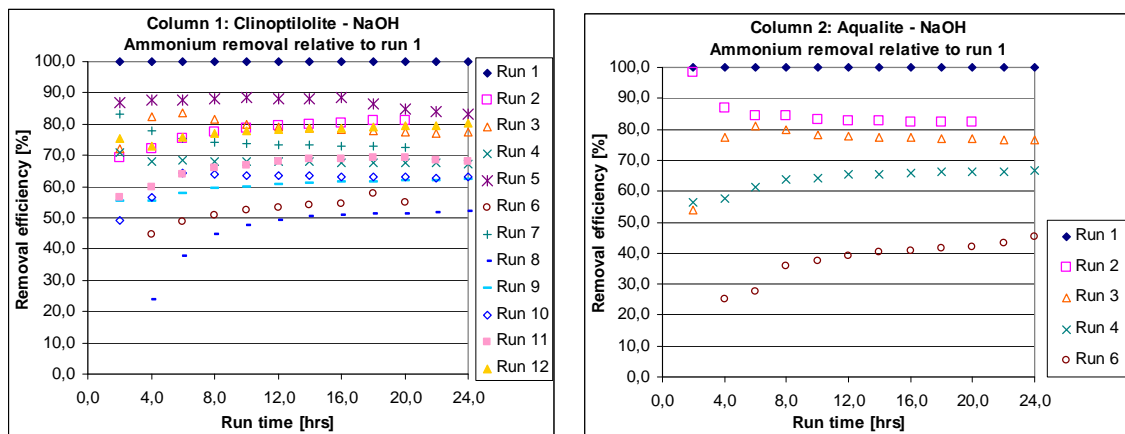


Figure 5-11: Removal efficiency of the runs compared to run 1 (Left: column 1, right: column 2)

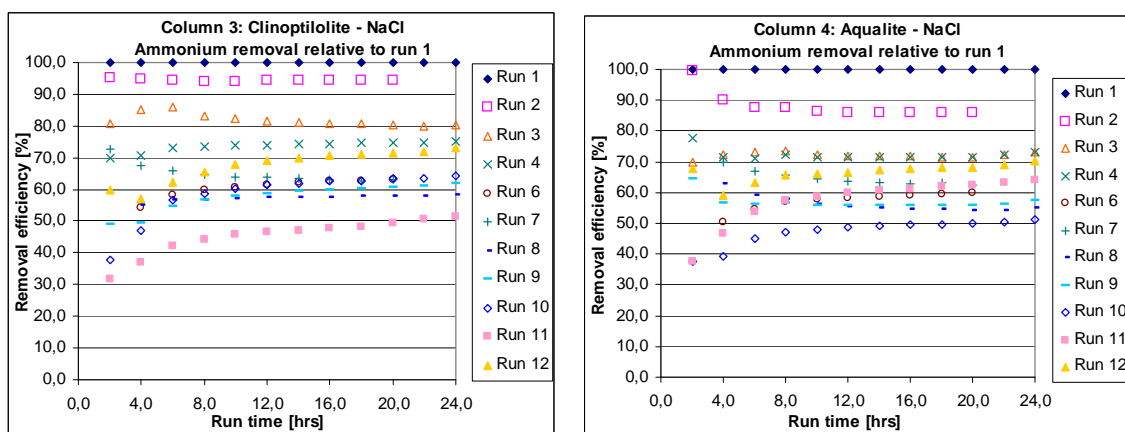


Figure 5-12: Removal efficiency of the runs compared to run 1 (Left: column 3, right: column 4)

Both Figure 5-11 and Figure 5-12 show that regardless of which regenerant is used, the removal capacity drops after the first regeneration. The number of regenerations does not seem have an effect on the capacity though. In case of column 1, 3 and 4, which all were regenerated 11 times, the twelfth run performs better than at least half of the earlier runs. The twelfth run with column 1, which regenerated with a fresh batch of NaOH every time, does show a slightly better result than the two columns regenerated with reused regenerant (80% vs 70%). Still, an efficiency of 70% after 11 regenerations with reused regenerant compared to the maiden run is a pretty decent result!

The efficiency graphs present a pretty clear picture of the loss in performance over time. Since they are established by dividing the amount of ammonium removed at a certain time during a certain run by the amount of ammonium removed at that same time during the maiden run, it is influenced by the bad rinsing after a regeneration cycle. So to gain a better understanding of why the adsorption capacity seems to reduce after a regeneration, a mass balance analysis has been made for a number of substances naturally present in the groundwater. This is done by analysing the used regenerant after a number of cycles. Besides that, the amount of ammonium removed during an adsorption cycle and the amount of regenerant used is also compared.

For the reused NaCl, the change in concentration and total amount of substance can tell something about the processes going on during the regeneration. The amount of substance found in both the used NaOH and NaCl give a better insight in the competition that those substances give the ammonium for adsorption sites.

The substances that were analysed are: NH_4^+ , K^+ , Ca^{2+} , Fe^{2+} , Mg^{2+} , Mn^{2+} and Na^+ . To give an idea of the ratio between the different ions, their average raw water concentrations are presented again in Table 5-5. The cation concentration each ion represents is given in the table as well.

Table 5-5: Average raw water concentrations of ions of interest

Well field Tiendweg 2003-2006		Average mg/l	Average mmol/l	Average Normality mmol electrons/l	Ratio compared to ammonium electrons ion/electrons NH_4^+
Ammonium	NH_4	5,7	0,32	0,32	1,00
Calcium	Ca	81,5	2,03	4,06	16,69
Iron	Fe	5,6	0,10	0,20	0,63
Potassium	K	2,7	0,07	0,07	0,22
Magnesium	Mg	10,7	0,44	0,88	2,75
Manganese	Mn	0,61	0,01	0,02	0,06
Sodium	Na	61,5	2,67	2,67	8,34

Column 1 - Clinoptilolite regenerated with 0,1 M NaOH

Table 5-6: Total ammonium and iron adsorbed during each run of Column 1 (Clinoptilolite)

Column 1 - Clinoptilolite NaOH			
	Total Ammonium adsorbed	Total iron adsorbed	Total electrons bonded
	mmol	mmol	mmol
Run 1	42,83		42,83
Run 2	18,32		18,32
Run 3	85,25		85,25
Run 4	19,13		19,13
Run 5	66,28		66,28
Run 6	12,26	6,01	24,28
Run 7	16,58	6,26	29,11
Run 8	69,71	20,57	110,86
Run 9	26,92	7,54	42,00
Run 10	63,23	15,64	94,50
Run 11	26,62	8,57	43,76
Run 12	24,81	8,34	41,50

Table 5-7: Total amount of ions (in mmol) found in the used regenerant after regeneration (Clinoptilolite - NaOH)

Column 1 - Clinoptilolite NaOH									
	Total NaOH added	Estimated Contact Time	Total Ammonium	Total Potassium	Total Calcium	Total Magnesium	Total Iron	Total Manganese	Total Sodium
	mmol	min	mmol	mmol	mmol	mmol	mmol	mmol	mmol
Regeneration 1	5*40=200	5*5							
Regeneration 2	7*40=280	3*7							
Regeneration 3	250,00	18,00							
Regeneration 4	250,00	18,00							
Regeneration 5	250,00	18,00							
Regeneration 6	250,00	18,00							
Regeneration 7	250,00	18,00							
Regeneration 8	290,00	15,50	24,20	0,73	0,96	0,17	-	-	53,33
Regeneration 9	290,00	15,50	22,56	1,48	0,87	0,09	0,03	-	125,57
Regeneration 10	275,00	16,40	25,00	1,13	0,29	-	0,03	-	111,04
Regeneration 11	250,00	18,00	25,00	1,13	0,45	-	0,03	-	95,00

Table 5-6 and Table 5-7 present the critical data of Column 1.

Table 5-6 shows how much ammonium and iron is adsorbed during one run, it also states how much that is in bonded electrons. This is important because to remove one iron or calcium ion two sodium ions are needed, where one ammonium ion only needs one sodium ion.

Table 5-7 shows how much regenerant is used per regeneration, the estimated contact time and the total amount of ions found in the used regenerant. The original amount of sodium in the regenerant

equals the amount of NaOH added. In the cases that the concentration of a certain ion was found to be below detection limit a dash is placed in the table.

Table 5-8: Used Sodium and removed electrons Column 1

	Sodium used mmol	Total electrons removed mmol
Regeneration 1		
Regeneration 2		
Regeneration 3		
Regeneration 4		
Regeneration 5		
Regeneration 6		
Regeneration 7		
Regeneration 8	236.67	27.19
Regeneration 9	164.43	26.01
Regeneration 10	163.96	26.75
Regeneration 11	155.00	27.09

In Table 5-8 the amount of sodium used during a regeneration and the amount of electrons that was removed by the sodium is listed. As can be seen, the amount of sodium used is much larger than the total amount of removed electrons that was measured. The remarkable thing is that it does not make much of a difference whether there was more than 235 mmol used or only 155 mmol. The removal still lies around 26 mmol, which is less than the total amount of ions adsorbed. This partly has to do with the fact that not all ions that were removed actually moved out of the column with the collected regenerant. Some stayed behind in the pores and were not measured.

Several ions species also had such low concentrations that they were not measured either. One of those ions is iron. Due to the fact that Fe^{3+} immediately reacts with hydroxide molecules and precipitates it is difficult to measure this ion. So although iron is adsorbed by the zeolites and the results show that iron is adsorbed again at about the same rate and efficiency every run (see Figure 5-13), it seems not much iron is removed from the zeolites during regeneration.

The ratio [sodium used] : [ammonium adsorbed] for this column lies in the region of 3,4 - 6,1.

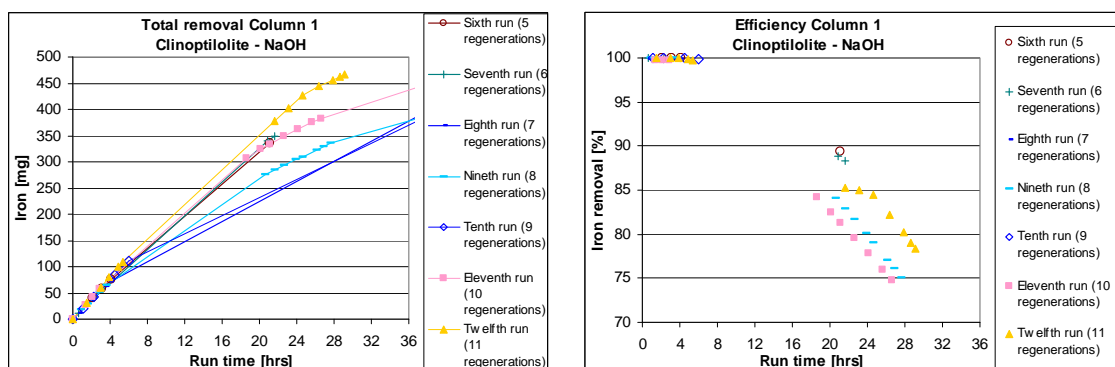


Figure 5-13: Total iron removal (left) and removal efficiency (right) for column 1

Column 3 and 4 - Clinoptilolite and Aqualite regenerated with recirculated NaCl

For column 3 and 4 a similar analysis has been made. The one big difference is that the regenerant used for the two columns is collected in one big tank. So all the ions removed from both columns are stored in the same solution.

Table 5-9: Total ammonium and iron removed during each run by columns 3 and 4

Column 3 - Clinoptilolite NaCl				Column 4 - Aqualite NaCl		
	Total Ammonium adsorbed	Total iron adsorbed	Total electrons bonded	Total Ammonium adsorbed	Total iron adsorbed	Total electrons bonded
	mmol	mmol	mmol	mmol	mmol	mmol
Run 1	44,83			48,51		
Run 2	22,48			22,73		
Run 3	96,43			99,70		
Run 4	22,76			24,49		
Run 5	83,74			86,28		
Run 6	14,79	4,22	23,23	15,62	4,12	23,86
Run 7	15,23	4,07	23,37	16,81	4,33	25,47
Run 8	75,73	21,05	117,84	77,14	20,22	117,59
Run 9	28,49	4,38	37,25	30,50	4,58	39,67
Run 10	70,07	15,98	102,03	62,10	14,10	90,31
Run 11	24,62	5,52	35,66	32,90	6,04	44,98
Run 12	23,67	6,93	37,54	25,11	6,80	38,71

Table 5-9 provides an overview of the total amount of ammonium and iron removed by column 3 and 4 during each run. When the data for both columns is compared, it can be seen that in general there is not much difference between the two types of material where these two ions are concerned.

Table 5-10: Total amount of ions found in NaCl solution after each regeneration

Regenerant in NaCl-tank (after regeneration cycle)									
	pH	Cummulative Ammonium mmol	Cummulative Potassium mmol	Cummulative Calcium mmol	Cummulative Magnesium mmol	Cummulative Iron mmol	Cummulative Manganese mmol	Sodium left over mmol	Extra added Sodium mmol
Original solution	11,30	0,00	0,00	0,00	0,00	0,00	0,00	36035,55	
Δ in 4 reg average		213,67 53,42	331,40 82,85	423,00 105,75	11,60 2,90	0,08 0,02	-	-7284,82 -1821,21	692,75
Regeneration 4	10,10	213,67	331,40	423,00	11,60	0,08	-	29443,48	
Sampling losses		8,54	13,26	16,92	0,46	0,00	-	1177,74	
Δ		48,89	18,62	178,37	21,89	0,03	-	-1252,11	
Regeneration 5	9,40	254,02	336,77	584,45	33,02	0,11	0,38	27013,63	
Sampling losses		10,58	14,03	24,35	1,38	0,00	0,00	1125,57	
Δ		13,06	-2,40	142,78	22,08	0,22	-0,25	-84,61	228,50
Regeneration 6	10,00	256,50	320,33	702,88	53,73	0,33	0,13	26031,95	
Sampling losses		11,15	13,93	30,56	2,34	0,01	0,01	1131,82	
Δ		67,58	-29,21	58,08	7,22	-0,27		-2249,64	
Regeneration 7	9,30	312,93	277,20	730,40	58,61	0,05	-	22650,50	
Sampling losses		14,22	12,60	33,20	2,66	-	-	1029,57	
Δ		55,94	-5,88	92,40	11,76			-1318,78	150,00
Regeneration 8	10,50	354,65	258,72	789,60	67,70	0,11	0,07	20452,15	
Sampling losses		16,88	12,32	37,60	3,22	0,00	0,00	973,90	
Δ		-61,63	-13,90	20,65	-4,69	0,07	0,00	-8382,12	7400,00
Regeneration 9	10,80	276,13	232,50	772,65	59,79	0,17	0,06	18496,13	
Sampling losses		16,00	9,78	34,80	2,77	0,01	0,01	786,09	
Δ		19,87	-7,47	32,15	-17,30	-0,01		-805,72	200,00
Regeneration 10	10,50	280,00	215,25	770,00	39,73	0,15	-	17104,33	
Sampling losses									
Δ									
Regeneration 11	11,00	-	-	-	-	-	-	-	-
Sampling losses									
Δ									

Table 5-10 presents the total amount of ions (in mmol) found in the NaCl solution after each regeneration. Since the change in concentration between two regenerations in general has the same order of magnitude as the loss of ions due to sampling, can not be neglected and thus they have been taken into account. Before the ninth regeneration the NaCl solution was replenished by adding 4 liters of 1,8 M NaCl at a pH of 11,25. This to compensate for the solution lost to the samples. Somehow this addition does not show in the measurements (see the orange cell). This might be due to a sampling or an analysis error.

Analysing the changes in amount of other ions present, provide a better insight in the adsorption and regeneration process.

The removal of ammonium is very unsteady. Some regeneration cycles do not remove much, others like regeneration 7, appear to remove much more ammonium than that was adsorbed during the corresponding adsorption run. There does not seem to be a relation between the ammonium removal and the pH, or the sodium concentration or the total amount of ammonium in the solution. Some other influence must cause the fluctuation.

Potassium is only present in the raw water in about one-fifth of the amount of ammonium present and one-thirtieth of the amount of calcium. The amount of potassium found in the regenerant does not suggest that though. On average the amount of potassium is one-third to half the amount of

calcium. This suggests that potassium is easily adsorbed to the zeolites but also very well removed again. If the amount of potassium in the regenerant becomes too high though, it appears that it starts re-adsorbing onto the zeolites. That, of course is a very negative effect.

With calcium this does not happen. Although the pH is relatively high and calcium precipitates as calcium carbonate at higher pH values, there is still quite some calcium present in the regenerant. At first the amount of calcium in solution rises quickly, but during the later regenerations, when calcium volumes become larger, this rise comes to a halt. This suggests either precipitation (which was found at the walls of the tank) or a decrease in calcium removal of the zeolites due to the competing effect from the calcium in the regenerant.

Although magnesium is present in the raw water in much larger concentrations than for example potassium, the amount found in the used regenerant only is a fraction of the amount of potassium found. There are three probable explanations. One is that magnesium barely is adsorbed by the zeolites. The second is that the regeneration does not have much effect on the removal of magnesium. The third is that magnesium precipitates and as a result is not measured any more. This last explanation is the reason that iron is not present in the regenerant, as is explained earlier in this section.

Manganese is barely present in the raw water to begin with. That it is practically not found in the regenerant is not very strange then.

The sodium levels are dropping very quickly. Per regeneration a minimum of 750 to 1000 mmol is used by the two columns together. One column uses at least 375 to 500 mmol sodium per regeneration. This is much more than was expected. As a result not enough sodium was added to keep the concentration up to standard. In the end, only half of the original sodium concentration is still present.

For these columns the ratio [sodium used] : [ammonium adsorbed] is approximately 6 to 8,5. The amount of NaOH that needed to be added after every regeneration was 8 to 10 grams. The loss of sodium per regeneration is roughly 1000 to 2200 mmol.

5.2.3. Influence of competition on the effectiveness regeneration

To obtain the information on the composition of the NaCl solution samples were taken from the regenerant in the tank before each regeneration. Besides that, samples have also been taken from the regenerant during the tenth and eleventh regeneration. During those regenerations the column effluent was also sampled before it entered the tank again. This way the effect of regeneration on the regenerant quality could be investigated more thoroughly.

Table 5-11 and Table 5-12 present the values found after analysis. Again the iron and manganese concentrations are very low.

Table 5-11: Concentration of ions found in the regenerant during the tenth and eleventh regeneration with NaCl

		10 T0	10 T15	10 T30	10 T60	11 T0	11 T15	11 T30	11 T60
		Before 10 th regeneration	15 min after start 10 th reg	30 min after start 10 th reg	60 min after start 10 th reg	Before 11 th regeneration	15 min after start 11 th reg	30 min after start 11 th reg	60min after start 11 th reg
NH₄⁺	mmol/l	14,67	16,33	18,33	18,33	16,00	17,89	18,67	19,83
Fe	mmol/l	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Na	mmol/l	967,83	993,91	991,30	970,43	977,39	958,70	980,00	957,83
Ca	mmol/l	39,75	42,75	43,50	45,00	44,00	45,50	47,25	49,00
K	mmol/l	12,05	12,74	12,58	12,12	12,30	12,34	12,58	12,28
Mg	mmol/l	3,13	2,98	3,00	2,94	2,27	2,22	2,36	2,25
Mn	mmol/l	0,01	<0,005	<0,005	<0,005	<0,006	<0,005	<0,005	<0,005
pH	-	11,00	10,20	10,10	10,50	11,00	10,20	10,20	11,00

Table 5-12: Concentration of ions found in the effluent of column 3 and 4 during the tenth and eleventh regeneration with NaCl

		10 T0	10 T15	10 T30	10 T60	11 T0	11 T15	11 T30	11 T60
		Before 10 th regeneration	15 min after start 10 th reg	30 min after start 10 th reg	60 min after start 10 th reg	Before 11 th regeneration	15 min after start 11 th reg	30 min after start 11 th reg	60min after start 11 th reg
NH₄⁺	mmol/l	11,33	18,33	20,00	16,67	2,64	19,06	19,44	19,83
Fe	mmol/l	0,15	0,01	0,01	0,06	0,20	0,01	0,01	0,02
Na	mmol/l	478,26	944,35	939,13	916,96	77,91	1016,52	970,87	1040,87
Ca	mmol/l	34,00	45,75	46,50	45,75	13,65	49,00	49,00	52,50
K	mmol/l	6,52	12,43	12,35	11,74	1,03	12,64	12,32	12,80
Mg	mmol/l	3,51	2,95	2,91	5,48	2,08	2,37	2,52	2,38
Mn	mmol/l	0,05	<0,005	<0,005	0,03	0,05	<0,005	<0,005	<0,005
pH	-	11,00	9,80	9,90	10,60	7,20	9,90	9,90	10,20

Figure 5-14 presents the results of the analyses of those samples for ammonium and potassium.

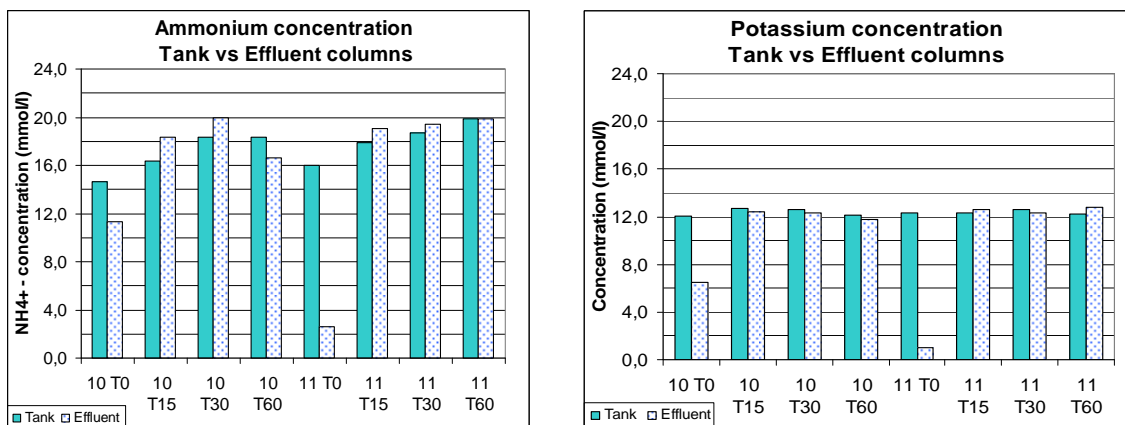


Figure 5-14: Ammonium (left) and potassium (right) concentrations in the NaCl tank and the effluent of column 3 and 4 during regeneration 10 and 11

The values on the horizontal axis refer to the moment during the regeneration when the sample was taken. The second row of Table 5-11 and Table 5-12 gives a more elaborate explanation of these values.

The most remarkable aspect of these graphs is the big difference between tank and effluent in the bars belonging to the beginning of a regeneration cycle (10 T0 and 11 T0). The logical thing to expect is that what goes in, must come out and more. In this case what went in, did not come out anymore. One explanation for this effect is that in the columns regenerant has mixed with residual raw water from the zeolites. This water contains so much less of the ions that levelling of the concentrations occurs.

A second explanation might be that the concentrations in the tank are so much higher than on the zeolites that the adsorption process continues. The amount of sodium present in the regenerant is not enough to stop that process. Ion-exchange can be a quick process, but earlier discussed results in this report conclude that it does take more than a couple of seconds to exchange a reasonable amount of ions. The gaps are really big, especially at the beginning of regeneration 11, so therefore the most likely explanation is dilution.

At the end of the cycle 10 there is again more ammonium going in, than that is coming out. This time dilution due to residual raw water can not be the cause, consequently it must be re-adsorption.

If the values for potassium are studied a little closer, it can be seen that its value does not change much anymore during both regenerations. It looks as though some sort of equilibrium has been established. This means that the potassium concentrations in the regenerant are so high and the affinity of the zeolites for potassium is so big that the regenerant is not strong enough anymore to remove potassium from the zeolites.

Since Figure 5-15 shows that calcium is removed during regeneration, it is very likely that the zeolites' affinity for calcium is much lower than for potassium and ammonium. This is in accordance with the affinity lists mentioned for clinoptilolite in (Cejka et al., 2007) and Aqualite's selectivity according to the MSDS provided by the distributor.

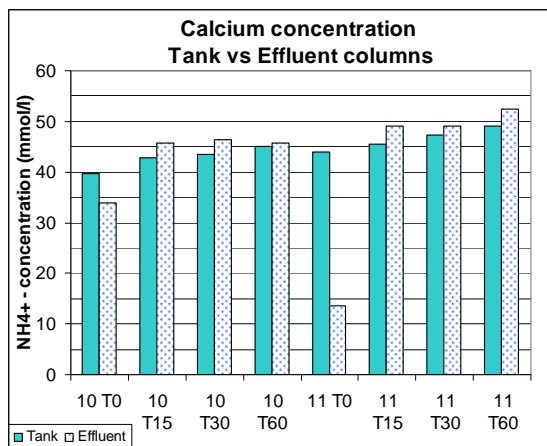


Figure 5-15: Calcium concentration in NaCl tank and effluent of column 3 and 4 during regeneration 10 and 11

So although it was expected that calcium and iron would interfere with the removal of ammonium and the re-use of regenerant it is in fact potassium that has the bigger influence.

5.2.4. Effectiveness of NaOH as regenerant

Figure 5-16 to Figure 5-19 show the progression in ammonium concentrations over the different regeneration cycles. A remark must be made about the long straight lines. They connect two back-to-back measurements, but they do not(!) represent the course of the concentration curve. Because of the long periods in between some measurements (sometimes up to 88 hours) the course of the curve is not always represented properly.

During Experiment 1 each regeneration with NaOH resulted in an improvement in performance of the columns. During this experiment, such an improvement was not noticed anymore. This can be seen in Figure 5-16 and Figure 5-17.

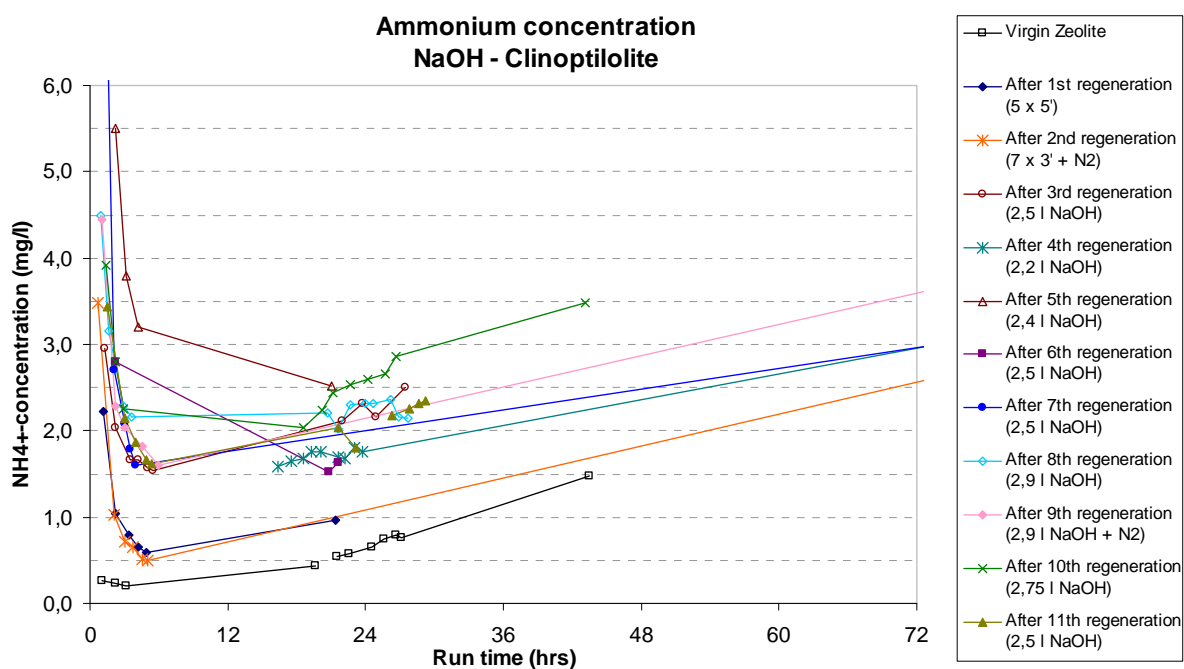


Figure 5-16: Progression in ammonium concentrations in the effluent of Clinoptilolite regenerated with NaOH

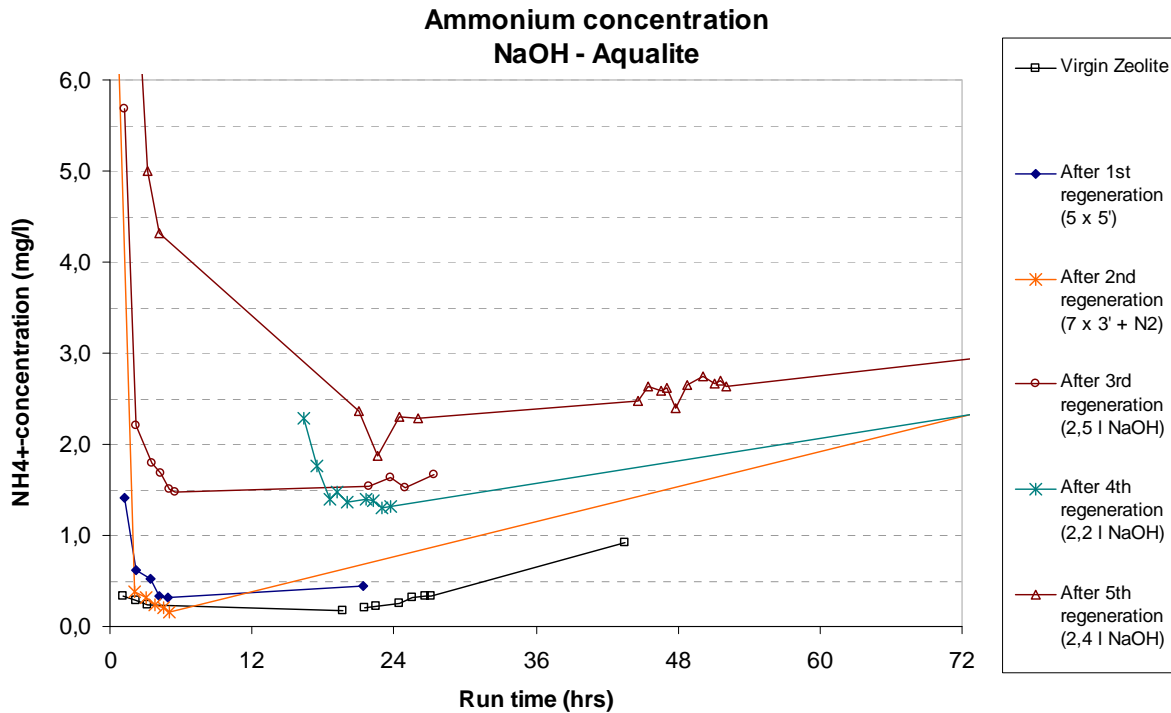


Figure 5-17: Progression in ammonium concentrations in the effluent of Aqualite regenerated with NaOH

The first two regenerations had very nice results, the ammonium concentrations came close again to the concentrations found with the virgin zeolite. After the second regeneration the regeneration method changed. The total amount of regenerant used stayed the same but instead of immersing the zeolites in NaOH and have them soak for a while, regenerant was introduced to the columns from the top. After seeping through the column the spent regenerant was collected at the bottom of the column and disposed of.

If not the amount of regenerant used made the difference, it must have been something else. It is likely that the regenerant was not able to make proper contact with the zeolites throughout the column because the column was not completely filled up with regenerant anymore. Preferential flow paths would lead to by-passing of part of the zeolites and gas bubbles could prohibit the regenerant from actually touching the zeolites. As a result, not all zeolite particles were regenerated properly. Naturally, this would lead to poorer removal values.

Although regeneration was not capable to restore the zeolites full adsorption capacity, there is no trend recognisable that suggests that the loss is irreversible or getting bigger over time.

The mass balance analysis also showed that the used amount of sodium was only roughly 235 mmol per regeneration while the columns regenerated with NaCl used much more. This confirms the idea that the regenerations have not been complete and a part of the adsorption sites has not been 'cleaned'.

5.2.5. Effectiveness and reusability of NaCl as regenerant

The zeolites regenerated with NaCl have not been regenerated with fresh regenerant every time. During the first regeneration cycle, the solution was fresh, but after that it has been re-used for another ten times. Figure 5-10 already showed that these regenerations were not as successful every time. Figure 5-18 and Figure 5-19 show the same.

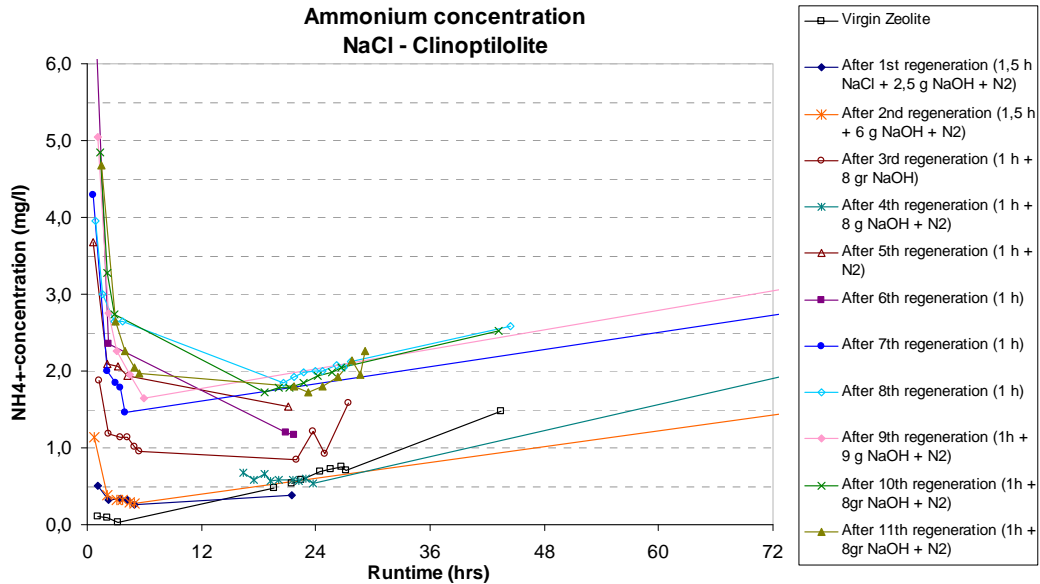


Figure 5-18: Progression in ammonium concentrations in the effluent of Clinoptilolite regenerated with NaCl

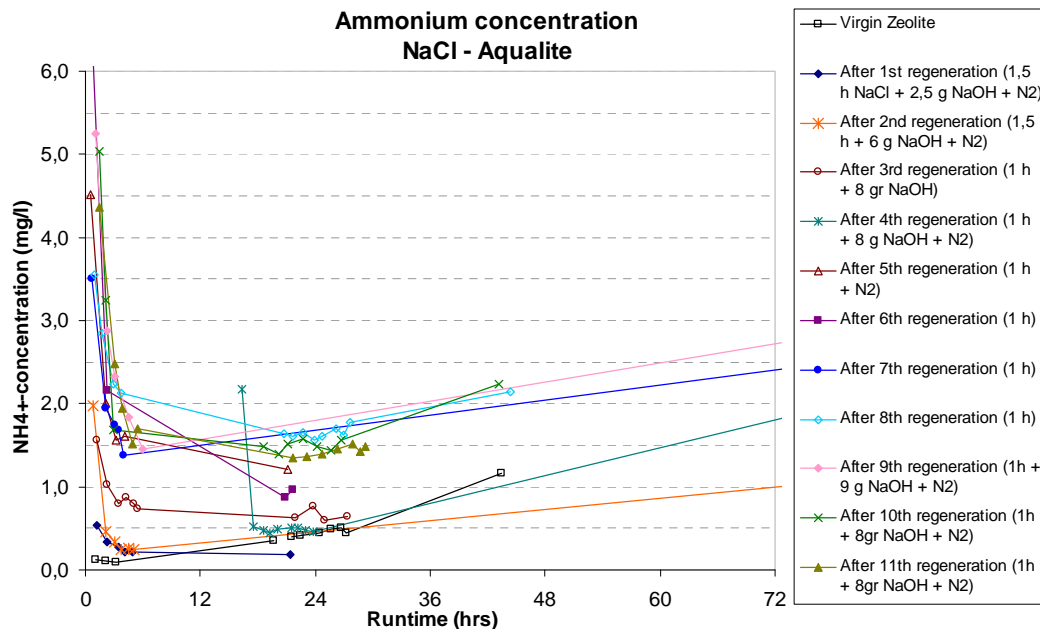


Figure 5-19: Progression in ammonium concentrations in the effluent of Aqualite regenerated with NaCl

Both graphs give the impression that the later regeneration cycles are not complete anymore. The lowest ammonium concentrations are at least 4 to 5 times higher than the ones found with the virgin

zeolite. Just as in Experiment 1 the split between better and worse regeneration results lies after the fourth regeneration.

In section 5.2.2 and 5.2.3 the composition of the regenerant has been discussed. One of the findings has been that the amount of sodium used per regeneration has been much higher than expected. As a result the sodium concentration dropped quickly. This might have influenced the regeneration. The other aspect of course is the concentration of ions the solution. Whether only one aspect or the combination of both has been the cause of the decreasing results can not be said. Extra research with regenerant containing a constant sodium level might give an answer to that question.

5.2.6. Impact of Fe²⁺ on ammonium removal

All literature found on ammonium removal with zeolites dealt with aerobe water. So although iron removal was mentioned a couple of times, it was always Fe³⁺ they were talking about. This difference in valence always has a big influence on ion-exchange abilities.

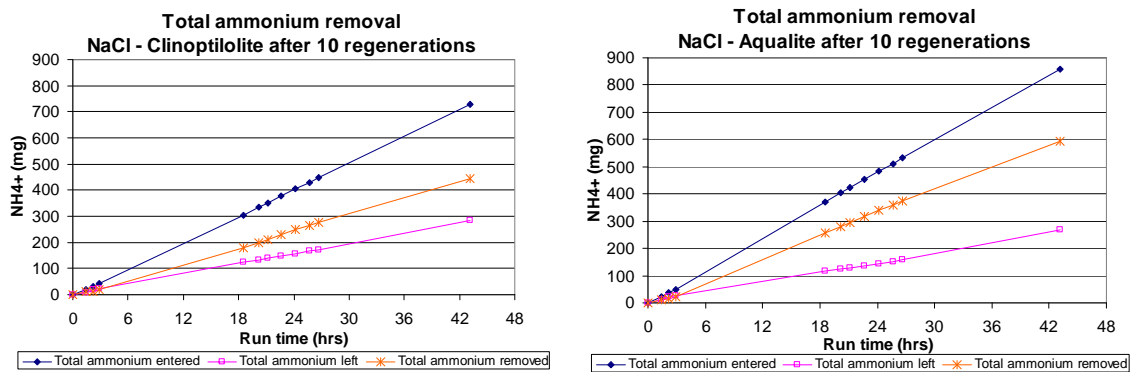


Figure 5-20: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 10 regenerations with NaCl

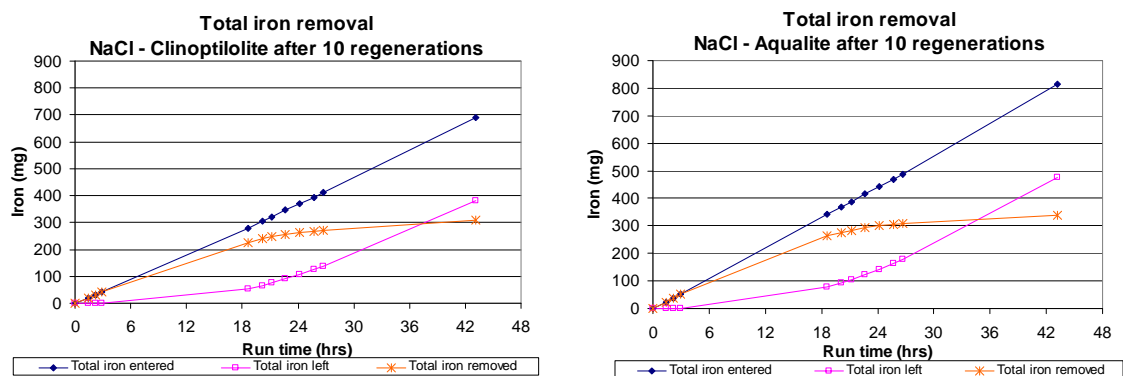


Figure 5-21: Iron removal by Clinoptilolite (left) and Aqualite (right) after 10 regenerations with NaCl

Figure 5-20 and Figure 5-21 show plots that are typical for ammonium and iron removal by the zeolites regenerated with NaOH. They clearly show a ceiling for iron removal after roughly 24 hours while the removal of ammonium is going on without any change. This shows that the iron-ions are not after the same bonding places as the ammonium ions. Therefore it can be concluded that Fe^{2+} is not a serious competition for ammonium.

5.2.7. Ammonium stripping while using NaOH

The idea with using a high-pH NaOH solution as regenerant was that the ammonium coming from the zeolite would be transformed to ammonia gas straight away (see paragraph 2.4 for theory). By blowing in nitrogen gas the NH_3 gas would be blown out leaving a solution with lower pH and only the competing ions. Most of the sodium originally present in the solution should be adsorbed by the zeolites. During Experiment 1 all regenerations have been executed with addition of nitrogen gas. The effect of the gas addition therefore could not be determined. Throughout Experiment 2, the addition of nitrogen has not been so regular. In fact only during regeneration 2 and 9 nitrogen has been added. It must be said that adding nitrogen while the columns were soaking in regenerant was easier than adding the gas while the regenerant was seeping through the columns. In the latter case the addition of gas would cause the regenerant to stop entering the columns. If the addition of nitrogen to the columns regenerated with NaOH makes a difference like it does with the regeneration using NaCl, it should be noticeable in the results. Figure 5-16 has been adapted slightly to make it easier to interpret. Some of the cycles that lay right on top of each other have been left out, resulting in Figure 5-22.

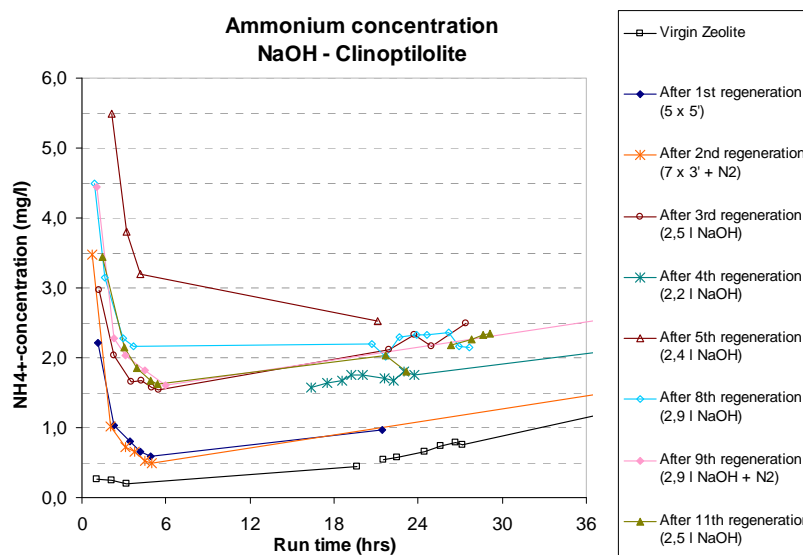


Figure 5-22: Ammonium concentrations in effluent of Clinoptilolite after regeneration with NaOH or NaOH and nitrogen gas

The only adaption to Figure 5-17 has been the change in time scale. This results in Figure 5-23.

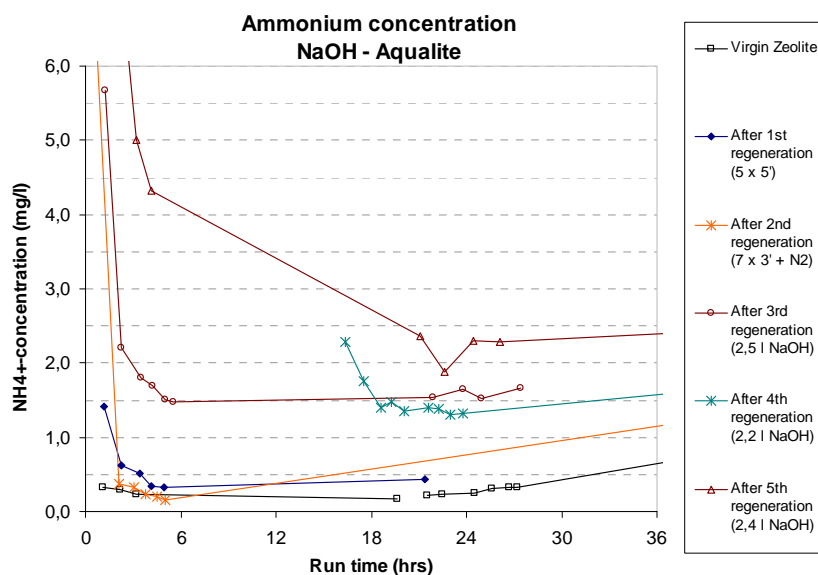


Figure 5-23: Ammonium concentrations in effluent of Aqualite after regeneration with NaOH or NaOH and nitrogen gas

In both cases it can be seen that the effluent after regeneration 2 has slightly lower ammonium concentrations than after regeneration 1. This might also be due to the use of more regenerant during the second regeneration. Which effect caused the difference is not clear, either way they are marginal.

The column containing clinoptilolite later was regenerated another time with the combination of NaOH and nitrogen gas. This time there is no distinctive difference between the regeneration with and without nitrogen either. It can only be concluded that the addition of nitrogen in the hope to improve regeneration by removing NH₃-gas from the regenerant did not have the desired effect. Whether the stripping of ammonia gas was successful can only be told after analyses of the regenerant.

Table 5-13: Ion concentrations in the effluent of column 1 during regeneration with NaOH

		Regeneration 8 (mix)	Regeneration 9 (mix)
NH₄⁺	mmol/l	8,33	7,78
Fe	mmol/l	0,00	0,01
Na	mmol/l	18,39	43,30
Ca	mmol/l	0,33	0,30
K	mmol/l	0,25	0,51
Mg	mmol/l	0,06	0,03
Mn	mmol/l	<0,001	<0,001
pH	-	12,00	13,00

Table 5-13 shows the results of analyses performed on column 1's regeneration effluent of regeneration 8 and 9. The regenerant was collected after passing through the column and the total effluent was sent to the lab for analyses. In both cases this was 2,9 litre. As can be seen in the table, the ammonium concentration of regeneration 9 is a little lower than the concentration of regeneration 8. The pH is higher and so is the sodium concentration. In paragraph 5.2.1 it was concluded that regenerations after longer runs had more difficulties with their performance than the regenerations after shorter ones. Unfortunately, regeneration 8 was a regeneration after a long run. The lower pH and sodium concentration might therefore also be caused by the higher amount of ammonium that had to be removed. This of course would automatically lead to a higher ammonium concentration in the effluent. With this knowledge in mind, the difference of 0,55 mmol/l is not significant enough to say that ammonium stripping in the column actually worked.

5.2.8. Ammonium stripping from the NaCl solution

The ammonium stripping has not only been tried on the columns regenerated with NaOH. It has also been tried on the NaCl solution, while the pH of the solution was high anyway.

Due to some logistical problems, the solution has not been blown through by nitrogen gas all the time. This does provide a possibility to investigate the differences though.

In the end nitrogen was added during the following periods:

- After regeneration 1 and during and after regeneration 2
- After regeneration 3 and during and after regeneration 4
- From 1 hour before regeneration 9 until the end of the experiments 8 hours a day

Table 5-14: Ammonium concentration in regenerant after regeneration with and without nitrogen

	pH of sample	Ammonium measured mmol	Difference including sample losses mmol
Regeneration 1	-		
Regeneration 2			
Regeneration 3			
Regeneration 4	10,10	213,67	
Regeneration 5	9,40	254,02	48,89
Regeneration 6	10,00	256,50	13,06
Regeneration 7	9,00	312,93	67,58
Regeneration 8	10,02	354,65	55,94
Regeneration 9	10,50	276,13	-61,63
Regeneration 10	10,02	280,00	19,87
Regeneration 11	11,00		

In Table 5-14 the found amount of ammonium is presented together with the difference with the next regeneration cycle and the pH. Although regeneration 6 did not seem to remove much regenerant,

this is not caused by nitrogen gas. It is more likely that it has something to do with a process condition.

The other two low values are regeneration 9 and 10. From regeneration 9 on, there was enough nitrogen available. The ammonium concentration in the solution was higher as well, because the earlier regenerations made sure extra ammonium was added. By raising the pH, ammonium is transformed into ammonia and switching on the nitrogen could help force the ammonia out.

The difference in total amount of ammonia present in the solution between regeneration 8 and 9 and 9 and 10 do suggest that the stripping had effect. The impact of the effect is hard to tell, since not enough data is available. The smell above the regenerant, when the nitrogen was switched on, also suggested the stripping had effect. This is hopeful since the theory in section 2.8 suggested that ammonium stripping is more or less impossible.

5.2.9. High pH and calcium precipitation

The risk of regenerating with a high pH solution is that calcium ions will start to precipitate as calcium carbonate. This might result in blocked pores and a reduction of ion-exchange capacity. It was already concluded that no trend was recognised in the deterioration of ion-exchange capacity. The loss in effectiveness between the second regeneration and the later one is believed to be caused mainly by a change in regeneration method. There is no reason to believe that precipitation took place or that it led to a loss in ion-exchange capacity. Whether it really had no effect at all can only be told after a microscopical examination of the used zeolites.

6. Conclusions and recommendations for future research

6.1. Conclusions

In chapter 3 the research objectives have been defined. In order to be able to draw conclusions, the objectives are listed here once more.

The focus of this research is the chemical regeneration of zeolites, after they have been used to remove ammonium from groundwater.

Main goals hereby are to:

- determine the effect of multiple regenerations on the ion-exchange capacity of the zeolites
- test the effectiveness of two types of regenerant: NaOH and NaCl
- find out whether it is possible to reduce the usage of chemicals by reusing the regenerant

While the regeneration is the main objective, a second objective can be expressed: To investigate whether removal of ammonium from anaerobic water is possible or that the Fe²⁺ present will interfere with the ion-exchange process.

In order to reach these goals several questions were asked and needed to be answered. This will be done in this section. Once the answers are given, a conclusion can be drawn about whether the objectives were met.

- *Can the zeolites be regenerated to their full potential?*

The long regeneration cycle in experiment 1 showed that if enough clean regenerant is used with a thorough contact to the zeolites it is possible to restore the zeolites to their full potential.

- *How much regenerant is needed to achieve that?*

The minimum amount necessary to achieve that has not been determined, but the mass balance analyses showed that 500 to 1.000 mmol Na⁺ was consumed during most NaCl regeneration and still the zeolites were not restored completely.

- *Is there a difference in performance between the zeolites regenerated with NaOH or NaCl?*

Most of the time the effluent quality of columns regenerated with NaCl was better than the effluent quality of the columns regenerated with NaOH at the same moment. The values always were in the same order of magnitude.

If a comparison is made between the amount of regenerant used with both methods it becomes clear that the regeneration with NaOH used significantly less regenerant (max 2,9 l

per column) than the NaCl regeneration (29,7 l). The total amount of sodium used with the NaOH regeneration was maximal $2,9 * 0,1$ M, this equals 290 mmol per column per regeneration. The NaCl solution started out with 1,8 M NaCl during Experiment 2. The mass balance made based on the chemical analyses of the used regenerant showed a minimum usage of 375 to 500 mmol per regeneration per column, but 1.000 mmol could also be used. So in fact, the NaCl-solution with a raised pH has a better result because the removal was better and the effluent quality of the water during the adsorption phase was better. The NaOH regeneration used less chemicals though and gained almost the same results.

- *Can the amount of chemicals needed for regeneration be reduced by stripping ammonium from regenerant and re-circulate the left-over stream?*

That ammonium can be stripped from a NaCl solution has been proven during these experiments. This can make it easier to re-use regenerant for a period of time.

- *What is the composition of the regenerant at the time it can not be used anymore and can it be disposed of easily?*

At the end of the experiments the regenerant showed elevated levels of potassium, calcium and magnesium. Sodium concentrations were lowered significantly. Ammonium concentrations were of course elevated, but the experiments also showed that stripping is possible.

Although problems were expected where calcium was concerned, in the end the limiting factor for reuse of regenerant seems to be the potassium concentration. If the concentration becomes too high, the ions begin to re-adsorb onto the zeolites. Since the zeolites tend to have at least an equal affinity for potassium as for ammonium, this is an unwanted effect. The disposal of industrial waste is something that the industry needs to discuss directly with the sewer manager and wastewater treatment plant. If extreme pH is a problem, this can be adjusted. In the end the raised salt concentration might be a bigger problem together with the amount of water disposed of every day.

- *What is the effect of Fe^{2+} on the removal of ammonium from groundwater?*

The iron present in anaerobic groundwater is being removed by the zeolites as well. Fortunately this process does not have a negative influence on the ammonium adsorption. The maximum capacity for iron adsorption is much lower than the maximum capacity for ammonium and once it is reached there is no significant change in adsorption rates where ammonium is concerned.

Now that the research questions have been answered, it can be determined whether the main goals have been reached.

Determine the effect of multiple regenerations on the ion-exchange capacity of the zeolites

During the 11 regenerations that have been performed for this research the biggest single loss in ion-exchange capacity has occurred during the first regeneration (10% loss compared to the virgin zeolite). After that first regeneration, the results have been varying but in general the capacity ended up in the region around 70% of its original capacity. Since one of the conclusions was that the regeneration was not complete yet, the efficiency could end up a little higher still.

Test the effectiveness of two types of regenerant: NaOH and NaCl

The two types have been tested and with the concentrations used the NaCl performed slightly better than the NaOH. The ammonium concentration in the effluent during adsorption phase stayed lower, but the adsorption capacity of the zeolites regenerated with NaOH stayed higher. On the other hand, the regenerations with NaCl used almost twice as many chemicals while performing only slightly better. Extra tests are needed to figure out what the exact differences are.

Find out whether it is possible to reduce the usage of chemicals by reusing the regenerant

It has been possible to re-use the same batch of chemicals 11 times and achieve a very constant result during that period. Analyses of the used regenerant showed that it was not possible to use all the sodium from the regenerant for regeneration. Some of it left the column. If the regenerant is not reused, the part that has not been used is thrown away. By reusing the regenerant, not everything has to be disposed of, resulting in fewer chemicals used.

Whether the reuse of the regenerant really results in a reduction of used chemicals can not be said from this study, since no comparison has been made with single use NaCl regenerant.

The efficiency drops encountered after some of the regenerations were mainly caused by pore rinsing of the zeolite after regeneration.

Investigate whether removal of ammonium from anaerobic water is possible or that the Fe^{2+} present in the water will interfere with the ion-exchange process.

The adsorption of ammonium from anaerobic water went very well. There has been no indication that the Fe^{2+} had a negative influence on the ammonium removal. The positive effect of this treatment was even that not only the ammonium was removed, the iron was removed as well.

6.2. Recommendations for future research

During research, every answered question leads to at least one new one. Together all the questions form the outline for future research.

During this research, two types of regenerant have been used, NaOH and NaCl. The concentration and pH have been different though. To give a clear answer to the question which regenerant really is better, the regenerants should be tested based on equal sodium concentration. The effect of pH can be tested by using two batches of regenerant with the same sodium concentration but different pH values.

In the end, the columns have been regenerated 11 times. During these regenerations the average loss in ion-exchange capacity has been approximately 30% with the biggest single loss of 10% after the first regeneration. What happens after the regenerant is replaced or if the zeolites are regenerated another 20 or 30 times is still unknown. In order to get the complete picture about the long-term usability of zeolites as ion-exchange medium in drinking water treatment, these are aspects that need to be looked into.

It was expected that calcium could pose a serious competition for ammonium and that problems could arise from regeneration with high pH. Calcium was removed by the zeolites, otherwise it would not have turned up in the used regenerant in the quantities that it was found in. The precipitation problems did not seem to occur though. To see whether calcium really did not block pores or influence the capacity of the zeolites in another way, microscopic investigations need to be conducted. The surface area of the zeolites has to be checked for scaling and blocked pores.

Unexpectedly potassium turned out to be the limiting factor in the reusability of the regenerant. It needs to be investigated whether something can be done to reduce the amount of potassium in the regenerant or whether for example a raise in sodium concentration can help increase the life expectancy of a batch of regenerant.

Rinsing of the zeolites after regeneration has been a real issue. If regenerant stays behind the raw water will not be treated properly and the filter's effluent can even become worse (higher concentrations of ions, pH raise). Tests must be performed to decide on a better way to rinse the zeolites.

7. Up-scaling to Treatment plant size

In the end, doing research just for the sake of research is nice, but the research is much more fun if, when the end result is positive, the subject being researched can be used in 'real life'.

In the case of ammonium removal with zeolites, research had already shown that the ammonium removal for drinking water purposes was possible. One of the aspects hampering full-scale implementation was the lack of knowledge about regeneration.

This research has proven that, with some adjustments to the used set-up, it is very well possible to remove ammonium from anaerobic groundwater with zeolites and regenerate them with re-used regenerant.

In this chapter, calculations will be made to see whether a full-scale ion-exchange system to remove ammonium is manageable. Important factors are: size of the system, needed amount of chemicals and costs

Because the used system is not giving completely satisfying results yet, some boundary conditions must be set and assumptions must be made to create the full-scale treatment facility. The facility is used to remove the majority of the ammonium and iron. The effluent will never have ammonium concentrations higher than 1 mg/l. The treated water will be aerated and filtered through the sand filters, which will remove the remaining ammonium and iron-flocs. The reusable NaCl solution will be used 10 times before it is worn out.

The following assumptions are made:

- With a contact time of 25 minutes the zeolites are capable of achieving the effluent quality demand for at least 24 hours, regardless of how many times the regenerant has been reused.
- If the sodium concentration in the NaCl-solution is kept at 1,8 M, the solution is capable of regenerating the filters back to required capacity 10 times.

Dimensioning of the filters

For the up-scaling calculations production data of Oasen's water treatment plant ZS Lekkerkerk has been used. The average yearly production for the last five years has been 2.944.536 m³. Which is 336 m³/h. The treatment plant has a clear water reservoir that serves as a buffer for the hours of peak demand and is filled up overnight, so the production is relatively constant.

With the formulas

$$EBCT = \frac{Q}{V} \quad (7.1)$$

where:

EBCT = Empty Bed Contact Time [h]

Q = flow rate [m³/h]

V = Volume of filter [m³]

and

$$v = \frac{Q}{A} \quad (7.2)$$

where:

v = filtration velocity [m/h]

Q = flow rate [m³/h]

A = surface area of the filter [m²]

the size of the filters can be calculated.

With a EBCT of 25 min (= 0,417 h) and a flow rate of 336 m³/h the needed volume of the filter is 806,4 m³. The filtration velocity v is set at 5 m/h (a common velocity for rapid sand filters). This leads to 2,1 m high filters and a needed surface area of 161 m².

With the necessary dimensions established, a closer look must be taken at the aspects concerning maintenance and regeneration. It is assumed that a filter only last 24 hours, so it has to be regenerated every 24 hours. The production has to continue though. This means multiple filters are necessary. If five filters should be able to filter all the water, their individual surface area should be 32,2 m². If the filter is shaped rectangular this implies a size of 4 by 8,1 m. A sixth filter of the same size would result in a complete system with the possibility to take one filter out of order without endangering the supply. The total footprint would be 193,2 m².

The six filters together contain 405,7 m³ of zeolites. In the granular form zeolites weigh 1.100 kg/m³. To fill the filters 446.292 kg is needed. Aqualite costs € 2,- per kg, clinoptilolite is expected to be cheaper. This would result in an investment cost of € 892.584,-. If the zeolites would last for only five years, the costs per m³ water produced would be 6 cents.

Regenerant

With larger filters, more regenerant is needed of course.

According to the mass balance analysis of the NaCl system the amount of sodium needed for regeneration was 6 to 8,5 times the adsorbed amount of ammonium.

The average ammonium concentration of the raw water is 6 mg/l. The water quality that is aimed for has an ammonium concentration of 1 mg/l. Per liter of produced water 5 mg of ammonium needs to be removed.

With a yearly production of 2.945.000 m³ a total of 14.725 kg of ammonium needs to be removed.

This equals 818.056 mol. In the worst case the total need for NaCl would be 6.953.476 mol or 406.361 kg. The cost price is € 203.181,- (€ 0,50 per kilo).

The mass balance also indicated that 40% of the used NaCl was needed in NaOH to keep the pH at the desired level. This is 2.781.390 mol or 111.256 kg of NaOH. At a price of € 1,75 per kg, the extra costs would be € 194.697,-.

Yearly, the total costs for regeneration chemicals add up to € 397.878,-. Per produced m³ this is € 0,14.

The analysis of the used NaOH regenerant showed that for every adsorbed mol of ammonium 3,4 to 6,1 mols of sodium were necessary. To remove the 818.056 mol of ammonium 4.990.142 mol or 199.606 kg NaOH is needed. This would cost € 349.310,-. Per m³ the extra costs would be € 0,12, which is slightly less than the costs for the NaCl regenerant.

Total costs

The total costs for a full-scale system (except for the investment cost) are the sum of the costs for the zeolites and the chemicals.

Based on a life-cycle of 5 years, the NaCl system would cost € 0,06 + € 0,14 = € 0,20 per m³.

The NaOH system would cost € 0,06 + € 0,12 = € 0,18.

Feasibility of the system in 'real-life'

The calculated production price of approximately € 0,20 per produced m³ is quite a lot compared to the price consumers pay (€ 1 - € 1,5 per m³). Remembered must be that in this price investment costs, pumping energy but also waste treatment costs are not concluded.

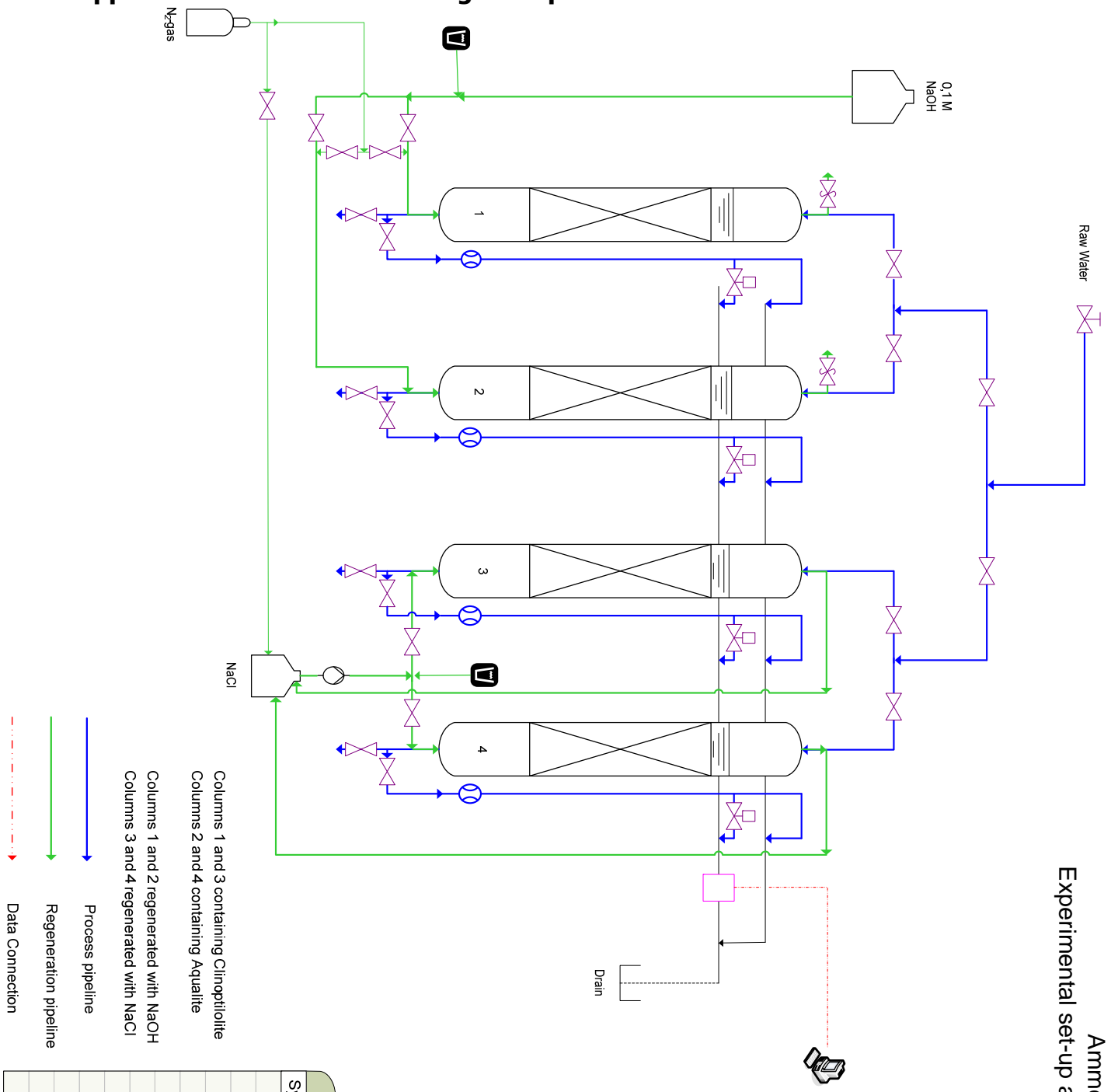
If this system was a replacement of an existing (and not optimally functioning) system, the price would be worth it. As it is, the ion-exchange is only an addition to an existing system. The sand filters are still needed to do the polishing. So as long as research does not prove that the amount of chemicals necessary can be reduced or that the system can be fine-tuned to produce a higher water quality standard in combination with longer run times, it stays a very promising technique but it will not be useful for drinkingwater treatment.

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Appendix A: Schematic drawing Set-up



Legend	
Symbol	Description
	Column with zeolite
	Pump
	Tank
	Nitrogen gas
	Tap
	Gate valve
	Relief valve
	Powered valve
	Ammonium Sensor
	PC
	Flow meter

Appendix B: Measuring report

This section will provide an overview of the measuring results obtained during the experiments. For both experiments the findings are discussed per regeneration cycle.

Experiment 1: Adsorption - Regeneration cycles with anaerobic groundwater EBCT \approx 6 min

General operating conditions

Bed height: approximately 70 cm (650 grams of zeolite)

Average flow rate: 6 l/h \sim 7,5 m/h \sim 10,7 BV/h

NaOH concentration: 0,1 M

NaCl concentration: 0,6 M (= 3,5%)

Number of regeneration cycles

NaOH: 6

NaCl: 7

Virgin zeolites

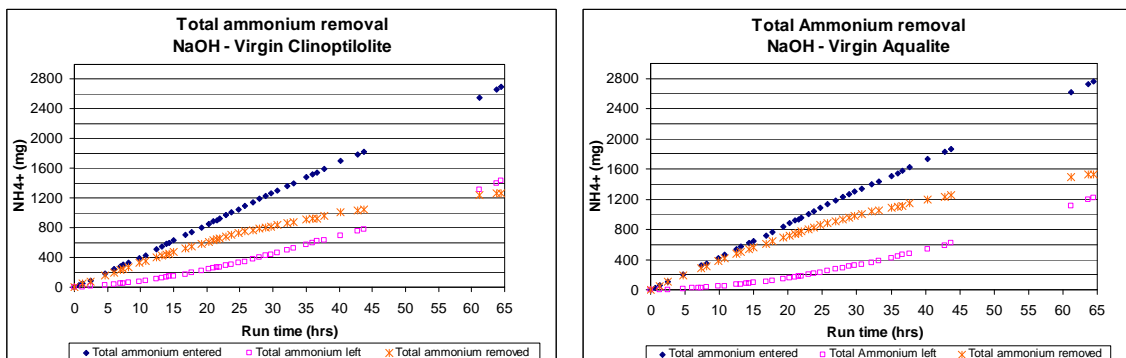


Figure 7-1: Ammonium removal by virgin Clinoptilolite (left) and Aqualite (right) in columns 1 and 2

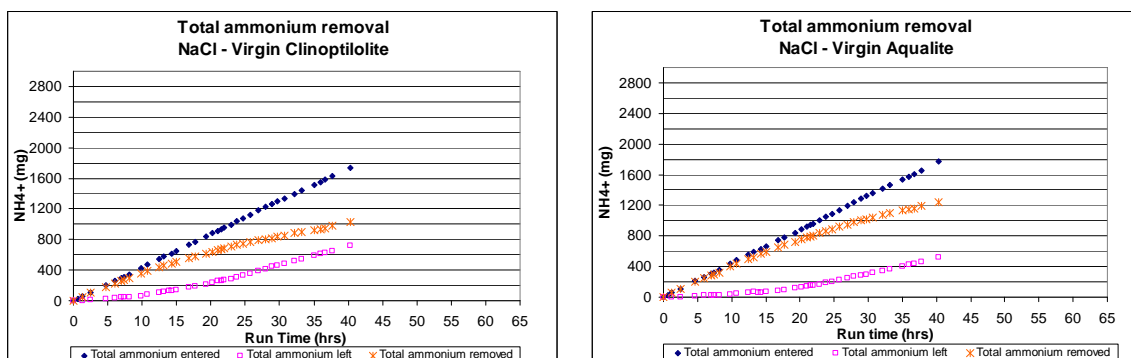


Figure 7-2: Ammonium removal by virgin Clinoptilolite (left) and Aqualite (right) in columns 3 and 4

The first adsorption test has been performed with untreated zeolites. This means that, provided that the flow velocity through the columns is equal, the results from both columns containing Clinoptilolite and both columns containing Aqualite should be the same.

In **Error! Reference source not found.** and Figure 7-2 the total amount of ammonium entered and removed are presented for all four columns.

Since the columns designated to be regenerated with NaOH have had a longer run time (approximately 65 hours) than the columns designated to be regenerated with NaCl (approximately 40 hours) a comparison is made between the columns for a run time of 5, 20 and 40 hours.

This results in the overview shown in Table 7-1. For the columns regenerated with NaOH, the results after a runtime of 60 hours are presented as well.

Table 7-1: Performance of the virgin zeolites

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	195	220	215	220
	Total NH ₄ ⁺ removed (mg)	160	200	185	200
	In mmol	8,9	11,1	10,3	11,1
	Effluent Concentration NH ₄ ⁺ (mg/l)	1,6	0,8	1,3	0,8
T = 20 hours	Total NH ₄ ⁺ entered (mg)	840	870	870	875
	Total NH ₄ ⁺ removed (mg)	605	715	635	745
	In mmol	33,6	39,7	35,3	41,4
	Effluent Concentration NH ₄ ⁺ (mg/l)	3,5	2,7	3,3	2,5
T = 40 hours	Total NH ₄ ⁺ entered (mg)	1690	1725	1725	1755
	Total NH ₄ ⁺ removed (mg)	1000	1195	1015	1235
	In mmol	55,6	66,4	56,4	68,6
	Effluent Concentration NH ₄ ⁺ (mg/l)	3,8	3,4	3,8	3,7
T = 60 hours	Total NH ₄ ⁺ entered (mg)	2550	2600	-	-
	Total NH ₄ ⁺ removed (mg)	1230	1475	-	-
	In mmol	68,3	81,9	-	-
	Effluent Concentration NH ₄ ⁺ (mg/l)	5,2	4,7	-	-

Because the zeolites in the columns are not influenced by any treatment yet, the columns containing the same material should give similar results.

Table 7-1 shows that the columns containing the same material do give similar results. The flow velocity has a small impact on the performance. The columns with the marginally higher velocity perform a little better during the first 5 hours of the experiment. The total removal is better (86% vs 82% for the Clinoptilolite) while the ammonium concentration in the effluent is lower.

At T = 20 hours, this difference has become smaller for the Clinoptilolite (73% vs 72%). The columns containing Aqualite on the other hand are not so similar as they were (85% vs 82% removal).

At T = 20 hours column 1 has a total load of 840 mg, this is 96,6% of the load column 3 has had.

The total ammonium removal of column 1 is 605 mg, this is 95,2% of column 3's.

Column 2 has had a total load of 870 mg, which is 99,4% of column 4's. The total ammonium removal is 715 mg, 96,0 % of the removal by column 4.

At T = 40 hours Column 1 removed 1000 mg (98,5% of column 3) of the entered 1690 mg (98,0%).

Column 2 removed 1195 mg (96,8%) of the 1725 mg (98,3%) entered.

So although there is a slight difference in performance between the columns containing the same zeolite, this can be accounted for by the difference in flow rate. This means that the basic set-up for the columns is identical enough to perform a comparative research.

In total ammonium removal the performance of Clinoptilolite stays behind the performance of Aqualite. At T = 20 hours and T = 40 hours column 2 and 3 have the same total ammonium load. Column 2, containing Aqualite, removed 82,2% while column 3 only removed 73,0% at T = 20 hours. At T = 40 hours, Clinoptilolite only removed 58,8 % of the ammonium entered, Aqualite removed 69,2%. The effluent quality for the Aqualite columns starts an awful lot better as well, in the end it is still better than the effluent of the Clinoptilolite columns but the relative gap is smaller.

Rate controlling diffusion

The first adsorption cycle was executed using virgin zeolites. Because it was expected that the rate of adsorption would be quick and the zeolite in the columns would be saturated after approximately eight hours, the columns were drained, flushed with drinking water for 5 minutes and filled with N₂-gas to prevent biological growth at the end of each day. This because it turned out that the columns were not saturated as quickly as expected.

Although the stopping and starting of the columns had a practical reason, it also functioned as a means to determine the rate-controlling diffusion mechanism.

As discussed in the paragraph 2.3.1, the way adsorption continues after an interruption tells a lot about the prevailing diffusion mechanism.

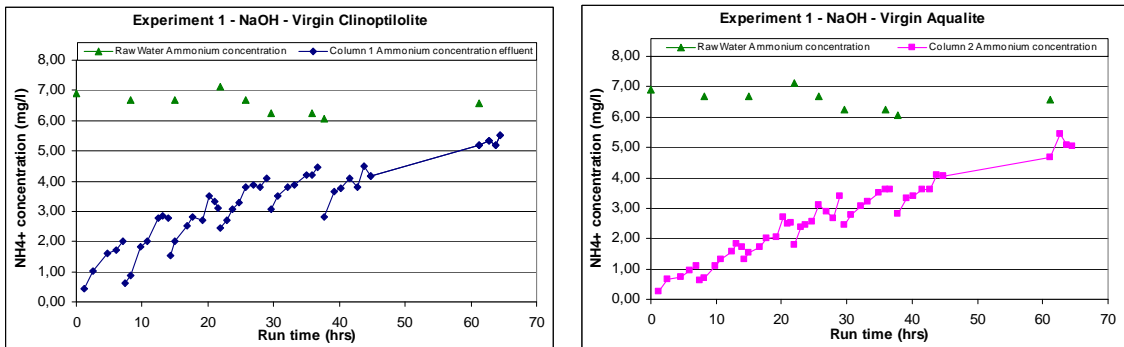


Figure 7-3: Effluent ammonium concentration Column 1 and 2

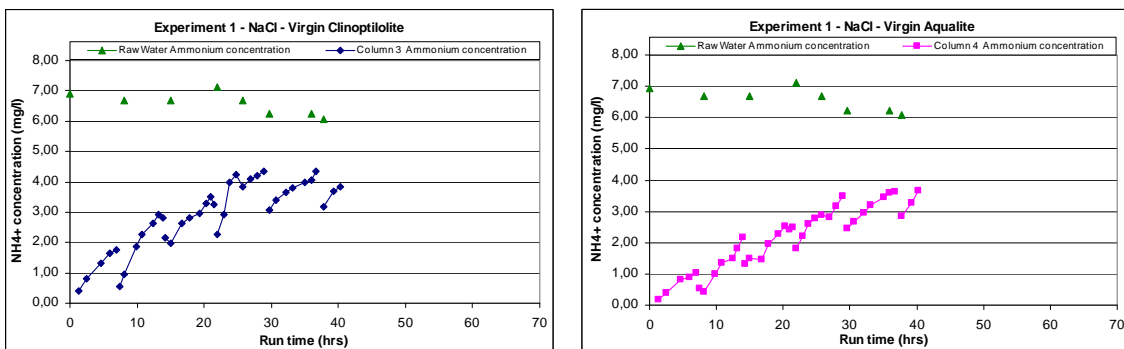


Figure 7-4: Effluent ammonium concentration Column 3 and 4

Figure 7-3 and Figure 7-4 show the ammonium concentration in the incoming (raw) water and the ammonium concentration in the water coming out of the columns (effluent). After each interruption, the effluent concentration is lower than it was the moment the columns were stopped.

Most of the time the raise in ammonium concentration is quicker just after start up than later in the cycle.

Regeneration 1

The main reason to start a regeneration is that the effluent quality does not meet the standards anymore. So the goal is to clean the system good enough to end up with a system that complies with the standards again for a significant period.

To see whether a regeneration was successful, one has to check the quality of the effluent after regeneration and monitor its development over time.

During the first regeneration the zeolites in column 1 and 2 have been surrounded by 0,5 liter of 0,1 M NaOH for 1 hour while nitrogen gas was blown through the columns to remove the formed NH_3 -gas. This means 50 mmol of NaOH has been in contact with the zeolite.

The total NH_4^+ removed by the Clinoptilolite has been 68,3 mmol, the Aqualite removed 81,9 mmol

Columns 3 and 4 have been regenerated by pumping through NaCl for 30 min with a velocity of 29,5 l per hour. A total of 14,75 l containing 600 mmol/l NaCl has passed each column, while the total NH_4^+ removal by the Clinoptilolite was 56,4 mmol and by the Aqualite 68,6 mmol.

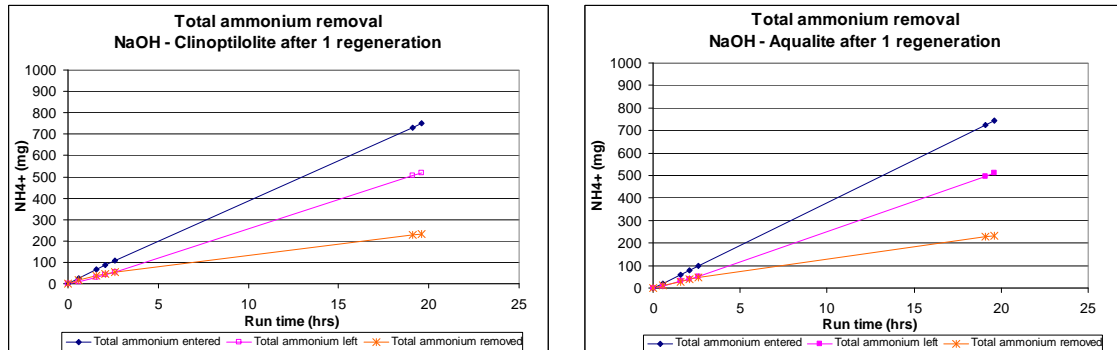


Figure 7-5: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 1 regeneration with NaOH

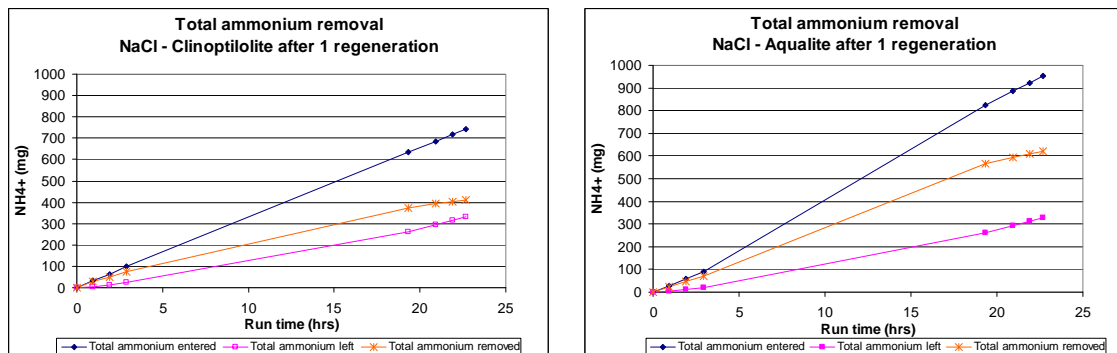


Figure 7-6: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 1 regeneration with NaCl

The performances of the columns are listed in Table 7-2. Since the run times are approximately 20 hours only the performances at a runtime of 5 hours and 20 hours are presented.

Table 7-2: Performance of the columns after 1 regeneration

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH_4^+ entered (mg)	200	190	170	155
	Total NH_4^+ removed (mg)	80	75	130	125
T = 20 hours	In mmol	4,4	4,2	7,2	6,9
	Effluent Concentration NH_4^+ (mg/l)	4,2	4,3	1,6	1,1
	Total NH_4^+ entered (mg)	770	765	655	850
	Total NH_4^+ removed (mg)	235	240	385	580
	In mmol	13,1	13,3	21,4	32,2
	Effluent Concentration NH_4^+ (mg/l)	5,2	5,1	4,2	3,6

Based on a simple mass balance sum, it is very unlikely that columns 1 and 2 have been regenerated to their full potential. They removed 68,3 mmol and 81,9 mmol respectively during their first cycle and the regeneration only added 50 mmol NaOH per column. In the ideal situation all regenerant is used to remove the NH_4^+ adsorbed on the zeolite. That would still leave 18,3 vs 31,9 mmol ammonium in the columns.

Unfortunately, the reality is not as ideal. The raw water used contains other cations, which are also adsorbed on the zeolites, therefore even less NaOH can be used to remove ammonium.

The performance stats of columns 1 and 2 in Table 7-2 show that the regeneration has been far from complete.

After 5 hours the amount of ammonium that entered the system is roughly the same as during the first run of the columns. The amount removed however by columns 1 and 2 is only 50% and 37,5% respectively of the amount removed during the first run. After 20 hours the amount removed by column 1 is only 38,9% of the removal during the first run, at column 2 the amount is only 33,6%. As said before, the effluent quality is an important parameter as to determine when a system should be regenerated. Before the first regeneration the effluent of column 1 contained 5,2 mg/l ammonium and the effluent from column 2 4,7 mg/l.

Five hours after the first regeneration, the effluent already contained 4,2 and 4,3 mg/l ammonium.

If this is compared to the effluent quality values of column 3 and 4 at the same moment, it even becomes clearer that the NaOH regeneration was not successful. The water contains 1,6 mg/l and 1,1 mg/l respectively, while right before regeneration the effluent of both columns contained about 4,0 mg/l ammonium.

Although the regeneration with NaCl has been much more successful than the regeneration with NaOH, it has not been able to restore the zeolites to their full potential.

At $T = 5$ hours, the ammonium removal in column 3 is 70% of the removal during the first run. The removal in column 4 is 62,5% of the removal during the first run.

At $T = 20$ hours, column 3 only removes 61% of the amount removed the first time but has been loaded with just 75% of the initial loading. Column 4 is loaded with about the same amount of ammonium and removes 78% of the amount removed during the first run.

The effluent quality of both columns after 20 hours is the same as it was after 40 hours during the first run.

Regeneration 2

During the second regeneration, 60 mmol of NaOH entered column 1 and 2 and only a little over 13 mmol had been removed during the run before regeneration. This means an 'overdose' of 47 mmol of NaOH.

However, there still was a minimum left-over of 18 and 32 mmol of the first regeneration. The expectancy for the performance of the columns after the second regeneration is that they should do slightly better than after the first regeneration. The removal results are shown in Figure 7-7 and Figure 7-8. Table 7-3 shows the performance values after the second regeneration.

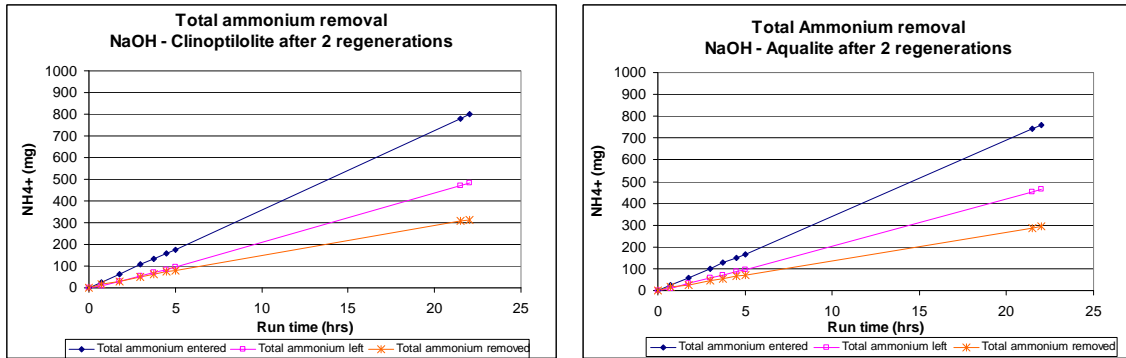


Figure 7-7: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 2 regenerations with NaOH

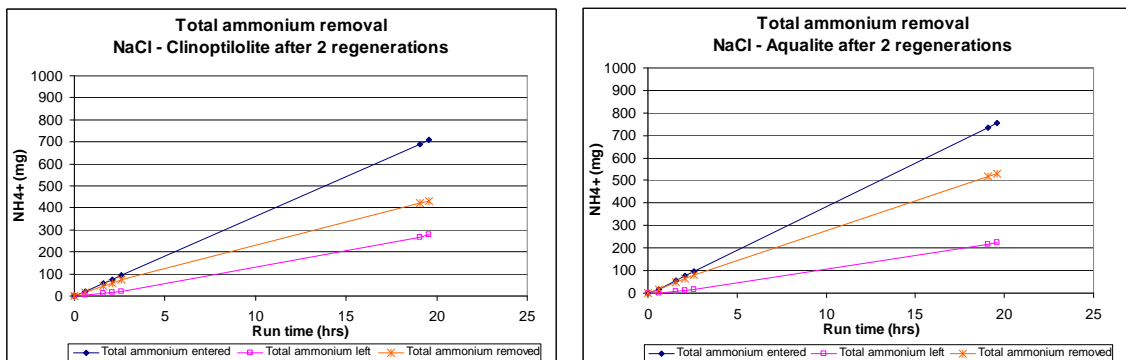


Figure 7-8: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 2 regenerations with NaCl

Table 7-3: Performance of the columns after 2 regenerations

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	174	166	183	198
	Total NH ₄ ⁺ removed (mg)	80	71	140	162
	In mmol	4,4	3,9	7,7	9,0
	Effluent Concentration NH ₄ ⁺ (mg/l)	3,7	3,6	1,6	1,4
T = 20 hours	Total NH ₄ ⁺ entered (mg)	725	690	723	770
	Total NH ₄ ⁺ removed (mg)	296	273	436	538
	In mmol	16,4	15,2	24,2	29,9
	Effluent Concentration NH ₄ ⁺ (mg/l)	5,1	5,2	3,8	2,6

When these values are compared with the values found after the first regeneration, the first noticeable thing is the change in flow rate. Only the fourth column has the same average flow rate as before, the rest all have lower rates.

As a result of that, the total loading is lower than before. The thing is though that although the total loading is lower, the total amount of NH_4^+ removed by columns 1 and 2 after 5 hours, is about the same as it was 5 hours after the first regeneration. This means that regeneration has improved the performance of column 1 and 2 compared to the cycle before.

After 20 hours, the improvement is even more noticeable. The total loading is lower, but the total removal has increased. The effluent quality has only improved a little bit at $T = 5$ hours. At $T = 20$ hours the effluent quality is the same as it was before.

The second regeneration with NaCl lasted 1 hour instead of 30 minutes. Here the results are noticeable as well. At $T = 5$ hours the total amount of ammonium that entered the system is higher than it was, but the total removal is higher as well. This is true for both columns and both for the actually removal and for the removal relative to the amount that entered the columns. At $T = 20$ hours the differences in performance (absolute and relative) are smaller, but still in favour of the second regeneration.

The effluent quality only starts to benefit from the regeneration during the later stages of the process. At $T = 5$ hours the effluent concentrations are about the same. At $T = 20$ hours, the effluent concentrations from the twice regenerated columns are significantly lower than those from the only once regenerated columns. (3,8 vs 4,2 and 2,6 vs 3,6 mg/l). This implies that the time available to load the zeolites has increased again.

Regeneration 3

During the third regeneration, columns 1 and 2 were soaked in 0,6 l of NaOH for 30 minutes (again 60 mmol NaOH per column), after which the columns were drained and nitrogen gas was blown in for another 30 minutes. Columns 3 and 4 were regenerated in the same manner, with the same (previously used) regenerant as during the second regeneration session, which means that another 29,5 l of NaCl solution has passed the columns.

After this regeneration, columns 1 and 2 have been used for 94 hours, of which only the first 5 were recorded. Columns 3 and 4 have been used for 22 hours after the third regeneration. The results are presented in Figure 7-8 and Figure 7-9.

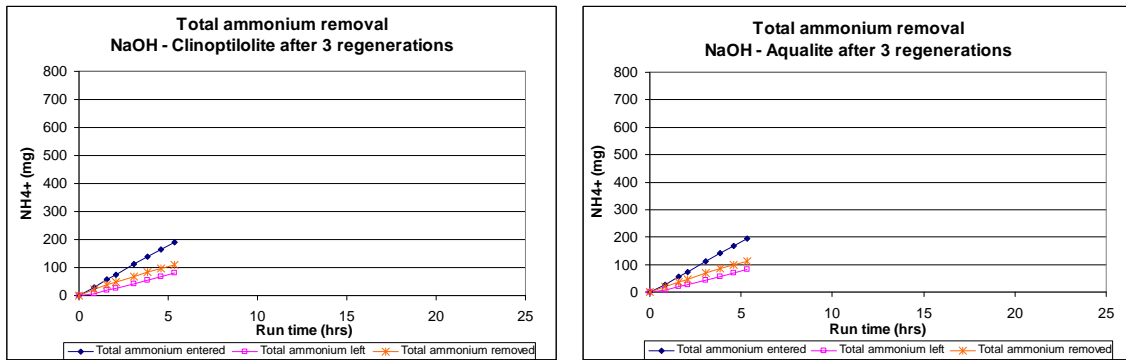


Figure 7-9: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 3 regenerations with NaOH

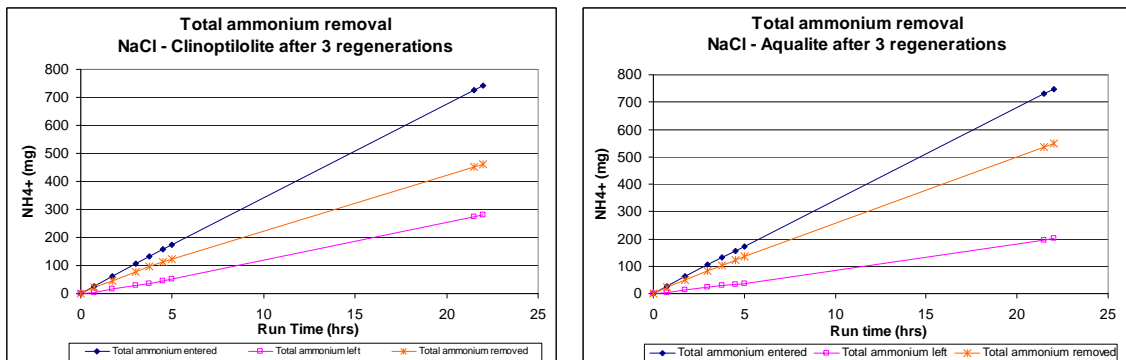


Figure 7-10: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 3 regenerations with NaCl

In Table 7-4 the performance values of the columns are listed.

Table 7-4: Performance of the columns after 3 regenerations

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	178	180	175	172
	Total NH ₄ ⁺ removed (mg)	103	105	125	135
T = 20 hours	In mmol	5,7	5,8	6,9	7,5
	Effluent Concentration NH ₄ ⁺ (mg/l)	3,5	3,5	2,0	1,3
	Total NH ₄ ⁺ entered (mg)	-	-	675	675
	Total NH ₄ ⁺ removed (mg)	-	-	430	505
	In mmol	-	-	23,9	28,1
	Effluent Concentration NH ₄ ⁺ (mg/l)	-	-	3,7	2,5

In Table 7-4 it can be seen that the total amount of ammonium removed at T = 5 hours actually is higher than it was at the same run time after the second regeneration. The effluent quality is better, but only just.

The columns regenerated by NaCl still perform better than the columns regenerated by NaOH. The total ammonium removal at T = 5 hours is lower than it was after 2 regenerations, but so is the total loading. The effluent quality after 5 hours is worse for the third regeneration than it was after the second regeneration. The effluent concentrations after 20 hours are the same (for a lower total loading). This implies that the zeolites have performed less well after the third regeneration than they did after the second.

Regeneration 4

During the fourth regeneration the approach towards the regeneration has changed for both regenerants.

Column 1 and 2 have been soaked in 0,6 l NaOH for 5 minutes after which the columns were drained and nitrogen gas was passed through for 10 minutes. This cycle has been repeated 3 times. Each column has been in contact with 180 mmol NaOH.

Columns 3 and 4 have been regenerated with previously used regenerant and a flow velocity of 15 l/h for one hour. Only 15 l of regenerant has passed the respective columns.

Columns 1 and 2 are now used again during 46 hours, columns 3 and 4 during 95 hours.

Unfortunately, only the performance of the first 5 hours is recorded. The removal results are shown I

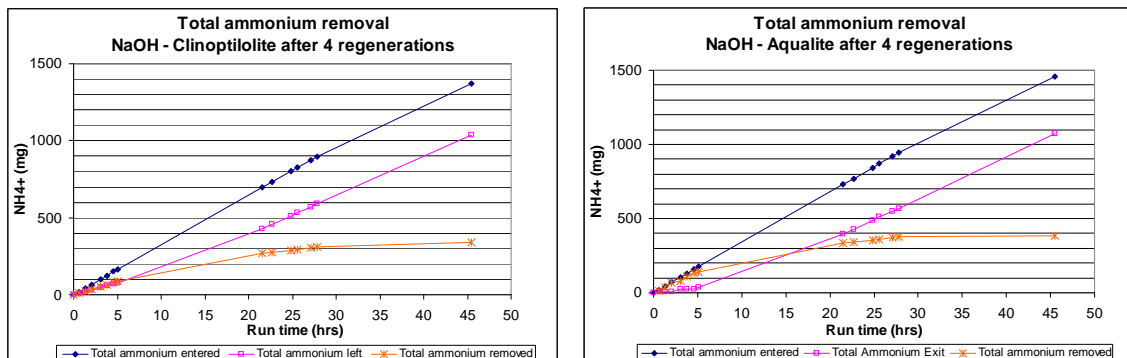


Figure 7-11: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 4 regenerations with NaOH

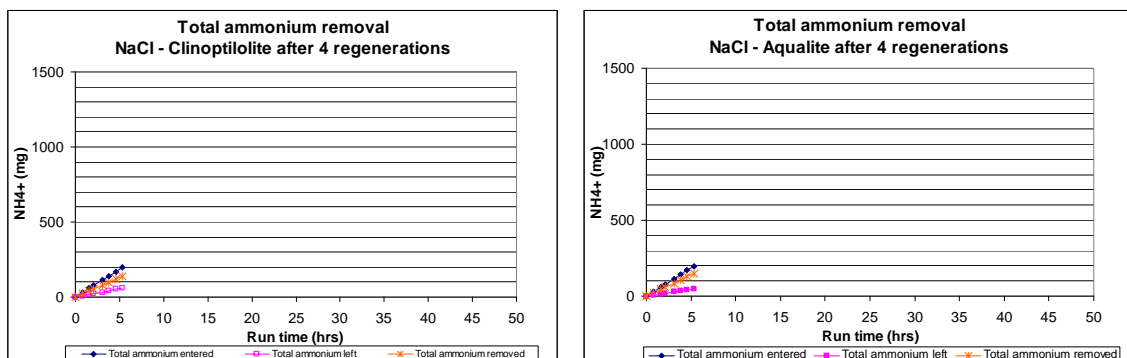


Figure 7-12: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 4 regenerations with NaCl

The performance of the columns is listed in Table 7-5.

Table 7-5: Performance of the columns after 4 regenerations

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	165	174	189	186
T = 20 hours	Total NH ₄ ⁺ removed (mg)	88	138	130	143
	In mmol	4,9	7,7	7,2	7,9
	Effluent Concentration NH ₄ ⁺ (mg/l)	3,1	2,9	2,6	1,7
T = 40 hours	Total NH ₄ ⁺ entered (mg)	685	720	-	-
	Total NH ₄ ⁺ removed (mg)	260	325	-	-
	In mmol	14,4	18,1	-	-
	Effluent Concentration NH ₄ ⁺ (mg/l)	4,6	4,6	-	-
	Total NH ₄ ⁺ entered (mg)	1248	1332	-	-
	Total NH ₄ ⁺ removed (mg)	330	380	-	-
	In mmol	18,3	21,1	-	-
	Effluent Concentration NH ₄ ⁺ (mg/l)	4,7	4,9	-	-

During the fourth regeneration columns 1 and 2 have been in contact with three times as much NaOH as during the previous regenerations. Columns 3 and 4 have been regenerated for 1 hour again, but know the flow velocity was turned down to half the velocity of the previous regenerations. This means that the same amount of regenerant passed through the columns as during the first regeneration cycle (half the time, twice the velocity).

It is expected that columns 1 and 2 give a better result after regeneration with so much more regenerant. The column containing Clinoptilolite doesn't do that. In fact in it gives a worse result when total removal is concerned. However, the effluent quality value after both 5 and 20 hours are much better than before. This of course is kind of strange when the total removal is lower than during previous cycles. If a closer look is taken at the progression of the ammonium concentration in the effluent (see Figure 7-13), it can be seen that those values start higher than they did during the cycle after the third regeneration. Besides that, the ammonium concentration in the raw water is lower as well (7,1 mg/l during the cycle after third regeneration and now between 5,9 and 6,2 mg/l)

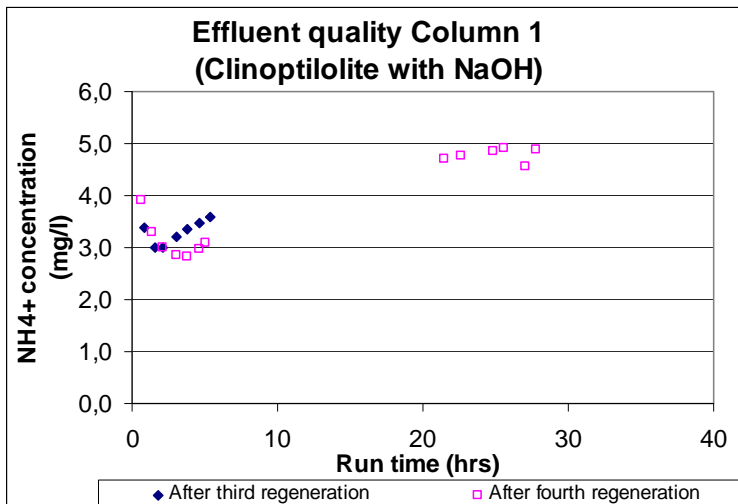


Figure 7-13: Ammonium concentration in effluent column 1 after third and fourth regeneration

Although the column containing Aqualite (column 2) actually performs better over all after the fourth regeneration than after third, the course the ammonium concentration in the effluent takes is similar to the one with Clinoptilolite. This can be seen in Figure 7-14.

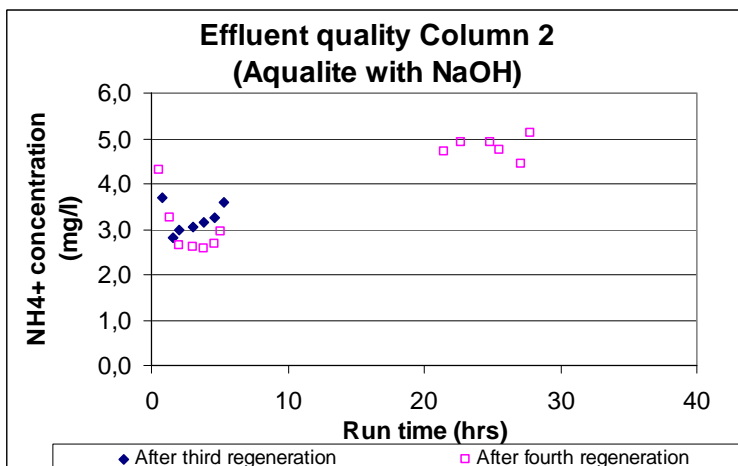


Figure 7-14: Ammonium concentration in effluent column 2 after third and fourth regeneration

Since the effluent concentrations are higher at the beginning than after an hour or two, it looks like the columns are not rinsed well enough after regeneration. It appears that the columns are still leaching regenerant containing ammonium from the pores of the zeolite.

The columns regenerated with NaCl do not perform as well as after the third regeneration. This could be expected since the first regeneration was not sufficient either. The set back in performance is not as big though as it was after the first regeneration. This leads to the (preliminary) conclusion that the amount of regenerant used is very important, the more the better. As long as there is an excess of regenerant though, time is necessary to remove all the adsorbed ions from within the pores.

Regeneration 5

During the fifth regeneration, columns 1 and 2 have been soaked in 0,6 l NaOH for 5 minutes after which the columns were drained and nitrogen gas was blown for 5 minutes as well. This has been repeated 4 times. In total 240 mmol NaOH has entered each column.

Columns 3 and 4 have been regenerated for 1 hour with the pre-used 0,6 M NaCl solution. The flow rate of the solution in the columns was 29,5 l/h. The day before regeneration, 1,55 g of NaOH (= 38,8 mmol) was added tot the solution and nitrogen gas has been introduced to the tank at a flow rate of 6 l/h for 18 hours.

After regeneration columns 1 and 2 have been loaded for about 23 hours, columns 3 and 4 for about 28 hours. The results are shown in Figure 7-15 and Figure 7-16.

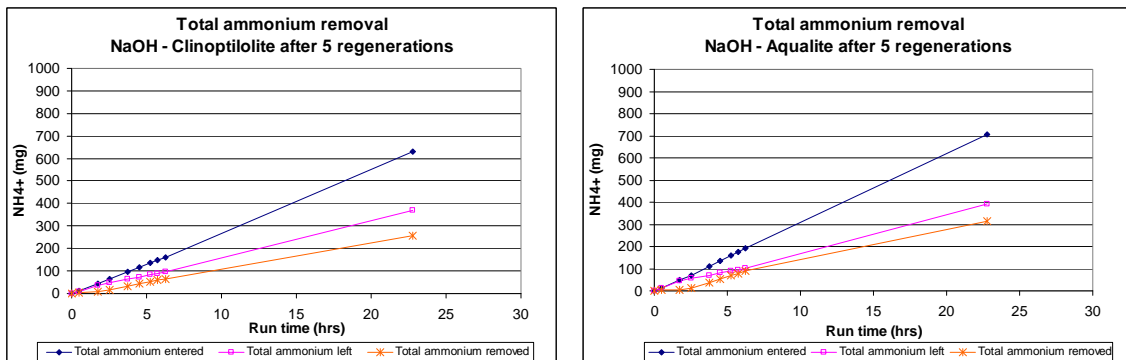


Figure 7-15: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 5 regenerations by NaOH

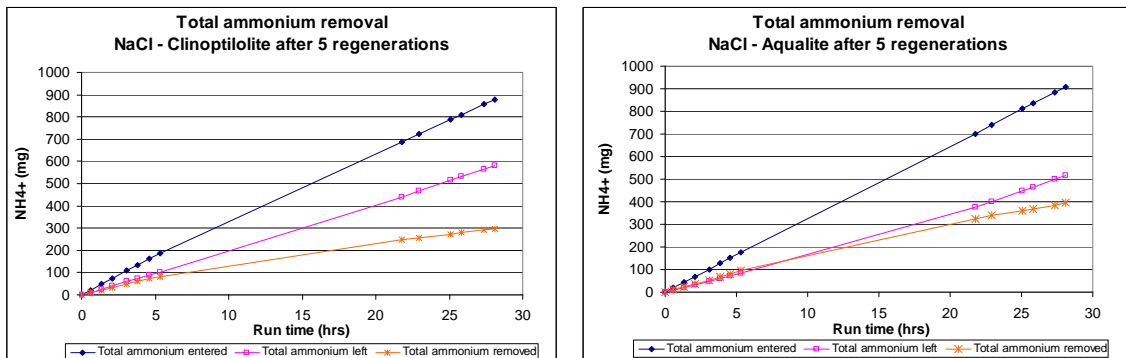


Figure 7-16: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 5 regenerations with NaCl

The performance of the columns is presented in Table 7-6.

Table 7-6: Performance of the columns after 5 regenerations

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	129	149	178	169
	Total NH ₄ ⁺ removed (mg)	49	64	79	90
	In mmol	2,7	3,6	4,4	5
	Effluent Concentration NH ₄ ⁺ (mg/l)	2,4	2,2	3,5	2,7
T = 20 hours	Total NH ₄ ⁺ entered (mg)	550	620	635	605
	Total NH ₄ ⁺ removed (mg)	230	280	235	285
	In mmol	12,8	15,6	13,1	15,8
	Effluent Concentration NH ₄ ⁺ (mg/l)	2,9	3,9	4,4	3,8
T = 25 hours	Total NH ₄ ⁺ entered (mg)	-	-	788	810
	Total NH ₄ ⁺ removed (mg)	-	-	270	361
	In mmol	-	-	15	20,1
	Effluent Concentration NH ₄ ⁺ (mg/l)	-	-	4,1	3,9

Again more NaOH has been used to regenerate columns 1 and 2. Now 240 mmol has been used per column, divided over four periods of 5 minutes followed by 10 minutes of nitrogen gas after drainage of the NaOH.

Until now the NaCl solution used has not been treated yet. So all removed ions are collected within the solution. To remove some of the ammonium from the solution and add a little sodium 1,55 g NaOH has been added to the regenerant 18 hours prior to the fifth regeneration. Nitrogen gas was added during that period to strip the gas from the solution. This method doesn't do much of course to remove other (competing) ions from the regenerant.

All above mentioned acts should help improve the performance of the zeolites after the fifth regeneration. The results are shown in Table 7-6.

After five hours of loading the total load onto column 1 and 2 has been relatively low. As a result the total removal stays behind as well. If we take a look at the ammonium concentration in the effluent, a definite improvement can be seen.

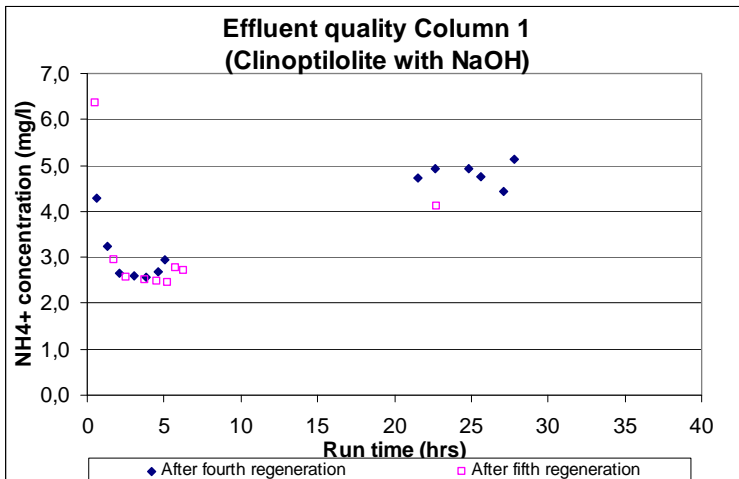


Figure 7-17: Ammonium concentration in effluent column 1 after fourth and fifth regeneration

Figure 7-17 demonstrates that the ammonium concentration in the effluent drops even more than after the fourth regeneration and the low level is held for a longer period of time, but the leaching effect just after the regeneration is also higher.

It was expected that the higher flow rate used during the fifth regeneration with NaCl should make the columns cleaner again and make them perform better than after the fourth regeneration. The extra added NaOH and nitrogen gas were supposed to help as well. As it turned out, this was not true.

The total ammonium entered after five hours of process was in the same order of magnitude as before. The removal however was less and the ammonium concentration in the effluent was higher. If the values after 20 hours of process are compared to those found after 3 regenerations, it can be seen that the fifth regeneration has not done a good job at all. The overview of the course the effluent quality takes during the last three cycles (see Figure 7-18) shows the same for both columns as well.

It is suspected that the regenerant is worn out.

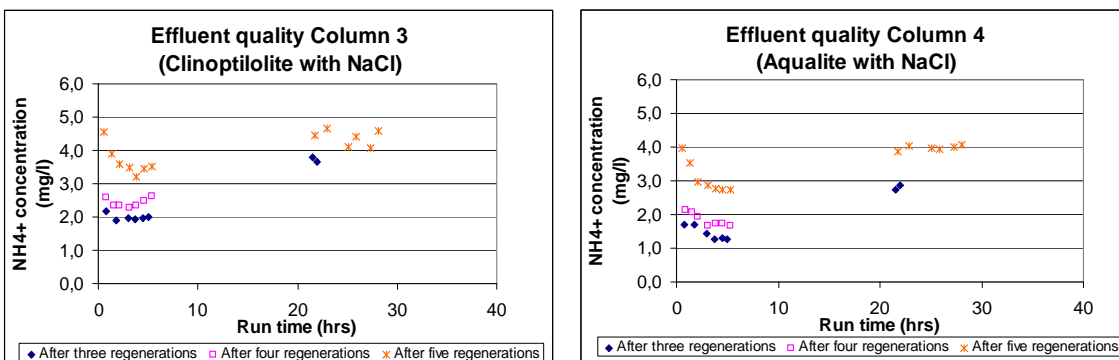


Figure 7-18: Effluent quality column 3 (left) and 4 (right) after three, four and five regenerations

Regeneration 6

This time columns 1 and 2 have been regenerated 5 times 5 minutes 0,6 l NaOH followed by 5 minutes nitrogen gas. Just as before, the NaOH solution was drained from the columns before the nitrogen was added.

In total 300 mmol NaOH was brought into the columns.

Columns 3 and 4 were regenerated for 18,5 hours with a fresh 0,6 M NaCl solution at a flow velocity of 20,2 l/h (up-flow). This means that 373,7 l of regenerant has passed the columns during that time.

After regeneration column 1 and 2 have been used again for about 94 hours, column 3 and 4 for about 23 hours. The total removal values are shown in

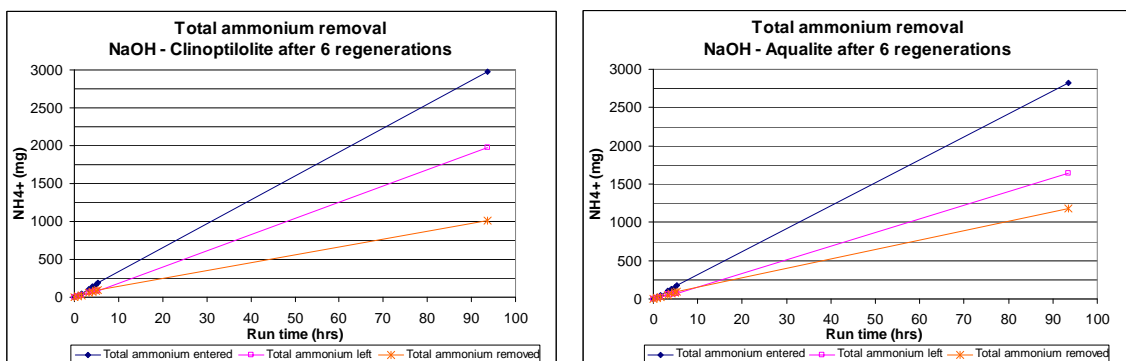


Figure 7-19: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 6 regenerations with NaOH

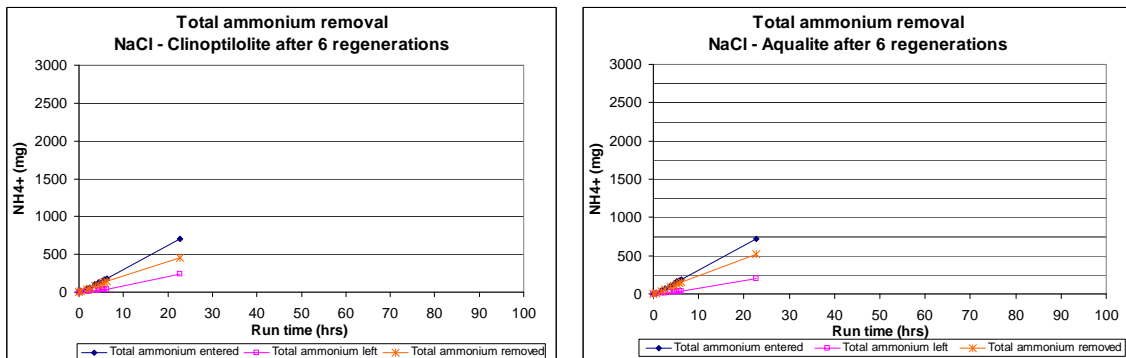


Figure 7-20: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 6 regenerations with NaCl

As usual, the performance is presented in Table 7-7. For comparison the values at T = 5 hours and T = 20 hours are given for all four columns. For columns 1 and 2 the estimated values for T = 90 hours are given as well.

Table 7-7: Performance of the columns after 6 regenerations

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	174	164	141	152
	Total NH ₄ ⁺ removed (mg)	91	91	111	123
	In mmol	5,1	5,1	6,2	6,8
	Effluent Concentration NH ₄ ⁺ (mg/l)	2,4	1,6	1,3	1,1
T = 20 hours	Total NH ₄ ⁺ entered (mg)	660	600	650	700
	Total NH ₄ ⁺ removed (mg)	250	290	435	505
	In mmol	13,9	16,1	24,2	28,1
	Effluent Concentration NH ₄ ⁺ (mg/l)	2,7	1,8	2,9	2,3
T = 90 hours	Total NH ₄ ⁺ entered (mg)	2900	2795	-	-
	Total NH ₄ ⁺ removed (mg)	995	1155	-	-
	In mmol	55,3	64,2	-	-
	Effluent Concentration NH ₄ ⁺ (mg/l)	5,2	5,2	-	-

As was already mentioned in the results section, columns 1 and 2 have been loaded for over 90 hours after the sixth regeneration. The reason why only the results at T = 5, T = 20 and T = 90 hours are discussed is that only the first six and the last 4 hours have been monitored. The graphs in the results section show a very nice straight line, but it is not sure that the processes actually evolved like that. Especially the total amount of ammonium removed has shown a sort of ceiling after 25 to 30 hours of operations. The evolution of the values still is a slow process therefore estimations at T = 20 and T = 90 hours are likely to be valid, but the gap in between is too big to say anything for sure about the rest.

The effluent quality of the columns at T = 5 hours is again better than before, the extra amount of NaOH added has paid off again. After 90 hours, the columns are pretty much saturated.

Columns 3 and 4 have made a huge improvement. The performance at T = 5 hours is only slightly worse than the performance of the virgin zeolites was at that time. The performance at T = 20 hours is comparable to the performance of the virgin zeolite. The total loading is lower after the 6 regeneration than it was with the virgin zeolite, but the performances are a little better as well.

This shows that the regenerant used during the first five regenerations was worn out and that it is possible to regenerate the zeolites back to their original capacity.

Regeneration 7

Only column 3 and 4 have been regenerated 7 times. The last time the columns were regenerated, they were regenerated for 1 hour again. The flow velocity was, as before, set at 29,7 l/h again. The

NaCl solution was the solution used during the 18,5 hour regeneration. The day before the seventh regeneration 1 g of NaOH (= 25 mmol) was added to the solution, after which nitrogen gas was added for 18 hours at a rate of 6 l/h.

After this regeneration the columns were loaded again for another 94 hours.

The results are presented in Figure 7-21.

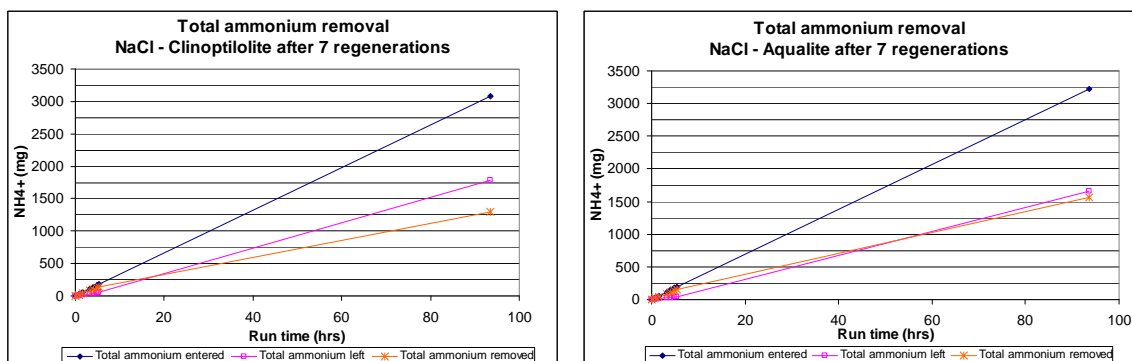


Figure 7-21: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 7 regenerations by NaCl

The performance values are listed in Table 7-8.

Table 7-8: Performance of the columns after 7 regenerations

		0,1 M NaOH		0,6 M NaCl	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	-	-	173	182
	Total NH ₄ ⁺ removed (mg)	-	-	124	140
	In mmol	-	-	6,9	7,8
	Effluent Concentration NH ₄ ⁺ (mg/l)	-	-	1,7	1,4
T = 20 hours	Total NH ₄ ⁺ entered (mg)	-	-	680	700
	Total NH ₄ ⁺ removed (mg)	-	-	300	420
	In mmol	-	-	16,7	23,3
	Effluent Concentration NH ₄ ⁺ (mg/l)	-	-	2,2	1,8
T = 90 hours	Total NH ₄ ⁺ entered (mg)	-	-	2965	3096
	Total NH ₄ ⁺ removed (mg)	-	-	1250	1499
	In mmol	-	-		
	Effluent Concentration NH ₄ ⁺ (mg/l)	-	-	5,0	4,7

The loadings are back to what they usually are. The columns show a slightly worse performance after 5 hours than they did after 6 regenerations, but the performances after 20 hours are definitely better.

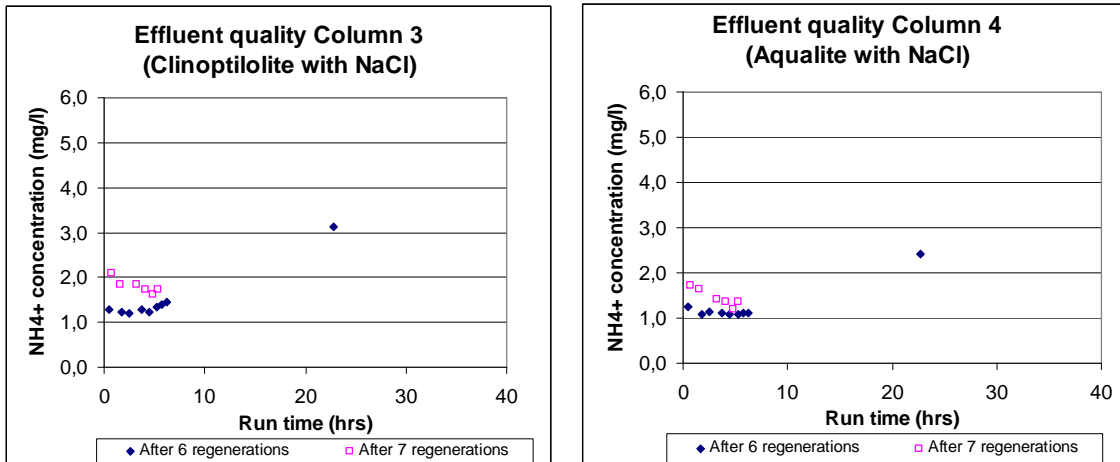


Figure 7-22: Effluent quality of column 3 (left) and column 4 (right) after 6 and 7 regenerations

The graphs in Figure 7-22 do not show a leaching problem they just confirm that the sixth regeneration was very good and that the seventh did well.

General conclusions

Based on the above discussed it can be concluded that there is a minimum amount of regenerant necessary to regenerate zeolites properly. It is possible to regenerate them to their full potential and it is also possible to reuse regenerants several times with a satisfactory result.

Generally, Aqualite does perform better than Clinoptilolite.

Experiment 2: Adsorption - Regeneration cycles with anaerobic groundwater EBCT \approx 17 min

General operating conditions

Bed height: approximately 110 cm

Average flow rate: 3,5 l/h ~ 4,4 m/h ~ 4,0 BV/h

NaOH concentration: 0,1 M

NaCl concentration: 1,8 M (= 10,5%)

pH NaCl solution: 11,2

Number of regeneration cycles

Clinoptilolite with NaOH: 11

Aqualite with NaOH: 5

Clinoptilolite with NaCl: 11

Aqualite with NaCl: 11

For the second series of experiments an EBCT of approximately 17 minutes was desired. Therefore the columns were filled zeolite up to 110 cm and the flow rate was reduced to 3,5 l/h on average. Columns 1, 2 and 4 went through 11 regeneration cycles. Column 2 was not regenerated after the 5 cycle anymore in order to establish a full breakthrough curve.

Just as during Experiment 1, two types of regenerant have been used. NaOH has been added at the same concentration of 0,1 M. The NaCl concentration had been tripled in strength to 1,8 M. Apart from that, the pH is raised to 11,25. An overview of the specifics of every regeneration cycle is given in Table 7-9. Regeneration cycles with the same properties have been given the same colour. Cycles for which samples have been sent to the Vitens Laboratories are marked with an asterisk (*).

Table 7-9: Overview of the regeneration specifics Experiment 2

	Duration of cycle after regeneration	0,1 M NaOH		1,8 M NaCl, pH = 11,25; 20 l recirculated	
		Column 1 - Clinoptilolite	Column 2 - Aqualite	Column 3 - Clinoptilolite	Column 4 - Aqualite
Regeneration 1	21,4 hours	5 x 5' NaOH, 5' N ₂ (~ ca 2 l NaOH)		1,5 h recirculation @ 29,7 l/h; N ₂ @ 6 l/h; 2,5 g NaOH added, during regeneration, 2 g added after regeneration	
Regeneration 2	117,5 hours	7 x 3' NaOH, 3' N ₂ (~ ca 2,8 l NaOH)		1,5 h recirculation @ 29,7 l/h; N ₂ @ 6 l/h; 3 x 2 g NaOH added	
Regeneration 3	27,4 hours	2,5 l NaOH down-flow seeping		1 h recirculation @ 29,7 l/h; total 8 g NaOH added; No N ₂ !	
Regeneration 4	136,25 hours	2,5 l NaOH down-flow seeping		1h recirculation @ 29,7 l/h; N ₂ @ 6 l/h; 2 g NaOH added before start, during regeneration 8 g NaOH added	
Regeneration 5	21,08 hours	2,5 l NaOH down-flow seeping		1 h recirculation @ 29,7 l/h; No N ₂ or NaOH added during regeneration	
Regeneration 6*	21,67 hours	2,5 l NaOH down-flow seeping	-	9 g NaOH added before 1h regeneration @ 29,7 l/h; No N ₂	
Regeneration 7*	117,5 hours	2,5 l NaOH down-flow seeping	-	1h recirculation @ 29,7 l/h; No N ₂ or NaOH added	
Regeneration 8*	44,4 hours	2,9 l NaOH down-flow seeping	-	6 g of NaOH added before 1 h recirculation @ 29,7 l/h; No N ₂ or NaOH added further	
Regeneration 9*	95,9 hours	2,9 l NaOH down-flow seeping; after rinsing 10' N ₂ blown through	-	Extra NaOH added before recirculation; N ₂ @ 6 l/h; 1h recirculation @ 29,7 l/h; 5 g NaOH added during circulation	
Regeneration 10*	43,17 hours	2,75 l NaOH through with 60 cm raw water still in column	-	1 h recirculation @ 29,7 l/h; N ₂ @ 6 l/h; in total 8 g NaOH added	
Regeneration 11*	29,17 hours	2,5 l NaOH through with 60 cm raw water still in column	-	4 g NaOH added before recirculation; 1 h @ 29,7 l/h; N ₂ @ 6 l/h; In total 8 g NaOH added	

From the fifth regeneration on not only the ammonium concentrations have been monitored, iron levels have been measured as well.

In order to draw final conclusions it is not necessary to discuss all regeneration cycles in detail. The cycles are not all the same in length, therefore two moments during the run have been picked to make a preliminary comparison of the performance of the columns. These moments are after 5 and 20 hours of loading the columns. Based on the values found at those times, the type of regeneration performed and the amount of data present, a selection has been made of cycles which will be discussed more elaborately.

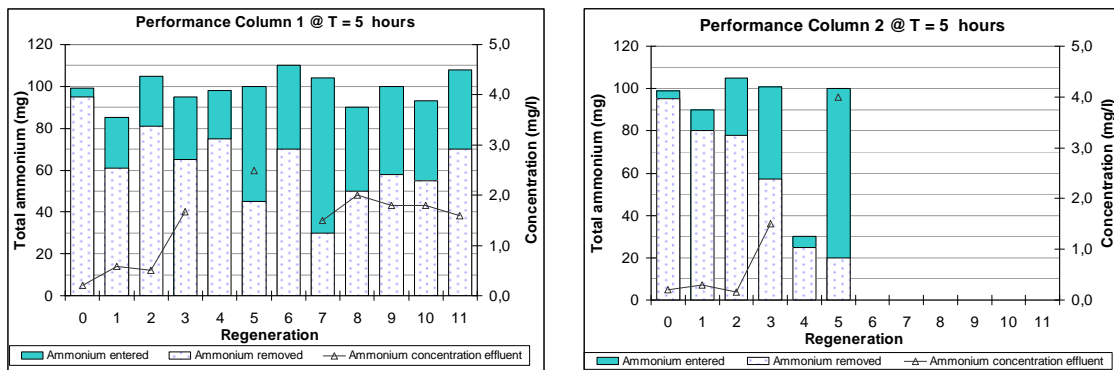


Figure 7-23: Performance of Column 1 (left) and 2 (right) after 5 hours of loading

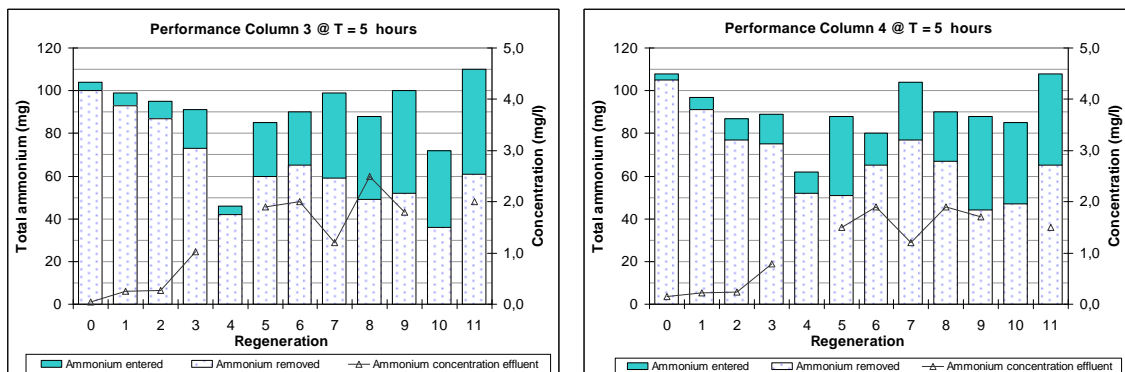


Figure 7-24: Performance of Column 3 (left) and 4 (right) after 5 hours of loading

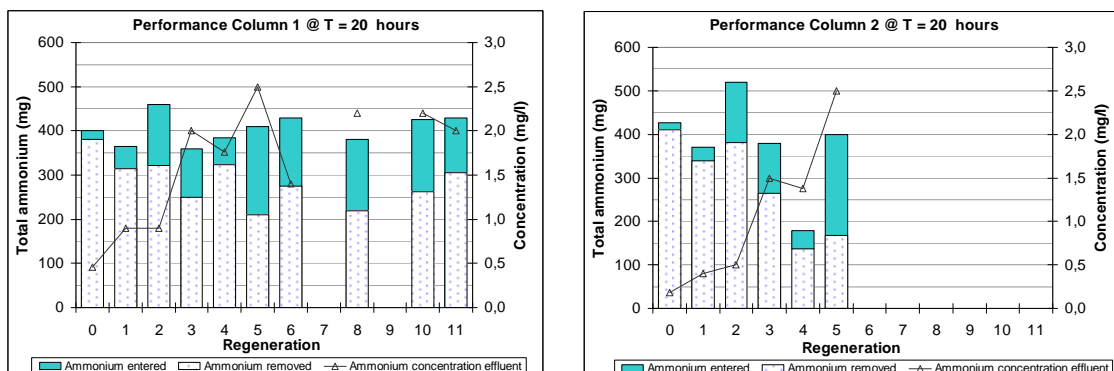


Figure 7-25: Performance of Column 1 (left) and 2 (right) after 20 hours of loading

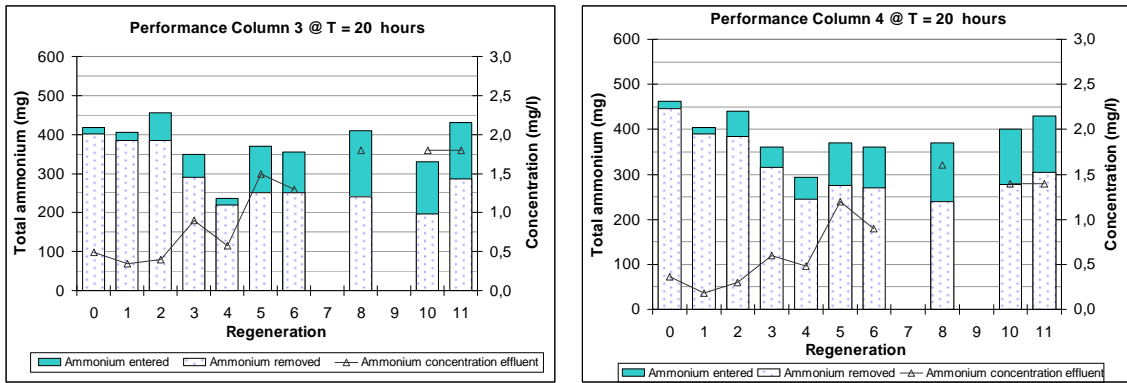


Figure 7-26: Performance of column 3 (left) and 4 (right) after 20 hours of loading

Figure 7-23 and Figure 7-24 the performance of the columns at T = 5 hours. Figure 7-25 and present the performance of the columns at T = 20 hours. The shaded bars show how much ammonium (in mg) has entered at that time, the dotted bars the amount of ammonium removed (in mg) by the zeolites. The line marked with triangles represents the ammonium concentration in the effluent of the columns at that time.

The cycles that will be discussed in the same manner as in the previous chapter are:

- Virgin zeolite
- Regeneration 1
- Regeneration 3
- Regeneration 5
- Regeneration 7 (only the first 5 hours)
- Regeneration 8
- Regeneration 10
- Regeneration 11

The cycles after regeneration 2, 4, 7 and 9 have been relatively long. While the rest of the cycles generally took between 20 and 45 hours, they all were longer than 95 hours.

Noticeable is that the cycles after those regenerations, so cycle 3, 5, 8 and 10 all have a higher than average effluent concentration after 5 hours and the total removal is lower as well. Although less prominent, this trend is still apparent after 20 hours. Since the performance increases again in the later cycle, it can be concluded that the regeneration after these long cycles is not complete.

Virgin zeolites

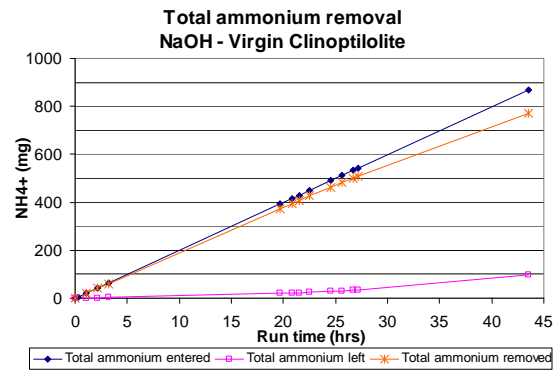
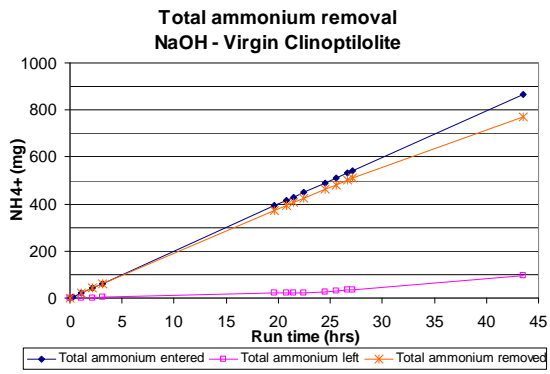


Figure 7-27: Total ammonium removal by virgin clinoptilolite in Column 1 (left) and by virgin Aqualite in Column 2 (right)

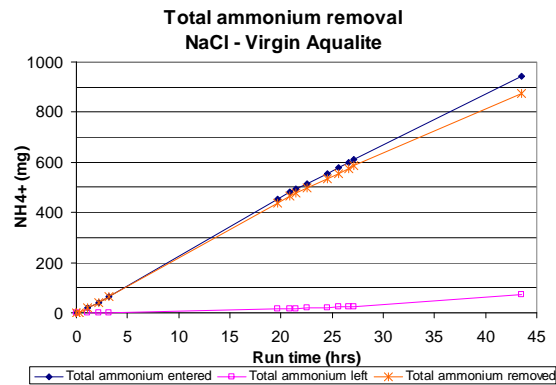
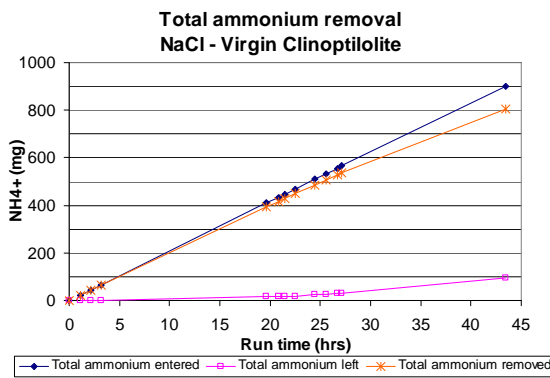


Figure 7-28: Total ammonium removal by virgin clinoptilolite in Column 3 (left) and virgin Aqualite in column 4 (right)

Table 7-10: Performance of the virgin zeolites

		0,1 M NaOH		1,8 M NaCl, pH 11,25	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	99	99	104	108
	Total NH ₄ ⁺ removed (mg)	95	95	100	105
	In mmol	5,3	5,3	5,6	5,8
	Effluent Concentration NH ₄ ⁺ (mg/l)	0,21	0,2	0,05	0,15
T = 20 hours	Total NH ₄ ⁺ entered (mg)	400	426	418	462
	Total NH ₄ ⁺ removed (mg)	380	411	402	446
	In mmol	21,1	22,8	22,3	24,8
	Effluent Concentration NH ₄ ⁺ (mg/l)	0,46	0,18	0,49	0,36
T = 40 hours	Total NH ₄ ⁺ entered (mg)	800	850	830	870
	Total NH ₄ ⁺ removed (mg)	720	800	750	810
	In mmol	40	44,4	41,6	45
	Effluent Concentration NH ₄ ⁺ (mg/l)	1,45	0,77	1,32	1,00
T = 43,5 hours	Total NH ₄ ⁺ entered (mg)	867	921	900	945
	Total NH ₄ ⁺ removed (mg)	771	863	807	873
	In mmol	42,8	47,9	44,8	48,5
	Effluent Concentration NH ₄ ⁺ (mg/l)	1,48	0,92	1,48	1,16

During the first experiments it was found that that the columns containing the same material, which are columns 1 and 3 and columns 2 and 4 performed more or less similar during the first cycle. This is expected to happen again during this experiment, since the columns all contain fresh zeolites again. Figure 7-27 and Figure 7-28 and the values in Table 7-10 show that this in fact is the case.

The first 5 hours the results are mixed, but in the end the columns containing Clinoptilolite (1 and 3) have a removal efficiency of 86% and 87% respectively. The columns containing Aqualite (2 and 4) removed 94% and 93%.

The difference between the columns is something else that could be expected after Experiment 1. Aqualite did perform better than Clinoptilolite. The ammonium concentrations found in the effluent of the columns underline this conclusion once more.

The new thing about this experiment compared to the Experiment 1 is the EBCT. The raised contact time should be able to increase the quality of the effluent due to a better ammonium removal. As a result of that, it should take longer before a certain threshold level in the ammonium concentration is reached.

If the effluent concentrations of the columns are compared to those found during the first experiment, it can be seen that the higher contact time has the desired effect.

During the first experiment the concentrations had nearly reached or even passed the 1,0 mg/l level at T = 5 hours. During the experiment with the longer contact time these values are only reached after approximately 40 hours. This is 8 times longer although the contact time has only increased 2,5 times!

Regeneration 1

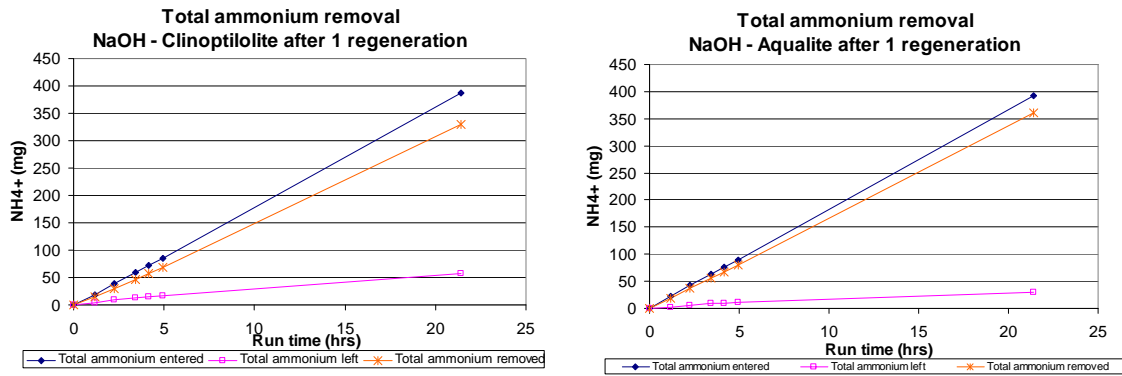


Figure 7-29: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 1 regeneration with NaOH

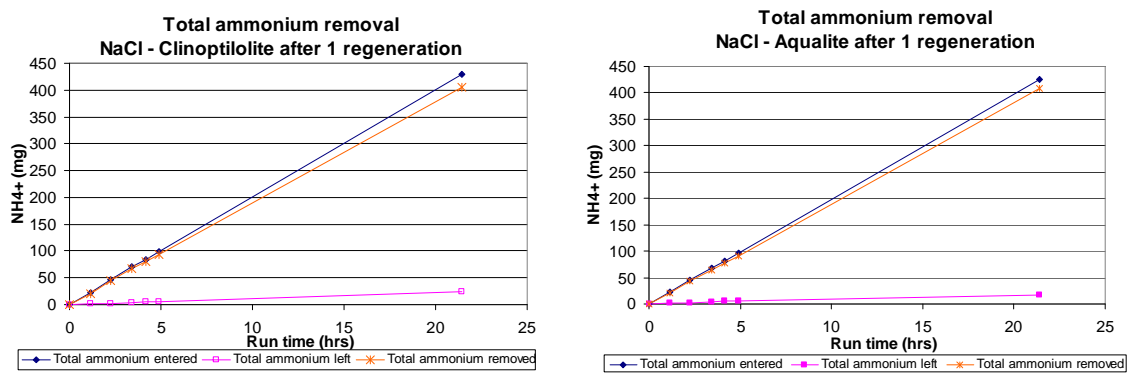


Figure 7-30: Total ammonium removal by Clinoptilolite (left) and Aqualite (right) after 1 regeneration with NaCl

Table 7-11: Performance of the zeolites after 1 regeneration

		0,1 M NaOH		1,8 M NaCl, pH 11,25	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	85	90	99	97
	Total NH ₄ ⁺ removed (mg)	69	80	93	91
	In mmol	3,8	4,4	5,2	5,1
	Effluent Concentration NH ₄ ⁺ (mg/l)	0,58	0,3	0,25	0,22
T = 20 hours	Total NH ₄ ⁺ entered (mg)	365	370	405	405
	Total NH ₄ ⁺ removed (mg)	315	340	385	390
	In mmol	17,8	18,9	21,4	21,7
	Effluent Concentration NH ₄ ⁺ (mg/l)	0,9	0,4	0,35	0,18
T = 21,4 hours	Total NH ₄ ⁺ entered (mg)	387	392	429	426
	Total NH ₄ ⁺ removed (mg)	330	361	405	409
	In mmol	18,3	20,1	22,5	22,7
	Effluent Concentration NH ₄ ⁺ (mg/l)	0,96	0,44	0,38	0,19

During the first regeneration column 1 and 2 have been filled up with NaOH 5 times 5 minutes. Each time after draining the regenerant, the columns have been blown through with N₂-gas. The total amount of NaOH that has passed the columns is approximately 2,0 l, which means 0,2 M of NaOH has passed the columns. Columns 3 and 4 have been regenerated for 1,5 hours at a rate of 29,7 l/h per column. The tank containing the NaCl solution was continuously blown through by nitrogen gas. During the regeneration the pH was corrected by adding 2,5 g of NaOH (~ 0,0625 mol). After regeneration an extra 2 g was added to remove more NH₄⁺ before the next regeneration.

Looking at the values in Table 7-11, it can be seen that although column 1 has the lowest amount of ammonium entered after 5 hours, the effluent quality is the poorest. Column 3 has the highest amount of ammonium entered, but is second in performance. After 21,4 hours of service this still is the case.

The columns' removal efficiency at that time is 85% for column 1, 92% for column 2, 94% for column 3 and column 4 has an efficiency of 96%.

Although column 4 still has a very low ammonium concentration in its effluent after 21,4 hours, the regeneration has not been able to restore the zeolites to their full potential. This is a little surprising since columns 1 and 2 each have been in contact with 200 mmol of NaOH and less than 50 mmol of ammonium was removed during the first cycle. This means that either the contact time with the zeolites or the NaOH concentration was too low to get a better result.

What is more important though, is the fact that the first few hours after regeneration all four columns have a heightened effluent concentration. Columns 1 and 2 even start with concentrations higher than the concentrations found at the end of the first cycle.

Apparently ammonium ions that have been loosened from the zeolites are still flushed out when a new loading cycle has started. The pH measurements performed on the first samples of effluent also show a heightened pH (> 9). This proves that the rinsing after regeneration is not sufficient, just as it was not sufficient during Experiment 1.

Since the rinsing time or method has not been changed during Experiment 2, it will stay insufficient. Therefore it will not be mentioned anymore while discussing any other regeneration cycle.

Regeneration 3

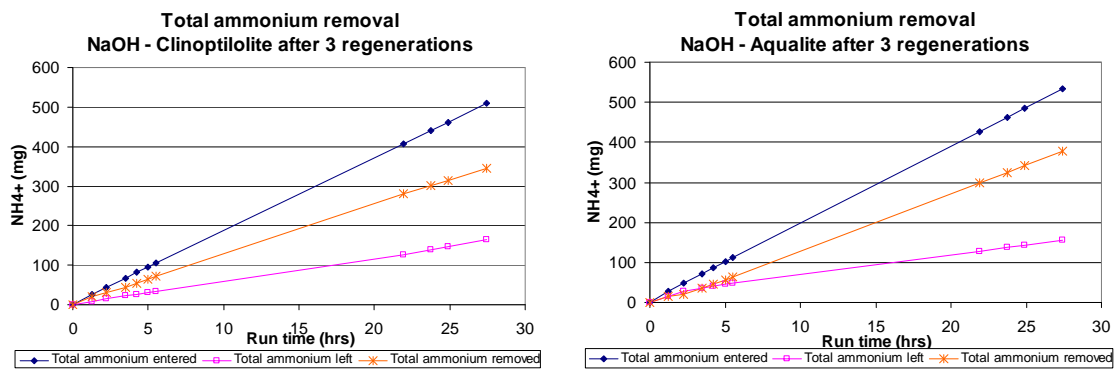


Figure 7-31: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 3 regenerations with NaOH

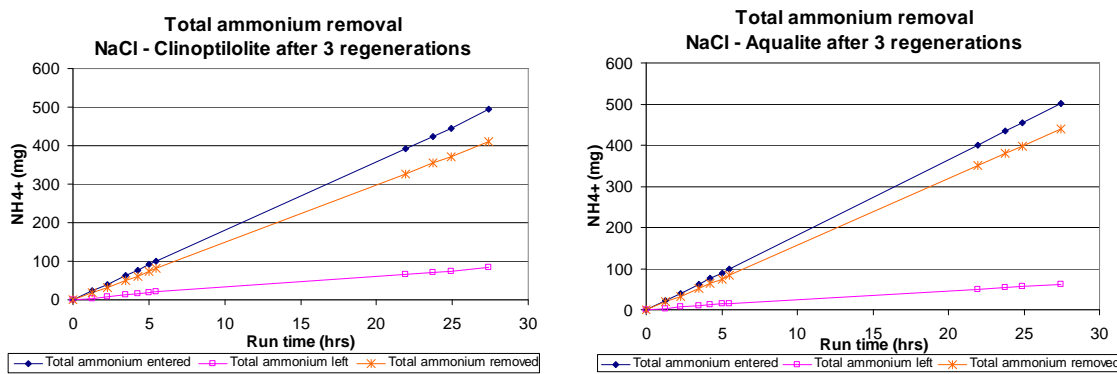


Figure 7-32: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 3 regenerations with NaCl

Table 7-12: Performance by the zeolites after three regeneration

		0,1 M NaOH		1,8 M NaCl, pH 11,25	
		Clinoptilolite	Aqualite	Clinoptilolite	Aqualite
T = 5 hours	Total NH ₄ ⁺ entered (mg)	95	101	91	89
	Total NH ₄ ⁺ removed (mg)	65	57	73	75
	In mmol	3,6	3,2	4,1	4,2
	Effluent Concentration NH ₄ ⁺ (mg/l)	1,57	1,51	1,02	0,79
T = 20 hours	Total NH ₄ ⁺ entered (mg)	360	380	350	360
	Total NH ₄ ⁺ removed (mg)	250	265	290	315
	In mmol	13,9	14,7	16,1	17,5
	Effluent Concentration NH ₄ ⁺ (mg/l)	2,0	1,5	0,9	0,6
T = 27,4 hours	Total NH ₄ ⁺ entered (mg)	510	533	494	502
	Total NH ₄ ⁺ removed (mg)	344	377	410	441
	In mmol	19,1	20,9	22,8	24,5
	Effluent Concentration NH ₄ ⁺ (mg/l)	2,5	1,66	1,6	0,64

The cycle after regeneration 2 has been a very long one, the columns have been loaded for 117,5 hours. This is 5,5 times longer than the cycle after regeneration 1. As a result the amount of ammonium removed by the zeolites is significantly higher as well (between 1500 mg and 1800 mg).

The third regeneration has to be a thorough one in order to clean the zeolites properly.

The method to regenerate columns 1 and 2 has changed. In stead of filling the columns up from below and emptying them out several times, they are now regenerated top down. In a continuous mode 2,5 l of NaOH is slowly passed through the columns. This way 250 mmol of NaOH is added. Columns 3 and 4 are regenerated for 1 hour at a flow rate of 29,7 l/h. During the regeneration 8 g of NaOH (~ 200 mmol) is added in 4 steps. The solution was not blown through with N₂-gas.

The first hours after regeneration the ammonium concentrations are really high compared to the earlier cycles, this can be seen in

Table 7-12. Although most columns have a lower ammonium concentration in the effluent after 20 hours than they had after 5 hours, the quality stays poorer than it used to.

If the graphs in Figure 7-31 and Figure 7-32 are compared, it is clear that all four columns have been loaded with approximately 500 mg of ammonium after 27,4 hours. However, the gap between the line that represents the ammonium (◆) entered and the line that represents the amount removed (*) is much bigger for the columns regenerated with NaOH than for those regenerated with NaCl. The efficiency numbers also represent that. Column 1 removed 67% of the entered ammonium, column 2 71%, column 3 83% and column 4 88%.

It can be concluded that a longer loading cycle needs a longer or stronger regeneration cycle. Based on the difference between the two types of regenerations it might be that the stronger regeneration does the trick. The NaCl solution contains 1,8 M of NaCl and is recycled for one hour at a rate of 29,7

l/h. This means that 29,7 l of NaCl is passed through the column with a theoretical total amount of 53,46 M of NaCl while during that same time 2,5 l of 0,1 M NaOH is passes through columns 1 and 2. This is only 0,250 M per column.

Regeneration 5

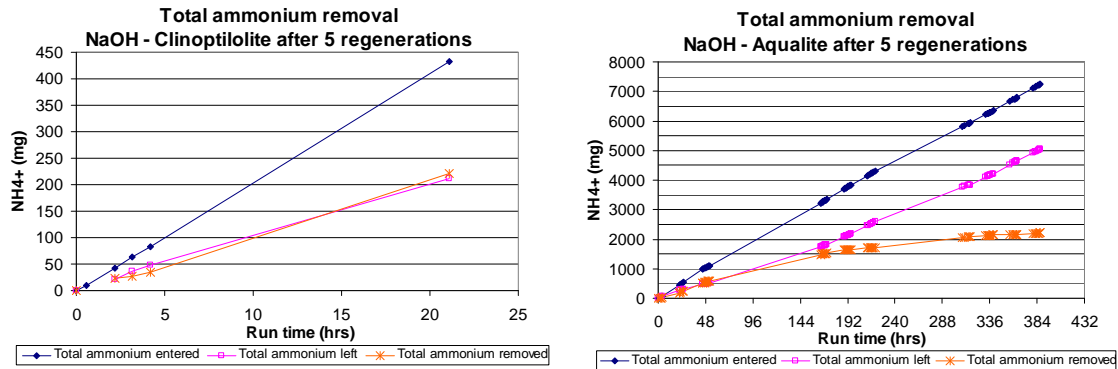


Figure 7-33: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 5 regenerations with NaOH

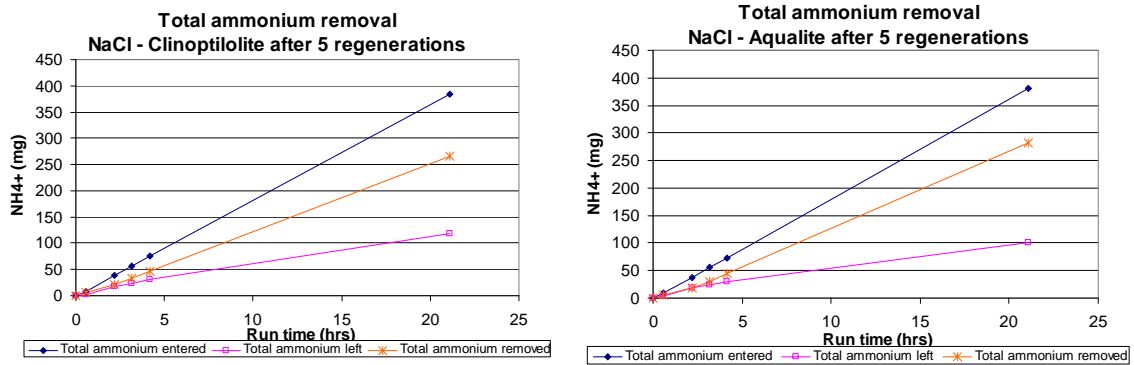


Figure 7-34: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 5 regenerations with NaCl

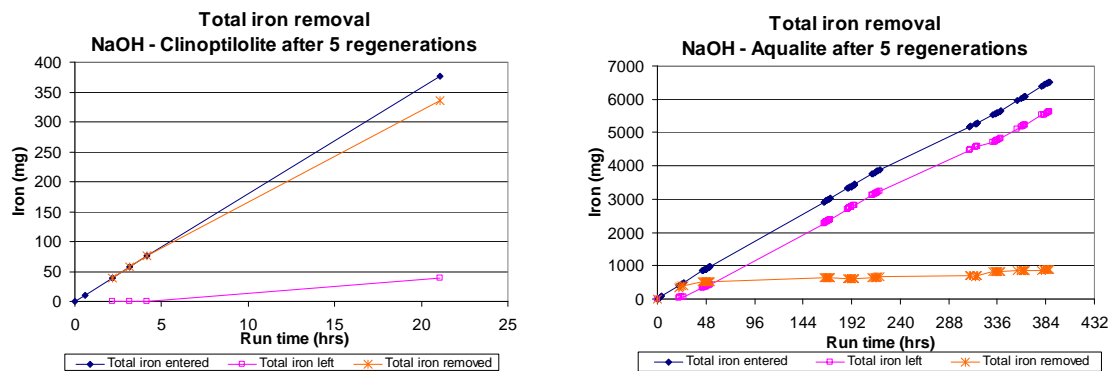


Figure 7-35: Iron removal by Clinoptilolite (left) and Aqualite (right) after 5 regenerations with NaOH

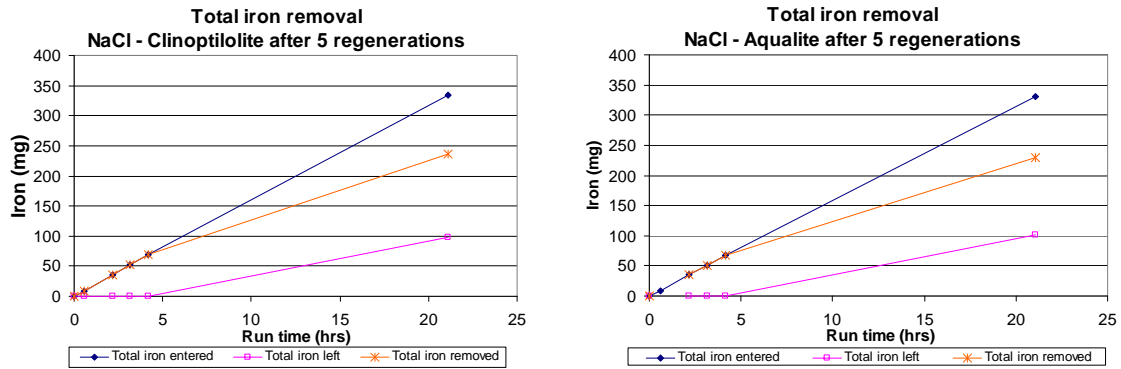


Figure 7-36: Iron removal by Clinoptilolite (left) and Aqualite (right) after 5 regenerations with NaCl

Table 7-13: Performance of the zeolite after five regenerations

		0,1 M NaOH				1,8 M NaCl, pH 11,25			
		Clinoptilolite		Aqualite		Clinoptilolite		Aqualite	
		NH ₄ ⁺	Fe	NH ₄ ⁺	Fe	NH ₄ ⁺	Fe	NH ₄ ⁺	Fe
T = 5 hours	Total amount entered (mg)	100	84	100	85	85	82	88	80
	Total amount removed (mg)	45	83	20	84	60	82	51	80
	In mmol	2,5	1,5	1,1	1,5	3,3	1,5	2,8	1,4
	Effluent Concentration (mg/l)	2,8	<0,10	4,0	<0,10	1,9	<0,10	1,5	<0,10
T = 20 hours	Total amount entered (mg)	410	350	400	370	370	320	370	310
	Total amount removed (mg)	210	320	167	330	250	235	275	205
	In mmol	11,7	5,8	9,3	6,1	13,9	4,2	15,3	3,7
	Effluent Concentration (mg/l)	2,5	1,3	2,5	1,1	1,5	3,8	1,2	3,9
T = 21,08 hours	Total amount entered (mg)	433	376	444	385	385	334	382	331
	Total amount removed (mg)	221	336	181	344	266	236	282	230
	In mmol	12,3	6,1	10,0	6,2	14,8	4,3	15,7	4,1
	Effluent Concentration (mg/l)	2,52	1,38	2,36	1,12	1,54	3,86	1,21	3,98
T = 48 hours	Total amount entered (mg)	-	-	1034	902	-	-	-	-
	Total amount removed (mg)	-	-	542	525	-	-	-	-
	In mmol	-	-	30,1	9,5	-	-	-	-
	Effluent Concentration (mg/l)	-	-	2,5	5,2	-	-	-	-
T = 168 hours	Total amount entered (mg)	-	-	2980	2980	-	-	-	-
	Total amount removed (mg)	-	-	1503	645	-	-	-	-
	In mmol	-	-	83,5	11,6	-	-	-	-
	Effluent Concentration (mg/l)	-	-	4,1	5,4	-	-	-	-
T = 387,42 hours	Total amount entered (mg)	-	-	7254	6518	-	-	-	-
	Total amount removed (mg)	-	-	2208	894	-	-	-	-
	In mmol	-	-	122,7	16,1	-	-	-	-
	Effluent Concentration (mg/l)	-	-	5,56	5,54	-	-	-	-

From this cycle on, not only ammonium concentrations have been measured, but iron levels as well. Besides this, it was also decided that Column 2, containing Aqualite, was not going to be regenerated anymore until the effluent concentrations reached the raw water concentrations. During earlier cycles the ammonium concentrations in the effluent never reached the level of the raw water. This means that the zeolites were never fully saturated. In order to create a full breakthrough curve more time was needed.

The decision to use column 2 for this was based on the fact that the NaOH regeneration never performed at the same level as the NaCl regeneration and not much is known yet about the performance of Aqualite. The other issue of course was the durability of the NaCl-solution while it was recycled. When one of those columns was taken out of regeneration service, it would mean that the NaCl solution would not be used as much anymore as before. This would influence the quality of the regenerant of course and so the time it would be reusable.

So although the Aqualite was not regenerated up to its full potential before starting the complete breakthrough curve, it would give a very good idea of what the material is capable of.

The cycle after the fourth regeneration was a long one (138 hours) again. This surely has affected the thoroughness of the fifth regeneration. When looking at Figure 7-33 and Figure 7-34 it is clear once more that the NaOH regeneration stays behind in performance.

The amount of ammonium that is removed by the zeolites is determined by subtracting the amount of ammonium that leaves the column from the amount that has entered the column at that time. If the rinsing after regeneration is not sufficient, the ammonium concentrations in the effluent start out really high. This means that there is practically no removal to start with. Therefore it can be concluded that the total removal is a nice indicator for the performance of the columns, but it does not mean much without knowledge about the effluent quality.

If a closer look is taken at Figure 7-35 and Figure 7-36, which represent the iron removal, it can be seen that these graphs show exactly the opposite from the ammonium graphs. The columns regenerated with NaOH have a better removal than those regenerated with NaCl.

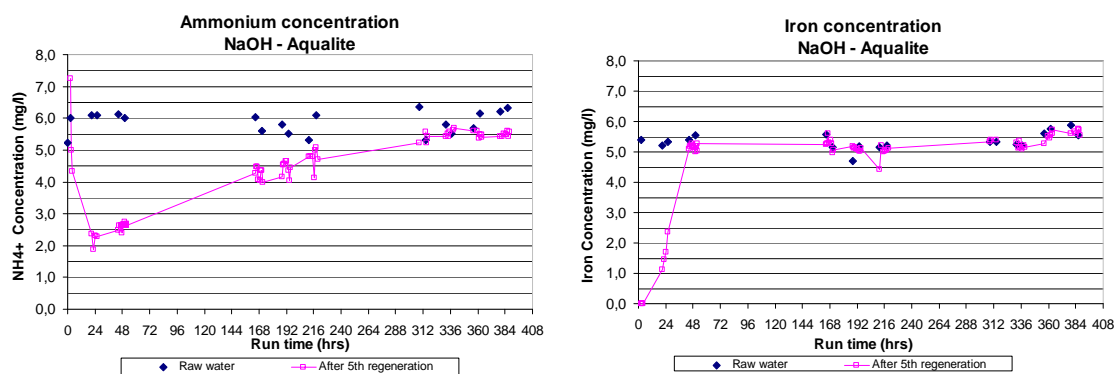


Figure 7-37: Ammonium (left) and Iron (right) concentrations in the raw water and effluent from Column 2 after 5 regenerations

The nice thing about the long run from column 2 is that both graphs clearly show that there is a ceiling regarding the amount of ions that can be removed by the zeolites.

Although the ammonium removal still is not there yet, the maximum level lies around 2500 mg. The iron removal reaches its maximum level of 500 after approximately 24 hours. The right graph of Figure 7-37 shows there is some leaching of iron going on in the later stages of the cycle. Around 192 hours the iron concentration in the effluent is higher than the concentration in the raw water. Later on, around 310 hours the same thing happens again. Both times the effluent concentration drops afterwards, after which iron is removed again. This is the reason that the total amount of iron removed in Figure 7-35 keeps rising slowly till the end of the run.

Besides that the effluent of the columns is tested for certain parameters, the regenerant is analysed as well.

Before starting the fifth regeneration a sample of the NaCl solution has been taken to test for ammonium, iron, sodium, calcium, potassium, manganese and magnesium. The first 250 ml of NaOH passing through column 1 and column 2 have been collected and tested for the same parameters as well.

This resulted in the values presented in Table 7-14.

Table 7-14: Water quality parameters NaCl regenerant after 4 regenerations

		NH₄⁺	Fe	Na⁺	Ca²⁺	K⁺	Mg²⁺	Mn²⁺	Total (excl Na⁺)
NaCl	mg/l	192,3	0,226	33860	846	647,8	14,152	0,002	
Solution	mmol/l	10,7	0,004	1472	21,15	16,57	0,58	0,036*10 ⁻³	49,00
Effluent	mg/l	6,66	0,37	69,9	42,035	4,75	5,635	0,215	
Column 1	mmol/l	0,37	0,007	3,04	1,05	0,12	0,23	0,004	1,78
Effluent	mg/l	6,68	0,425	107,8	42,01	6,85	6,42	0,155	
Column 2	mmol/l	0,37	0,008	4,69	1,05	0,18	0,26	0,003	1,87

This is the first time since the beginning of Experiment 2 that the regenerant has been analysed. Every new regeneration the NaOH solution is the same, since a fresh badge is used every time. The NaCl solution, however, has been reused four times already. This means that all the ions that have been removed until now are accumulating in the solution. The only exception is NH₄⁺. By raising the pH and adding nitrogen gas, this ion should be removed from the solution.

During the four regenerations a total of 28,5 g of NaOH has been added to the solution. This equals 0,7 mol. The experiments started with a tank containing 20 l 1,8 M NaCl and 1,4 g NaOH (= 0,035 mol). The total amount of sodium in the original solution is 36,04 mol. After four regenerations the concentration has dropped to 1,472 mol/l. Assuming that the tank still contains 20 l of solution, this equals 29,44 mol.

During four regenerations 36,04 - 29,44 = 6,6 mol of Na⁺ has been consumed.

Since the regenerant was made with demi water, the only ions present at first were Na^+ and Cl^- . All other ions now present in the water were once attached to the zeolites. The total amount of 'foreign' cat ions present before the fifth regeneration is 49,00 mmol/l. This equals 980 mmol or 0,98 mol. Those ions contain 70,7 mmol/l of positive electrons, which equals 1,4 mol. If it is assumed that all those electrons were connected to the zeolite before regeneration, 1,4 mol of Na^+ would have been enough to replace them. Apparently there was a need for another 5,2 mol of Na^+ for other purposes. Partly this can be explained because some of the regenerant stays behind after regeneration and is flushed out either during the rinsing or during the new loading phase. A second explanation is that the analysis does not cover all cations that might have been attached to the zeolites. This way a certain amount of ions, such as heavy metals, might be present in the regenerant because sodium ions forced them to leave the zeolites. The third explanation is that there used to be more NH_4^+ present in the regenerant. Due to the high pH of the solution and the nitrogen gas blown through, NH_3 gas is forced to leave the regenerant, leaving a gap in the mass balance. The third explanation is the one most likely, or at least the one with the greatest impact on the mass balance.

Regeneration 7

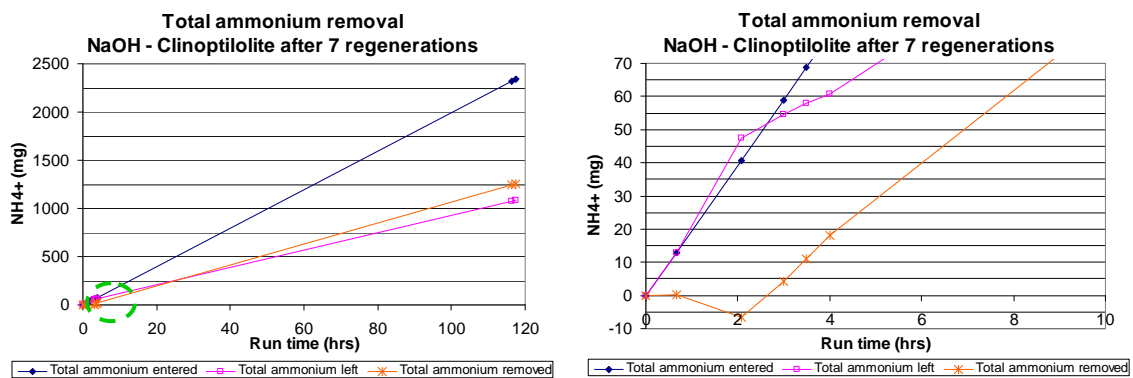


Figure 7-38: Ammonium removal by Clinoptilolite after 7 regenerations with NaOH (left: complete; right: detail)

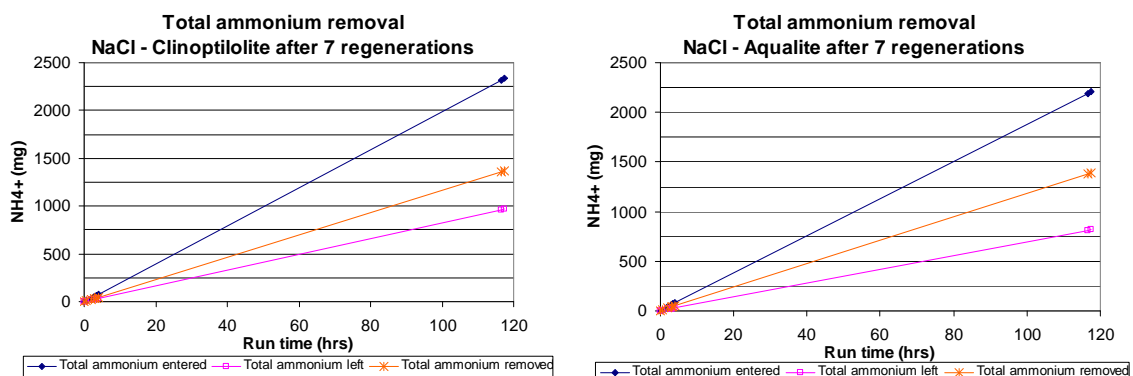


Figure 7-39: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 7 regenerations with NaCl

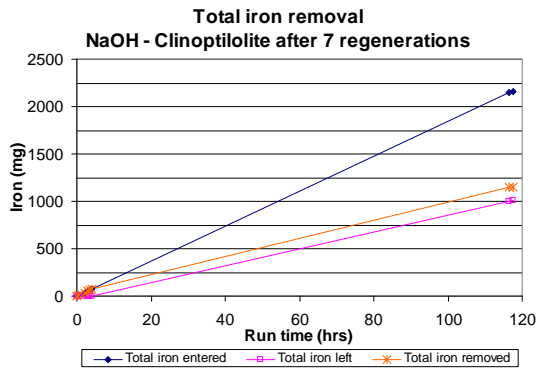


Figure 7-40: Iron removal by Clinoptilolite after 7 regenerations with NaOH

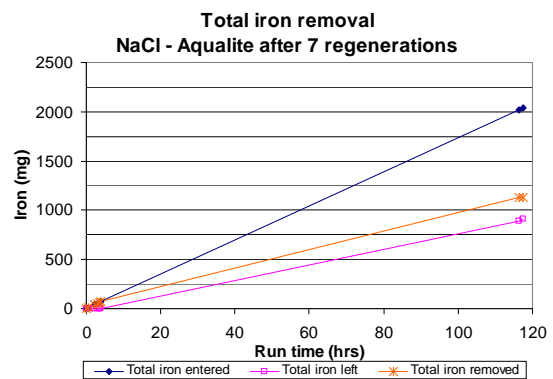
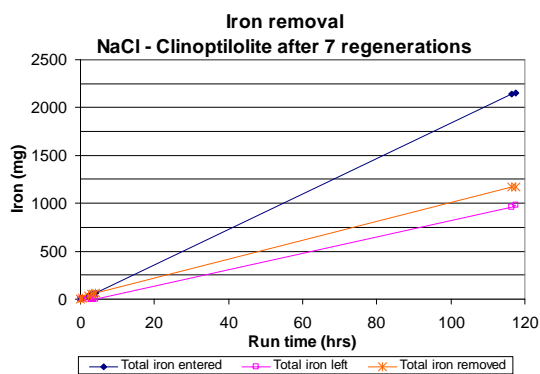


Figure 7-41: Iron removal by Clinoptilolite (left) and Aqualite (right) after 7 regenerations with NaCl

Table 7-15: Performance of the zeolites after seven regenerations

		0,1 M NaOH				1,8 M NaCl, pH 11,25			
		Clinoptilolite		Aqualite		Clinoptilolite		Aqualite	
		NH ₄ ⁺	Fe	NH ₄ ⁺	Fe	NH ₄ ⁺	Fe	NH ₄ ⁺	Fe
T = 5 hours	Total amount entered (mg)	104	95	-	-	99	90	104	95
	Total amount removed (mg)	30	83	-	-	59	79	77	85
	In mmol	1,7	1,5			3,3	1,4	4,3	1,5
	Effluent Concentration (mg/l)	1,5	<0,10	-	-	1,2	<0,10	1,2	<0,10
T = 115 hours	Total amount entered (mg)	2290	2110	-	-	2285	2110	2155	1990
	Total amount removed (mg)	1230	1147	-	-	1343	1173	1368	1127
	In mmol	68,3	20,7			75	21,2	76	20,3
	Effluent Concentration (mg/l)	3,8	5,3	-	-	3,5	5,0	3,0	5,0
T = 117,5 hours	Total amount entered (mg)	2343	2164	-	-	2335	2157	2205	2037
	Total amount removed (mg)	1255	1149	-	-	1363	1176	1388	1130
	In mmol	69,7	20,7			75,7	21,2	77,1	20,4
	Effluent Concentration (mg/l)	3,84	5,50	-	-	3,64	5,24	3,88	5,16

The cycle after the seventh regeneration has lasted 117,5 hours. From those hours, only the first four hours were monitored closely. In the graphs in Figure 7-38 to Figure 7-41 the gap between T = 4 hours and T = 116,5 hours is represented by a line. This line is only a straight connection between the points measured. It definitely does not represent the actual progression in concentrations.

Because of those insecurities in the measurements, only the results found during the first four hours will be discussed.

Column 3 and 4 behaved like they usually do. Iron concentrations during the first hours were below detection limits and ammonium concentrations started relatively high, but then dropped to average levels.

Column 1 however, had some very striking values for the effluent concentration. Figure 7-42 shows that the value found after 2/3 of an hour is higher than 12 mg/l. At that same time the ammonium concentration in the raw water is only 6 mg/l. As a result there is a negative removal of ammonium, as can be seen in Figure 7-38. More ammonium is leaving the column than that entered it. This can only be the case when the regeneration has not been complete and the rinsing has not been thorough. The regenerant left in the zeolite's pores removes ammonium from the zeolite and also prohibits new ammonium to attach to the zeolite. Eventually all the ammonium that entered the column is flushed out together with the left-over regenerant containing more ammonium.

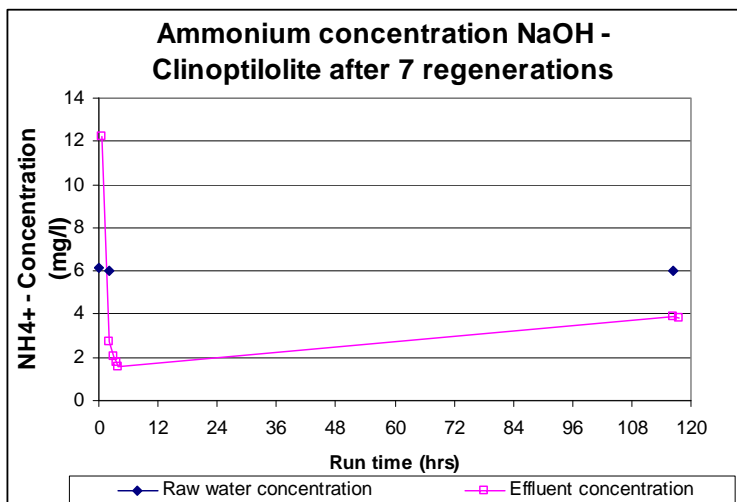


Figure 7-42: Ammonium concentration from Column 1 after 7 regenerations

Regeneration 8

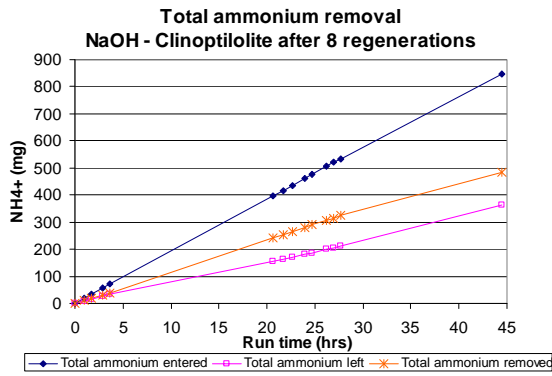


Figure 7-43: Ammonium removal by Clinoptilolite after 8 regenerations with NaOH

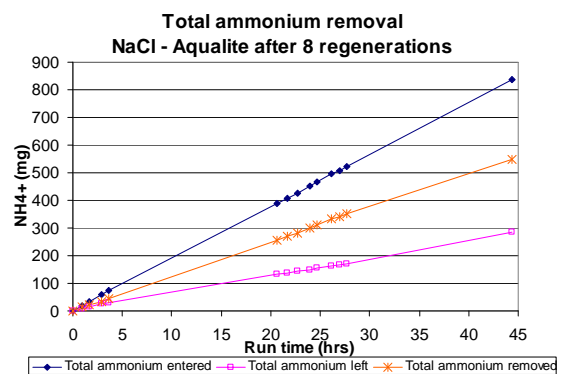
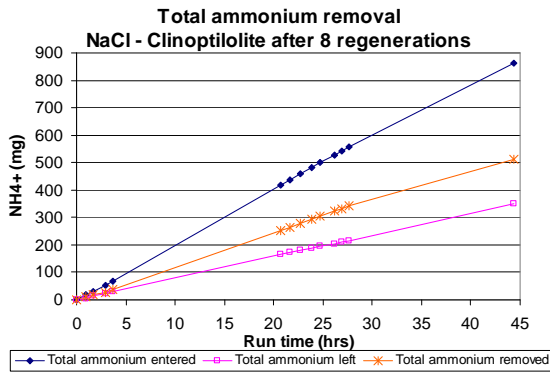


Figure 7-44: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 8 regenerations with NaCl

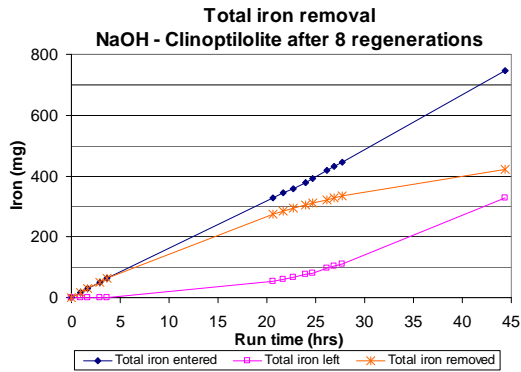


Figure 7-45: Iron removal by Clinoptilolite after 8 regenerations by NaOH

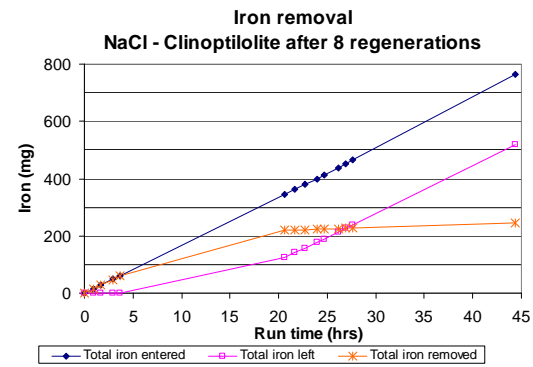
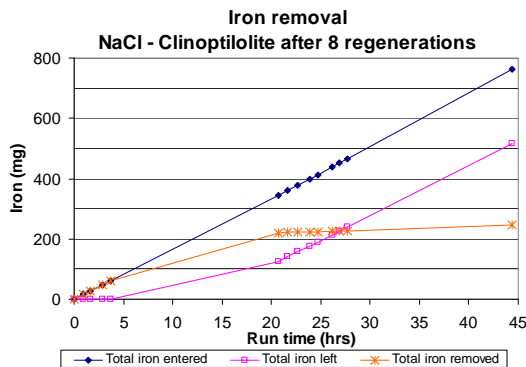


Figure 7-46: Iron removal by Clinoptilolite (left) and Aqualite (right) after 8 regenerations with NaCl

Table 7-16: Performance of the zeolites after eight regenerations

		0,1 M NaOH				1,8 M NaCl, pH 11,25			
		Clinoptilolite		Aqualite		Clinoptilolite		Aqualite	
		NH₄⁺	Fe	NH₄⁺	Fe	NH₄⁺	Fe	NH₄⁺	Fe
T = 5 hours	Total amount entered (mg)	90	78	-	-	88	77	90	81
	Total amount removed (mg)	50	75	-	-	49	70	67	75
	In mmol	2,8	1,4			2,7	1,3	1,2	1,4
	Effluent Concentration (mg/l)	2,0	<0,10	-	-	2,5	<0,10	1,9	<0,10
T = 20 hours	Total amount entered (mg)	380	312	-	-	410	340	370	312
	Total amount removed (mg)	220	260	-	-	240	210	240	213
	In mmol	12,2	5,0			13,3	3,8	13,3	3,8
	Effluent Concentration (mg/l)	2,2	1,9	-	-	1,8	1,9	1,6	3,7
T = 25 hours	Total amount entered (mg)	482	396	-	-	505	420	455	390
	Total amount removed (mg)	295	303	-	-	310	230	300	222
	In mmol	16,4	5,5			17,2	4,1	16,7	4,0
	Effluent Concentration (mg/l)	2,3	2,5	-	-	2,0	4,8	1,6	4,6
T = 44,4 hours	Total amount entered (mg)	847	748	-	-	964	763	835	741
	Total amount removed (mg)	485	421	-	-	513	245	549	256
	In mmol	26,9	7,6			28,5	4,4	30,5	4,6
	Effluent Concentration (mg/l)	3,04	4,26	-	-	2,58	4,84	2,14	4,56

The very clear graphs in Figure 7-43 to Figure 7-46 show once again that both Clinoptilolite and Aqualite have a higher capacity for ammonium than for iron. After 20 hours, but also after 40 hours of running the removal of ammonium still has a straight line. Where the removal of iron is concerned though, there is a big change in direction of the removal lines after approximately 20 hours. The exact moment when breakthrough starts to happen, is hard to say of course, since there is a big gap between the measurements taken at around T = 5 hours and T = 20 hours. As said, there is not much difference between the two types of zeolite. There is a difference though between the two types of regeneration. Figure 7-45 and Figure 7-46 show that the column regenerated with NaOH has better iron removal skills than the columns regenerated with NaCl. This is probably due to the build-up of iron and other ions in the NaCl solution. The competition that is a result hereof makes it hard to remove all the iron from the zeolite. The NaOH that is used is fresh every time, so a better removal is achieved.

Regeneration 10

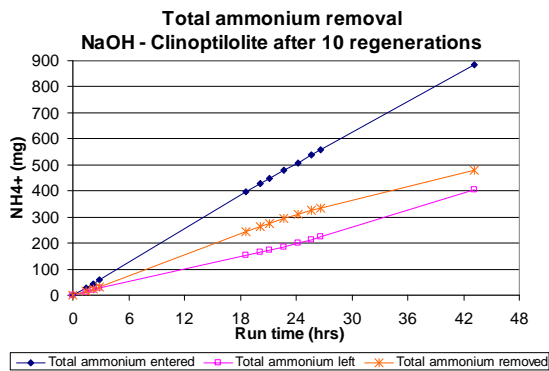


Figure 7-47: Ammonium removal by Clinoptilolite after 10 regenerations with NaOH

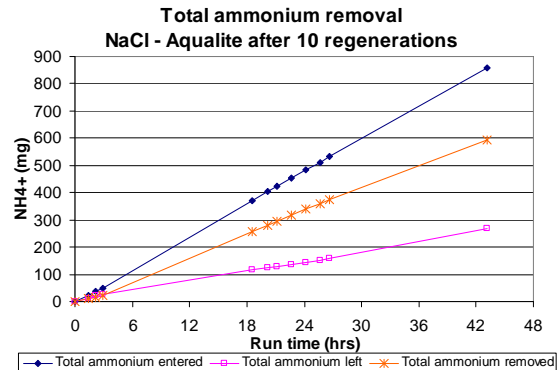
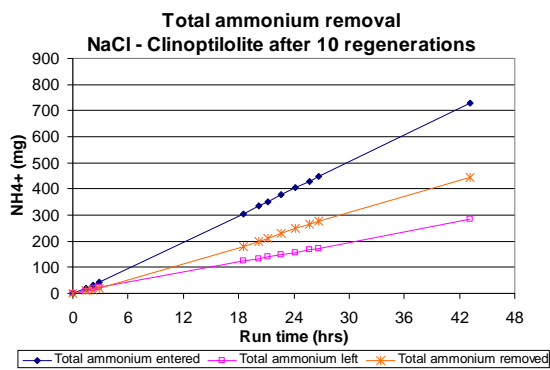


Figure 7-48: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 10 regenerations with NaCl

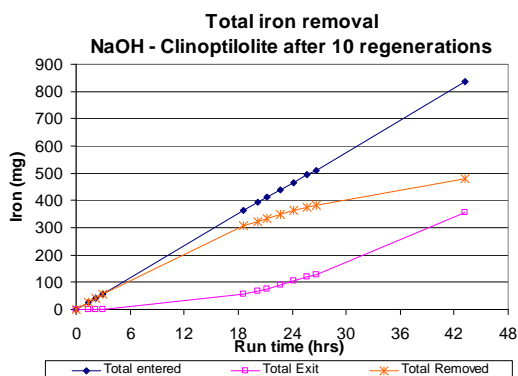


Figure 7-49: Iron removal by Clinoptilolite after 10 regenerations with NaOH

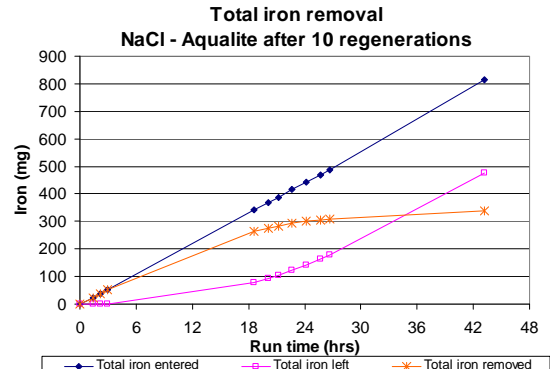
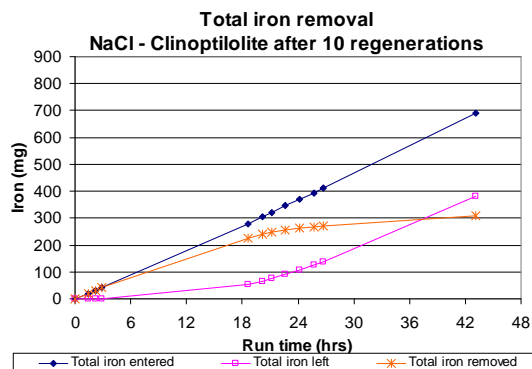


Figure 7-50: Iron removal by Clinoptilolite (left) and Aqualite (right) after 10 regenerations with NaCl

Table 7-17: Performance of the zeolites after ten regenerations

		0,1 M NaOH				1,8 M NaCl, pH 11,25			
		Clinoptilolite		Aqualite		Clinoptilolite		Aqualite	
		NH ₄ ⁺	Fe	NH ₄ ⁺	Fe	NH ₄ ⁺	Fe	NH ₄ ⁺	Fe
T = 5 hours	Total amount entered (mg)	93	90	-	-	72	69	85	81
	Total amount removed (mg)	54	84	-	-	36	63	47	78
	In mmol	3	1,5			2	1,1	2,6	1,4
	Effluent Concentration (mg/l)	1,8	<0,10	-	-	N/A	<0,10	N/A	<0,10
T = 20 hours	Total amount entered (mg)	425	390	-	-	330	303	400	366
	Total amount removed (mg)	262	321	-	-	197	237	278	275
	In mmol	14,6	5,8			10,9	4,3	15,4	5,0
	Effluent Concentration (mg/l)	2,2	2,1	-	-	1,8	2,8	1,4	3,1
T = 25 hours	Total amount entered (mg)	520	490	-	-	420	384	500	455
	Total amount removed (mg)	316	373	-	-	260	266	349	305
	In mmol	17,6	6,7			14,4	4,8	19,4	5,5
	Effluent Concentration (mg/l)	2,6	3,0	-	-	1,9	4,0	1,4	4,2
T = 43,2 hours	Total amount entered (mg)	885	836	-	-	728	689	860	813
	Total amount removed (mg)	479	479	-	-	443	308	592	337
	In mmol	26,6	8,6			24,6	5,6	32,9	6,1
	Effluent Concentration (mg/l)	3,48	4,76	-	-	2,52	5,52	2,24	5,54

Regeneration 11

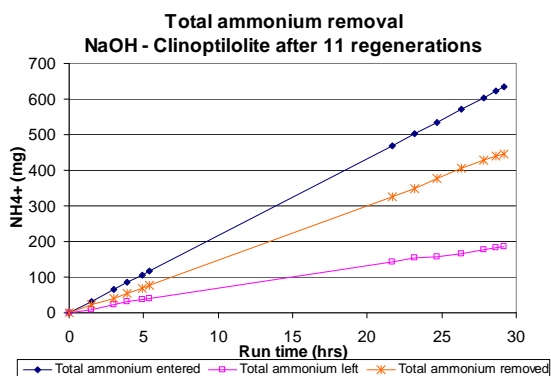


Figure 7-51: Ammonium removal by Clinoptilolite after 11 regenerations with NaOH

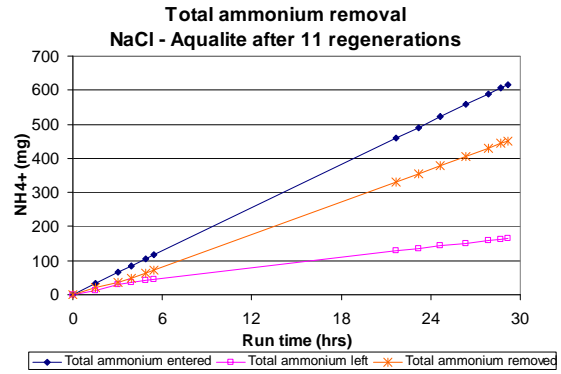
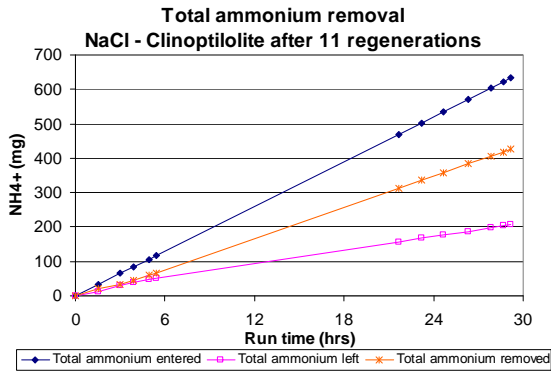


Figure 7-52: Ammonium removal by Clinoptilolite (left) and Aqualite (right) after 11 regenerations with NaCl

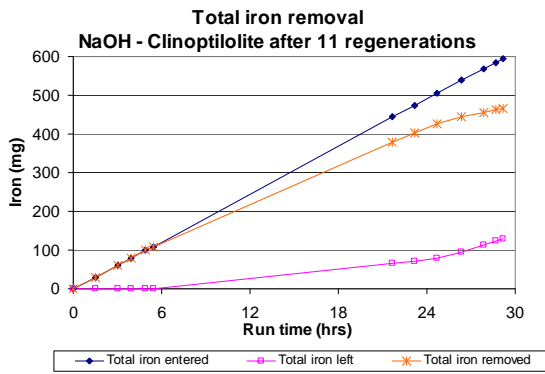


Figure 7-53: Iron removal by Clinoptilolite after 11 regenerations with NaOH

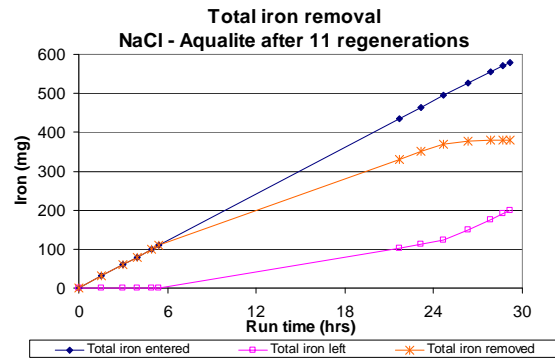
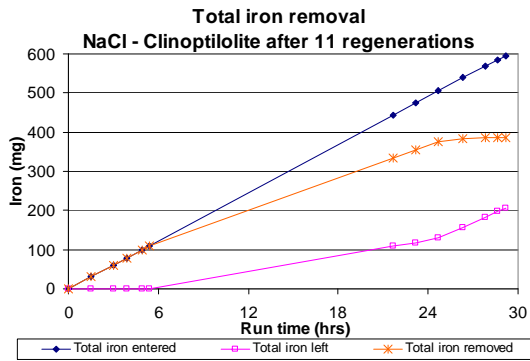


Figure 7-54: Iron removal by Clinoptilolite (left) and Aqualite (right) after 11 regenerations with NaCl

Table 7-18: Performance of the zeolites after eleven regenerations

		0,1 M NaOH				1,8 M NaCl, pH 11,25			
		Clinoptilolite		Aqualite		Clinoptilolite		Aqualite	
		NH₄⁺	Fe	NH₄⁺	Fe	NH₄⁺	Fe	NH₄⁺	Fe
T = 5 hours	Total amount entered (mg)	108	100	-	-	110	100	108	100
	Total amount removed (mg)	70	99	-	-	61	99	65	99
	In mmol	3,9	1,8			3,4	1,8	3,6	1,8
	Effluent Concentration (mg/l)	1,6	<0,10	-	-	2,0	<0,10	1,5	<0,10
T = 20 hours	Total amount entered (mg)	430	410	-	-	430	410	430	405
	Total amount removed (mg)	305	350	-	-	286	315	305	310
	In mmol	16,9	6,3			15,9	5,7	16,9	5,6
	Effluent Concentration (mg/l)	2,0	2,2	-	-	1,8	3,7	1,4	3,6
T = 25 hours	Total amount entered (mg)	540	510	-	-	540	510	530	500
	Total amount removed (mg)	385	430	-	-	365	378	390	372
	In mmol	21,4	7,8			20,3	6,8	21,7	6,7
	Effluent Concentration (mg/l)	2,0	2,9	-	-	1,8	4,4	1,4	4,4
T = 29,2 hours	Total amount entered (mg)	633	595	-	-	633	595	617	580
	Total amount removed (mg)	447	466	-	-	426	387	452	380
	In mmol	24,8	8,4			23,7	7,0	25,1	6,9
	Effluent Concentration (mg/l)	2,34	3,5	-	-	2,26	5,32	1,48	5,2

The graphs belonging to regeneration 10 (Figure 7-47 to Figure 7-51) and regeneration 11 (Figure 7-51 to Figure 7-54) Show the same results as the ones belonging to regeneration 8. After approximately 20 hours the removal of iron is starting to fail whereas the removal of ammonium is still going strong. There is no sign that the rate at which ammonium is removed changes when the iron removal is starting to weaken. This shows that iron and ammonium are not directly competing for the same adsorption sites in the zeolites.

Results analyses Regenerant by Vitens Laboratories

The removal and concentration values found during all cycles show that the regenerations are not completely successful. The removal values for ammonium slowly drop while the effluent concentrations slowly rise. This is also illustrated by the overview of ammonium concentrations per column shown in Figure 7-56 to Figure 7-58.

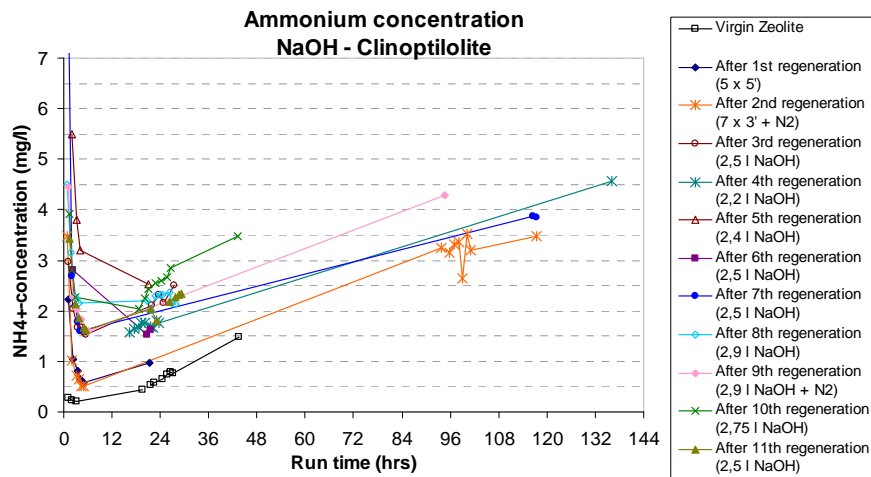


Figure 7-55: Progression of ammonium concentration in effluent of Clinoptilolite regenerated with NaOH

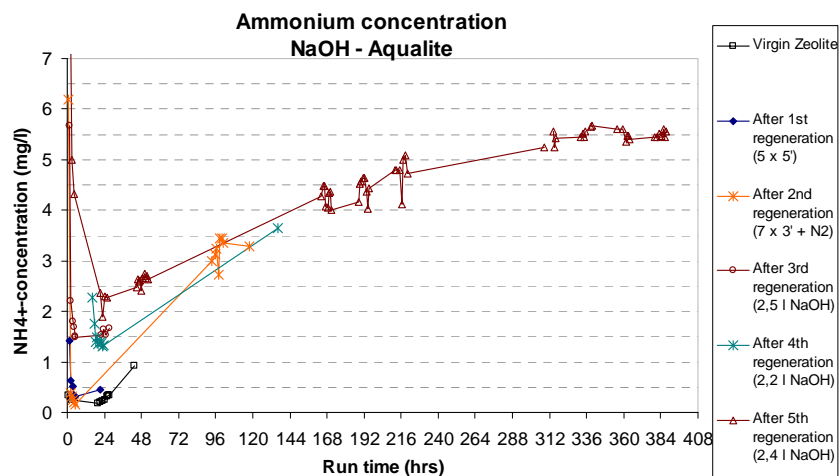


Figure 7-56: Progression of ammonium concentrations in effluent of Aqualite regenerated with NaOH

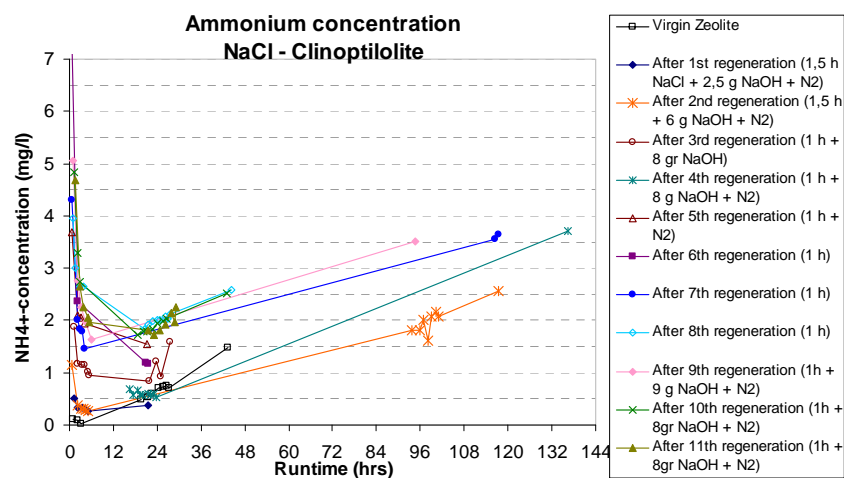


Figure 7-57: Progression in ammonium concentration in effluent of Clinoptilolite regenerated with NaCl

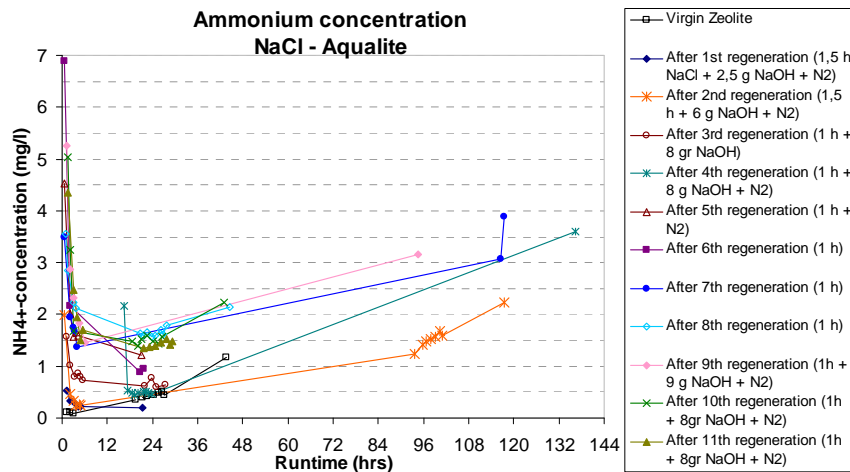


Figure 7-58: Progression in ammonium concentrations in effluent of Clinoptilolite (left) and Aqualite (right) after regeneration with NaCl

The first three cycles all show a pretty decent result. The concentrations after the first and the second regeneration are close to the ones found with the virgin zeolite. After that the concentrations are rising from approximately 0,5 mg/l to 1,5 mg/l as lowest concentration. For columns 1 and 2 this probably has to do with the change in regeneration type. First the columns were soaked in NaOH for a short period, then the column was emptied, nitrogen was blown in for a couple of minutes and the cycle was repeated for a number of times. After the second regeneration the NaOH the columns were slowly flushed, top-down, with NaOH. That did not have the same effect as the soaking, maybe because the zeolites were not immersed in regenerant as completely as they were when they were soaking.

The deterioration in regeneration with the NaCl has most likely to do with the build up of ions in the regenerant. After eight cycles 4 liters of new NaCl was added to the regenerant because all the samples taken from the tank lowered the level of regenerant in the tank significantly. Both graphs in Figure 7-58 show that the ninth regeneration had a better result in cleaning the zeolites than the eighth. The most likely explanation is the lowering of average concentrations of competing ions in the solution.

The evolution of the concentration of these ions is shown in Table 7-19.

Table 7-19: Concentration of ions found in NaCl solution between fourth and twelfth regeneration

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	after 4th reg (with N2)	After 5th reg with N2 (before adding 9,14 g NaOH)	After 6th regeneration - No N2	After 7th regeneration - No N2 (before adding 6g NaOH)	24 h after 8th reg - No N2 (before 4 l 1,8M NaCl, 8,02 g NaOH)	1h after 9th reg with N2	98 hours after 9th reg - No N2 (before adding NaOH)	before 10th reg with N2 (45 min after adding NaOH)	During 10th reg with N2 t15	During 10th reg with N2 t30	during 10th reg with N2 t60	45 hours after 10th reg - with N2	during 11th reg with N2 t15	During 11th reg with N2 t30	During 11th reg with N2 t60
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
NH4+	10,68	13,23	13,94	17,78	21,11	20,00	13,67	14,67	16,33	18,33	18,33	16,00	17,89	18,67	19,83
Fe	0,00	0,01	0,02	0,00	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Na	1472,17	1406,96	1414,78	1286,96	1217,39	982,61	915,65	967,83	993,91	991,30	970,43	977,39	958,70	980,00	957,83
Ca	21,15	30,44	38,20	41,50	47,00	43,50	38,25	39,75	42,75	43,50	45,00	44,00	45,50	47,25	49,00
K	16,57	17,54	17,41	15,75	15,40	12,23	11,51	12,05	12,74	12,58	12,12	12,30	12,34	12,58	12,28
Mg	0,58	1,72	2,92	3,33	4,03	3,46	2,96	3,13	2,98	3,00	2,94	2,27	2,22	2,36	2,25
Mn	0,000	0,002	0,007	<0,001	0,004	0,007	0,003	0,005	0,004	0,004	0,004	<0,006	<0,005	<0,005	<0,005
pH	10,10	9,40	10,00	9,30	10,50	10,80	10,00	11,00	10,20	10,10	10,50	11,00	10,20	10,20	11,00

Before the samples were taken, the tank was stirred in order to suspend the deposits on the bottom of the tank. A lot of the ion-compositions with a low solubility were attached to the tank wall though. Iron for example can only be present in Fe²⁺ as long as there are no oxidants present. The moment there is a very small amount of oxidant, such as oxygen, present it will be reduced to Fe³⁺. This ion is not soluble under basic conditions, because it quickly reacts with OH⁻ ions to the insoluble Fe(OH)₃ complex. This might explain why there is so little iron present in the tank. The same reasoning can be applied to manganese. Manganese easily reacts with the same OH⁻ ions and not much manganese is present in the raw water to begin with.

The other six parameters from Table 7-19 are plotted in graphs represented in Figure 7-59 to Figure 7-61.

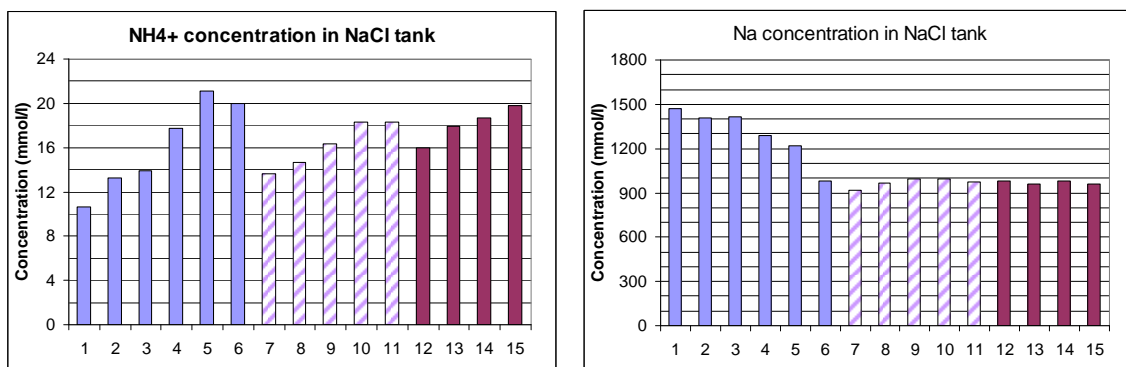


Figure 7-59: Ammonium and Sodium concentration in the NaCl tank during Experiment 2

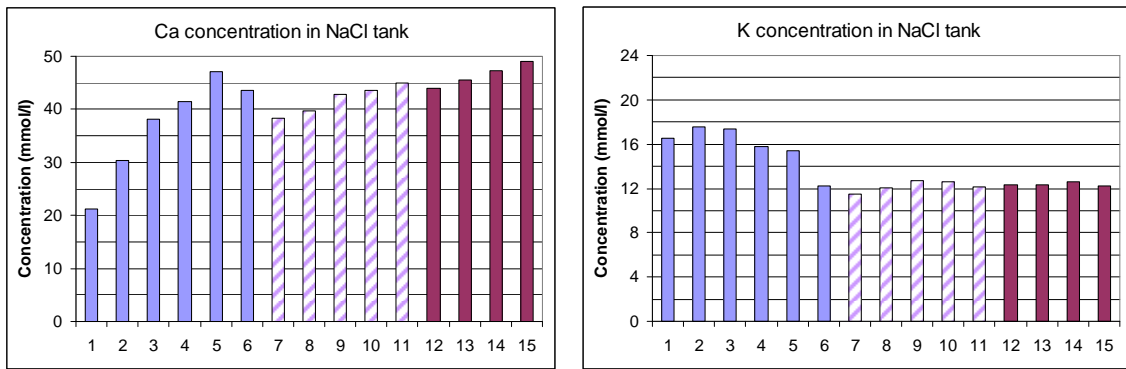


Figure 7-60: Calcium and Potassium concentration in the NaCl tank during Experiment 2

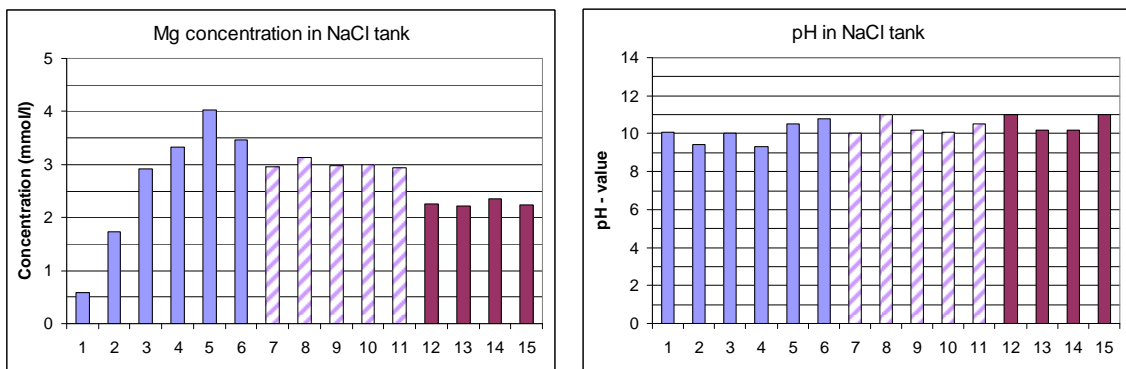


Figure 7-61: Magnesium concentration and pH in the NaCl tank during Experiment 2

The numbers below the bars refer to the description belonging to the same number in Table 7-19. The bars are separated into three groups. The group most left are values found in samples taken during the fifth to ninth regeneration. All samples taken before and during the tenth regeneration are striped. The values found in the samples taken during the eleventh regeneration are darker in colour.

The bar numbers 3, 4 and 5 belong to regeneration cycles where no nitrogen gas was added to the NaCl-solution in the tank. The sample belonging to number 7 was taken four days after the last regeneration. During that regeneration nitrogen gas was added, but a couple of hours afterwards it was switched off for 3 days until two and a half hours before taking the sample.

The sole purpose of adding nitrogen gas is to remove ammonium from the solution by forcing the ammonia gas out. Although this stripping is not easy, the plot in Figure 7-59 does show that the ammonium concentration stays lower when nitrogen gas is used than when no nitrogen is added. Columns 3, 4 and 5 show rising concentrations while columns 6 and 7 show that the concentrations are lower again. So even though the nitrogen gas was switched of for a period of time, it still managed to push out a significant amount of nitrogen gas. The main reason why the ammonium levels are rising from bar 7 to 11 and 12 to 15 again is that a lot of ammonium has been added during the regeneration cycle. The samples are taken during that period as well. Because ammonium

is not easy to strip, it will take a while before a significant amount has been removed. This is also shown by the drop in concentration between bar 11 and 12.

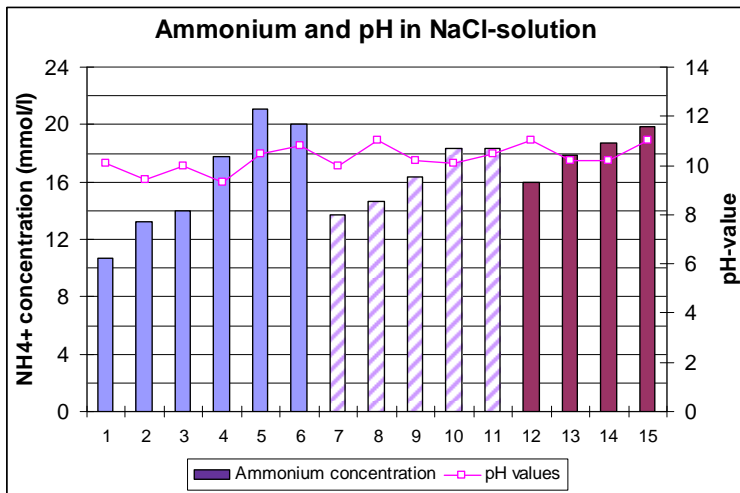


Figure 7-62: Ammonium concentration and pH in NaCl solution

The pH-value of course is strong factor in the stripping of ammonium as well. The plot in paragraph 2.4 already showed that at a pH of 9,25 50% of the ammonium present in a solution will actually be ammonia. At a higher pH the equilibrium will shift towards the ammonia side. More ammonia will be present than ammonium. To see whether the pH of the solution made a difference in the amount of ammonium present in the regenerant, ammonium concentrations and pH have been plotted in the same graph. This graph is shown in Figure 7-62. What can be seen is that usually when the pH drops, the ammonium concentration increases. The other way around this rule does not necessarily apply. In cases 2 -> 3, 4 -> 5, 7 -> 8 and 14 -> 15 the pH goes up, but the ammonium concentration in the tank as well. Therefore it can be concluded that in this pH range (9,3 – 11) the pH has less influence on the ammonium concentration than the nitrogen gas added.

Figure 7-58 showed that the lowest ammonium concentrations in the effluent of column 3 and 4 rose over the number of regenerations. The conclusion was that the regenerant was losing its effectiveness. When looking at Figure 7-59 to Figure 7-61 there are several possibilities to why that is the case. The initial sodium concentration was 1800 mmol/l. After four regenerations there is less than 1500 mmol/l left and during regeneration 10 and 11 the sodium concentration fluctuates around 1000 mmol/l. Other important facts are that the big competitors for binding spots on the zeolite potassium and calcium are abundantly present in the regenerant. Calcium concentrations are approximately twice as high as ammonium concentrations, potassium concentrations are a little lower than ammonium concentrations but in the same order of magnitude. This is not unexpected, because the MSDS provided by the distributor of Aqualite already showed that potassium is second in ion-exchange priority order. Only ammonium has a higher priority.

Effluent concentrations Column 3 and 4 during regeneration

During regeneration 10 and 11 samples were not only taken from the regenerant, the effluent of the columns has been monitored as well.

Table 7-20: Ion concentrations in the effluent of Column 3 and 4 during regeneration 10 and 11

	1-7	8	9	10	11	12	13	14	15
		before 10th reg with N2 (45 min after adding NaOH)	During 10th reg with N2 - t15	During 10th reg with N2 - t30	during 10th reg with N2 - t60	45 hours after 10th reg - with N2	during 11th reg with N2 t15	During 11th reg with N2 - t30	During 11th reg with N2 - t60
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
NH4+	N/A	11,33	18,33	20,00	16,67	2,64	19,06	19,44	19,83
Fe	N/A	0,15	0,01	0,01	0,06	0,20	0,01	0,01	0,02
Na	N/A	478,26	944,35	939,13	916,96	77,91	1016,52	970,87	1040,87
Ca	N/A	34,00	45,75	46,50	45,75	13,65	49,00	49,00	52,50
K	N/A	6,52	12,43	12,35	11,74	1,03	12,64	12,32	12,80
Mg	N/A	3,51	2,95	2,91	5,48	2,08	2,37	2,52	2,38
Mn	N/A	0,046	0,003	0,003	0,029	0,050	<0,005	<0,005	<0,005
pH	N/A	11,00	9,80	9,90	10,60	7,20	9,90	9,90	10,20

These values are shown in Table 7-20. The quality of the regenerant in the tank is a result of regenerating column 3 and 4 at the same time. The tank is a mix of the effluent of both columns. Therefore the samples taken from the effluent are taken as a mix of both columns as well. In order to keep the values comparable the lay-out of Table 7-20 is the same as the lay-out of Table 7-19 only the first seven columns are combined.

Noticeable is that the first regenerant exiting the columns is low on sodium and ammonium, but really high on iron. It also has a lower pH. The big differences in values found in the first effluent of regeneration 10 (column 8 in the table) and regeneration 11 (column 12 in the table) are probably due to the fact that the sample taken during the 10th regeneration was twice as big as the one taken during the 11th. As a result the effect of the first moments of regeneration is stronger in regeneration 11's sample.

Effluent regeneration column 1

What was done for column 3 and 4 during the last two regenerations has been done for column 1 since regeneration 5. The findings are presented in Table 7-21.

Table 7-21: Ion concentrations in effluent of column 1 during regeneration

	1	2	3	4	5	6	7	8	9	10
	5th reg 1st 250 ml	reg 6 1st 250 ml	reg 6 last 250 ml	Regenera tion 8 (mix)	Regenera tion 9 (mix)	reg 10 1st 300ml	Reg 10, after 1 l	Reg 10, last 300 ml	Reg 11, 1st 120 ml	Reg 11, after 1 l
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
NH₄⁺	0,37	26,45	33,83	8,33	7,78	0,37	12,00	9,33	1,24	12,06
Fe	0,01	0,00	0,00	0,00	0,01	0,07	0,01	0,01	0,02	0,01
Na	3,04	13,54	47,37	18,39	43,30	2,37	35,87	52,96	2,69	37,13
Ca	1,05	0,43	0,20	0,33	0,30	1,50	0,15	0,08	0,53	0,18
K	0,12	0,24	0,59	0,25	0,51	<0,15	0,40	0,51	<0,36	0,45
Mg	0,23	0,12	0,01	0,06	0,03	0,29	<0,02	<0,02	0,08	<0,06
Mn	0,004	0,001	0,000	<0,001	<0,001	0,007	<0,002	<0,002	<0,05	<0,05
pH	7,30	12,00	12,00	12,00	13,00	-	12,30	12,90	9,70	12,70

The loss of sodium in the first moments of regeneration is very noticeable again, but also the immense drop in pH. The NaOH solution started with a pH of 13 and a sodium concentration of 100 mmol/l. Approximately 97% of the sodium in the first 250 ml of regenerant is consumed by the zeolites. At the end of the regeneration this is around 50%.

Delft University of Technology

Faculty of Civil Engineering and Geoscience

Department of Water Management

Section of Sanitary Engineering

Stevinweg 1

2628 CN Delft

www.drinkwater.tudelft.nl