Investigation of Resin Regeneration in the Suspended Ion Exchange (SIX®) System

Jihyon Im
University of New Hampshire, Durham

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Investigation of Resin Regeneration in the Suspended Ion Exchange (SIX®) System

Abstract
This research investigated 1) evaluation and optimization of the SIX® anion exchange regeneration efficiency and 2) compatibility of cation exchange for hardness removal and shared-regeneration with the current anion exchange regenerant. The first objective was addressed by comparing the effects of three variables on desorption efficiencies: regenerant volume, salt concentration, and contact time. Sorption studies were performed to quantify resin blinding, and removal kinetics were established and compared. The second part of this research tested a strong acid cation resin for softening performance and regenerability with sodium chloride regenerant.

Inefficient DOC and nitrate desorption were observed as larger regenerant volume and higher salt concentration were required than sulfate and bicarbonate desorption. This indicated organic and nitrate accumulation on the resin, so the follow-up adsorption kinetics study compared its effects on target removal performance. The study also investigated desorption equilibrium, equivalent balance, and sorption kinetics observed during regeneration. Finally, the tested cation exchange resin achieved the desired hardness removal but was incompatible for sodium chloride regeneration, highlighting the complexity of resin selection for shared-regeneration. This report includes a comprehensive overview of the background, techniques, results and conclusions related to this investigation of resin regeneration.

Keywords
Drinking Water, Ion Exchange, Natural Organic Matter, Regeneration, Softening, Treatment, Environmental engineering, Civil engineering
INVESTIGATION OF RESIN REGENERATION IN THE SUSPENDED ION EXCHANGE (SIX®) SYSTEM

By

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Bachelor of Science in Environmental Engineering, University of New Hampshire, 2013

THESIS

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In
Civil Engineering

September, 2015
This thesis has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering by:

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Dr. M. Robin Collins, P.E., Professor of Civil and Environmental Engineering

On 12 June, 2015

Original approval signatures are on file with the University of New Hampshire Graduate School.
DEDICATION

I would like to dedicate this thesis to the following people for many special reasons.

**First of all, my family.** Everything I know about work ethic, responsibility, motivation, and kindness came from my parents, Kum Lee Farr and Ronald Farr. I will always be grateful for their unconditional support for my decisions in pursuing an engineering career and a Master’s degree and also their patience and trust throughout the past years that sometimes involved solo travel in foreign countries, missed flights, and turning strangers into friends.

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ABSTRACT

INVESTIGATION OF ANIONIC AND CATIONIC RESIN REGENERATION IN THE SUSPENDED ION EXCHANGE® (SIX®) SYSTEM

by

Jihyon Im

University of New Hampshire, September 2015

This research investigated 1) evaluation and optimization of the SIX® anion exchange regeneration efficiency and 2) compatibility of cation exchange for hardness removal and shared-regeneration with the current anion exchange regenerant. The first objective was addressed by comparing the effects of three variables on desorption efficiencies: regenerant volume, salt concentration, and contact time. Sorption studies were performed to quantify resin blinding, and removal kinetics were established and compared. The second part of this research tested a strong acid cation resin for softening performance and regenerability with sodium chloride regenerant.

Inefficient DOC and nitrate desorption were observed as larger regenerant volume and higher salt concentration were required than sulfate and bicarbonate desorption. This indicated organic and nitrate accumulation on the resin, so the follow-up adsorption kinetics study compared its effects on target removal performance. The study also investigated desorption equilibrium, equivalent balance, and sorption kinetics observed during regeneration. Finally, the tested cation exchange resin achieved the desired hardness removal but was incompatible for sodium chloride regeneration, highlighting the complexity of resin selection for shared-regeneration. This report includes a comprehensive overview of the background, techniques, results and conclusions related to this investigation of resin regeneration.
CHAPTER 1

1 Introduction

1.1 PWN Water Supply Company North Holland and PWN Technologies

Provincial Waterworks of North Holland (PWN) was established in 1920 to supply drinking water to the province of North Holland through groundwater extraction from the dunes region. This groundwater source originally met the drinking water needs, and adequate treatment was not complex. However, the increasing demand over the years put pressure on the dune’s groundwater supply. This led to the construction of the Andijk water treatment plant (WTP) in 1968 to utilize a surface water source, the Ijssel Lake that is fed by the River Rhine,

The focus of this research is on Andijk WTP under the ownership of PWN and its pilot facility operated by PWN Technologies. PWN Technologies was founded as a subsidiary of PWN and a drinking water research company to make the utility’s innovations in water treatment available to other water companies. The revenues are invested in the research and development programs to further develop advanced and sustainable solutions in water treatment.

Since its opening in 1968, Andijk WTP has gone through multiple upgrades, as summarized by Figure 1. The original treatment scheme included microstraining, breakpoint chlorination, coagulation, sedimentation, rapid sand filtration (RSF), and post chlorination prior to distribution. This system was upgraded ten years later in 1978 by implementing a pseudo moving bed granular activated carbon (GAC) filtration step after RSF. GAC filtration mitigated taste and order problems and prevented the passage of disinfection by-products from the breakpoint chlorination. This treatment series remained unchanged until 2004 when PWN installed
the first full-scale advanced oxidation process (AOP) with ultraviolet and hydrogen peroxide (UV/H\textsubscript{2}O\textsubscript{2}). This step acts as a barrier against organic and pathogenic micro pollutants found in the Ijssel Lake, and the high UV dose provided advanced disinfection that eliminated the need for breakpoint chlorination. Since the AOP implementation after RSF, the GAC filters are used to remove the residual H\textsubscript{2}O\textsubscript{2}, any residual toxicity from organic compounds and assimilable organic carbon (AOC).

![Figure 1, Andijk WTP treatment process upgrades from 1968 to 2014](image)

The most recent major upgrade project, Andijk III, became operational in May 2014 with the first full-scale application of Suspended Ion eXchange (SIX\textsuperscript{®}) and Ceramic Filtration (CeraMax\textsuperscript{®}). SIX\textsuperscript{®} replaces coagulation and sedimentation and achieves removal of not only dissolved organic carbon (DOC) but also nitrate and sulfate. The ceramic microfiltration step,
which replaces RSF, removes suspended particles and colloidal matters and allows for vigorous cleaning regimes and high backwashing pressures. With these new processes, Andijk III is designed to have a capacity of 120,000 m$^3$ or 32 million gallons per day, produce a higher quality of water than conventional treatment, and increase the overall treatment efficiency and also the AOP specifically. This research is focused on the SIX® process, which is further discussed in detail in the next section.

1.2 Suspended Ion eXchange (SIX®)

1.2.1 Treatment

Ion exchange is a reversible process that removes contaminants in drinking water through ionic sorption on a resin made of synthetic polymers. The undesirable ionic constituents in the feed water are replaced by the inert ions attached to the ion exchange resin. In the SIX® process, the main constituent of removal is natural organic matter (NOM), specifically the dissolved organic carbon (DOC) fraction. Overall, SIX® achieves the goal of increasing the efficiencies of the later treatment processes. DOC removal by SIX® improves the AOP process efficiency by increasing UV-Transmittance (UVT) and lessening the AOC production and reduces fouling potential for the ceramic membrane. Nitrate is another parameter that affects the efficiency of the AOP operation as it leads to nitrite formation and interferes with the degradation of pollutants at high concentrations (Martijn, et al. 2009).

Since NOM found in the Ijssel Lake, or the feed water matrix, is negatively charged, SIX® utilizes anion exchange resin to remove not only NOM, but also other anionic constituents such as nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$), bicarbonate (HCO$_3^-$), phosphate (PO$_4^{3-}$), etc. The SIX® pilot uses the Lewatit VPOC 1071 (VPOC) anion exchange resin, which was selected by a
previous investigation for its favorable target constituent removal, regenerability, and flexibility as a non-proprietary resin. VPOC exchanges the inert chloride ions (Cl\(^-\)) for the anions present in the water, and the chloride ions are adsorbed to the resin surface as a result.

Traditional ion exchange systems comprise of fixed-bed units, which are inefficient at treating surface water, due to resin blinding, or fouling, from the organics and colloidal mater. Resin blinding can lead to slower removal kinetics and clogging of the pores on the resin. Therefore, to prevent the resin blinding, SIX\(^\circledast\) utilizes a cyclic design in which the resins are kept in suspension. In addition, all the resins are regenerated after each pass through the system prior to additional use, which helps reducing the biofilm formation and limiting the amount of remaining (non) target anions on the resin surface. The SIX\(^\circledast\) pilot system, shown in Figure 2, was utilized in this research as the source of the used resin (also referred as “spent” resin) and regenerated resin (also referred as “fresh” resin).

![Figure 2, SIX\(^\circledast\) pilot system](image-url)
Figure 3 illustrates the flow diagram of the SIX® pilot system with the hydraulic range from 25 m³/hour to 50 m³/hour. The pilot system includes two resin contact reactors, one Lamella separator, two regeneration vessels, and two fresh resin holding tanks. The feed water enters the pilot system, and resin is dosed from the fresh resin tanks to reach a concentration between 4-20 mL resin/L depending on the raw water quality. The mixture of the feed water and the resin travels through a series of two cylindrical completely stirred tank reactors that act as a plug flow reactor. These reactors consist of overhead paddle mixers that agitate the water to allow for thorough distribution of the resin and adequate contact time. After the contact reactors, the resin is separated out by a Lamella separator where all of the used resin is settled in a basin and sent through a regeneration process. The resin is regenerated with a concentrated sodium chloride (NaCl) salt solution at a concentration of ~30 g-Cl⁻/L in the regeneration vessels. The regenerated or fresh resin that has been returned to the chloride form is stored in the fresh resin tanks until it is injected to the feed water again.

![Figure 3, SIX® pilot flow schematic](image)

Figure 4 shows the historical SIX® pilot data on DOC and nitrate removal from 12/5/2012 to 3/12/2014. The graphs include the SIX® influent and effluent concentrations and
the corresponding percent removal values. These data show that seasonal fluctuations affect the influent nitrate concentrations and consequently nitrate removal. The effluent nitrate concentration ranges between 1 and 6 mg/L after treatment, increasing from October to late March and decreasing through spring and summer. On the other hand, the DOC removal performs more consistently throughout the year with the effluent concentration ranging between 2 and 4 mg/L.

![Figure 4, 2012-2014 Historic SIX® pilot nitrate (top) and DOC (bottom) removal data](image)

It is important to note that the SIX® pilot has achieved more or less the same magnitude of DOC removal steadily throughout the years since 2010 when the pilot monitoring first had started. However, nitrate removal performance has been slightly deteriorated. The pilot data
from 2010 to 2012 in Figure 5 show that the effluent nitrate concentration after SIX® treatment used to range between 0.5 and 4 mg/L.

Figure 5, 2010-2012 Historic SIX® pilot nitrate (top) and DOC (bottom) removal data

1.2.2 Regeneration

The spent resin is regenerated with sodium chloride salt solution at concentrations of ~30 g-Cl/L. The goal of SIX® regeneration is to desorb the anions that were removed in the SIX® reactors and adsorbed onto the resin, such as DOC, nitrate, sulfate, and bicarbonate. Highly concentrated salt solutions allow the exchange of the binding sites between chloride ions in the salt solution and the adsorbed anions while sodium ions remain unaffected in the solution. However, because SIX® is a single pass process where 100% of the resin is settled and regenerated before additional use, the resin is not completely spent prior to regeneration.
Therefore, desorption can occur to a greater extent, requiring lower salt concentrations in the regenerant solution.

A counter current method is utilized in the SIX® pilot regeneration, and this involves recycling regenerant salt solutions up to five times. The spent resin is first introduced to the most heavily used regenerant salt solution (five times used) and subsequently washed with the less used and newer regenerant each time (four times used → three times used → two times used → once used). The resin is finished with the cleanest, “virgin” regenerant solution. After each regeneration cycle, the batches of the used regenerant solution are recycled and stored in separate tanks until the next regeneration cycle. Figure 6 shows the five regenerant storage tanks, which are also indicated in the regeneration flow schematic in Figure 7. The typical system operations aim for the resin to be fully regenerated before it is dosed back into the feed.
The spent regenerant exiting the regeneration vessels goes through a train of extensive treatment steps with the goals of reducing waste water volumes and creating opportunities for salt recovery and reuse. The spent regenerant treatment begins with a biological denitrification process to reduce the levels of nitrate that have been rinsed off the resin during regeneration. In spite of high salinity and low brine temperature in winter nitrate levels exceeding 300 mg NO$_3^-$/L can be reduced for more than 98% with this treatment process (Koreman and Hogeboezem, *Biological Denitrification of High Saline Ion Exchange Regenerant* 2011). Mainly responsible for this removal is the microorganisms called Pseudomonas stutzeri. Biological denitrification is followed by nanofiltration that separates DOC and larger ions, such as sulfate, phosphate, and other multivalent ions, from the sodium and chloride that pass through the membranes. The nanofiltration concentrate is then sent to dynamic vapor recompression (DVR) for further salt recovery while the permeate is recycled for regeneration. The treatment processes are summarized in Figure 8. After both nanofiltration and DVR steps, a concentrate or brine remains. Treatment and recovery of spent regenerant and disposal of this brine are ongoing research objectives of PWN Technologies. The current brine disposal method employed by the
full-scale WTP includes deep well injection for the first few years of operation until a more sustainable alternative is fully developed.

![Flow diagram of regenerant fluid treatment](image)

*Figure 8. Flow diagram of regenerant fluid treatment (Vaudevire, et al. 2012)*

1.2.3 **Salt Use**

Production of salt used for SIX® resin regeneration is one of the dominant contributors to the energy demand in the pretreatment system (Bogosh, et al. 2010). Therefore, minimizing salt usage during regeneration and also volume of brine waste is important for economic and environmental benefits. Over the course of years, regeneration research and the resulting process optimization, such as recycling spent regenerant solutions, have achieved significant reduction in salt use as shown by the SIX® pilot data in Figure 9. However, the fate of the chloride ion during the entire SIX® process, including treatment and regeneration, must be better understood for minimizing the overall chloride demand of the system.
Chloride use and selectivity of the current resin during the removal of anions have been studied previously, and the results indicated that adsorption of non-target anions (i.e. sulfate and bicarbonate) can have a significant impact in the chloride requirements for regeneration (Roakes 2013). Figure 10 shows the percentage of desorbed chloride ions attributed to each anion that was removed at a resin dose of 16 g/L and contact time of 30 minutes. Only 20% of the available chloride ions are utilized to remove the target constituents (i.e. DOC and nitrate) while 80% was used in non-target ion adsorption. For optimization of the regeneration process, the current resin’s chloride efficiency on desorption also should be investigated to fully understand the fate of the chloride ion.
1.3 Softening

1.3.1 Current Practice - Chemical Softening

Prior to entering the treatment facility, the raw water is softened with caustic soda (NaOH) to remove hardness comprised of calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)). The presence of hardness is related to aesthetic issues of water and causes scale in pipes and hot-water heaters, high soap consumption, and the deterioration of fabrics (Crittenden, et al. 2005). Hardness is typically achieved in water treatment by chemical precipitation, ion exchange or membrane process.

At Andijk WTP, chemical softening is applied by dosing 0.4 kg-NaOH/m\(^3\)-water when the raw water enters the reservoir, as shown by Figure 11. This causes the formation of calcium and magnesium sludge that settles out to the bottom, and the water is then recarbonated with compressed carbon dioxide, which is injected in the inlet channel to the treatment plant.

*Figure 11, Current softening process diagram*

As a result of softening, about 1 mmol/L of total hardness is removed, achieving 40% reduction, and calcium is removed more preferably than magnesium. More information on the
current performance of the chemical softening practice is presented in Table 1. The hardness levels are fairly stable in the influent water throughout the year and observed up to \(~2.5\) mmol/L in the reservoir, so a high volume of NaOH is required to soften the water to the desired level of \(~1.5\) mmol/L.

### Table 1, Hardness removal by current softening process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>IJssel Lake</th>
<th>Post-Softening</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hardness (as CaCO(_3))</td>
<td>(~2.5) mmol/L</td>
<td>(~1.5) mmol/L (40% reduction)</td>
</tr>
<tr>
<td></td>
<td>250 mg/L</td>
<td>150 mg/L</td>
</tr>
<tr>
<td>Hardness Speciation</td>
<td>Ca(^{2+}): 80% Mg(^{2+}): 20%</td>
<td>Ca(^{2+}): 65% Mg(^{2+}): 35%</td>
</tr>
</tbody>
</table>

It should be noted that production of caustic soda is energy intensive, and thus, the large quantity required for softening accounts for high energy demand. The current chemical softening practice is the second highest in energy consumption when compared to the rest of the treatment processes (Bogosh, et al. 2010). If an alternative treatment process to chemical softening is pursued, similar removal performance achieved by the current practice would be necessary.

1.3.2 **Cation Exchange**

The largest application of ion exchange to drinking water treatment is in the area of softening as cation exchange has a long history of use for effective removal of calcium, magnesium, and other polyvalent cations in exchange for sodium. The main features of cation exchange resin are high chemical and physical stability, high exchange capacity, rapid exchange kinetics, a high degree of reversibility, and long life (Clifford, Sorg and Ghurye 2011).

Since ion exchange can be used for removing not only DOC, but also hardness, and Andijk WTP needs to accomplish reductions of both, the combination of anion exchange resin
and cation exchange resin may be considered for removals of both DOC and hardness. There is limited research on the effects of combined ion exchange, but recent studies showed that high removals of DOC and hardness were achieved in groundwater and nanofiltration (NF) membrane concentrates using the ion exchange combination in completely mixed tanks (Comstock and Boyer 2014). The main benefit of combined ion exchange in Andijk would be the efficient use of the current salt regenerant because cation exchange would utilize the sodium ions that are unaffected in the anion exchange process. This would also reduce the amount of treatment needed for the brine waste, due to the decreased sodium content. Other potential benefits include minimizing chemical requirements such as caustic soda; reducing the need for reservoir dredging and sludge removal due to the calcium and magnesium solids buildup; minimizing footprint if simultaneous removals are possible in the same vessels; and generating only one waste stream from removing multiple contaminants in a single process.
CHAPTER 2

2 Research Description

2.1 Challenges

2.1.1 Anion Exchange

The two challenges associated with the current anion exchange treatment are evaluation of the current resin regeneration efficiency and investigation of optimizing the regeneration process regarding salt use and contact time.

The goal of the SIX® regeneration process is to desorb the anion constituents removed from the influent water off of the resin exchange sites and return the resin to the chloride form so it can be reused and provide consistent DOC and nitrate removal. Ensuring the stability of the SIX® resin performance involves minimizing resin blinding from organic or inorganic matter coating the resin surface. Resin blinding can cause slower removal kinetics and is an indicator of incomplete desorption during regeneration. Therefore, the challenge presented is to evaluate the current efficiency of the SIX® pilot regeneration by investigating the extent of the blinding on the resin and its effects on the resin’s removal performance of the target constituents.

A comprehensive investigation of the regeneration process should clarify the sorption relationship between salt and the anionic constituents to be exchanged off the resin surface by the salt. There is limited knowledge on the extent of desorption that occurs for each anion. Furthermore, the effects of key process parameters such as salt concentration and contact time on desorption are not fully understood. This information can elucidate salt use efficiency during desorption and optimization of operational conditions and thus the overall process.
2.1.2 Cation Exchange

The sustainability issues with the current softening practice and the experience with the anion exchange technology have presented the opportunity of using cation exchange as a means of removing hardness. The challenges associated with cation exchange as an alternative are the resin’s target constituent removal and compatibility with the sodium chloride solution used for SIX\textsuperscript{®} regeneration. The resin performance must be comparable to the current level of total hardness reduction achieved by chemical softening. In addition, it is crucial that the resin is regenerable with the SIX\textsuperscript{®} regenerant solution to utilize sodium as the counter anion. Two cation exchange resins have been evaluated for hardness removal by a previous research, Lewatit MDS 1368 and Lewatit MonoPlus S 1567 (Roakes 2013). They showed desirable performance by achieving the required removal, but more evaluation is needed in resin regenerability.

2.2 Objectives

The overall goal of this research is to evaluate the ion exchange regeneration process in the SIX\textsuperscript{®} system to achieve process optimization in both anion exchange pretreatment and possible cation exchange softening. Both phenomena of adsorption and desorption during regeneration will be investigated in depth to address the above-mentioned challenges. The following objectives specify the information to be provided by this research on the efficiency of anion exchange resin regeneration and the compatibility of cation exchange as a softening alternative.

The first objective is to assess the regeneration efficiency of the SIX\textsuperscript{®} pilot. The extent of resin blinding will be characterized and quantified through bench-scale column tests. Maximum desorption off the spent resin will be achieved through a series of multiple regeneration cycles,
and the water matrix of the resulting spent regenerant will be studied. This would be followed by a series of jar tests to determine the effects of the resin blinding on target constituent removal by obtaining removal kinetics for NOM/DOC and nitrate.

The second objective is to define the relationship between regeneration process parameters (i.e. salt concentration and contact time) and magnitude and rate of sorption. Both jar tests and column tests are performed to monitor desorption behaviors of DOC, nitrate, sulfate, and bicarbonate and adsorption of chloride using a wide range of salt concentrations. This would provide information on the chloride demand of the current resin and the exchange rate between chloride and the anionic constituents through analyzing the desorption kinetics.

The third objective is to evaluate the performance of Lewatit 1131S cation exchange resin (1131S) in both adsorption and desorption. 1131S was chosen for this investigation due to its promising ease of regeneration. The resin’s removal capabilities of calcium and magnesium and its regenerability with sodium chloride regenerant will be analyzed. The results will be used for comparing 1131S to the previously tested cation resins for a softening alternative.
CHAPTER 3

3 Literature Review

3.1 Ion Exchange

Ion exchange, a process in which ions attached to a stationary functional group exchange for ions in a solution, is considered as a nonconventional process since it is not widely used in large-scale plants. In water treatment, ion exchange removes dissolved ionic constituents that can cause aesthetic and health issues and primarily used for water softening and demineralization (e.g. removal of Ca$^{2+}$, Mg$^{2+}$, Na$^{+}$, Cl$^{-}$, SO$_{4}^{2-}$, NO$_{3}^{-}$) (Crittenden, et al. 2005). The ion adsorption and desorption phenomena are complex but can be conceptualized by theories of thermodynamics, reaction kinetics, ionic chemistry, and fluid mechanics (Wachinski 2005).

Ion exchange involves the insoluble solid phase or ion exchanger that can be made of natural origin such as kaolinite and montmorillonite minerals or a synthetic material such as polymeric resin. The use of ion exchange and inorganic adsorbents for full-scale applications has increased in water treatment with much attention placed on conventional synthetic ion exchange resins (Asano, et al. 2007). Two basic components of an ion exchange resin are a cross-linked polymer matrix and charged functional groups. The usual matrix is polystyrene cross-linked for structural stability with 3 to 8 percent divinylbenzene, and Figure 12 shows a schematic of an organic cation-exchanger bead comprising the two components. It should be noted that the open spaces in the structure illustrated by the schematic are much tighter in an actual resin bead.
The exchanger resins have charged functional groups attached to this matrix by covalent bonding. The four categories of common functional categories are strongly acidic (e.g. sulfonate, $-\text{SO}_3^-$); weakly acidic (e.g. carboxylate, $-\text{COO}^-$); strongly basic (e.g. quaternary amine, $-\text{N}^+(\text{CH}_3)_3$); and weakly basic (e.g. tertiary amine $-\text{N}((\text{CH}_3)_2$). Figure 12 shows chemical structures of a strongly acid cation exchanger with a sulfonate group on the left and a strongly basic anion exchanger with a quaternary amine functional group on the right. The type of the functional group on the exchanger dictates the charge of the bonding sites and thus the charge of the counter ion.
These functional groups are fixed on the resin’s external and/or internal surface and associated with counter ions that have an opposite charge to the functional groups. The counter ion is a cation for a negative functional group and an anion for a positive functional group. Chloride (Cl\(^-\)) and sodium (Na\(^+\)) are used most commonly as counter ions in anion exchange and cation exchange, respectively, because they readily exchange with contaminant ions (Maul, et al. 2014). These mobile counter ions are attached to each of the charged functional group by electrostatic attraction to remain electroneutrality at all times not only within the exchange material, but also in the aqueous solution. This electroneutrality can be maintained because ions are exchanged on an equivalence basis, so they do not degrade or change form during the resin usage (Wachinski 2005). The cation and anion exchange processes between solution and resin are described by Equation 1 and Equation 2.

\[
\begin{align}
    n[R^-]Na^+ + M^{n+} & \leftrightarrow [nR^-]M^{n+} + Na^+ \quad \text{Equation 1} \\
    n[R^+]Cl^- + M^{n-} & \leftrightarrow [nR^+]M^{n-} + Cl^- \quad \text{Equation 2}
\end{align}
\]

The overbar refers to the immobile resin phase, R represents the functional group, Na\(^+\) and Cl\(^-\) are the presaturant ions associated with the resin before exchange, M\(^{n+}\) is the counter ion.
in solution being exchanged out of solution, and \( n \) is the charge on the counter ion in solution. These equations assume an ideal ion exchange condition where ions are adsorbed by their full valence.

### 3.2 Regeneration

As shown by Equation 1 and Equation 2, ion exchange comprises a reversible process between a resin and a liquid. The reaction towards the right is favorable during resin usage and contaminant removal, but this direction reverses during regeneration that forces it towards the left with a highly concentrated regenerant. High concentrations of the mobile counter ions are necessary in the regenerant, due to the resin’s low affinity for them. Consequently, the resin discharges contaminant ions in exchange for more highly concentrated mobile counter ions in the regenerant (Wachinski 2005). This process restores the initial ionic form of the resin, so it can be reused and continue with the removal process.

Depending on the specific resin and its characteristics, resins are regenerated with salts, acids, or basis. As a result of chloride and sodium being the most common counter ions in ion exchange, highly concentrated sodium chloride (NaCl) salt solution is required for regeneration. Regeneration of exhausted ion exchange resin with sodium chloride is well-documented and used widely in full-scale practice, due to the high solubility, low human toxicity, and low cost of sodium chloride (Rokicki and Boyer 2011).

Also, studies have demonstrated the benefits of sodium chloride as a regenerant agent, compared to alternative regenerant chemicals. Sodium chloride has shown to require a lower amount of equivalents than hydrochloric acid (HCl) to achieve the same level of regeneration (Valverde, et al. 2006). In regenerating anion exchange resin exhausted with nitrate and cation
exchange resin exhausted with calcium, sodium chloride had an equivalent efficiency compared
to potassium and bicarbonate salts, but it demonstrated the lowest environmental burden and

However, the disposal of waste streams with high concentrations of sodium chloride
poses significant disadvantages since it can increase the salinity in the natural and engineered
systems. Disposal methods employed by some softening plants include discharge into sanitary
sewer or directly into ocean, evaporation ponds, and brine disposal wells (Wachinski 2005). The
associated impacts include inhibition of biological processes in a wastewater treatment plant,
adverse impacts on the receiving waters and their aquatic organisms and ecosystems, and
damages to soil structure and plant growth in case of land application (Maul, et al. 2014).
Greater effort should be placed on treatment, reduction and reuse of the sodium chloride content
of waste regenerant to maximize the benefits of upstream and operational phases of regeneration.
Volume minimization of the effluent regenerant waste is especially important due to its polluting
capabilities.

Effective resin regeneration is vital in ensuring optimal performance of the ion exchange
process, but the study of the regeneration is empirical and dependent on the resin type and the
ions to be considered (Valverde, et al. 2006). In addition, regeneration of ion exchange resins
used to remove NOM can be problematic because of the strong attraction that the aromatic
portion of the anions possesses for the aromatic resin matrix (American Water Works
Association 1999). However, this problem is partially solved using acrylic-matrix strong base
anion resins, such as those found in SIX®.

The factors dominating the operational impacts in the SIX® system are salt demand and
regenerant disposal (Bogosh, et al. 2010). Thus, reducing salt use and subsequent treatment and
discharge of the regenerant waste are the key areas for optimization in the ion exchange process. These areas can be improved by either implementing brine reclaim operations or reducing the quantity of salt application during regeneration. However, the tradeoffs are that they both can result in decreased treatment capacity through loss of bed volumes treated per cycle and increased leakage (Flodman and Dvorak 2012).

The efficiency of regeneration is evaluated in terms of meeting the process objective, which is the restoration of the exchange capacity of the resin. Resins with lower cross-linkage are typically easier to regenerate while strongly acidic cation and strongly basic anion exchange resins are more difficult to regenerate because they require more regenerant than the stoichiometric quality (Wachinski 2005). The regeneration process can be optimized by analyzing concentration profiles of the different ions substances in the regenerant stream. For an accurate optimized design of the ion exchange process, the ability to predict the regeneration effluent concentration history is crucial. This requires knowledge of not only the basic equilibrium parameters, but also the kinetic parameters of the charged resin with respect to the regenerant. The concentration profiles are graphical representations produced by analyzing samples taken at various time intervals during regeneration and plotting the results as a function of time to determine trends. They can be a useful tool in providing information on regeneration time, rinsing stage, and resin condition (Strydom and Schutte 2003).

Specific related parameters to monitor for improving the regeneration process include the desorption rate of the ionic constituents, the number of regenerant bed volumes required to restore the resin’s removal capacity, and its related contact time. These parameters are translated to important aspects of the ion exchange operation. Desorption rate of the ionic constituents is related to the efficiency of the regeneration process while the number of regenerant bed volumes
needed is a function of the operational cost that includes the required chemicals (Chowdiah and Foutch 1995).

For example, Figure 14 from a study with resin charged with copper demonstrates the number of bed volumes of regenerant solution required to meet desired regeneration efficiency. It also shows that higher external sodium chloride concentration in the regenerant solution increases percent regeneration due to the electroselectivity effect, but this effect reduces at high concentrations, indicating excessive salt use is not needed at concentrations higher than 6 wt% (Valverde, et al. 2006). Additionally, when evaluating the operational aspects of the ion exchange process, not only the direct use of the regenerant chemicals, but also the need for high purity water required for rinsing the resin after regeneration should be considered (Gordon 2011).

![Figure 14](image)

*Figure 14, Influence of the NaCl concentration in regenerant on the level of fixed-bed regeneration; Amberlite IR-120 in Cu form, F=5.7 BV/h; T=298K (Valverde, et al. 2006)*

### 3.3 Kinetics

The reaction rate is a vital element for a sorption process as it determines the residence time required for the desired reaction or performance. Establishing this relationship between an
ion’s concentration and time allows evaluation and comparison if the sorption performance in ion exchange. The Lagergren’s kinetics equation, which is a pseudo first order equation for liquid-solid adsorption with a non-zero equilibrium value, has been most widely used for the adsorption of an adsorbate from an aqueous solution (Ho 2004). The SIX® system has been modeled by the Lagergren equation in previous studies, and it has shown to be a good fit (Koreman, Personal correspondence 2014) and is summarized as follows (Lito, et al. 2012):

\[
\frac{dq_t}{dt} = k_{p1}(q_{eq} - q_t)
\]

Where \( q_{eq} \) is the adsorption capacities at equilibrium, \( q_t \) is the adsorption capacity at time \( t \), and \( k_{p1} \) is the pseudo first order rate constant (min\(^{-1}\)).

When modified, the following equation can be used to describe a linear relationship with a slope of \( k \) using ion concentrations in aqueous form:

\[
k_{p1} \times t = \ln \left( \frac{C_o - C_{eq}}{C_t - C_{eq}} \right)
\]

Where \( C_o \) is the initial concentration, \( C_t \) is the concentration at time \( t \) (min), and \( C_{eq} \) is the concentration at equilibrium. The values for equilibrium concentrations were obtained from samples taken after 24 hours of contact time.

This modified equation can be used to build best-fit kinetic models for not only DOC and nitrate concentrations, but also UVT values, due to its linear relationship with DOC. The slope of this linear fit is the k-value for the tested resin concentration and used for further kinetic analysis.

In addition, a pseudo second order equation was applied to some data for kinetic fit comparison, which is expressed by:

\[
\frac{dq_t}{dt} = k_{p2}(q_{eq} - q_t)^2
\]
Where \( k_{p2} \) is the pseudo second order rate constant (\( \text{min}^{-1} \)). This equation can be modified to:

\[
k_{p2} \times t = \frac{(C_o - C_t)}{(C_t - C_{eq})(C_o - C_{eq})}
\]

### 3.4 Selectivity

As Equation 1 and Equation 2 describe, stoichiometry plays a crucial role in ion exchange as the charge balance during the exchange process must be maintained between the resin and the solution. This means that the net charge of ions adsorbed onto the resin (e.g. contaminant constituent such as DOC) must equal the net charge of ions desorbed off the resin (presaturant chloride) (Wachinski 2005). Quantifying the amounts of ions adsorbed and desorbed during the exchange process can identify the chloride demand and use of the ion exchange process. Stoichiometry suggests that the sum of the ionic equivalents adsorbed onto the resin during ion exchange treatment or regeneration is equal to the sum of the equivalents desorbed. For example, if DOC is removed from a solution by anion exchange resin, the decrease in the aqueous-phase concentrations of DOC must equal the increase in the aqueous phase concentration of chloride in terms of equivalents (Boyer and Singer 2008).

However, this ideal stoichiometric approach does not always hold true. Changes in certain parameters such as pH have demonstrated a shift in the number of ionic equivalents taken up by the resin (Boyer and Rokicki 2011). The expected stoichiometric ion exchange was not observed with Andijk WTP as only 1.3 equivalents of chloride were required to adsorb one equivalent of a sulfate ion, as shown by Table 2. One equivalent of a sulfate ion is expected to require 2 equivalents of chloride due to its divalent property.
Table 2. Anionic stoichiometric coefficients with SIX® resin and Andijk water matrix (Roakes 2013)

<table>
<thead>
<tr>
<th>Anion</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>HCO$_3^-$</th>
<th>%UVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient (K$_{anion}$)</td>
<td>1.331</td>
<td>0.9173</td>
<td>0.8234</td>
<td>-0.02981</td>
</tr>
<tr>
<td>P-Value (&lt;0.05 significant)</td>
<td>&lt;0.0001</td>
<td>0.0003</td>
<td>&lt;0.0001</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

Although ion exchange is a stoichiometric process, not all ions are exchanged equally. Resins have a certain affinity or preference for ions in aqueous solution, and this affinity or preference for a given resin is called selectivity. Divalent ions are typically preferred over monovalent ions, and ions with the same valence have different preferences by the resin depending on properties such as size and hydration (Crittenden, et al. 2005). The preference an ion exchange resin has for one ion over the other is calculated by a selectivity coefficient (K$_s$) or separation factor, as shown by the following equations.

\[ \bar{A} + B \rightarrow \bar{B} + A \]

\[ K = \frac{[\bar{B}][A]}{[A][\bar{B}]} \]

A and B are ions while overbar denotes the resin phase. Selectivity coefficients are based on molar concentrations and stoichiometry and are similar in theory to equilibrium constants (American Water Works Association 1999). They can depend on many factors, including the valence, properties (size, pore structure, functional group, etc.) of resin and its saturation, the concentration and nature (size, charge and hydrophobicity) of the ion in the raw water (Crittenden, et al. 2005).

The order in which ions are preferred by a particular resin is called a selectivity sequence. With the exception of special-purpose resins that are designed to exhibit unique selectivity sequences, the commercially available cation and anion exchange resins demonstrate similar
selectivity sequences. Some general rules govern these selectivity sequences, such as the resin preference for the ion with the highest charge and least degree of hydration (Clifford, Sorg and Ghurye 2011). For commercially available resins in typical water conditions, the selectivity sequence is \( \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- \sim \text{HCO}_3^- \) for anion exchange resins and \( \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ \) for cation exchange resins (Crittenden, et al. 2005).

### 3.5 Shared Cation and Anion Exchange Regeneration

DOC and hardness are prevalent in water supplies and pose challenges for drinking water treatment. There is the need for advanced treatment processes that can achieve high reductions in DOC due to the issues with disinfection byproduct formation and membrane fouling (Gray, et al. 2007; Al-Amoudi 2010). Challenges associated with the presence of hardness in drinking water production include reversible and irreversible fouling of membranes and scale formation (Jin, Huang and Hoek 2009). Ion exchange encompasses removals of both anionic and cationic contaminants, but it has traditionally been used in drinking water treatment as either anion exchange alone or cation exchange alone (Indarawis and Boyer 2013).

Recent studies began exploring sequential and combined anion and cation exchange treatment and simultaneous regeneration of anion and cation exchange resins (Apell and Boyer 2010; Indarawis and Boyer 2013; Comstock and Boyer 2014). These studies found that hardness cations, DOM, and sulfate interact differently in separate anion and cation exchange processes in sequential treatment compared to the combined treatment. Both systems observed satisfactory DOM, hardness, and sulfate in synthetic water, ground water, and NF membrane concentrates. However, most of these studies focused on removal aspect of combined ion exchange, and the only study that investigated the simultaneous regeneration tested with a proprietary resin,
Magnetic Ion Exchange® (MIEX®) (Apell and Boyer 2010). Additional concerns raised from these studies include bicarbonate and sulfate precipitation in calcium containing waters in sequential treatment and decreased separation factors for anion exchange during combined ion exchange.

Previous research at Andijk WTP found that two cation exchange resins, Lewatit MDS 1368 (S1368) and Lewatit MonoPlus S 1567 (S1567) achieved the required hardness removal easily with low resin concentrations and short contact times (Roakes 2013). The desirable removals were accomplished after 18 minutes of contact time at 4 g/L of S1368 resin concentration and after 20 minutes at 6 g/L of S1567, but overall S1368 performed significantly better with faster kinetics and lower predicted equilibrium values. Subsequently, a follow-up investigation evaluated the regeneration performance by the two resins, and the results are presented in Figure 15.
Figure 15 shows the efficiencies of resin regeneration achieved by a range of sodium chloride salt concentrations. The two resins that are capable of the desirable hardness reduction require substantial amounts of sodium chloride salt to desorb the removed calcium and magnesium and put the resins back in the sodium form. The current salt concentration in the SIX® regenerant is ~50 g-NaCl/L. Therefore, alternative cation exchange resins with lower salt demand must be investigated and selected.
CHAPTER 4

4 Methods and Materials

4.1 Materials

4.1.1 Anion Exchange Resin

Lewatit® VP OC 1071, the resin product currently used in the SIX® system and thus tested in this research, is a strongly basic, gelular Type I anion exchange resin supplied by the German chemical company, Lanxess. The manufacturer recommends the resin for demineralization and organic matter removal, especially from surface water. The resin comes in chloride form and consists of a cross-linked polyacrylamide matrix. The listed total capacity is 1.25 equivalents per liter of resin with 55-61% water retention. The density of the resin is approximately 1.09 g/mL, which is greater than the density water and therefore indicates that the resin has a good settling capability. Further information of the resin can be found in the product information sheet in Appendix A: Resin and Chemical Product Information Sheets.

4.1.2 Cation Exchange Resin

Lewatit® K 1131 S is a strongly acidic, gel-type, polymer-based resin supplied by Lanxess. Due to the resin’s very narrow bead size distribution, it is an ideal heterogeneous catalysis for organic reactions. The manufacturer listed applications include bisphenol-A production, condensation and esterification of small polar molecules, and hydrolysis of ether and esters. The resin comes in hydrogen form and consists of a cross-linked polystyrene matrix with the sulfonic acid functional group. The resin beads are transparent and consist of the listed total
capacity of 5.0 equivalents per liter of resin and 78-82% water retention. Further information of the resin can be found in the product information sheet in Appendix A: Resin and Chemical Product Information Sheets.

4.1.3 Regeneration Column

The bench-scale resin regeneration set-up was designed at the pilot plant. The set-up, as shown in Figure 16, includes a design of the vertical regeneration column with piping from a salt solution that was drawn to the regeneration column by a peristaltic pump. The regeneration vessel has a diameter of 3 cm and a height of 35 cm with the bed volume of 750 mL. The influent tubing is attached at the bottom of the column and can be removed to drain the column for sample collection or cleaning purposes. The peristaltic pump is a Masterflex® L/S Digital Economy Drive from Cole-Parmer Instrument Company; Model Number 77200-60. The peristaltic pump could operate with a flow of 20mL/min-480mL/min and would draw the salt solution to the regeneration vessel making the solution have an upward flow.

![Figure 16, Bench-scale regeneration column](image)
The piping attached at the top of the regeneration vessel allows the regenerant solution to travel back to the original beaker for recirculation of the salt solution. This mimicked regenerant reuse of the current SIX® regeneration system as one volume of regenerant solution was recirculated for five times in the column system. The contact time was 30 minutes for each of the five cycles. In order to achieve the five circulations, the pump was operated at 3.5 L/30 minutes, or 7 L/hour for 30 minutes. This flow rate was chosen to achieve long enough empty bed contact time (EBCT) that would result in five cycles through the column, as shown by the following calculation:

\[ EBCT = \frac{\text{Volume of Empty Bed}}{\text{Flow}} = \frac{750\text{mL}}{7000\text{mL/hour}} = 0.107\text{ hour} = 6.43\text{ minutes} \]

\[ \# \text{ of Cycles Achieved in 30 minutes} = \frac{30\text{ minutes}}{6.43\text{ minutes}} = 4.7\text{ cycles} \approx 5\text{ cycles} \]

4.1.4 Jar Test Apparatus

The jar test apparatus used for adsorption and desorption kinetics study is a ZR4-6. The apparatus has 6 stirring paddles that may spin at the rate or at individual speeds. The mixing speed may range from 20-900 rpms. Six rectangular jars were used, each with a maximum volume of 1.5L. An image of the jar test apparatus is shown in Figure 17.
4.1.5 **Resin Loading Vessel**

The resin loading vessel was used to put the cation exchange in sodium form since it originally comes in hydrogen form and then load the resin with hardness for the regeneration study. The vessel has a cylindrical shape, a volume of 130 liters, and an electric paddle mixer attached to the top. The paddle mixer can be adjusted to reproduce the mixing conditions in the SIX® pilot system. The tank has a port at the top for filling and resin dosing and a drain at the bottom for draining and sampling the water and recovering the resin.

4.1.6 **Salt**

The sodium chloride salt used in the desorption study was supplied by Kloek Zout B. V. company located in Dordrecht, Netherlands. The salt is 99% pure, and the rest of the composition includes calcium (0.2%), sulfate (0.7%), and magnesium (0.1%). The average grain size of the salt is between 1.5-3.2 mm. Further information on the salt can be found in Appendix A: Resin and Chemical Product Information Sheets.
4.1.7 **Water Matrices**

4.1.7.1 **Deionized Water Matrix**

Deionized water is supplied by Het Waterlaboratorium (HWL), an accredited laboratory that is further described in 4.2.7. Deionized water is assumed to contain no significant amount of ionic species and is a base for the water matrix used to create the salt regenerant solution for the desorption study. The regenerant water matrix is prepared with deionized water by adding a known mass of sodium chloride salt.

4.1.7.2 **Andijk Pilot Matrix**

The influent water to the SIX® pilot system was used in the adsorption jar tests for both anionic and cationic removals. This water had been softened with caustic soda prior to entering the pilot facility, as described by 1.3.1 Current Practice - Chemical Softening, and was collected from the sample port pan-pi-LEWA-V0.

4.1.8 **UV-Spectrophotometer**

A HACH DR-5000 Spectrophotometer was used for in-house UVT-254, DOC, nitrate, sulfate, chloride, sodium, calcium, magnesium, and total hardness measurements. 1-cm cuvettes were used for UVT-254 measurements, and analysis for the rest of the constituents were completed in conjunction with appropriate Hach test kits. More information on in-house chemical analysis is provided in 4.2.6.
4.2 **Laboratory Methods**

4.2.1 **Regeneration Experiment Procedure**

1. 750 mL of spent resins sampled from the SIX® pilot system was measured and put in regenerating column

2. 1100 mL of regenerant was prepared using deionized water and the amount of sodium chloride salt calculated to achieve the chloride concentration to be tested (~60 g Cl/L)

3. 1000 mL of the regenerant solution was poured into a beaker while the peristaltic pump was set up to draw from it at 3.5 L/30 minutes, or 7 L/hour, in an up-flow direction for 30 minutes. The regenerant was continuously recirculated after it traveled through the column

4. The side of the column was tapped occasionally to keep the hydraulics through the resin bed consistently (some channeling and bubbles occurred)

5. After 30 minutes, the pump was turned off, and the regenerant was drained and collected from the bottom of the column.

6. The spent regenerant was collected as much as possible by gravity and the laboratory vacuum- suction set-up

7. The final volume of the spent regenerant was recorded, if any occurred, in order to account for the dilution factor in data analysis

4.2.2 **Jar Test Procedure – Adsorption**

1. Prepared the resin accordingly:
   - Virgin resin: Hydrated in a beaker at least overnight in deionized water
- Fresh resin: Sampled from the fresh resin tank in the SIX® pilot and rinsed with deionized water
- Column-regenerated resin: Rinsed with distilled water

2. Removed resin from beaker with a spoon, draining it against the side of the glass
3. Weighed out the desired amount of resin and store in watch glass for dosing
4. Sampled SIX® influent water by filling 10 liter jerry can.
5. Filled jars to 1,5 L mark and overfilled jars if the initial sample was to be drawn from them
6. Took initial samples down to the 1,5 L mark using the sample port attached to each jar
7. Set jar tester to mixing at 200 rpm
8. Dosed resin by pouring from watch glass
9. Sampled using labeled plastic test tubes at staggered sample times, which allowed for running multiple jars
10. If equilibrium samples were taken, the jar test was run over night. Jar tester ran for a maximum of 10 hours so in the morning the jar tester was restarted until sampling time
11. Filtered all samples using 30 mL syringes and 0.45 um filters for analysis

4.2.3 Jar Test Procedure – Desorption

1. Sampled ~5 L of spent resin from the collection cone from Lamella separators of the SIX® pilot
2. Drained the water off the resin as much as possible using a metal filter and a funnel and place the drained resin in a separate container
3. Filled each jar with 700 mL of drained resin
4. Set the jars aside and prepared >800 mL of the regenerant solutions for the desired salt concentrations using sodium chloride and deionized water

5. Measured out 800 mL of the prepared regenerant solutions while the rest was stored for initial sample analysis

6. Set jar tester to mixing at 300 rpm

7. Dose regenerant solution by pouring from Erlenmeyer flask

8. Sampled using diameter 185 mm filter paper and funnel into labeled plastic test tubes at staggered sample times which allowed for running multiple jars.

9. If equilibrium samples were taken, the jar test was run over night. Jar tester ran for a maximum of 10 hours so in the morning the jar tester was restarted until sampling time

4.2.4 Resin Loading Procedure

1. Measured 1,2 liters of virgin resin

2. Filled “loading vessel” to the 100 liter mark and turned paddle mixer on

3. Took initial sample from bottom drain

4. Dosed resin by pouring it in from glass beakers, rinsing residual resin with deionized water

5. Let mix for 12 minutes after dosing

6. After 12 minutes of mixing, took final sample and emptied tank through a mesh screen, so as to catch the resin being washed out

7. Resin left in the bottom of the tank was recovered by rinsing it out with water that had been saved while draining
8. “Spent resin” was hydrated with deionized water and stored overnight in ~2 degree Celsius refrigerator

4.2.5 **Sampling Procedure**

1. Using 35 mL syringe, drew from jar at midpoint between the paddle shaft and the jar wall and about 4 cm below the water surface

2. Sample was filtered, using 0.45 um filters, into plastic sample test tubes, from which samples for analysis were taken

3. All in-house analyses were completed directly after sampling. Samples for HWL were stored in a refrigerator at ~2 degrees Celsius and collected the next day when possible

4.2.6 **In-house Chemical Analysis**

Once the samples were filtered through a 0.45 um filter into the sample vials that had been rinsed with deionized water and dried, the UV-Spectrometer described in 4.1.8 was used to obtain measurements for the parameters of interest, including UVT. The spectrophotometer was also used to measure the following constituents in conjunction with appropriate Hach test kits:

- DOC
- Nitrate
- Sulfate
- Chloride
- Sodium
- Hardness (calcium and magnesium)

The product information and procedures of the test kits for measuring these constituents are provided in Appendix B: In-house Chemical Analysis Procedures.
In-house bicarbonate measurements were taken from raw samples through performing titrations. The amount of acid consumed from pH 8.3 to 4.5 was recorded and converted to the concentration of bicarbonate present in the sample. The titration and calculation procedure is also included in Appendix B: In-house Chemical Analysis Procedures.

4.2.7 Het Waterlaboratorium N.V. Haarlem

Het Waterlaboratorium (HWL) is located in Haarlem, Netherlands and is independent from PWN. Samples were sent to the lab to analyze for constituents that could not be analyzed accurately at the Pilot Facility.

HWL is accredited by the Dutch Accreditation Council RvA. The lab followed the ISO/IEC 17025:2005 requirements to be accredited and they are accredited until 1 January 2015. The registration number of the lab is L 404. The certificate of the lab can be seen in Appendix C: HWL Certificate.

4.2.8 Kinetics

The following steps describe fitting the Lagergren model using experimental data and a pseudo first order equation as an example.

1. For each resin concentration,

   \[ \ln \left( \frac{C_0 - C_{eq}}{\left(\frac{C_0 - C_{eq}}{C_{eq}} - C_{eq}\right)} \right) \]

   was plotted against time, with the values for \( C_{eq} \) either obtained experimentally or established by trial and error using an iterative approach until the best fit to the experimental data was found (An example graph is shown for multiple column-regenerated resin at a concentration of 4 g/L)
2. The slopes of the above linear fit represent the first order adsorption rate constant or (k-value). k-values were then calculated for all resin concentrations according to this method (see table below).

<table>
<thead>
<tr>
<th>C_{resin}</th>
<th>4 g/L</th>
<th>6 g/L</th>
<th>8 g/L</th>
<th>12 g/L</th>
<th>16 g/L</th>
<th>20 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>k-values</td>
<td>0.0128</td>
<td>0.02</td>
<td>0.0242</td>
<td>0.0373</td>
<td>0.0499</td>
<td>0.0557</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9812</td>
<td>0.99</td>
<td>0.9961</td>
<td>0.9861</td>
<td>0.9873</td>
<td>0.9802</td>
</tr>
</tbody>
</table>

3. Subsequently the various k-values were plotted against resin concentration, which in turn results in another linear plot. The slope of this linear fit was recorded as the normalized k-value. In the example below $k_{\text{normalized}}$ is 0.030 ($R^2=0.98$).
4.3 Experimental Design

4.3.1 Anionic Desorption Efficiency during Regeneration

The purpose of this experiment was to investigate the efficiency for the SIX® pilot regeneration process of the current anion exchange resin. In order to achieve this goal, resin blinding, which in this context indicates that the resin surface is still partially covered by anions other than chloride, was assessed and quantified.

One bed volume (~750 mL) of fresh resins sampled from the SIX® pilot system was regenerated in the bench-scale column over 13 regeneration cycles. Each of the 13 regeneration cycles used a virgin salt solution (~60 g Cl⁻/L) and a 30 minute contact time. The multiple regeneration cycles with virgin regenerants ensured maximum desorption of the anions adsorbed on the resins. The experiment ended after 13 regeneration cycles as no further change, or reduction, of the color in the spent regenerant solution could be observed.

It should be noted that although the first regeneration cycle was designed to represent the bench-scale version of the current SIX® pilot regeneration process, a different salt concentration was used with opposite flow direction and also a higher regenerant volume. The regenerant concentration in the pilot system is ~30 g Cl⁻/L while the regenerant volume is only 40% of the bed volume. The concentration of 60 g Cl⁻/L was chosen because desorption curves investigated in Chapter 4.3.3 Chloride Demand were observed to level off after ~50 g Cl⁻/L. This indicated that up to this salt concentration, desorption was improved, but the effects were limited at concentrations higher than that. Furthermore, the regenerant volume used in the experiments was 1,000 mL, which equals 133% of the bed volume (1,000 mL/750 mL-BV). However, in order to achieve continuous regenerant recirculation, the regenerant volume had to be higher than the bed volume, due to the additional volume taken up by filters and tubing in the column set-up.
The measured parameters included:

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>· Chloride (Cl⁻)</td>
<td>· DOC</td>
</tr>
<tr>
<td></td>
<td>· Nitrate (NO₃⁻)</td>
</tr>
<tr>
<td></td>
<td>· Sulfate (SO₄²⁻)</td>
</tr>
<tr>
<td></td>
<td>· Bicarbonate (HCO₃⁻)</td>
</tr>
</tbody>
</table>

The adsorption and desorption of the anions were quantified by measuring the change in their concentrations before and after each regeneration cycle. This enabled the evaluation of mass balance between the adsorbed chloride ions from the virgin regenerant and the desorbed anions in the spent regenerant. All the samples were analyzed by Het Waterlaboratorium (HWL) in Haarlem.

4.3.2 Anionic Adsorption Efficiency during Removal

The purpose of this experiment was to investigate the effects of regeneration on the adsorption efficiencies of the current anion exchange resin. The experiment aimed to bring insight into the effects of regeneration with larger salt volumes on the target constituent removal of the resin. This was achieved by assessing how the DOC and nitrate removal capacities from SIX® influent water differed among the virgin, fresh, and multiple column-regenerated resins. Virgin resin has never been used or recycled since its production, and this represents that the resin is first time in use. Fresh resin sampled from SIX® pilot has been used for treatment and regenerated. Multiple-column-regenerated resin was a product of the previous experiment from 4.3.1 Anionic Desorption Efficiency and had undergone 13 regeneration cycles until maximum desorption was observed. These three resins represent the direct results of different levels of regeneration, with the virgin resin being the most ideal condition with no risk of blinding from
previous use. They allow comparing the effects of brine volume applied during regeneration on adsorption efficiencies.

The parameters, all measured by in-house analysis methods, included:

**Adsorption:**
- $UVT_{254}$ (DOC)
- $NO_3^-$

The parameter of $UVT_{254}$ (1 cm) was used as a surrogate for DOC because it is the most practical and economical metric for quantifying DOC. The experiment consisted of three runs, and each run consisted of six jars with resin concentrations of 4, 6, 8, 12, 16, and 20 g/L with sample times at 0, 2, 4, 8, 12, 20, and 30 minutes as well as an equilibrium time of 24 hours.

4.3.3 Chloride Demand

The main objective for this study was to investigate the chloride demand of the current anion exchange resin when regenerated with a range of salt concentrations. This would determine the optimal salt concentration that results in most efficient desorption and provide insight into the exchange phenomena between chloride and the different anion constituents.

Chloride demand of the spent resin was tested by a series of column experiments to examine the relationship between salt concentration and anion desorption during regeneration. The SIX® pilot system currently utilizes regenerant strength of about 30 g-Cl/L. In this study, a range of salt concentrations from 10 to 193 g-Cl/L was used to regenerate one bed volume (~750 mL) of spent resins sampled from the SIX® pilot system for a contact time of 30 minutes. The regenerant solutions were prepared using deionized water and salt, which ensured that salt concentration is the only independent variable in the study. The tested increments of salt
concentrations were \( \approx 10 \text{ g-Cl/L} \), and total 23 column experiments were completed. Replicate runs were performed for several data points to increase confidence in the results.

The measured parameters included:

<table>
<thead>
<tr>
<th>Adsorption:</th>
<th>Desorption:</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Chloride (Cl(^-))*</td>
<td>* DOC</td>
</tr>
<tr>
<td></td>
<td>* Nitrate (NO(_3^{-}))*</td>
</tr>
<tr>
<td></td>
<td>* Sulfate (SO(_4^{2-}))*</td>
</tr>
<tr>
<td></td>
<td>* Bicarbonate (HCO(_3^{-}))*</td>
</tr>
</tbody>
</table>

The results allowed quantification of chloride adsorption and corresponding desorption of the anion constituents and thus, evaluation of chloride efficiency of regeneration at the tested salt concentration. Regeneration efficiency achieved by the observed chloride uptake was evaluated in terms of anion desorption and also the effects of the initial salt strength.

4.3.4 Regeneration Sorption Kinetics

The purpose of this study was to investigate the kinetics of desorption taking place during regeneration of the current anion exchange resin. It is important to examine how fast the sorption processes are occurring in the interest of process optimization. This goal was achieved in this study by investigating the desorption kinetics of DOC and sulfate over a range of contact time during regeneration as well as monitoring the corresponding chloride adsorption. In addition, this study included salt concentration as a factor and aimed to confirm the relationship between anion desorption and initial chloride concentrations from Chapter 4.3.3 Chloride Demand.

The parameters, all measured by in-house analysis methods, included:

<table>
<thead>
<tr>
<th>Adsorption:</th>
<th>Desorption:</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Chloride (Cl(^-))*</td>
<td>* UV(_{254}) (DOC)</td>
</tr>
<tr>
<td></td>
<td>* Sulfate (SO(_4^{2-}))*</td>
</tr>
</tbody>
</table>
Only two desorption parameters (DOC and sulfate) were recorded due to the large number and volumes of samples that would have been required for analysis of all anionic constituents of concern. DOC and sulfate were chosen as the parameters since DOC is the main target constituent of SIX® treatment process, and the previous data showed that sulfate is highly preferred by the current anion resin. DOC desorption was represented by the change in UVT$_{254}$. Since the samples were diluted to be in the detection limit, and its water matrix was changed from dilution, the calculated relationship between UV T% values and DOC concentrations is disturbed. However, the linear relationship between UV T and DOC still holds true for a given dilution factor, and thus, the diluted results still can be evaluated to provide insight into DOC desorption over time.

The experiment was divided into preliminary and follow-up runs. The preliminary experiment included two desorption jar tests, one for DOC desorption (change in UV T) and the other for sulfate desorption. Chloride adsorption was investigated in both runs. Since the preliminary investigation revealed that significant both adsorption and desorption occurred before the shortest contact time tested (6 minutes), a follow-up investigation was performed with shorter contact times to analyze sorption of DOC, sulfate, and chloride. In addition, the follow-up investigation included testing a new salt type, potassium chloride, to observe possible effects in UV T reduction, which were unexpected since chloride is the counter ion involved in the exchange process.

The preliminary runs consisted of SIX® jars with liquid (regenerant) to solid (resin) ratio of 1.2 from the pilot regeneration process and chloride concentrations of ~9, 30, 65, 90, 140, and 165 g/L with sample times at 0, 6, 12, 18, 30, and 60 minutes as well as an equilibrium time of
24 hour. The follow-up run used a smaller range of chloride concentrations (~15, 30, and 60 g/L) and sample times (2, 5, 10, and 30 minutes).

4.3.5 Hardness Adsorption

The purpose of this investigation was to assess if the desired removal of hardness could be achieved by Lewatit K 1131 S cation exchange resin. Jar experiments were performed to observe change in hardness, represented by the sum of calcium and magnesium, from influent and effluent water of the SIX® pilot system. First, the preliminary investigation tested un-rinsed virgin in hydrogen (H+) form. Once the desired removal was observed, a follow-up investigation was performed with virgin resin that was rinsed with sodium chloride solution at a concentration of ~100 g-NaCl/L, which put the resin in sodium (Na+) form.

The parameters, all measured by in-house analysis methods, included:

**Adsorption:**
- Calcium (Ca²⁺)
- Magnesium (Mg²⁺)
- Total hardness (dH°)

The experiment consisted of three runs. The preliminary investigation included two runs, one with SIX® influent water and the other with SIX® effluent water. Both runs tested resin concentrations of 4, 6, 8, 12, 16, and 20 g/L with sample times at 0, 2, 4, 8, 12, 20, and 30 minutes as well as an equilibrium time of 24 hour. The follow-up investigation was carried out to check that the resin in Na⁺ form would also achieve the comparable removal performance observed in the preliminary investigation with the resin in H⁺ form. The resin concentrations of 8, 12, and 16 g/L were chosen from the preliminary results with sample times at 0, 2, 6, 12, 30 minutes.
4.3.6 **Hardness Desorption**

The purpose of this investigation was to measure the hardness desorption achieved by and evaluate if 1131 S is a more suitable cation exchange resin choice compared to the previously tested resins, Lewatit MDS 1368 (MDS 1368) and Lewatit MonoPlus S 1567 (S 1567). The cation exchange resin’s regenerability with sodium chloride is an important parameter in compatibility with the current treatment system. The SIX® treatment is an anion exchange system regenerated with sodium chloride, and it would be most economically and environmentally beneficial for the cation system to share this regenerant stream.

Jar experiments were performed to observe the increase in hardness, which is the sum of calcium and magnesium, and decrease in sodium that gets adsorbed onto the resin. Therefore, the parameters, analyzed by HWL, included:

**Desorption:**
- *Calcium (Ca\(^{2+}\))*
- *Magnesium (Mg\(^{2+}\))*
- *Sodium (Na\(^{+}\))*

Before the desorption jar-test, the resin was preloaded at the resin concentration of 12 g/L for 12 minutes to achieve the 1 mmol/L of total hardness adsorption on the resin. The resin loading vessel described in 4.1.5 was used, and the experimental procedure is described in 4.2.4. The experiment consisted of three runs tested the salt concentrations of 44, 68, 89, 123, and 173 g-Cl/L with sample times at 2, 4, 8, 12, 20, and 30 minutes as well as an equilibrium time of 24 hour.
CHAPTER 5

5 Results and Discussions

5.1 Anionic Desorption Efficiency during Regeneration

In this section, the current efficiency for the SIX® pilot regeneration process of the Lewatit VP OC 1071 anion exchange resin was investigated in terms of anion desorption. The following data were collected over a week, from 2-24-2014 to 2-28-2014, to evaluate by performing multiple regeneration cycles to one bed volume of spent resin. This investigation also aimed to study the effects of regenerant volume on anion sorption.

5.1.1 Chloride Adsorption

The experimental approach of this study was to regenerate the resins multiple times with a series of virgin salt solutions of the same chloride concentration, which was selected to be 60 g Cl/L. Virgin salt solutions were prepared in several batches because the number of regeneration cycles required for complete anion desorption was initially unknown. Their initial chloride concentrations ranged from 57.6 to 63.7 g Cl/L with the average concentration of 59.9 g Cl/L.

Figure 18 shows the cumulative concentrations of chloride adsorbed over one series of the 13 regeneration cycles, after which no further change in color was observed in the spent regenerant, indicating maximum desorption was achieved on the resin. The concentration of chloride adsorbed during each cycle was calculated with the equation:

\[ C_o - (C_f \times Dilution \ Factor) = C_{adsorbed} \]

Where \( C_o \) is the initial chloride concentration of the virgin regenerant, \( C_f \) is the final chloride concentration of the spent regenerant, and \( C_{adsorbed} \) is the change in chloride concentration due to
regeneration and thus the concentration adsorbed on the resin. Dilution factor was applied to account for the moisture of the hydrated resin and calculated by the equation:

\[
\text{Dilution Factor} = \frac{V_{f,\text{regen}}}{V_{o,\text{regen}}} \quad ; \quad V_{o,\text{regen}} = 1000 \text{ mL}
\]

Where \(V_{f,\text{regen}}\) is the final volume of the spent regenerant measured after a column experiment, and \(V_{o,\text{regen}}\) is the initial volume of the virgin regenerant and was prepared to be 1000 mL for every experiment. In this section, dilution factors ranged from 0.99 to 1.02, demonstrating that the dilution effect was negligible.

The cumulative concentration of chloride adsorbed after 13 regeneration cycles added up to 36.9 g/L, and most chloride adsorption took place during the first regeneration cycle (19.5 g/L out of 36.9 g/L). After the first cycle, chloride adsorption decreased significantly, but the amount of chloride used during the first cycle only made up for 52.7% of the total amount of chloride used up in the 13 cycles. This indicates that significant amount of additional chloride ions were adsorbed to the resins throughout the subsequent cycles to perform further regeneration. Anion desorption that corresponds to these chloride adsorption data is analyzed in the next sections, providing insight into exchanges between chloride ions and the anion constituents during these regeneration cycles.
5.1.2 Anion Desorption

Along with chloride adsorption, desorption of DOC, nitrate, sulfate, and bicarbonate from regeneration was measured. The total desorption value was calculated by measuring the change in the anion concentration in the spent regenerant after each of the 13 regeneration cycles and summing them up for the accumulated desorption value. The total desorption values after 13 regeneration cycles are summarized for all anions in Table 3.

Table 3. Total accumulated concentrations of anionic desorption after 13 regeneration cycles

<table>
<thead>
<tr>
<th>Total Desorption, g/L</th>
<th>DOC</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Bicarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.79</td>
<td>4.8</td>
<td>5.9</td>
<td></td>
</tr>
</tbody>
</table>

Dilution factors, discussed in Chapter 5.1.1, were also applied to the desorption values for a fair comparison with chloride adsorption. Figure 19 shows desorption efficiency on the
right-axis, which is the percentage value of the accumulated anionic concentration at each cycle, with 100% desorption represented by the maximum desorbed concentration after 13 cycles.

Overall, the data show that most of the anion desorption occurred well before the last regeneration cycle for all the four constituents. For sulfate and bicarbonate, the increase of the cumulative concentrations rapidly slowed down after each cycle, especially compared to the first cycle. However, this process was more gradual for DOC and nitrate as their cumulative concentrations still increased steadily after the first cycle. Eventually leading to no or very low concentrations of the desorbed anions in the spent regenerant, maximum desorption was accomplished, which is represented by the stabilized curves in Figure 19. Unlike the chloride adsorption data that did not demonstrate a conclusive equilibrium curve in Figure 18, the equilibrium curves were observed in the desorption data of all the four anions.

However, it is important to note that the number of regeneration cycles, or the volume of virgin regenerant solution, required to reach maximum desorption differed among the anion constituents. The curves show that sorption equilibrium was achieved very quickly after the second or third cycle for sulfate and bicarbonate while at least seven regeneration cycles were required for full desorption of DOC and five cycles for nitrate. Especially for DOC, the equilibrium curve is not as clearly established as those of the other three constituents even after 13 cycles that used a significant volume, 13 L, of virgin regenerant solution, indicating that DOC may be continuously desorbed in slight amount. This may have partially contributed to the lack of a conclusive equilibrium curve in chloride adsorption.

Another explanation for the continuous chloride adsorption may be related to different levels of chloride demand required to desorb certain DOC fractions. As Section 5.3.3 Anion
Equivalent Balance discusses the possibility of some sulfate ions adsorbing to the resin only one of the two charges, the chloride demand of DOC may be too complex to be defined by one equivalent factor (1.97 from previous research). Literature suggests that DOC during ion exchange removal can be divided into three categories: (1) not removed, (2) less-preferred than sulfate, and (3) more-preferred than sulfate (Clifford, Sorg and Ghurye 2011). This difference in preference is originated from the diversity and complexity of NOM and can translate to varying chloride demand for desorption. Some portion of DOC may be more preferred during earlier regeneration cycles and thus requires less chloride while the rest may require much more chloride ions. Since nitrate, bicarbonate, and sulfate have all reached equilibrium with no further desorption observed after the first few cycles, it can be assumed that the continuous chloride adsorption is controlled by DOC desorption, specifically the certain fractions of DOC that has higher chloride demand than the fractions that came off the resin more easily during the earlier regeneration cycles.
It is essential to evaluate the efficiency of the resin regeneration from the first cycle when compared to the observed maximum desorption because one regeneration cycle in this study is a bench-scale representation of the regeneration process that the spent resin experiences in the pilot system. Maximum desorption represents complete regeneration of the resin (100%...
efficiency) and thus allows an analysis of the first regeneration cycle for its completeness of desorption or regeneration. Comparing desorption efficiencies from the first cycle to the rest of the desorption data allows the calculation of how blinded the resin still is after one cycle of regeneration treatment. Figure 19 highlights desorption efficiencies of the first regeneration cycles, but Figure 20 includes them for all the 13 cycles to emphasize the significance of first cycle desorption in terms of complete regeneration. The results show that only 36% of the observed maximum desorption for DOC and 49% for nitrate are accomplished during the first regeneration cycle. These values are significantly lower when compared to the results for sulfate (85%) and bicarbonate (68%).

It is hard to compare these results to the data in current literature since the need for analyzing the levels of these four anionic constituents in ion exchange brine is unique to Andijk WTP. However, the current resin used in this study has demonstrated a chloride efficiency of 20% during removal, meaning 80% of total chloride exchange is attributed to removing sulfate and bicarbonate (Roakes 2013). High chloride demand during adsorption can be translated to high chloride demand during desorption that can slow down sulfate and bicarbonate from coming off the resin. This high chloride demand for sulfate and bicarbonate observed during adsorption and also the resin’s general preference for divalent ions like sulfate (Crittenden, et al. 2005) may predict the opposite of the results from this experiment. The divalent preference expects the resin to hold onto sulfate ions stronger than monovalent ions like nitrate.

However, it has been reported that divalent sulfate can be the first to be stripped from the resin during regeneration because of the selectivity reversal that occurs in high-ionic-strength salt solution (Clifford and Liu 1993). In addition, higher desorption efficiencies for sulfate and bicarbonate might be explained by their larger concentration gradient between the resin phase
and aqueous (regenerant) phase. Regeneration is a process that exchanges ions between these two phases by reversing the equilibrium through increasing one ionic concentration, such as chloride in this case. As shown by Table 3, the total desorbed concentrations of sulfate (4.8 g/L) and bicarbonate (5.9 g/L) are higher than those of DOC (1.8 g/L) and nitrate (0.79 g/L). Compared to these concentrations on the resin phase, there was no sulfate, DOC, and nitrate and very little bicarbonate present in the prepared regenerant solution. Thus, the differences in the concentration gradients were larger for sulfate and bicarbonate, and this may have provided higher driving force of the ion transport between the two phases.
Furthermore, Figure 21 highlights the inefficiency of DOC desorption in comparison to nitrate, sulfate, and bicarbonate desorption. Not only substantial sulfate desorption occurs in the first cycle, but also essentially full desorption is accomplished after the third cycle (99%).
regeneration cycles lead to total 95% desorption efficiency for bicarbonate and 90% for nitrate while achieving only 63% of DOC desorption efficiency is achieved. DOC desorption does not obtain 90% efficiency until the sixth cycle (Figure 19). This translates into twice more virgin regenerant volume required to accomplish 90% desorption for DOC than for sulfate, bicarbonate, and even nitrate.

![Cycle Efficiency Comparison](image)

*Figure 21, Comparison of desorption efficiencies from 1st, 2nd, and 3rd cycles*

DOC and nitrate are the target constituents of removal in the SIX® pretreatment process, and these findings show that it is more difficult to desorb DOC and nitrate, requiring more salt solution for complete desorption off the used resin. This indicates the current regeneration of the resins are not as efficient in desorption of these target constituents, especially DOC, compared to that of sulfate and bicarbonate. The slower desorption of DOC is not surprising as its higher chloride demand during adsorption has already been observed on a carbon-basis (Roakes 2013), and DOC can have diverse structures of carbon chains (Bhatnagar, et al. 2011). This makes DOC a more complex compound to analyze in sorption than inorganic constituents like sulfate and
nitrate. In addition, irreversible fouling by negatively charged natural organic matter is a well-documented issue and requires large volumes of regenerant and rinses to restore the resin’s capacity (Crittenden, et al. 2005).

Consequently, the effects of this incomplete desorption of the target anions must be examined to determine if the adsorption capacities, or removal kinetics, of the resin are compromised as a result. For this reason, Section 5.2 Anionic Adsorption Efficiency during Removal investigates this subject by comparing the removal kinetics of the resin that underwent the multiple regeneration treatment in this experiment and achieved full anion desorption to those of virgin and fresh resins.

5.1.3 Anion Sorption in Equivalent

In order to evaluate the efficiency of chloride used to desorb the anion constituents, all the anions involved in the exchange process were converted to the unit of equivalent, or specifically milliequivalent in this analysis. More detailed information can be obtained then on the usage and distribution of the adsorbed chloride ions. This information is also used to determine the ratio of the adsorbed chloride that was utilized to desorb the target constituents, DOC and nitrate, which represents the true efficiency of the regeneration process. Analyzing in equivalent allows a fair comparison between the number of chloride ions adsorbed and anions desorbed including each ion’s valence. For the conversions from mass to equivalent, the valence numbers of 2 for sulfate and 1 for nitrate and bicarbonate were used. For DOC, the selectivity coefficient value of 1.97 was used, which was calculated from previous research using the influent water matrix to the SIX® pilot system and the current resin (Roakes 2013). This information is summarized in the following table:
Table 4. Equivalence factors used in conversion from mass to equivalent

<table>
<thead>
<tr>
<th>Anion</th>
<th>DOC</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalence factor</td>
<td>1.97</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 22 details the distributions of the four anionic concentrations (DOC, nitrate, sulfate, and bicarbonate) in desorption in terms of milliequivalent per liter (meq/L) of regeneration solution. The data show that compared to the non-target constituents, desorption of nitrate accounts for an insignificant portion of the total equivalent desorption while DOC takes up the dominant portion. This indicates that a lot more chloride milliequivalents are utilized to desorb DOC rather than the other three constituents. This is consistent with the results of another equivalent analysis performed over a range of salt concentrations in Section 5.3.3 Anion Equivalent Balance.

Figure 22, Concentrations of nitrate, DOC, sulfate, and bicarbonate desorbed in meq/L accumulated at each of the 13 regeneration cycles (initial regenerant concentration=60 g·Cl⁻/L)

Figure 23 compiles the adsorption data from Figure 18 and desorption data from Figure 22 in milliequivalents per liter. The sum of the four anionic concentrations represents total desorption, which is depicted by the red bars. This value is theoretically equal to the
concentration of total chloride ions used for adsorption during regeneration, shown by the blue bars, when compared in the equivalent unit. This relationship is represented by the following equation:

\[ N_{\text{adsorbed}} = N_{\text{desorbed}} \]
\[
N_{\text{Cl}^-} = N_{\text{DOC}} + N_{\text{NO}_3^-} + N_{\text{SO}_4^{2-}} + N_{\text{HCO}_3^-}
\]

N denotes equivalent concentration, or normality, of the compound written in subscript. Due to the small magnitude of the values, milliequivalents per liter (meq/L=mN) was used as a unit.

Figure 23, Comparison between total chloride adsorption, all anion desorption, and target anion (DOC+nitrate) desorption in meq/L over 13 regeneration cycles

This anion equivalent balance is not achieved at most cycles in Figure 23, as denoted by the gaps between the red and blue bars, with the exceptions of the first and second cycles. This gap increased throughout the cycles, indicating more equivalents were adsorbed than desorbed, according to the chloride equivalent coefficients in Table 4. The equivalent gap may be related to the selectivity coefficient values used for equivalent conversion and occurs in the subsequent
regeneration experiments as well. Therefore, it is further investigated and discussed in Section 5.3.3 Anion Equivalent Balance.

Finally, the green bars in Figure 23 that represent the target anion desorption (DOC and nitrate) must be highlighted. Although Figure 22 shows the dominant equivalent desorption of DOC, Figure 23 shows that overall less than half of the chloride equivalents adsorbed during regeneration are utilized to desorb the target constituents. During the first cycle, the chloride efficiency of target anion desorption was 40.9%, as only 115.5 of total 282.1 meq/L of adsorbed chloride ions were used to desorb DOC and nitrate. This efficiency increased over time slightly, mainly due to the increasing DOC desorption over the cycles.

5.2 Anionic Adsorption Efficiency during Removal

In this section, three resins at different stages of regeneration were analyzed for their DOC and nitrate removal capabilities. The three resin conditions included:

- Virgin resin that has never been used or recycled since its production
- Fresh resin that has been used for treatment and regenerated by the SIX pilot
- Multiple column-regenerated resin that had gone 13 regeneration cycles until maximum desorption was observed from the previous experiment in Section 5.1.

These three resins represent the direct results of different levels of regeneration, with the virgin resin being the most ideal condition with no risk of blinding from previous use. They allow comparing the effects of brine volume applied during regeneration on adsorption efficiencies. UVT was used as a surrogate parameter for DOC as they are linearly related to each other for the typical range of Andijk water matrices, and higher UVT indicates less remaining DOC.
The following data were collected in three days; the first day, 3-5-2014, included the virgin resin run while the fresh resin run was performed on the second day, 3-10-2014, and the column-regenerated run on the third day, 3-19-2014. Table 5 shows initial concentrations of UVT, nitrate, and sulfate in the samples of the SIX® pilot influent water used for experiment on each day.

Table 5, Initial concentrations of SIX® pilot influent water matrix

<table>
<thead>
<tr>
<th>Resin Type / Date</th>
<th>Virgin</th>
<th>Fresh</th>
<th>Multiple-Column-Regen.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVT%</td>
<td>74.7</td>
<td>74.3</td>
<td>74.3</td>
</tr>
<tr>
<td>NO₃⁻ (mg/L)</td>
<td>7.75</td>
<td>7.77</td>
<td>7.56</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>46.1</td>
<td>50.9</td>
<td>53.5</td>
</tr>
</tbody>
</table>

5.2.1 DOC Adsorption

Change in UVT was plotted for each resin type and resin concentration over time in Figure 24. Despite slight deviations at the beginning of the curves for virgin and fresh resins, overall higher resin concentrations and longer contact time led to larger UVT increase, or DOC removal. The only exception is the 16 g/L resin concentration run with virgin resin whose UVT increase is higher than the 20 g/L resin concentration. The 16 g/L resin concentration data may have been subjected to errors during the UVT analysis since the increasing UVT trend from low to high resin concentration is clear and consistent at the rest of the tested resin concentrations. The resin weighted for this jar may have been sampled from an especially dry part of the batch or there could have been errors associated with pipetting the samples into the cuvettes for UVT analysis. In general, virgin resin showed highest UVT increase, and this becomes more evident with increasing contact time.
Figure 24. Adsorption graphs for UVT, tested with virgin, fresh, and multiple column-regenerated resins at six resin concentrations over time.

Also, for most of the contact time duration, fresh resin achieves higher UVT increase than column-regenerated resin, but the difference between the two becomes much smaller at longer contact time after ~20 minutes. Ion exchange equilibrium is evidenced by the flat region of the curve that plots concentration over time (Becker 2006). In previous research that investigated the current SIX® resin, the establishment of this flat region has been observed to start before or around 30 minutes. In addition, 24 hours has been used as an equilibrium contact time for experiments performed at PWN as it is considered to be long enough to fully achieve the
ion exchange equilibrium. UVT values measured after 24 hours in Figure 25 show that the highest UVT values were recorded by column-regenerated resin performance, followed by comparable UVT levels from virgin and fresh resins.

Figure 25, UVT measured at equilibrium (after 24 hours) over resin concentration

Overall, these results indicate that applied multiple cycle regeneration did not improve DOC removal capacities of the fresh resin within the practical contact time duration. This conclusion is also supported by Figure 26 which shows the calculated removal efficiencies for DOC, using UVT as a surrogate, by fresh and multiple column-regenerated resins with 100% removal represented by virgin resin performance. This representation helps analyze easily if the multiple cycle regeneration increased DOC adsorption by comparing the removal efficiencies of fresh and multiple column-regenerated resins. The data were extracted from the runs with resin concentrations of 12, 16 and 20 g/L and contact time of 30 minutes because they are the actual parameters applied in the SIX® process.

As Figure 26 shows, at all three resin concentrations, both multiple column-regenerated and fresh resins showed almost identical removal performance, indicating that the higher degree
of regeneration did not necessarily improve the DOC adsorption capabilities of fresh resin. The UVT data for virgin resin at 16 g/L resin concentration were much higher than expected by the trend and consequently reduced the removal efficiencies of fresh and multiple column-regenerated resins. However, these data were still included in Figure 26 as they contribute to the point that multiple regeneration cycles did not improve the resin’s DOC removal performance.

![Figure 26](image.png)

**Figure 26.** Percent removal efficiency for UVT/DOC comparing virgin, fresh and multiple column-regenerated resins (Virgin resin performance set as 100% removal; contact time = 30 minutes)

### 5.2.2 Nitrate Adsorption

Nitrate removal was plotted over time per each resin type and resin concentration in Figure 28. Similar to the UVT results, virgin resin consistently accomplished the highest nitrate removal at all resin concentrations. However, column-regenerated resin demonstrated comparable removal performance throughout the tested resin concentrations and contact times. The removal achieved by fresh resin was significantly lower than virgin and column-regenerated resins, and moreover, nitrate concentration even increased at 4, 6, and 20 g/L resin concentrations. This desorption could be caused by the nitrate built up on the resin, due to the
current practice of inefficient regeneration in the SIX® pilot, which was demonstrated by how only 49% of total nitrate present on the spent resin was desorbed during the first regeneration cycle with 51% still left on the resin (Section 5.1.2 Anion Desorption). Deteriorated nitrate removal has been observed on a pilot-scale since the regeneration process had started reusing salt regenerant up to five times. This regeneration is less rigid than the previous system whose oldest salt regenerant was only twice-used. As observed on a bench-scale in this experiment, the resin’s DOC removal performance was unaffected, and this is also consistent from the SIX® pilot data that did not observe deterioration in DOC reduction. These results on bench-scale and pilot-scale indicate that nitrate is the first victim of lower salt use rather than DOC as lower salt use results in blinding of the nitrate adsorption sites rather than the DOC adsorption sites on the resin.
This conclusion is highlighted by Figure 28, which follows the same set-up as Figure 26. With virgin resin’s nitrate removal performance established as 100% efficiency, multiple column-regenerated resin removed far more nitrate (>90%) than fresh resin. Fresh resin only achieved ~40% removal efficiency when desorption interferences caused by nitrate blinding were not significant. As previously explained, these desorption interferences were only observed in fresh resin adsorption and resulted in negative efficiency in Figure 28 at resin concentration of 20 g/L by increasing the nitrate concentrations. It should be noted that the fresh resin used for
testing both DOC and nitrate removals came from the same batch of the resin that was sampled from the SIX® pilot system. The desorption interferences observed with nitrate and not DOC may be related to the inefficient regeneration process affecting nitrate adsorption sites more than DOC adsorption sites.

Figure 28, Percent removal efficiency for nitrate comparing virgin, fresh and multiple column-regenerated resins (Virgin resin performance set as 100% removal; contact time = 30 minutes)

Figure 29 presents the removal achieved at equilibrium measured after 24 hours versus resin concentrations. The nitrate concentrations at equilibrium are the highest for fresh resin, indicating the least nitrate removal. Highest nitrate removal was achieved by virgin resin, and lower, yet comparable, removal occurred with multiple column-regenerated resin. Despite the interferences from desorption, or increased nitrate concentrations, that occurred at resin concentrations 4, 6, and 20 g/L at shorter contact times, Figure 29 shows that the effects of these interferences were removed after 24 hours. It is unlikely that this increased nitrate concentration was contributed by analytic errors since it occurred at half of the tested resin concentrations. This might be one of the phenomena contributing to the overall decrease in nitrate removal performance of the SIX® pilot system. Nitrate was not efficiently desorbed during the SIX® pilot
regeneration and thus prevented adsorption during treatment, but at some point during the 24 hours, this undesirable desorption was completed. Figure 29 shows that higher nitrate removal evidently occurred at higher resin concentration for all resin types, but even after the desorption interferences vanished, fresh resin still maintained its unfavorable adsorption capabilities.

![Netrate concentrations measured at equilibrium (after 24 hours), plotted over resin concentration](image)

**Figure 29.** Nitrate concentrations measured at equilibrium (after 24 hours), plotted over resin concentration

5.2.3 Kinetics Comparison

Adsorption kinetics of the three resins were investigated to further evaluate their performances. Figure 30 plots the k-values, described in Section 3.3, of the UVT increase, or DOC adsorption, versus the tested concentrations of virgin, fresh, and column-regenerated resins.

First, the high $R^2$ values (0.9718, 0.9607 and 0.9811) from the linear fits indicate that Lagergren’s pseudo first order equation describes the adsorption kinetics of all the three resins well. Faster removal kinetics, characterized by higher normalized k-values, represents lower contact times needed to achieve the same removal. The normalized k-value, the slope of the linear fit, was the highest for virgin resins, 0.0048 min$^{-1}$. Fresh resin exhibited the k-value of
0.0037 min\(^{-1}\) while the column-regenerated resin had the lowest k-value of 0.0030 min\(^{-1}\). Therefore, fastest adsorption kinetics were accomplished by virgin resin, followed by fresh resin and column-regenerated resin, respectively, reiterating the findings from the analysis in Section 5.2.1 DOC Adsorption.

![Graph showing linear fits of pseudo first order k-values for UVT increase, or DOC removal, by virgin, fresh, and column-regenerated resins, calculated with experimental equilibrium concentrations.]

The linear fits of the k-values for nitrate removal by virgin and column-regenerated resins are presented in Figure 31. Pseudo second order equation was applied for the k-value calculations since the data did not fit pseudo first order kinetics, as seen in Appendix D: Supplemental Data. Also, it should be noted that the kinetics evaluation of the fresh resin adsorption was not feasible because the experimental data showed desorption, or increased nitrate concentrations, at half of the tested resin concentrations. The overall k-values of 0.0105 L·(g·min\(^{-1}\)) for virgin resin and 0.0082 L·(g·min\(^{-1}\)) for column-regenerated resin confirm the faster adsorption kinetics by virgin resin observed in Section 5.2.2 Nitrate Adsorption.
Figure 31, Linear fits of pseudo second order k-values for nitrate removal by virgin and column-regenerated resins, calculated with theoretical equilibrium concentrations

In conclusion, this investigation of anion adsorption found that the maximum desorption achieved by multiple cycle regeneration with larger regenerant volumes did not improve DOC removal of the fresh resin, as shown by the UVT data and kinetics evaluation. Virgin resin always accomplished most DOC and nitrate removal when compared to fresh and column-regenerated resins. However, the study found that nitrate removal of the column-regenerated resin was higher and also more consistent than that of the fresh resin, most likely improved by the higher degree of desorption performed during regeneration. There are many other factors that affect DOC and nitrate adsorption kinetics and were not included in the scope, such as other constituents in the water matrix like sulfate and bicarbonate. However, the results of this study still demonstrate that inefficient regeneration can compromise nitrate removal, but not necessarily DOC removal.
5.3 Chloride Demand

In this section, the relationship between the salt concentration and regeneration capabilities of the current resin was analyzed. The monitored parameters included chloride, DOC, nitrate, sulfate, and bicarbonate. The results allowed quantification of chloride adsorption and corresponding desorption of the anion constituents and thus, evaluation of chloride efficiency of regeneration at the tested salt concentration.

5.3.1 Anion Sorption

A range of salt concentrations from 9.68 to 192.8 g-Cl⁻/L, in ~10 g-Cl⁻/L increments, was tested to regenerate one bed volume (~750 mL) of spent resins sampled from the current SIX® pilot system over a 30 minute contact time. Figure 32 shows the concentrations of chloride adsorbed onto the resins over the different initial salt concentrations, both in terms of grams of chloride per liter. The concentrations of chloride adsorbed \( (C_{\text{adsorbed}}) \) were calculated by the equation explained in the previous chapter:

\[
(C_o \times DF_{ads}) - C_f = \frac{q}{L} = C_{\text{adsorbed}}
\]

Where \( C_o \) is the initial chloride concentration of the virgin regenerant, \( C_f \) is the final chloride concentration of the spent regenerant, and \( C_{\text{adsorbed}} \) is the concentration adsorbed on the resin. Dilution factor for chloride adsorption (\( DF_{Cl} \)) of 0.824 was applied to account for the moisture of the hydrated resin, and this dilution factor was measured for this column set-up and is consistent with the one used by a previous study (Friend-Gray 2009). See Appendix D: Supplemental Data for the dilution factor calculation and comparison.

The graph also includes the corresponding resin exchange capacity, expressed in grams of chloride per milliliter of resin and calculated by the equation:
\[ \frac{C_{\text{adsorbed}} \times V_{\text{o,regen}}}{V_{\text{Resin}}} = \frac{mg}{L} \times \frac{L}{mL} = \frac{mg}{mL} = \text{Exchange Capacity} \]

Where \( C_{\text{adsorbed}} \) is the calculated concentration adsorbed on the resin, \( V_{\text{o,regen}} \) is the initial volume of the virgin regenerant, 1000 mL, and \( V_{\text{Resin}} \) is the gross volume of the regenerated resin, which was 750 mL in all experiments.

Figure 32 plots concentrations of chloride adsorbed on the left axis versus initial chloride concentration used for regeneration. The right axis represents the resin exchange capacity, which was calculated with the adsorption data (left axis) and volume of resin used for the regeneration runs. The results show that higher initial salt concentration in the virgin regenerant leads to higher chloride adsorption during regeneration. Over the tested concentration range, neither a linear fit of the data nor an exponential relationship results in a strong correlation coefficient (R²), but both do show the general trend. The scatter in the data may have been caused by the seasonal variation that was concluded to play an important role in anion desorption in the next section or potential errors from making dilutions of the samples, which was necessary for the chloride analysis.
Figure 32. Concentrations of chloride adsorbed after 30 minute contact time over a range of initial chloride concentration in the virgin regenerant and the corresponding resin exchange capacity calculated (L/S ratio = 1.33)

The data for desorption of DOC, nitrate, sulfate, and bicarbonate corresponding to these results of chloride adsorption are presented in Figure 33
Figure 33 and Figure 34 expressed in terms of grams of constituents per liter of regenerant solution. For these desorbed concentrations, volumetric dilution factors were applied to account
for the change in the regenerant volume before and after the regeneration. Therefore, the total desorbed concentration and the dilution factors were calculated by the equations:

\[
(C_f \times DF_{des}) - C_o = \frac{\Delta V}{L} = C_{desorbed}
\]

Where \(C_o\) is the initial anion concentration of the virgin regenerant, which was assumed to be zero for all anions except bicarbonate, \(C_f\) is the final anion concentration in the spent regenerant, \(DF_{des}\) is the dilution factor for anion desorption, and \(C_{desorbed}\) is the concentration desorbed off the resin.

\[
DF_{des} = \frac{V_{f, regen}}{V_{o, regen}}; \quad V_i = 1000 \text{ mL}
\]

Where \(V_{f, regen}\) is the final volume of the spent regenerant, and \(V_{o, regen}\) is the initial volume of the virgin regenerant and was prepared to be 1000 mL for every experiment. In this section, desorption dilution factors ranged from 1 to 1.072.

The results are separated into three groups by the date of the experiments, as explained in Table 6. This categorization was done to alienate the seasonal variation of the influent water characteristics, which imposed noticeable effects on the desorption curves.

<table>
<thead>
<tr>
<th>Category</th>
<th>Start</th>
<th>End</th>
</tr>
</thead>
<tbody>
<tr>
<td>Week 1-2</td>
<td>1-31-2014</td>
<td>2-13-2014</td>
</tr>
<tr>
<td>Week 3-4</td>
<td>2-17-2014</td>
<td>2-24-2014</td>
</tr>
<tr>
<td>Week 5-6</td>
<td>3-17-2014</td>
<td>4-1-2014</td>
</tr>
</tbody>
</table>

From Figure 32 to 35, the difference in chloride adsorption and anion desorption can be compared visually. They show that anion desorption does not follow the same relationship as chloride adsorption. For all the four anion constituents monitored, the desorbed amount did not continue to increase with salt strength used. In all the seasonal categories, the decreasing
significance of the role that the initial salt concentration plays in anion desorption is apparent after ~60 g-Cl\(^{-}/L.

Also, DOC, nitrate, and sulfate curves show that the anion desorption increases gradually from winter to spring. Although the desorption curves level off at similar initial salt concentrations, it is clear that the actual amounts of desorbed anions increased over the weeks. This increase was gradual from Week 1-2 to Week 3-4 (from the end of January to the end of February) and became more drastic during Week 5-6 (from mid-March to early April). This demonstrates that desorption is influenced by seasonal variations, which can develop from several sources. The historical SIX® pilot data have observed rapidly increasing concentrations of nitrate and sulfate in the influent water from January to April, which would result in higher nutrient loading on the resin. In addition, the increasing temperature of the influent water can influence the anion loading on the resins for both DOC and nutrients since temperature affects both the hydraulics and kinetics of ion exchange operation.
Figure 33. Concentrations of DOC, nitrate, and sulfate desorbed by different initial chloride concentrations in virgin regenerant, expressed in g/L (contact time = 30 minutes, L/S ratio = 1.33)
Figure 34, Concentrations of bicarbonate desorbed by different initial chloride concentrations in virgin regenerant, expressed in g/L (contact time = 30 minutes, L/S ratio = 1.33)

Figure 35 and Figure 36 represent these same desorption data, but they are expressed in terms of milliequivalents, so a fair comparison of desorbed quantities of the four anion constituents can be made. Also, the data are plotted over the concentrations of chloride adsorbed, not initial chloride concentrations. This helps evaluate how significant the desorbed amounts are in terms of the adsorbed amounts of chloride.
Figure 35. Concentrations of DOC, nitrate, and sulfate desorbed over concentrations of chloride adsorbed, expressed in meq/L (contact time = 30 minutes, L/S ratio = 1.33)
Similar to the findings of Figure 33 and Figure 34, these equivalent data show that higher chloride adsorption does not necessarily equal higher desorption of the anion constituents. For DOC, nitrate, and sulfate, desorption seems to stabilize after ~150 meq-Cl\(^{-}\)/L was adsorbed, which occurred at initial chloride concentrations of 50~60 g/L. In addition, the amount of nitrate desorbed was insignificant when compared to the rest of the anions in equivalent. The nitrate desorption is almost an order of magnitude lower, ranging between 1 and 13 meq/L while DOC, sulfate, and bicarbonate desorption occurred close to or higher than 100 meq/L.

5.3.2 Regenerant Concentration on Desorption Efficiency

The SIX\(^{\circledast}\) pilot system utilizes the regenerant concentration of ~30 g-Cl\(^{-}\)/L to desorb the removed anions and replace them with chloride ions. Therefore, the desorption performance at this chloride concentration should be analyzed to evaluate the regeneration efficiency of the current process.

Figure 37 aims to accomplish this analysis by comparing the total anion desorption efficiencies observed at different initial regenerant concentrations of chloride, or salt. The graph
set the anion desorption achieved by the highest chloride concentration as maximum or 100% desorption, and using this as a benchmark, desorption efficiencies were calculated for lower chloride concentrations. The data used for this analysis were extracted from the results presented in the previous section and obtained from four regeneration column runs, each of which tested one salt concentration and monitored all the five anions involved in sorption. Since seasonal variation was concluded as a contributing factor in anion desorption, comparing data only from the runs that were performed in the same time category ensured eliminating its effects as much as possible. All the runs compared in this analysis were performed in Week 3-4.

![Initial chloride concentrations and desorption efficiencies](image)

*Figure 37. Anion desorption efficiencies for different initial chloride concentrations in regenerant*

The results in Figure 37 show that regeneration with 30 g Cl-/L salt solution achieved less than 50% of maximum DOC and nitrate desorption. Their desorption efficiencies increased gradually with higher chloride concentration, but a considerably different trend is observed with sulfate and bicarbonate desorption. 78% of total sulfate desorption and 90% of total bicarbonate
desorption were achieved by 30 g Cl/L salt solution, and these represent significantly better performance when compared to DOC and nitrate desorption. These findings are consistent with the results of the evaluation of the current regeneration efficiency with multiple-cycle testing from Section 5.1.2, which found that maximum desorption for DOC and nitrate required more regeneration cycles, or larger volume of regenerant and amount of salt, than for sulfate and bicarbonate. This study can conclude that when compared to sulfate and bicarbonate, to achieve efficient desorption DOC and nitrate require not only larger regenerant volume, but also higher regenerant concentration.

Furthermore, the results from this investigation highlight the critical aspects of the SIX® pilot regeneration process: The current regeneration process with 30 g Cl/L brine is not desorbing the target anionic constituents, DOC and nitrate, efficiently, and this can be contributed by the interferences from sulfate and bicarbonate that are seemingly preferred in desorption. Additionally, the results indicate that due to the inefficient regeneration, significant amounts of DOC and nitrate are getting built up on the resin surface. The effects of this anionic accumulation on removal performance were investigated in Section 5.2.

5.3.3 Anion Equivalent Balance

Some of the desorption data from Figure 35 and Figure 36 are compiled in Figure 38 to compare the equivalent contributions of the four anions to total desorption in terms of percentage. The data are plotted over the initial chloride concentrations used for regeneration. Since bicarbonate was not measured for all the experiments, only the data sets with all four anion concentrations recorded were used for this analysis. First, Figure 38 reiterates the previous findings from Section 5.1 on the distribution of anion desorption: In comparison, largest
equivalent desorption takes place with DOC and sulfate while nitrate equivalent desorption is insignificant. However, more importantly, Figure 38 shows that the percent contributions of the four anions are relatively constant regardless of the salt concentration and total desorption amount. The data cover initial chloride concentrations from 29.9 to 188 g/L, and total desorbed equivalents range from 204 to 561 meq/L. Yet the percent desorption values of the target anions, DOC and nitrate, remain at ~40% throughout the salt concentration ranges.

**Figure 38, Percent contributions of the four anions (nitrate, DOC, sulfate, bicarbonate) to total desorption compared in equivalent**

Figure 39 plots both the desorbed anion concentrations from Figure 37 and the corresponding concentrations of adsorbed chloride, both in terms of meq/L, over the tested initial salt concentration range. Blue bars show the adsorbed chloride concentrations while red bars represent the summed concentrations of the four anions (nitrate + DOC + sulfate + bicarbonate) desorbed. Theoretically, the concentration of four anion constituents desorbed during regeneration should equal the concentration of chloride ions adsorbed, when compared in the molar equivalents, as explained in Chapter 5.1.3. Thus, data were analyzed for this equivalent
balance check, but they were only from the experiments that met the following two conditions: The experiments were carried out in the same time category; and bicarbonate levels were measured to account for all the four desorbed anion constituents. 

![Graph showing comparison between chloride adsorbed and all anions (DOC, nitrate, sulfate and bicarbonate) desorbed in meq/L over initial chloride concentrations (Sulfate valence electron number = 2 for all salt concentrations).](image)

Figure 39. Comparison between concentrations of chloride adsorbed and all anions (DOC, nitrate, sulfate and bicarbonate) desorbed in meq/L, over the initial chloride concentrations (Sulfate valence electron number = 2 for all salt concentrations)

The results show that overall equivalent balance between adsorption and desorption is achieved at the initial chloride concentrations of 59.1 and 156.4 g/L. Theoretically, the number of total anionic equivalents desorbed by chloride ions during regenerant should equal the number of chloride equivalents adsorbed on the resin from the regenerant solution. However, at lower initial concentrations, the magnitude of anion desorption was higher than that of chloride adsorption, indicating that the chloride efficiency was high with more equivalents desorbed than adsorbed. Meanwhile the opposite was observed at high initial salt concentrations as gaps were created by a higher number of equivalents in chloride adsorption than in anion desorption, indicating some degree of chloride losses.
These results indicate that the chloride efficiency in desorption generally decreased with increasing salt concentration, as more anion equivalents than expected were desorbed at lower salt concentrations. This unanticipated phenomenon can be linked to the number of valence electrons used for the equivalent calculations. For example, in all equivalent calculations, the valence electron number of 2 was used for sulfate from its negative charge of two. Sulfate ions are assumed to adsorb to the resin surface with its two electrons available for chemical bonding. This divalent property makes sulfate ions more preferred by anion resins than monovalent ions such as nitrate and bicarbonate. However, previous research performed stoichiometry experiments to verify this value in the Andijk water matrix and found the selectivity coefficient of 1.33 for sulfate, which is much lower than expected (Roakes 2013). This finding indicates that some sulfate ions are adsorbed on the resin surface with only one of the available two electrons, reducing the average coefficient value from 2 down to closer to 1.

This partially explains the higher desorption efficiencies at lower salt concentrations since the sulfate ions bonded with only one electron are easier to desorb. At higher salt concentrations, this desorption efficiency is expected to decrease for many possible reasons. Since sulfate ions may stay adsorbed with only one bond, this indicates that one chloride ion can be exchanged to break only one of the two bonds, thus failing to completely desorb the sulfate ion as the second bond remains. This means that some chloride ions are taken up by exchange sites without necessarily desorbing any anions.

The same theory of chloride losses could apply to other surface active groups present on fresh resin, such as DOC (calculated selectivity coefficient in Andijk water matrix = 1.97) and carboxylic and hydroxylic compounds. Literature suggests that equilibrium constants for inorganic ions during ion exchange reactions do not vary significantly with solution conditions,
but equilibrium constants for organic ions have been reported to change with conditions such as resin loading (Crittenden, et al. 2005). Especially for DOC, the results from Section 5.1.3 Anion Sorption in Equivalent showed that some fractions of DOC may be less preferred and thus have different equivalent factors. This means that the DOC fraction that is more difficult to desorb and requires higher regenerant volume or concentration has higher equivalent factors (>>1.97).

Other resin characteristics that should be discussed for DOC desorption include resin porosity and the type of diffusion that may be happening during regeneration. The current SIX resin is a gel type resin that exhibits microporosity, allowing ion exchange to take place deeper in the resin than the surface. In addition, two types of diffusion should be considered in the ion exchange process. The first is called film diffusion, which describes movement of ions from a surrounding solution to the surface of an ion exchange particle. The second is internal or pore diffusion that represents the ion movement from the surface to the interior of an ion exchange particle. It has been found that in dilute solutions, film diffusion is usually the controlling reaction in ion exchange while in more concentrated solutions, such as spent regenerant with high concentrations of competing anions, internal diffusion is controlling (Reichenberg 1953). Internal diffusion of DOC that typically consists of complex structures with carbon chains may be a contributing factor in its varying chloride demand and difficulty in desorption.

It is important to recognize the potential influences of pH on both adsorption and desorption of ion exchange. The phenomena with the changing selectivity coefficients for sulfate and DOC may be a function of pH, which would not be surprising since pH can influence many important variables. For example, pH controls the ratios between sulfuric acid and sulfate in the water, and any presence of sulfuric acid (HSO₄⁻) during treatment would cause adsorption on the resin with one exchange site due to its one negative charge. Charge and
hydrophobic/hydrophilic function of DOC are also dependent on pH, and these characteristics contribute to removal performance, kinetics, and chloride demand during adsorption and desorption. Therefore, it might be worthwhile to investigate how different pH levels affect the desorption efficiencies during regeneration. For example, pH increase can be achieved by addition of sodium hydroxide, another type of regenerant often investigated in studying resin regeneration (Blaney, Cinar and SenGupta 2007) (Nur, et al. 2014).

Since varying selectivity coefficients for non-monovalent anions presented a plausible theory, the same data from Figure 39 were plotted again with different valence electron numbers used for equivalent conversion, and the results are included in Figure 40. The calculations involved the valence number of 1 for initial chloride concentrations under 50 g/L and 2 for higher. 50 g/L was selected because despite continuously increasing chloride adsorption, the desorption curves investigated in previous sections stabilize around this salt concentration, therefore suggesting the beginning of chloride losses. The valence number of 1 is considered as the lowest assumed limit and 2 as the highest assumed limit for the sulfate ion due to its bonding structure. Even with the application of varying valence numbers, the same conclusion is made: the desorption efficiencies of chloride is highest at lower salt concentrations, and chloride losses start to occur as the salt concentration increases.
Figure 40. Comparison between concentrations of chloride adsorbed and all anions (DOC, nitrate, sulfate and bicarbonate) desorbed in meq/L, over the initial chloride concentrations with varying valence numbers

This trend was observed not only in the results in Figure 39 and Figure 40, but also in the data that were excluded, due to the lack of bicarbonate measurements and also different experimental dates. Figure 41 presents all sorption data to show the consistent equivalent imbalance. Although bicarbonate was not measured for every experiment, the average value of the existing bicarbonate data was calculated (82.0 meq/L) and substituted for only the purpose of this analysis. This was a reasonable assumption since as seen in Figure 34 of the bicarbonate desorption curves, bicarbonate data were not significantly influenced by the initial salt concentration or seasonal variation. In addition, the data from Figure 39 and Figure 40 are illustrated by lighter colors for comparison.

Overall Figure 41 is in close agreement with the findings of Figure 39 and Figure 40. High chloride efficiencies are observed at lower salt concentrations as desorption is higher than adsorption. But not all high salt concentration data showed lower equivalent desorption than adsorption as they did in Figure 39 and Figure 40, indicating chloride loses in the rest of the
results were not as significant. However, the same conclusion still remains that chloride efficiency generally decreases with increasing salt concentrations.

Figure 41. Comparison between concentrations of chloride adsorbed and DOC, nitrate, sulfate, and bicarbonate desorbed in meq/L, over the initial chloride concentrations (average value was used when no data were available for bicarbonate). Lighter colors indicate the data also included in Figure 9 and Figure 10.

5.4 Regeneration Sorption Kinetics

In this section, the DOC and sulfate desorption kinetics of the spent resin from the current SIX® pilot system were analyzed. UVT was used as a surrogate parameter for DOC as they are linearly related to each other within a broad range of UVT values, and higher UVT indicates less remaining DOC. The samples for UVT analysis were diluted by the factor of 200 because the DOC concentrations desorbed into brine are typically too high for the UVT analysis range.
The following data were collected in three days. Preliminary desorption investigation took place on 4-25-2014 and 4-30-2014. The first day included a jar test and analyzed DOC desorption (change in UVT) while sulfate desorption was studied on the second day. Chloride adsorption was investigated on both days. Since this preliminary investigation revealed that significant both adsorption and desorption occurred before the shortest contact time tested (6 minutes), a follow-up investigation was performed on 5-19-2014 with shorter contact times to analyze sorption of DOC, sulfate, and chloride. In addition, the follow-up investigation included testing a new salt type, potassium chloride, to observe possible changes in UVT reduction.

5.4.1 DOC Desorption

5.4.1.1 Preliminary Investigation

Figure 42 presents the results from the jar test that regenerated spent resin at six salt concentrations (9.0~162 g-Cl/L), and the UVT data are plotted over time. The samples were diluted by the factor of 200 as the resulting brine from the regeneration experiments were too low for in-house analysis using the Hach machine. The results show that generally higher salt concentrations led to larger UVT reduction and thus more DOC desorption. Continuous UVT reduction was observed throughout the sample times even up to 1,440 minutes at all concentrations except the lowest chloride concentration of 9.0 g/L, which reached a desorption equilibrium quickly as no significant additional UVT reduction was observed after 6 minutes. In addition, UVT reduction improved significantly between the chloride concentrations of 32.0 and 70.0 g/L. It is not surprising that higher salt concentrations generally led to higher DOC desorption, but these findings show that most desorption occurred within the first 6 minutes, establishing equilibrium rather quickly.
The significance of desorption that occurs for the first 6 minutes of contact time is highlighted by Figure 43. Desorption efficiencies at 6 minutes were calculated using the maximum desorption observed at equilibrium (t = 1,440 minutes) and setting it as 100% desorption for each salt concentration. The results reiterate that UVT reduction for the first 6 minutes was substantial ranging from 59 to 97% of maximum desorption. Also, higher UVT reduction was achieved within 6 minutes by increasing salt concentrations. 9.0 g-Cl\(^{-}/L\) is the exception to this trend because essentially no further desorption occurred after 6 minutes, as seen from Figure 42; the UVT values were 97.9% after 6 minutes and 98.0% after 1,440 minutes. Therefore, the data for 6.8 g-Cl\(^{-}/L\) is not compatible for a comparison with the other salt concentrations where desorption equilibrium was achieved at later contact times and recorded by decreasing UVT values.
The same UVT data were plotted over the salt concentrations per sample time to evaluate the effects of salt concentration on DOC desorption, as shown in Figure 44. Not only does this graph show that UVT reduction increased with contact time consistently throughout the salt concentrations, but also that the effects of increasing salt concentrations diminished after $60 \text{ g Cl}^-/\text{L}$. This combination contributes to the shape of the curve that is observed at all contact times. UVT reduction increased almost linearly until $\sim 60 \text{ g Cl}^-/\text{L}$ where all the curves stabilized, indicating DOC desorption was not improved by higher salt concentration after this point. There are only a limited number of exchange sites on the resin surface. Once these sites are taken up by chloride ions that desorb the anion contaminants as much as physically and chemically possible, desorption is slowed down and eventually stopped. This is assumed to take place around $\sim 60 \text{ g Cl}^-/\text{L}$, indicating that there is no additional benefit to increasing the salt level after this concentration. This finding is consistent with the conclusions from the previous column-tests where between 50 and 60 g-Cl\(^-\)/L the desorbed amounts of DOC, nitrate, and sulfate...
stopped increasing when seasonal variations were alienated. In addition, Figure 44 highlights the diminishing returns of increasing contact time on DOC desorption after 6 minutes as most UVT reduction took place within the first 6 minutes.

![Figure 44, Change in UVT over initial chloride concentrations during spent resin regeneration (dilution factor of 200)](image)

5.4.1.2 Follow-up Investigation

Since the preliminary investigation showed that significant desorption took place within the first 6 minutes, this follow-up investigation measured UVT reduction at shorter contact times to obtain clearer and more informative desorption curves. The same experimental procedures were followed, but only three chloride concentrations of 16, 31, and 62 g/L were used for their practicality. In addition, potassium salt was tested under the same conditions to investigate if UVT reduction could be improved by a different salt type.

The results are presented in Figure 45 and demonstrate the decreasing UVT levels more clearly. This run used 2 minutes as the shortest contact time, and although UVT levels continued to decline through 30 minutes, it is evident that substantial DOC desorption was achieved during
those 2 minutes. In addition, it can be seen that the performance of potassium chloride was very similar to that of sodium chloride. Although they are two different forms of salts, both potassium chloride and sodium chloride dissociate to a cation (K$^+$ and Na$^+$) and a chloride ion with one negative charge, thus similarly preferred by the resin for both salts. However, the data with potassium chloride can be perceived as the duplicate set, illustrating that the desorption data were consistent even with another chloride salt form.

![Change in UVT over time](image)

**Figure 45. Change in UVT over time during spent resin regeneration with two types of salt, sodium chloride (NaCl) and potassium chloride (KCl), and three salt concentrations (dilution factor of 200)**

### 5.4.1.3 Desorption Kinetics

The Langergren’s pseudo first and second order equations were applied to describe the kinetics of UVT reduction or DOC desorption that occurred in the preliminary runs. The same analytic procedures from Section 3.3 Kinetics were applied for k-value calculations. Figure 46 shows the results for kinetics analysis of UVT reduction with a pseudo second order equation. The results for pseudo first order kinetics are included in Appendix D: Supplemental Data, and
the comparison between the two equations showed the pseudo second order equation was a better fit for UVT reduction.

Figure 46, Pseudo second order kinetic fits for UVT reduction at all salt concentrations tested from preliminary runs, calculated with experimental equilibrium concentrations.
The kinetics fit results in Figure 46 shows that between 32 and 144 g-Cl/L, second order kinetics describe UVT reduction well with the $R^2$ values ranging between 0.8621 and 0.9699. The linear fits were not as strong at 9.0 g and 162 g Cl/L mainly because as seen by Figure 42, their desorption curves do not show the gradual decrease in UVT as well as the other salt concentrations. Distinct changes in UVT values are needed for accurate statistical analysis of kinetic fits. For example, very little UVT reduction occurred with 9.0 g-Cl/L because this was the lowest salt concentration tested and thus already expected to lead to least desorption. Furthermore, this least desorbed amount was diluted as part of the analytic procedure, which contributed to covering up any change in UVT that may have occurred. But overall, between 32 and 144 g-Cl/L, k-values did not change significantly.

Therefore, since almost no change in desorption was observed at 9.0 g-Cl/L, the k-values calculated at all the salt concentrations except 9.0 g-Cl/L were plotted in Figure 47. Although the $R^2$ value of the k-value for 162 g-Cl/L was low, it was included in Figure 47 since significant removal occurred, and the data points followed a linear trend.

The plotted pseudo second order k-values in Figure 47 show that desorption did not consist of a linear fit that was observed in adsorption (Section 5.2.3). The k-values seem to increase exponentially at salt concentrations higher than 140 g-Cl/L, but it should be noted that the $R^2$ value of this k-value at 140 g-Cl/L is -0.49. This is extremely low, but the k-value was included in Figure 47 as the data points for 140 g-Cl/L in Figure 46 still followed the linear trend unlike those for 9.0 g-Cl/L.
Furthermore, the kinetic analysis of the UVT reduction observed during the follow-up run confirms the pseudo second order fit, as shown in Figure 48. Their k-values were close to the ones calculated from the preliminary runs with high $R^2$ values. Analyses of desorption kinetics are important for determining the performance of the SIX® regeneration system and for the evaluation of different operational variables such as regenerant type or salt concentration. Overall, the kinetics results suggest that the rates of DOC desorption are not drastically different over the range of concentrations from 32 to 144 g-Cl/L while a different type of kinetics other than pseudo second order occurs at the lowest and highest salt concentrations tested.
Figure 48, Pseudo second order kinetic fits for UVT reduction from follow-up run, calculated with experimental equilibrium concentrations

5.4.2 Sulfate Desorption

5.4.2.1 Preliminary Investigation

Figure 49 presents the results from the jar test that regenerated spent resin at six salt concentrations (9.5~169 g-Cl/L), and the sulfate data are plotted over time. The results show that generally higher salt concentrations led to larger sulfate desorption, with the exception of the highest concentration of 169 g-Cl/L. Desorption of this salt concentration was lower than those of the next three lower salt concentrations (141, 94, and 61 g-Cl/L) until 60 minutes. Similar equilibrium trends were observed as the UVT data because most sulfate desorption occurred before 6 minutes. This is more extreme for the lowest salt concentrations (9.5 and 30 g-Cl/L) where the equilibrium state seemed to have been achieved before 6 minutes as the sulfate concentrations never increased throughout the contact time duration. For the rest of the concentrations, their desorption curves are more clear with increasing sulfate concentrations that represent additional desorption taking place.

Regarding the results for 169 g-Cl/L, the unexpected low desorption may have been contributed by analytic issues such as potential errors in making dilutions or procedural issues.
during weighting of the resin that may have led for this particular jar to have more wetter and heavier resins than the rest. Since this was the highest salt concentration tested, another cause could be that salt might not have been fully dissolved into the solution before the experiment was performed. The salt may have finished dissolving completely during the test which would explain the increased desorption at 24 hours. In addition, these data at 169 g-Cl/L could be another representation of the decreasing influence that salt concentration past ~60 g-Cl/L has on sulfate desorption. The sulfate desorption data from Week 5-6 in Section 5.3.1 show that the amount of desorption is especially inconsistent toward high salt concentrations unlike the sulfate data from Week 1-2 and Week 3-4 and the rest of the anionic consistent data that demonstrated clear plateaus.

![Sulfate Desorption Graph](image)

*Figure 49. Change in sulfate over time during spent resin regeneration with different salt concentrations*
The significance of sulfate desorption that occurs for the first six minutes of contact time is highlighted by Figure 50. Desorption efficiencies at 6 minutes were calculated in the same way as DOC desorption efficiencies in Figure 43. The maximum desorption observed at equilibrium (t = 1,440 minutes) was set as 100% desorption for each salt concentration. The results reiterate that sulfate desorption for the first 6 minutes was substantial ranging from 49 to 96% of maximum desorption. However, unlike DOC desorption efficiencies which improved with increasing salt concentrations, Figure 50 shows the opposite. Less percent desorption was achieved by higher salt concentrations. This can be explained by the fact that at higher salt concentrations, desorption equilibrium was achieved later, increasing the difference in desorbed amount between 6 minutes and 1,440 minutes, as seen by Figure 49.

![Percent Desorption at t=6 minutes](image)

*Figure 50. Percent desorption of sulfate achieved after 6 minutes compared to the equilibrium desorption after 1,440 minutes (100% desorption)*

The same sulfate data were plotted over the salt concentrations per sample time to evaluate the effects of salt concentration on sulfate desorption with contact time, as shown in Figure 51. Similar to the findings from Figure 45 that plotted UVT data over initial salt concentrations, the sulfate results also showed that the amount of desorption increased with
contact time, and the effects of increasing salt concentrations diminished between 40 and 60 g-
Cl/L. Both UVT and sulfate analyses show that desorption increased almost linearly until these
turning point concentrations (~60 g-Cl/L from UVT analysis) where all the curves started to
stabilize, indicating desorption was not improved by higher salt concentration after this point.

![Sulfate Desorption over Initial Cl- Concentrations](image)

**Figure 51. Change in sulfate over initial chloride concentrations during spent resin regeneration**

### 5.4.2.2 Follow-up Investigation

Figure 52 presents the data from the follow-up investigation that measured the sulfate
concentrations at shorter contact times to obtain clearer and more informative desorption curves.
These results demonstrate the increasing sulfate levels more gradually than from the preliminary
investigation. Similar to UVT desorption, it is evident that substantial sulfate desorption was
achieved already within the first two minutes. This is especially true for the lower salt
concentrations, 12 and 24 g-Cl as their equilibrium states are reached shortly after 2 minutes. In
addition, the different salt types did not influence desorption performance significantly,
consistent with the UVT results from Chapter 5.4.1.2. The desorbed concentrations were
sometimes slightly higher for sodium chloride samples, but the differences were insignificant.

\[ \text{Figure 52, Change in sulfate over time during spent resin regeneration with two types of salt, sodium chloride (NaCl) and potassium chloride (KCl), and three salt concentrations} \]

5.4.2.3 Desorption Kinetics

The Langergren’s pseudo first and second order equations were applied to describe the
kinetics of sulfate desorption from the preliminary runs. The same analytic procedures from
Chapter 3.3 Kinetics were applied for k-value calculations. Figure 53 shows the results for
kinetics analysis of sulfate desorption with a pseudo second order equation. The results for
pseudo first order kinetics are included in Appendix D: Supplemental Data, and the comparison
between the two equations showed that the pseudo second order equation was a better fit for
sulfate desorption.
Figure 53, Pseudo second order kinetic fits for sulfate desorption at all salt concentrations tested from preliminary runs, calculated with theoretical equilibrium concentrations

The kinetics fit results in Figure 53 shows that between 61 and 169 g-Cl\(^-\)/L, second order kinetics describe sulfate desorption well with the \(R^2\) values ranging between 0.8904 and 0.9853. The linear fits were weak at 9.5 g and 30 g Cl\(^-\)/L with their k-values and \(R^2\) values being much lower. Figure 54 shows the exponential fit of the absolute k-values calculated from Figure 53.
With UVT data, since the initial value was 100% and decreased over time during regeneration, the resulting k-value at each regenerant concentration was positive. However, with sulfate data, the initial value was 0 g/L as no sulfate was present in virgin salt regenerant, and this value only increased as sulfate ions desorbed into the regenerant solution. This resulted in negative k-values, and therefore use of their absolute values was necessary in order to fit the exponential equation, which is not possible with negative k-values.

This means that the highest absolute value in Figure 54 is translated to the lowest k-value, but the y-axis of the graph was reversed so the data points are plotted in the same way that they would with raw k-value data points. The k-values of 9.5 and 30 g-Cl⁻/L were excluded in this analysis due to their negative R² values and non-linear trends. Figure 53 shows that the k-values of sulfate desorption fit an exponential equation with the R² value of 0.7912. The k-values exponentially increased at much lower concentrations (~30 g-Cl⁻/L) unlike DOC desorption which exponentially increased at high salt concentrations.

![Figure 54, Exponential fit of absolute pseudo second order k-values for sulfate desorption during preliminary run of Lewatit VPOC jar-test regeneration](image-url)
Furthermore, the kinetic analysis of sulfate desorption observed during the follow-up run confirms the pseudo second order fit, as shown in Figure 55. Their k-values were close to the ones calculated from the preliminary runs with high $R^2$ values, and the absolute k-values also fit an exponential equation well even with a higher $R^2$ value. The exponential fit is presented in Figure 56.

![Figure 55](image1.png)

*Figure 55, Pseudo second order kinetic fits for sulfate desorption from follow-up run, calculated with theoretical equilibrium concentrations*

![Figure 56](image2.png)

*Figure 56, Exponential fit of absolute pseudo second order k-values for sulfate desorption during follow-up run of Lewatit VPOC jar-test regeneration*

Overall the results from this study showed that the rate of sulfate desorption increase at lower salt concentrations. This study also demonstrated that the kinetics analysis for desorption
during regeneration is more challenging than for adsorption during treatment. Lagergren’s first and second order equations were chosen to fit the desorption data as they describe ion exchange removal well, especially with the SIX® pilot data. In addition, there has been no previous study that attempted to describe the kinetics of desorption during ion exchange regeneration. However, the changes that the tested water matrices go through during treatment and regeneration are vastly different in terms of the magnitude and rate of change. During the jar test for nitrate removal in Section 5.2.2 Nitrate Adsorption, the initial nitrate concentration was 8 mg/L with the effluent concentration being 3~6 mg/L (Figure 27). This equals to 2~5 mg/L of nitrate removal in 30 minutes. Compared to this small concentration change in the water matrix, the total desorbed concentrations of nitrate in regenerant solution that started at 0 mg/L of nitrate ranged from 100 to 800 mg/L after 30 minutes of regeneration (Figure 33). It is important to note that the magnitude of DOC and sulfate concentration change in the regenerant solution before and after the regeneration cycle was much larger. In conclusion, these rapidly increasing concentrations of the competing ions play a significant role in the kinetics of desorption of one constituent during regeneration, making it more challenging to calculate desorption k-values than adsorption k-values during treatment.

5.4.3 Chloride Adsorption

5.4.3.1 Preliminary Investigation

In addition to DOC and sulfate desorption, chloride adsorption was also monitored over time, and Figure 57 shows the results from both preliminary runs. Similar to the desorption curves, Figure 57 also shows that significant chloride adsorption occurred within the first 6 minutes. The degree of adsorption accomplished within the first 6 minutes is larger for higher
salt concentrations. However, all chloride concentrations reached the equilibrium state shortly after 6 minutes, generally before 18 minutes of contact time. This is consistent with the DOC and sulfate desorption data where significant desorption took place in 6 minutes.

\[\text{Figure 57, Chloride adsorption achieved by a range of salt concentrations}\]
The data for some of the higher chloride concentrations (70, 89, 144 and 169 g-Cl\(^{-}/L\)) have some degree of noise around 12 minutes. This could have been caused by the increasing dilutions applied for higher concentrations. Since the analytic range for chloride only measured up to 1000 mg/L, or 1 g/L, the dilution factors presented in Table 7 were applied. The samples from 70 to 169 g-Cl\(^{-}/L\) runs that had slight noise in data were much more diluted than those from 9.5 to 32 g-Cl\(^{-}/L\) with much smoother curves. Although most curves in Figure 57 are satisfactory in providing insight on desorption equilibrium, they shows that inconsistencies associated with making dilutions for sample analysis can affect the accuracy of sorption results.

<table>
<thead>
<tr>
<th>Initial Concentration (g-Cl(^{-}/L))</th>
<th>9.5 &amp; 9</th>
<th>30 &amp; 32</th>
<th>70 &amp; 61</th>
<th>89 &amp; 94</th>
<th>144 &amp; 141</th>
<th>162 &amp; 169</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution Factors</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

5.4.3.2 Follow-up Investigation

Figure 58 presents the data from the follow-up investigation that measured the chloride concentrations at shorter contact times to obtain clearer and more informative adsorption curves. These results demonstrate the decreasing chloride levels more gradually than from the preliminary investigation. For the salt concentrations of 16 g-Cl\(^{-}/L\), the equilibrium state seems to have been attained almost directly after 2 minutes. This suggests that most of the needed chloride adsorption for regeneration occurred within several minutes, which is a compatible conclusion to the previous sulfate and DOC desorption results. For 62 and 63 g-Cl\(^{-}/L\), a higher degree of adsorption was achieved, but at all concentrations it took only ~5 minutes to reach equilibrium. It should be noted that this is much shorter than the current regeneration time of 30 minutes in the SIX\(^{\text{®}}\) pilot system. Moreover, these results show that the different salt types of
sodium chloride and potassium chloride did not affect either desorption or adsorption of the anions.

![Figure 58](image)

*Figure 58. Chloride adsorption achieved by a range of chloride concentrations with two types of salt, sodium chloride (NaCl) and potassium chloride (KCl), and three salt concentrations.*

5.5 Hardness Adsorption

The following hardness data were collected in a series of three experiments to evaluate Lewatit K 1131 S cation exchange resin. The first two experiments investigated the un-rinsed virgin resin’s capability of hardness removal from the Andijk water matrix. However, this un-rinsed virgin resin in hydrogen form is not suitable for use in full-scale application because adsorption of hydrogen ions can lead to a significant pH change in the water. Therefore, the virgin resin was rinsed with sodium chloride solution to be put in sodium form. This rinsed resin was used for the third experiment to confirm hardness removal to provide a more accurate measure of calcium and magnesium reduction. This follow-up investigation aimed to also conclude the required resin concentration and contact time for the next section on regeneration.
evaluation. The initial hardness concentrations in the tested water are listed in Table 8, demonstrating that the initial water qualities were similar for the three experiments.

Table 8, Initial hardness concentrations in the tested SIX® water matrix

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Preliminary (H+)</th>
<th>Follow-Up (Na+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+} (mg/L)</td>
<td>45.5</td>
<td>43.5</td>
</tr>
<tr>
<td>Mg^{2+} (mg/L)</td>
<td>7.86</td>
<td>11</td>
</tr>
<tr>
<td>Total Hardness (mmol/L CaCO_3)</td>
<td>1.46</td>
<td>1.5</td>
</tr>
<tr>
<td>Total Hardness (mg/L CaCO_3)</td>
<td>146</td>
<td>150</td>
</tr>
</tbody>
</table>

5.5.1 Preliminary Investigation – Virgin Lewatit K 1131 S

The average hardness results from the two experiments are plotted over time for the tested resin concentrations in Figure 59. The hardness concentration measured after each contact time interval is expressed in terms of millimoles of calcium carbonate (CaCO_3) per liter of the tested water matrix (mmol/L) using the right axis. The left axis is used to demonstrate the corresponding percent reduction of hardness from the average initial concentration of 1.48 mmol/L (1.46 mmol/L for the first run and 1.5 mmol/L for second run). Figure 60 shows the corresponding percent removals of calcium and magnesium to provide more insight into total hardness removal. Generally, longer contact time and higher resin concentration led to lower hardness concentration and thus, higher total hardness removal.

The magnesium data are fairly noisy with the data points not showing consistent trends as calcium data do and also their larger standard deviation error bars. This noise can be explained by two different reasons. First, the initial magnesium concentration (11 mg/L maximum) is much lower than the initial calcium concentration (45.5 mg/L maximum). Therefore, the same change in concentration is converted to be much larger percent change for magnesium than calcium (i.e. a change of 1 mg/L in concentration equals 9% and 2% change in percent removal for magnesium and calcium, respectively, using maximum initial values). In addition, the Hach
The cuvette test that was used for hardness analysis is not as accurate with magnesium measurements. The test calculates the magnesium concentration by subtracting the calcium concentration from the total hardness measurement. This lack of actually measuring the magnesium concentration leaves room for error. The manual for this hardness test kit actually recommends using another test kit specifically designed for magnesium analysis at low magnesium concentrations and high calcium levels.

Figure 59. Preliminary investigation with Lewatit K 1131 S in hydrogen form - total hardness concentrations expressed in mmol/L as CaCO3 on the right axis and the corresponding percent removal on the left axis.
Figure 60, Preliminary investigation with Lewatit K 1131 S in hydrogen form - percent removal of calcium and magnesium

Although the current chemical softening accomplishes hardness reduction of 40%, or 1 mmol/L, the desired percent hardness reduction in these experiments is higher (68%) because the tested water was already softened and had lower initial hardness concentrations. Softened water
was used for this study because the post-softening sampling ports were readily available, and the objective of this experiment included not only evaluating the resin’s general removal capacity, but also comparing it to the previously investigated resins which were tested also with the softened SIX® pilot water. However, using raw Ijssel Lake water before softening is a more representative water matrix for the purpose of scaling up. Since the initial hardness concentration is higher in raw Ijssel Lake water, larger removal is expected as the driving force for ion exchange increases with larger concentration gradient between the resin and aqueous phases. However, the current softening process does not remove magnesium, so the magnesium level in this water was the same as in the full-scale even though its interaction with calcium concentrations during adsorption is important. Therefore, due to the use of the post-softening water, the required 1 mmol/L of hardness removal equals ~68% of total reduction in this study at the given initial concentrations.

Figure 61 presents the same hardness results, but they are expressed in the concentrations of total hardness removed in the unit of mmol/L as CaCO₃, calculated for each sample time by different resin concentrations. The target removal is highlighted by a horizontal red line to denote the parameter combinations that perform equivalently or better than 1 mmol/L adsorption and thus are compatible to the current performance of the chemical softening process.

First, the results show that at all resin concentrations, fastest adsorption is observed at shortest contact times, and it slows down over time. Also, Figure 61 demonstrates that the resin concentrations of 4 and 6 g/L are impractical because the target removal was never accomplished even after 30 minutes. However, there were still a reasonable number of parameter combinations that achieved the required hardness removal (after 8 minutes for 20 g/L; after 12 minutes for 16 and 12 g/L; and after 20 minutes for 8 g/L). Therefore, this preliminary study can conclude
that Lewatit K 1131 S cation exchange resin was suited for hardness removal at practical resin concentrations and contact times in Andijk water matrix and thus deserved further investigation.

Figure 61, Preliminary investigation with Lewatit K 1131 S in hydrogen form - total hardness removal in mmol/L as CaCO3

5.5.2  Follow-up Investigation – Rinsed Lewatit K 1131 S

Lewatit K 1131 S had to be further analyzed since the resin was initially supplied in hydrogen form and thus must be tested in sodium form since the SIX® regenerant solution is comprised of sodium chloride. The resin rinsed by a highly concentrated sodium chloride solution (~100 g-NaCl/L) underwent the same adsorption test as the preliminary investigation. The resin was tested at concentrations of 8, 12 and 16 g/L since these concentrations were considered most practical from the preliminary results.

Figure 62 shows the hardness removal achieved in mmol/L and also percent reduction while Figure 63 plots the percent calcium and magnesium reduction. The data point for 8 g/L
Resin concentration at 2 minutes in Figure 62 is higher than expected as the removal at this concentration should be lower than at 12 and 16 g/L. Specifically, the magnesium data are noisy at 8 g/L in Figure 63, so this may have been caused by an analytic issue with the test kit. Overall, equivalent total hardness removal was achieved by the resin in sodium form, compared to the results observed in the preliminary investigation with the resin in hydrogen form.

Figure 62. Follow-up investigation with Lewatit K 1131 S in sodium form - total hardness concentrations expressed in mmol/L as CaCO3 on the right axis and the corresponding percent removal on the left axis.
Consequently, it is not surprising that Figure 64 also presents total hardness removal consistent to the data in Figure 61. Hardness reduction of close to or higher than 1 mmol/L was observed after 12 minutes with 12 and 16 g/L of resin concentrations. It is difficult to conclude with 8 g/L since the target removal could have been met anytime between 12 minutes and 30 minutes depending on where the adsorption curve started to stabilize. Regardless, it is determined that 1 mmol/L removal is achieved by 8 g/L resin concentration before 30 minutes,
which is consistent with the results from the resin in hydrogen form in Figure 61 where 1 mmol/L removal was met shortly after 20 minutes at the same resin concentration.

![Graph showing hardness removal vs contact time for different resin concentrations.]

Figure 64, Follow-up investigation with Lewatit K 1131 S in sodium form - total hardness removal in mmol/L as CaCO3

Overall, this set of investigations concluded that Lewatit K 1131 S is a suitable option for hardness reduction in Andijk water matrix. Equivalent removals to chemical softening’s performance were observed both in the resin’s initial hydrogen form and in the sodium form. The removal performance in sodium form was compared to the two resin types in Figure 66 that were tested by previous research (Roakes 2013). This comparison shows poorer performance by Lewatit 1131 S which suggests that further research and more detailed comparisons are needed. Since, Lewatit 1131 S met the required hardness removal, a regeneration investigation was carried out to further test the resin’s compatibility with the current SIX® system.
Figure 65. Hardness removal comparison between Lewatit 1131 S (resin under evaluation) and Lewatit S 1368 and S 1567 (previously tested resins (Roakes 2013). Cr = resin concentration.
### 5.6 Hardness Desorption

The following hardness data were collected on 6-6-2014 to monitor desorption of calcium and magnesium from preloaded cation exchange resin 1131 S and adsorption of sodium from the regenerant solution.

#### 5.6.1 Hardness Desorption

Regenerability of the resin can be analyzed by calculating how much of hardness that was adsorbed onto the resin was able to desorb into the regenerant. More regenerable resins are capable of higher degrees of desorption during regeneration. Therefore, hardness adsorption that occurred on the tested resin during preloading must be quantified first to evaluate the magnitude of desorption. The hardness adsorption onto the resin during preloading was calculated using the following equation:

\[
\frac{C_0 - C_{\text{final}}}{C_{\text{resin}}} = \frac{mg}{L} - \frac{mg}{mL} = \frac{mg}{mL} = C_{\text{adsorbed}}
\]

Where \(C_0\) is initial concentration of the water that undergoes hardness removal, \(C_{\text{final}}\) is the final concentration of the water after hardness removal, \(C_{\text{resin}}\) is the resin concentration in the water being treated, and \(C_{\text{adsorbed}}\) is the mass of constituent adsorbed per volume of resin. As a result, the following pre-loaded hardness concentrations were calculated:

| Table 9. Preloaded concentrations of hardness on Lewatit 1131 S for desorption study |
|--------------------------|----------|--------------------------|
| Total Hardness           | 7.807    | mg/mL as CaCO\(_3\)     |
| Ca\(^{2+}\)              | 1.950    | mg Ca\(^{2+}\)/mL resin |
| Mg\(^{2+}\)              | 0.711    | mg Mg\(^{2+}\)/mL resin |
Similarly, the hardness desorption off the resin during regeneration was calculated using the following equation:

\[
\frac{(C_{\text{final}} - C_0) \cdot V_{\text{regen}}}{V_{\text{resin}}} = \frac{(\frac{mg}{L} - \frac{mg}{L}) \cdot L}{mL} = \frac{mg}{mL} = C_{\text{desorbed}}
\]

Where \( C_0 \) is initial concentration in the regenerant, \( C_{\text{final}} \) is the final concentration of the regenerant, \( V_{\text{regen}} \) is the volume of the regenerant used, \( V_{\text{resin}} \) is the volume of resin regenerated, and \( C_{\text{desorbed}} \) is the mass of constituent desorbed per volume of resin.

These preloaded or adsorbed concentrations and desorbed concentrations were used to calculate the percentage desorption values from the hardness data of the jar-test regeneration experiment. The results of these percent desorption values for total hardness, calcium, and magnesium are shown in Figure 66. Higher salt concentration led to higher percent desorption of total hardness, calcium and magnesium ranging between 26–65%. In addition, similar to the desorption results from the anion investigations, these hardness data also showed that desorption involves fast kinetics. Most desorption occurred within minutes, and equilibrium was reached before 10 minutes for all salt concentrations.
Figure 66. Percent desorption of total hardness (up), calcium (bottom left) and magnesium (bottom right) over a range of regenerant concentrations (g-Cl\textsuperscript{-}/L).

However, this desorption performance must be compared to the data obtained with the previously tested resins to evaluate if 1131 S is a better resin choice for regeneration with sodium chloride. This comparison is demonstrated in Figure 67 and shows that 1131 S achieved comparable calcium desorption but poorer magnesium desorption. It should be noted that unlike the magnesium data from the adsorption tests, the samples from these desorption experiments
were analyzed by HWL, which significantly improved the quality of the magnesium data, making this desorption comparison more reliable. However, the fact that the resin is initially in hydrogen form puts 1131 S at a disadvantage with S 1567 and 1368 that come in sodium form. During the hardness loading procedure with the virgin 1131 S resin mixing in SIX® influent water, a significant change in pH (down to negative values) was observed in the water due to the adsorption of the hydrogen ions. Changes in pH like this would not be desirable on pilot or full-scale operation.

Therefore, overall, it can be concluded that 1131 S is not as regenerable as the other two resins, but it is important to note that 1131 S’s poor magnesium desorption occurred at relatively high salt concentrations (>100 g-NaCl/L). Up to 100 g-NaCl/L, which equals 55 g-Cl⁻/L, 1131 S’s both magnesium and calcium desorption performances were similar to S 1567 and 1368. If 1131 S is to be considered for pilot or full-scale testing, further study should be carried out past these preliminary experiments.

![Figure 67. Percent desorption of calcium and magnesium by the previously tested resins (S 1567 and 1368) and resin under evaluation in this study (1131 S)](image-url)
5.6.2 Sodium Adsorption

Changing levels of sodium corresponding to the hardness desorption results are presented in Figure 68. The data show that generally increasing salt concentrations led to higher sodium adsorption. In addition, similar to the chloride adsorption that was observed in the anion exchange investigation, adsorption equilibrium was reached quickly. Sodium concentrations stopped declining before 10 minutes indicating that most adsorption occurred within minutes. Again these data reiterate that equilibrium is reached quickly during regeneration both in adsorption and desorption.

![Figure 68, Corresponding sodium concentrations to hardness desorption in Section 5.6.1](image_url)

*Figure 68, Corresponding sodium concentrations to hardness desorption in Section 5.6.1 Hardness Desorption*
CHAPTER 6

6 Conclusions and Recommendations

This chapter includes conclusions from the research findings and recommendations to suggest how these findings may be applied and where future research on these topics can be directed. Each of the six research topics is addressed individually.

6.1 Anionic Desorption Efficiency during Regeneration

This research showed that with a given regenerant volume, the current resin desorbs sulfate and bicarbonate more efficiently than DOC and nitrate. This was indicated by the larger volumes of sodium chloride regenerant required for achieving the same desorption efficiency and the especially low desorption efficiencies observed for DOC and nitrate during the first cycle. In comparison, maximum desorption for DOC occurred much later, requiring two and three times more than what the other three constituents needed. The order of the anions requiring from most regenerant volume to least for maximum desorption was: $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{DOC}$.

6.2 Anionic Adsorption Efficiency during Removal

When virgin, fresh, and multiple column-regenerated resins were compared for DOC and nitrate removal, the results shed some light on important effects of the current regeneration system and resin performance. Virgin resin achieved the highest DOC removal, followed by fresh resin and then multiple column-regenerated resin. The same order was also observed in the
kinetics analysis as virgin resin had the fastest kinetics, followed by fresh resin and multiple column-regenerated resin. This indicates that 13 cycles of regeneration with virgin regenerant did not improve the resin’s DOC removal capacity, implying no detrimental effects were caused by the current regeneration regimes. Therefore, it can be concluded that the SIX® regeneration practices under the current pilot conditions are adequate for DOC removal performance.

In the nitrate removal experiments, fresh resin performed significantly worse than virgin and column-regenerated resin. These results show that the pilot plant resin’s nitrate removal capacity has been significantly impacted. Virgin resin accomplished most nitrate removal at all resin concentrations, but multiple column-regenerated resin demonstrated comparable removal performance. This shows that the diminished capacity, represented by the fresh pilot plant resin performance, can be restored by applying a higher degree of regeneration as the removal capacity increased significantly with multiple column-regenerated resin.

6.3 Chloride Demand

When tested over a range of salt concentrations, adsorption results found that chloride uptake by the resin increased with regenerant salt concentration, but desorption of DOC, nitrate, sulfate, and bicarbonate did not follow the same trend. The decreasing significance of the role that the initial salt concentration played in anion desorption was apparent after ~60 g-Cl−/L. In addition, desorption was found to be heavily influenced by seasonal variations. From winter to late spring, the amount of desorption doubled and in some cases even tripled over the weeks, and this increase was most drastic toward the late spring.

Equivalent balance between adsorption and desorption was not achieved at most of the tested and analyzed concentrations. At lower salt concentrations, higher chloride efficiency was
observed as more anion equivalents than expected were desorbed. At higher salt concentrations, the gaps in equivalent balance were not as significant, but chloride loss occurred at some concentrations as equivalent desorption was lower than adsorption. Overall, the data support that chloride efficiency in desorption generally decreases with increasing regenerant concentrations. This phenomenon can be linked to atypical adsorption of sulfate that may bond to the resin with one exchange site instead of the expected two for a divalent ion. This would directly contribute to chloride efficiency during regeneration as desorbing a sulfate ion bonded with one exchange site would increase the efficiency. However, inefficient chloride adsorption is also possible if a chloride equivalent breaks only one of the two bonds, and the sulfate ion remains on the resin with the second bond. Overall the results support that the selectivity coefficient of sulfate can be less than the expected 2 and may change depending on the regeneration condition (e.g. salt concentration). This is also possible for DOC that may require higher number of chloride equivalents for the DOC fractions that are less preferred and more difficult to desorb.

6.4 Regeneration Sorption Kinetics

The kinetics study determined the Lagergren’s pseudo second order equation as a good fit for both DOC and sulfate desorption. Both chloride adsorption and anion desorption involved fast kinetics at all the tested concentrations with between 49% and 97% of total desorption being achieved within the first 6 minutes of experiments. During these 6 minutes, higher salt concentration in general led to faster desorption of DOC, but for sulfate, fastest desorption occurred at the lowest concentrations. When tested at the current regenerant concentration of \(~30 \text{ g-Cl}^-/\text{L}\), considered as a “low” concentration, almost all sulfates (95% of total desorption) were desorbed in the first 6 minutes, much before the current SIX® pilot and full-scale plant’s
regeneration contact time (30 minutes). Although most significant DOC desorption (59%) occurred within the first 6 minutes, further regeneration over 30 minutes accomplished significant additional DOC desorption. These results reiterate the finding that sulfate is preferentially desorbed compared to DOC. The equilibrium for sulfate desorption was observed at ~60 g-Cl/L, which is consistent to the previous finding, while this concentration was slightly higher, ~70 g-Cl/L, for DOC desorption.

6.5 Hardness Adsorption

Preliminary research using Lewatit K 1131 S cation exchange resin found it was capable of the necessary hardness reduction in the Andijk water matrix at practical resin concentrations and contact times. Two scenarios that achieved the needed 68% removal while the resin is in sodium form include 12 g/L and 16 g/L of resin concentrations after 12 minutes of contact time. However, comparing these results to the two resin types that were tested by a previous research showed poorer performance demonstrated by Lewatit K 1131 S. Regardless, the resin met the required hardness removal and thus was evaluated further on its regenerability.

6.6 Hardness Desorption

Similar to sorption results with the SIX® anion exchange resin, regeneration of the cation exchange resin demonstrated fast hardness desorption and chloride adsorption. Desorption equilibrium occurred within 10 minutes of contact time in all scenarios. Regeneration with sodium chloride solution desorbed between 26% and 65% of the preloaded hardness over a wide range of regenerant concentrations. When these results were compared to the previously tested resins, Lewatit K 1131 S achieved comparable calcium and magnesium desorption at practical
regenerant concentrations. However, at high salt concentrations, the resin’s desorption performance for magnesium declined and it can be concluded that Lewatit K 1131 S has poorer regenerability. Therefore, a search for more compatible resin alternatives for cation exchange softening must be continued with a focus on regenerability.

6.7 Recommendations

The following recommendations fall under two general topics: anion exchange resin and cation exchange resin.

Anion exchange resin recommendations are:

- Seasonal variation should be further investigated as it was determined as an influential factor in anion desorption. The column experiments of multiple regeneration cycles and the subsequent jar tests to compare the removal capacities may produce different results if they are carried out during a different season other than winter. Also, significantly increased desorption of DOC, nitrate, and sulfate was evident from winter to spring. Thus the relationship between the salt concentration and regeneration capabilities of the current resin should be revisited in summer and fall for a complete picture of the effects of seasonal variation.

- The matrix effect can contribute to creating the seasonal variation and thus the role it plays on desorption selectivity should be examined to shed more light on the ion exchange mechanisms.

- Future efforts should be expended on the factors affecting the selectivity coefficients of non-monovalent ions, including sulfate and DOC. The results from this research support
that the selectivity coefficient of sulfate can be less than the expected 2 for divalent ions and may change depending on the regeneration condition while for some DOC fractions that are more difficult to desorb, it could be significantly higher than 1.97.

- Some degree of permanent resin blinding was observed physically (e.g. failure to restore the original color in all the resins despite maximum desorption being achieved) and indicated by the kinetics results (lower k-values for multiple column-regenerated resin than for virgin resin in both DOC and nitrate removals). This blinding issue must be addressed for the long-term SIX® operation.

- pH is an important parameter in both adsorption and desorption of ion exchange, especially for NOM. Therefore, in future experiments, pH should be more carefully considered and its relationship with desorption efficiencies should be investigated.

Cation exchange resin recommendations are:

- Other cation exchange resins should be investigated. Evaluation of the three cation exchange resins emphasized that the challenge lies in the resin regenerability with sodium chloride.

- Using a magnesium-specific test kit for in-house method or utilizing HWL’s expertise is recommended for magnesium analysis when high levels of calcium and low levels of magnesium are expected (e.g. adsorption or removal test with cation exchange resin).

- In the future experiments, cation exchange resins should be tested with the raw Ijssel Lake water for assessing their hardness reduction capacities. This research used the pilot influent water which had been already chemically softened. Using the raw source water
with higher influent concentrations may have effects on the resin’s removal kinetics and provide more representative results.

Salt use recommendations are:

- Since it was concluded that higher salt concentration (around 60 g-Cl\(^{-}/L\)) during regeneration is very effective with respect to desorption, 60 g-Cl\(^{-}/L\) would be preferred to the current concentration of 30 g-Cl\(^{-}/L\). For economic reasons, this would only be feasible if chloride recovery by means of additional treatment becomes possible, which is a topic of ongoing research at PWN.
7 Bibliography


Friend-Gray, Owen. 2009.


http://books.google.nl/books?id=AtlIBmlc018C&pg=PA102&lpg=PA102&dq=a253/a203&sourc=bl&ots=NKpS1c0aI0&sig=cmL9kHF1OCUX8HoUOejwvAQRWNg&hl=en&sa=X&ei=zsVQYSMCPKb1AWS6oHIcQ&redir_esc=y#v=onepage&q&f=true.


APPENDICES
Lewatit® VP OC 1071 is a strongly basic, gelular anion exchange resin (type I) based on an acrylvinylbenzene copolymer of special bead size distribution. Due to its acryl structure Lewatit® VP OC 1071 stands for effective adsorption and desorption of naturally occurring organic substances. Its very high total capacity and outstanding mechanical stability together with the excellent resistance to cosmic shock makes it unique for all demineralization applications especially if a low silica leakage is required.

Lewatit® VP OC 1071 is especially suitable for:

- demineralization of water for industrial steam generation operated with co-current or modern counter-current systems like e.g. Lewatit® WS System, Lewatit® Litbed System or Lewatit® Rinsebed System
- removing of organic matter, especially from surface water
- lifetime extension of acid baths in the surface finishing industry (acid retardation process)

The special properties of this product can only be fully utilized if the technology and process used correspond to the current state-of-the-art. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

**General Description**

<table>
<thead>
<tr>
<th>Ionic form as shipped</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Functional group</td>
<td>quaternary amine, type I</td>
</tr>
<tr>
<td>Matrix</td>
<td>crosslinked polycrylamide</td>
</tr>
<tr>
<td>Structure</td>
<td>gel type beads</td>
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<tr>
<td>Appearance</td>
<td>white, translucent</td>
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**Physical and Chemical Properties**

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<th>Metric Units</th>
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<tbody>
<tr>
<td>Uniformity Coefficient*</td>
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</tr>
<tr>
<td>Bead size*</td>
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<tr>
<td>Effective size*</td>
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<tr>
<td>Total capacity*</td>
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<tr>
<td>Volume change CI -&gt; OH</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Storability of the product</td>
<td>max. years 2</td>
</tr>
<tr>
<td>Storability temperature range</td>
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* Specification values subjected to continuous monitoring.
Recommended Operating Conditions*

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<tr>
<td>Operating pH-range</td>
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<td>Specific pressure drop (15 °C)</td>
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<tr>
<td>Pressure drop</td>
<td>max. kPa</td>
</tr>
<tr>
<td>Linear velocity operation</td>
<td>max. m/h</td>
</tr>
<tr>
<td>Linear velocity backwash (20 °C)</td>
<td>approx. m/h</td>
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<tr>
<td>Bed expansion (20 °C, per m/h)</td>
<td>approx. vol. %</td>
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<tr>
<td>Freeboard backwash (extern / intern)</td>
<td>vol. %</td>
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<td>Regenerant</td>
<td>NaOH</td>
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<td>Counter current regeneration level</td>
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<tr>
<td>WS-System concentration</td>
<td>approx. wt. %</td>
</tr>
<tr>
<td>Linear velocity regeneration</td>
<td>approx. m/h</td>
</tr>
<tr>
<td>Linear velocity rinsing</td>
<td>approx. m/h</td>
</tr>
<tr>
<td>Rinse water requirement slow / fast</td>
<td>approx. BV</td>
</tr>
<tr>
<td>Co current regeneration level</td>
<td>approx. g/l</td>
</tr>
<tr>
<td>Co current regeneration concentration</td>
<td>approx. wt. %</td>
</tr>
<tr>
<td>Rinse water requirement slow / fast</td>
<td>approx. BV</td>
</tr>
</tbody>
</table>

* The recommended operating conditions refer to the use of the product under normal operating conditions. It is based on tests in pilot plants and data obtained from industrial applications. However, additional data are needed to calculate the resin volumes required for ion exchange units. These data are to be found in our Technical Information Sheets.

Additional Information & Regulations

**Safety precautions**

Strong oxidants, e.g. nitric acid, can cause violent reactions if they come into contact with ion exchange resins.

**Toxicity**

The safety data sheet must be observed. It contains additional data on product description, transport, storage, handling, safety and ecology.

**Disposal**

In the European Community ion exchange resins have to be disposed, according to the European waste nomenclature which can be accessed on the internet-site of the European Union.

**Storage**

It is recommended to store ion exchange resins at temperatures above the freezing point of water under roof in dry conditions without exposure to direct sunlight. If resin should become frozen, it should not be mechanically handled and left to thaw out gradually at ambient temperature. It must be completely thawed before handling or use. No attempt should be made to accelerate the thawing process.

This information and our technical advice – whether verbal, in writing or by way of trials – are given in good faith but without warranty, and this also applies where proprietary rights of third parties are involved. Our advice does not release you from the obligation to check its validity and to test our products as to their suitability for the intended processes and uses. The application, use and processing of our products and the products manufactured by you on the basis of our technical advice are beyond our control and, therefore, entirely your own responsibility. Our products are sold in accordance with the current version of our General Conditions of Sale and Delivery.
**Lewatit® K 1131 S Product Information from Lanxess® (1 of 2)**

Lewatit® K 1131 S is a strongly acidic, gel-type, polymer-based resin in spherical bead form with a very narrow bead size distribution and ideally suited as a heterogeneous catalyst for organic reactions.

It has a low degree of crosslinking, good mechanical stability and gives optimum performance in polar media.

Lewatit® K 1131 S is suitable for the following applications:
- Bisphenol-A production
- Condensation and esterification of small polar molecules
- Hydrolysis of ether and esters

The special properties of this product can only be fully utilized if the technology and process used correspond to the current state-of-the-art. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

### General Description

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### Physical and Chemical Properties

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<td>Total capacity*</td>
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<tr>
<td>Fine beads*</td>
<td>max. vol %</td>
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<tr>
<td>&lt;= 0.42mm</td>
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<tr>
<td>Fine beads*</td>
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<td>5</td>
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<td>&lt;= 0.84mm</td>
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<td></td>
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<tr>
<td>Coarse beads*</td>
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<tr>
<td>&gt; 1.41mm</td>
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<td>Bulk density (± 5 %)</td>
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<td>-20 - 40</td>
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</table>

* Specification values subjected to continuous monitoring.
Additional Information & Regulations

**Safety precautions**
Strong oxidants, e.g. nitric acid, can cause violent reactions if they come into contact with ion exchange resins.

**Toxicity**
The safety data sheet must be observed. It contains additional data on product description, transport, storage, handling, safety and ecology.

**Disposal**
In the European Community ion exchange resins have to be disposed, according to the European waste nomenclature which can be accessed on the internet-site of the European Union.

**Storage**
It is recommended to store ion exchange resins at temperatures above the freezing point of water under roof in dry conditions without exposure to direct sunlight. If resin should become frozen, it should not be mechanically handled and left to thaw out gradually at ambient temperature. It must be completely thawed before handling or use. No attempt should be made to accelerate the thawing process.

This information and our technical advice – whether verbal, in writing or by way of trials – are given in good faith but without warranty, and this also applies where proprietary rights of third parties are involved. Our advice does not release you from the obligation to check its validity and to test our products as to their suitability for the intended processes and uses. The application, use and processing of our products and the products manufactured by you on the basis of our technical advice are beyond our control and, therefore, entirely your own responsibility. Our products are sold in accordance with the current version of our General Conditions of Sale and Delivery.
Sodium Chloride Product Information from Kloek®

Kloek Meadow Salt Natural

> When meadow grass is used for grazing and silage production it is desirable to maintain the sodium (Na) content in grass by means of fertilizer.
> Sodium makes grass tastier. This results in greater grass take-up and grass utilization and this has an effect on the general health of your cattle.
> Providing a good supply of sodium (Na) for dairy cattle is important for, among other things, reducing the salt content in the milk, fertility, controlling the water balance and certain enzyme functions.
> The growth rate and sodium take-up of the grass drop at lower rates of nitrogen fertilizer application. It is important to continue to optimally utilize the grass produced, particularly when grass production is dropping as a result of reduced fertilizer application. [Source: NIM]
> Sodium addition also results in better grazed land.

### CHEMICAL COMPOSITION

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<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Content</th>
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<tr>
<td>Sodium Chloride (NaCl)</td>
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<td>59</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>%</td>
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</tr>
<tr>
<td>Sulfate (SO4)</td>
<td>%</td>
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</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>%</td>
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</table>

* on a dry base

### PARTICLE SIZE DISTRIBUTION AND BULK DENSITY

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<th>Content</th>
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<td>&gt; 3,2 mm</td>
<td>%</td>
<td>&gt; 15</td>
</tr>
<tr>
<td>1,5 – 3,2 mm</td>
<td>%</td>
<td>78</td>
</tr>
<tr>
<td>&lt; 1,5 mm</td>
<td>%</td>
<td>&lt; 7</td>
</tr>
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</table>

* Bulk density Kg/m³

| Differences in particle size distribution in separate samples may occur due to transport and storage.

### PACKAGING UNITS

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<tr>
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<tbody>
<tr>
<td>10265</td>
<td>25 kg</td>
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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>25 kg</td>
<td>7</td>
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<table>
<thead>
<tr>
<th>Layers per pallet</th>
<th>Pieces per layer</th>
<th>Bags per pallet</th>
<th>Grass/net (t) weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>49 bags</td>
<td>7</td>
<td>49 bags</td>
<td>1263 kg / 1225 kg</td>
</tr>
</tbody>
</table>

GMP registration no.
Complementary registration no:
Contains no allergens
Contains no GMOs (genetically modified organisms)

These product specifications may be subject to changes.
Appendix B: In-house Chemical Analysis Procedures

Sulfate Measurement Procedure from Hach® (1 of 3)

**Table 388 Instrument-specific information**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Powder pillows</th>
<th>AccuVac Ampule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample cell</td>
<td>Sample cell</td>
</tr>
<tr>
<td>DR 6000</td>
<td>2495402</td>
<td>2427606</td>
</tr>
<tr>
<td>DR 5000</td>
<td>2495402</td>
<td>2427606</td>
</tr>
<tr>
<td>DR 3900</td>
<td>2495402</td>
<td>2427606</td>
</tr>
<tr>
<td>DR 3800, DR 2800, DR 2700</td>
<td>2495402</td>
<td>2122800</td>
</tr>
</tbody>
</table>

Before starting the test:

1. Adjust the standard curve for each new lot of reagent (Standard solution method).
2. For best results, calibrate the instrument with each new lot of reagent (see Calibration).
3. For best results, measure a reagent blank value for each new lot of reagent (follow the procedure using deionized water in place of the sample). Subtract the reagent blank value from the final results or enter the value as a reagent blank adjust for automatic subtraction.
4. Filter highly colored or turbid samples using filter paper and a funnel. Use this sample in step 2 and 5.
5. The Pour-Thru Cell cannot be used with this procedure.
6. SulfateVer® 4 contains barium chloride. The final solution will contain barium chloride (D005) at a concentration regulated as a hazardous waste by the Federal RCRA. Refer to a current MSDS for safe handling and disposal instructions.
7. Use a blank AccuVac® Ampule in place of the sample cell in Step 5, if necessary.
Sulfate Measurement Procedure from Hach® (2 of 3)

Collect the following items:

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Pillow Test:</td>
<td></td>
</tr>
<tr>
<td>SulfAVer® 4 Reagent Powder P</td>
<td>1</td>
</tr>
<tr>
<td>Sample Cells (see Instrument-</td>
<td>2</td>
</tr>
<tr>
<td>specific information)</td>
<td></td>
</tr>
<tr>
<td>AccuVac Test:</td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>Ampuls</td>
<td></td>
</tr>
<tr>
<td>Beaker, 50-mL</td>
<td>1</td>
</tr>
<tr>
<td>Sample Cells (see Instrument-</td>
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<tr>
<td>specific information)</td>
<td></td>
</tr>
<tr>
<td>Stopper</td>
<td>1</td>
</tr>
</tbody>
</table>

See Consumables and replacement items for reorder information.

SulfAVer 4 powder pillow procedure

1. Select the test. Insert an adapter if required (see Instrument-specific information). Refer to the user manual for orientation.

2. Prepared sample: Fill a sample cell with 10 mL of sample.

3. Add the contents of one SulfAVer 4 Reagent Powder Pillow to the sample cell. Swirl vigorously to dissolve the powder. White turbidity will form if sulfate is present.

4. Start the instrument timer. A five-minute reaction time will begin. Do not disturb the cell during this time. Note: Accuracy is not affected by undissolved powder.

5. Blank preparation: Fill a second sample cell with 10 mL of sample.

6. When the timer expires, wipe the blank and insert it in the cell holder (fill lines face right).

7. ZERO the instrument. The display will show: 0 mg/L SO₄²⁻

8. Within five minutes after the timer expires, wipe the cell and insert the prepared sample in the cell holder. READ the results in mg/L SO₄²⁻. Clean sample cells with soap and a brush.
Sulfate Measurement Procedure from Hach® (3 of 3)

Interferences

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<th>Interfering Substance</th>
<th>Interference Level</th>
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<tr>
<td>Calcium</td>
<td>Greater than 20,000 mg/L as CaCO₃</td>
</tr>
<tr>
<td>Chloride</td>
<td>Greater than 40,000 mg/L as Cl⁻</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Greater than 10,000 mg/L as CaCO₃</td>
</tr>
<tr>
<td>Silica</td>
<td>Greater than 500 mg/L as SiO₂</td>
</tr>
</tbody>
</table>

Sample collection, preservation and storage

Collect samples in clean plastic or glass bottles. Samples may be stored up to 7 days by cooling to 4 °C (39 °F) or lower. Warm to room temperature before analysis.

Method performance

<table>
<thead>
<tr>
<th>Program</th>
<th>Standard</th>
<th>Precision 95% Confidence Limits of Distribution</th>
<th>Sensitivity Concentration change per 0.010 Abs change</th>
</tr>
</thead>
<tbody>
<tr>
<td>660</td>
<td>40 mg/L SO₄²⁻</td>
<td>30–60 mg/L SO₄²⁻</td>
<td>0.4 mg/L SO₄²⁻</td>
</tr>
<tr>
<td>685</td>
<td>40 mg/L SO₄²⁻</td>
<td>32–48 mg/L SO₄²⁻</td>
<td>0.7 mg/L SO₄²⁻</td>
</tr>
</tbody>
</table>

Summary of method

Sulfate ions in the sample react with barium in the Sulfaver 4 and form a precipitate of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. Test results are measured at 450 nm.

Required reagents

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity/Test</th>
<th>Unit</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfaver® 4 Reagent Powder P</td>
<td>1</td>
<td>100/pkg</td>
<td>2100769</td>
</tr>
<tr>
<td>OR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfaver® 4 Sulfate Reagent</td>
<td>1</td>
<td>25/pkg</td>
<td>2509025</td>
</tr>
<tr>
<td>AcuVac® Ampules</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Required apparatus

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
<th>Unit</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcuVac® snapper</td>
<td>1</td>
<td>each</td>
<td>2405200</td>
</tr>
<tr>
<td>Beaker, 50 mL</td>
<td>1</td>
<td>each</td>
<td>50041H</td>
</tr>
<tr>
<td>Sample cell, 10 mL, round, 25 x 54 mm</td>
<td>1</td>
<td>each</td>
<td>2122500</td>
</tr>
<tr>
<td>Sample cell, 10 mL, round, 25 x 60 mm</td>
<td>1</td>
<td>each</td>
<td>2427506</td>
</tr>
<tr>
<td>Sample cell, 10 mL, square, matched pair</td>
<td>2</td>
<td>2/pkg</td>
<td>2495025</td>
</tr>
<tr>
<td>Stopper</td>
<td>1</td>
<td>6/pkg</td>
<td>173106</td>
</tr>
</tbody>
</table>
Nitrate Measurement Procedure from Hach® (3 of 3)
Water Hardness Calcium/Magnesium

Principle
Calcium and magnesium ions react with metal phthalate to give a violet dye.

Range of Application
Flaw and drinking water, surface water, boiler water, process control

Storage Information
The test reagents are stable at +15 to +25°C up to the expiry date given on the package.

Interferences
There are no known interferences when the tests are used with drinking water and boiler water.

For your Information
Calcium and magnesium levels below the measuring range given here (< 1 °dH) can be determined with the Cuvette Test LCK 327 residual hardness.

Special Note
Measurement units of water hardness ('dH):

Definition:
1 degree water hardness, german ('°) = 10 mg CaO/L
1 degree water hardness, french ('°) = 10 mg CaCO₃/L
1 degree water hardness, english ('°) = 14.3 mg CaCO₃/L

Conversion Table

<table>
<thead>
<tr>
<th>mmol/L CaCO₃</th>
<th>°G</th>
<th>°T</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mmol/L CaCO₃</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>°G</td>
<td>1.18</td>
<td>1.00</td>
<td>1.78</td>
</tr>
<tr>
<td>°T</td>
<td>0.10</td>
<td>0.50</td>
<td>1.00</td>
</tr>
<tr>
<td>°C</td>
<td>0.14</td>
<td>0.79</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Application to all types of photometer
Water Hardness Calcium/Magnesium Edition 06/1997

Pipette into the cuvette test
Buffer solution A (LCK 327 A) 4.0 mL
Close cuvette and invert a few times until the freeze-dried contents are dissolved. After 2 min thoroughly clean the outside of the cuvette and evaluate.

Evaluation
Water hardness, calcium and magnesium determination
1. Insert sample cuvette (see procedure).
Display: "CA/MG". (CADAS 20/50, ISIS 9000)
2. Remove sample cuvette.
Into the same cuvette pipette
Water sample 0.2 mL
Close cuvette, invert a few times and thoroughly clean the outside of the cuvette.
3. After 30 sec insert sample cuvette again.
4. Remove sample cuvette.
Into the same cuvette pipette
Masking solution B (LCK 327 B) 0.2 mL
Close cuvette, invert a few times and thoroughly clean the outside of the cuvette.
5. After 30 sec insert sample cuvette again.

Application:
CADAS 30/50, ISIS 9000
The results for calcium/magnesium/hardness can be called up one after another by pressing the key under the display symbol → → → →.
Bicarbonate Measurement and Calculation from Titration

1. Sampled 100 mL of the spend regenerant solution in a clean beaker
2. Placed the beaker on a stir plate with a stir bar inside
3. Adjusted the water flow so the stir bar is spinning and creating a small vortex without splashing
4. Placed a calibrated pH probe in the beaker outside of the vortex and recorded the initial pH of the sample
5. Added drops of sodium hydroxide (25% NaOH) using a pipet to increase the pH of the sample to at least 10.3 and recorded the amount of base added and the new pH of the sample
6. Added a drop of hydrochloric acid (10% HCl) using a titrator. Each drop ranged from 0.03 to 0.3 mL depending on how rapidly the pH level was changing.
7. Waited until the pH stabilized
8. Recorded the new pH and the volume of HCl added to the sample
9. Repeated Step 6 and 7 until ~pH 2 was reached
10. Calculated the total volume of HCl consumed from pH 8.3 to pH 4.5. Interpolation of data may be necessary to account for the exact pH level.
11. Convert this volume of HCl to moles per liter (mol/L) of HCl
12. Assuming 1 mole of HCl reacted with 1 mole of bicarbonate (HCO₃⁻), convert the calculated mol/L from Step 11 to grams per liter (g/L) of HCO₃⁻. This is the concentration of bicarbonate present in the sample.
13. Multiplied the calculated concentration from Step 12 with the following factor of dilution caused by addition of NaOH and HCl:
\[
\text{Dilution factor} = \frac{V_{\text{Sample}} + V_{\text{NaOH}} + V_{\text{HCl}}}{V_{\text{Sample}}}
\]

Example Calculation:

- Initial pH of sample = 7.93; 0.90 mL of 25% NaOH added; New pH = 11.08
- Following data were collected

<table>
<thead>
<tr>
<th>Volume of HCl added</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.846</td>
<td>8.3</td>
</tr>
<tr>
<td>5.95</td>
<td>4.55</td>
</tr>
<tr>
<td>6.004</td>
<td>4.42</td>
</tr>
</tbody>
</table>

- Interpolation for pH 4.5 needed

Appendix C: HWL Certificate
The Dutch Accreditation Council RvA, by law appointed as the national accreditation body for The Netherlands, hereby declares that accreditation has been granted to:

Het Waterlaboratorium N.V.

Haarlem

The organisation has demonstrated to be able to generate technical valid results in a competent way and work according to a management system.

This accreditation is based on an assessment against the requirements as laid down in ISO/IEC 17025:2005.

The accreditation covers the activities as specified in the authorized annex bearing the registration number.

The accreditation is valid provided that the organisation continues to meet the requirements.

The accreditation with registration number:

L 404

is granted on 27 October 2010

This declaration is valid until

1 January 2015

The accreditation has been granted for the first time on

1 January 2003

The Chief Executive

Ir. J.C. van der Poel

Appendix D: Supplemental Data
Linear fits of pseudo first order k-values for nitrate removal by virgin and column-regenerated resins, calculated with theoretical equilibrium concentrations. Pseudo second order was determined as a better fit in Chapter 5.2.3. The kinetics evaluation of the fresh resin adsorption was not feasible because the experimental data showed desorption, or increased nitrate concentrations, at half of the tested resin concentrations.

![Linear Fits Diagram]

\[ y = 0.0179x \quad R^2 = -1.239 \]

\[ y = 0.0039x \quad R^2 = 0.853 \]
Linear fits of pseudo first order k-values for DOC desorption during regeneration of the current SIX resin, calculated with experimental equilibrium concentrations. Pseudo second order was determined as a better fit in Chapter 5.4.1.3.

- **9.0 g Cl-/L**
  - $y = 0$
  - $R^2 = \#N/A$

- **32 g Cl-/L**
  - $y = 0.0685x$
  - $R^2 = 0.6048$

- **70 g Cl-/L**
  - $y = 0.0983x$
  - $R^2 = -2.422$

- **89 g Cl-/L**
  - $y = 0.1176x$
  - $R^2 = -2.119$

- **144 g Cl-/L**
  - $y = 0.1191x$
  - $R^2 = -2.515$

- **162 g Cl-/L**
  - $y = 0.1829x$
  - $R^2 = -47.21$
Linear fits of pseudo first order k-values for sulfate desorption during regeneration of the current SIX resin, calculated with theoretical equilibrium concentrations. Pseudo second order was determined as a better fit in Chapter 5.4.2.3.
Dilution factor calculation and comparison

This section describes the procedure used to determine and validate the dilution factor caused by resin hydration.

The exact regeneration column set-up described in 4.1.3 Regeneration Column was prepared, and the same procedure from 4.2.1 Regeneration Experiment Procedure was followed to repeat column experiments with virgin resin. Using virgin resin ensured that the chloride concentration in the regenerant solution should remain constant throughout the experiments, and any change in this concentration was a result of dilution.

The following table shows the observed initial and final chloride concentration measured before and after column experiment and the dilution factors calculated from the results. The average dilution factor is 0.824.

<table>
<thead>
<tr>
<th>Salt Concentration (Cl-g/L)</th>
<th>Initial (undiluted)</th>
<th>Final (diluted)</th>
<th>Dilution Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100.2</td>
<td>80.2</td>
<td>0.836</td>
</tr>
<tr>
<td></td>
<td>178.3</td>
<td>144.9</td>
<td>0.813</td>
</tr>
</tbody>
</table>

Average Dilution Factor 0.824

In addition, a previous study found that 1,000 mL of hydrated resin consisted of 275 mL of water (Friend-Gray 2009). Using this ratio (multiplier of 0.275), a bed volume of 750 mL of hydrated resin consists of 206.3 mL of water (0.275 × 750 mL = 206.3 mL).

During each column experiment, one bed volume of 750 mL of hydrated resin was regenerated with 1,000 mL of virgin sodium chloride solution. The total liquid volume then must include this initial virgin regenerant volume (1,000 mL) and the hydrated portion on the resin (206.3 mL). Therefore, the total liquid volume involved in a column experiment sums to 1,206.3 mL.

The dilution factor is calculated as:

\[
Dilution \ Factor = \frac{V_o}{V_f} = \frac{1,000 \ mL}{1,206.3 \ mL} = 0.829
\]

This calculated dilution factor of 0.829 is very close to the observed dilution factor of 0.824. The observed dilution factor of 0.824 was applied to adjust the concentration of chloride adsorbed on the resin.