Recovery of magnesium from RO concentrate for struvite production

Master Thesis

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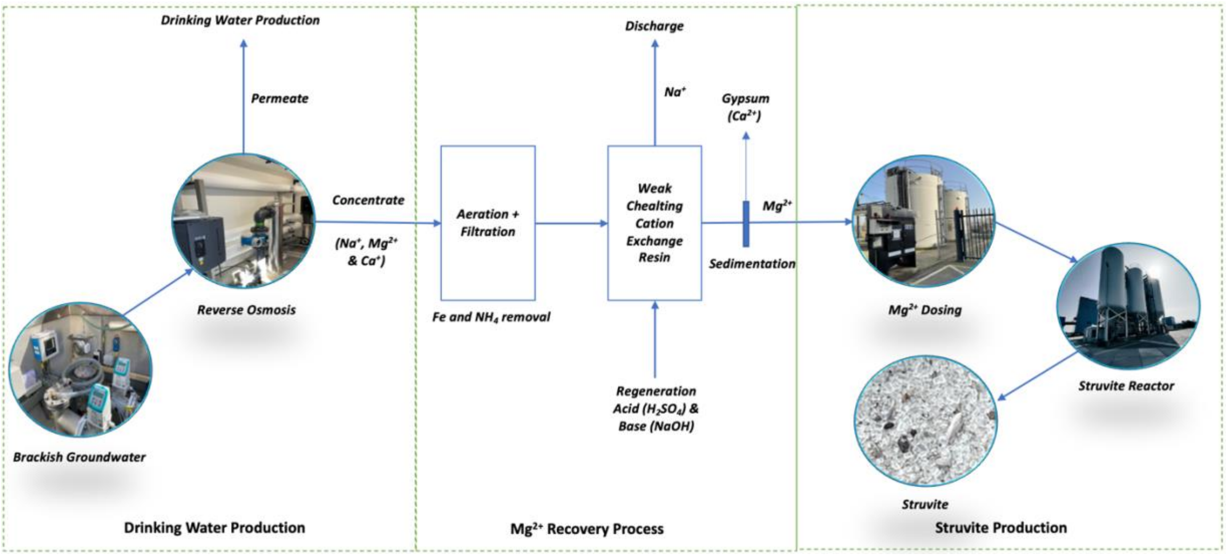
Abstract

Magnesium is one of the most critical natural resources and 96% of magnesium used in Europe is imported. The present study investigated possible ways of implementing circularity in the magnesium cycle within the borders of Waternet, a water utility in the Netherlands. The wastewater treatment plant at Amsterdam-West produces struvite from anaerobic digestate. The production of struvite requires 4400 tons of 32% $MgCl_2$ annually. At the same time, a reverse osmosis (R.O.) process treating brackish groundwater for drinking water production produces a concentrate rich in magnesium ions. This R.O. concentrate, after being treated by aeration and filtration to remove iron and ammonium, is considered for use in the wastewater struvite recovery process. Technologies for recovering magnesium from this R.O. concentrate were investigated in this study. After analyzing the constraints of the magnesium dosing system, the struvite reactor, and the R.O. concentrate composition, two technologies were selected for the study of Mg^{2+} recovery: Nano-filtration (N.F.) and Ion exchange. The present study investigated both these processes via software simulations and laboratory experiments. The study revealed that while the N.F. process is not viable, the cation exchange using a weak chelating resin AmberLite IRC747 in Na^+ form (regeneration with H_2SO_4 and NaOH) is possible when the resin is saturated with divalent cations. The regenerant stream (produced via acid regeneration) is a sodium-free stream having gypsum precipitates. After gypsum separation, the process created an Mg^{2+} dose with a concentration of 4.45 g/l. This study developed a 1 step process for extracting Mg^{2+} from RO concentrate.



Graphical Abstract

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Abbreviations

R.O.	Reverse Osmosis
R.C.	Reactive Crystallization
T.L.R.	Technology Readiness Level
TDS	Totally Dissolved Solids
E.D.	Electro-Dialysis
IEM	Ion Exchange Membrane
Z.D.D.	Zero Discharge Desalination
EFC	Eutectic Freeze Crystallization
Mm^3	Million Meter Cube
CSTR	Continuous Stirred Tank Reactor
Aq	Aqueous
Na^+	Sodium Ion
Mg^{2+}	Magnesium ion
Ca^{2+}	Calcium Ion
Fe^{2+}	Ferrous Ion
Fe^{3+}	Ferric Ion
K+	Potassium Ion
Cl-	Chlorine ion
SO_4^{2-}	Sulfate Ion
NH_4OH	Ammonium Hydroxide
$MgCl_2$	Magnesium Chloride
$MgCO_3$	Magnesium Carbonate

$Mg(OH)_2$	Magnesium Hydroxide
$MgSO_4$	Magnesium Sulfate
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium Carbonate
$Ca(OH)_2$	Calcium Hydroxide
$CaSO_4$	Calcium Sulfate / Gypsum
Na_2SO_4	Sodium Sulfate
Na_2HPO_4	Disodium Phosphate
NaCl	Sodium Chloride
Na_2SO_4	Sodium Sulfate
Na_2CO3	Sodium Carbonate
CO_2	Carbon Dioxide
BV	Bed Volume
VMD	Vacuum Membrane Distillation

Chapter 1:

Introduction

This Chapter introduces the motivation and the framework guiding this research. The research aims and the research questions are derived in this chapter through a detailed problem statement. Thereafter, the methodology adopted for the research is elaborated upon. In the last section, summary and structure of the research is shown.

Chapter 1 INTRODUCTION

1.1 Motivation

This study focuses on resource recovery and circularity in the water sector. One of the companies effectively targeting this is Waternet. Waternet is a public utility operating in the water sector in Amsterdam and its surroundings. It deals with the city's water management and water treatment. Waternet is owned by the municipality of Amsterdam and the regional water authority Amstel, Goi, and Vecht. It caters to about 1.3 million people. The mission of Waternet is: "Together, we get more out of water." It purifies wastewater, produces drinking water, and keeps surface water clean. It is the only utility in the Netherlands that takes care of the entire water cycle. In addition, the utility focuses on making all these processes more sustainable and circular. With a focus on climate adaptation and a circular economy, the utility is actively looking at new areas for resource recovery from the present and future waste streams. The use of magnesium is one of the critical areas identified for introducing circularity in the water treatment sector.

The utility operates the wastewater treatment plant located at Amsterdam-West (Fig 1.1). One of the important parts of the wastewater treatment process is the production of struvite (magnesium ammonium phosphate) from anaerobic digestate. For this, a full-scale struvite reactor is installed in the plant. The struvite produced in this struvite reactor is sold to a fertilizer company. This ensures that not only an important resource is recovered from the sludge, but it is also economically beneficial. To produce struvite, about 4300 tons of 32% of magnesium chloride is dosed yearly at Amsterdam-West. This magnesium dose is bought from the market. In the future, the supplier is expected to stop the supply of magnesium chloride, due to the widespread magnesium shortage in Europe. About 96% of the magnesium used in Europe is imported, making it one of Europe's most critical raw materials (EU Commission, 2020). Instead of finding a new supplier, Waternet is looking to develop a new way to recover magnesium from one of its future waste streams. This would establish a unique source for magnesium hence ensuing circularity in its life cycle and would potentially be economically beneficial.

Waternet also has a drinking water production plant in Weesperkarspel, Amsterdam (Fig 1.1) which currently utilizes water from Bethunepolder to produce drinking water. The utility plans to use brackish seepage groundwater in the future for drinking water production. For this purpose, the utility has started a pilot plant at Horstermeerpolder in North Holland (Fig 1.1), close to Amsterdam. The pilot plant contains a reverse osmosis (R.O.) unit to treat brackish water. A candle filter is attached before the R.O. unit to account for the sudden rise in sediment concentration. The pilot plant would treat brackish seepage groundwater, and the permeate would be used for drinking water production at Weesperkarspel, Amsterdam. The pilot plant in the future would result in a full-scale drinking water production plant. The target is to potentially treat 8 Mm^3 of brackish groundwater annually.

The concentrate produced from R.O. would be between 1.6 Mm^3 and 3.2 Mm^3 annually. The concentrate stream of such type is generally considered a waste stream, which is to be discarded at a cost. The cheapest option to deal with the concentrate stream is river discharge, but it often requires extensive permits, which may not be renewed in the future. The second cheapest option is to send it to a wastewater treatment plant. Still, the discharge volume and the total dissolved solids (TDS) concentration could affect the downstream operations of a wastewater treatment plant. The current plan with this R.O. concentrate stream is to treat it with aeration and filtration to remove iron and ammonia, and then discharge it either to the wastewater treatment plant or the wastewater treatment plant's effluent to a river.

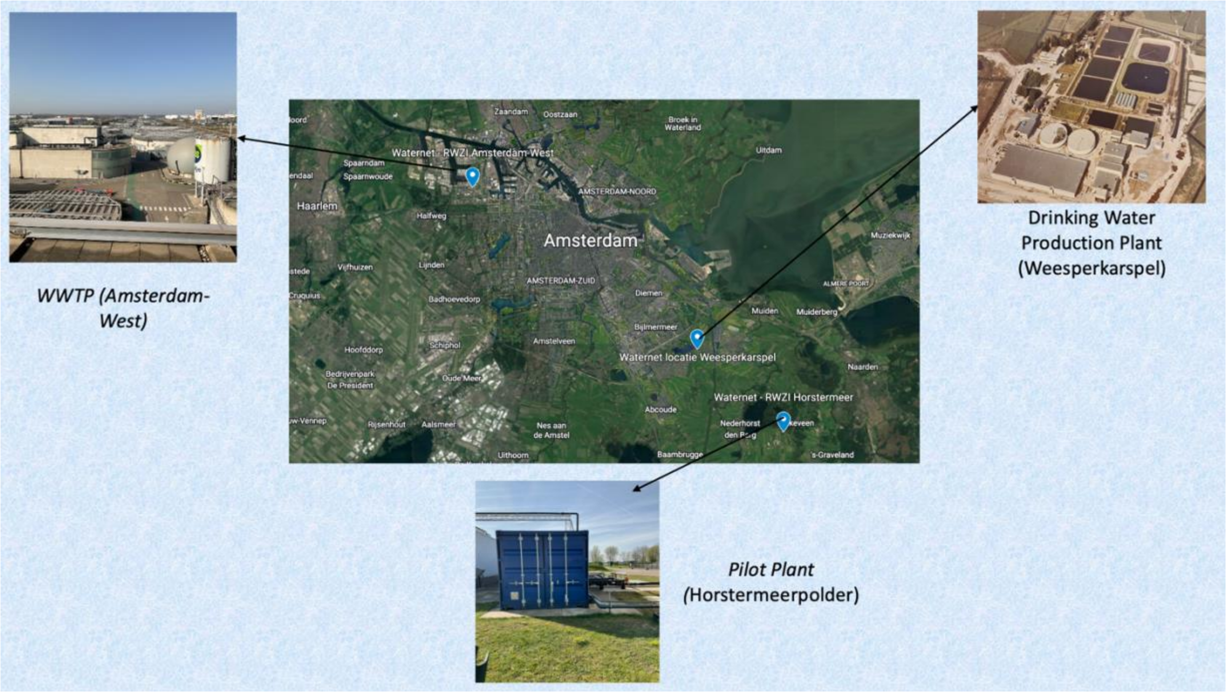

Figure 1.1: Waternet Plant Locations

This concentrate is similar to seawater brine and therefore it is rich in magnesium. Hence this could be a potential source of magnesium, which could then be used for struvite production. This would create circularity within the borders of Waternet. This thesis aims to figure out a way to achieve this, i.e., to recover magnesium from the concentrate stream of the reverse osmosis plant treating brackish groundwater and to use that for struvite production in the wastewater treatment plant at Amsterdam-West. The process flow chart is shown in Figure 1.2.

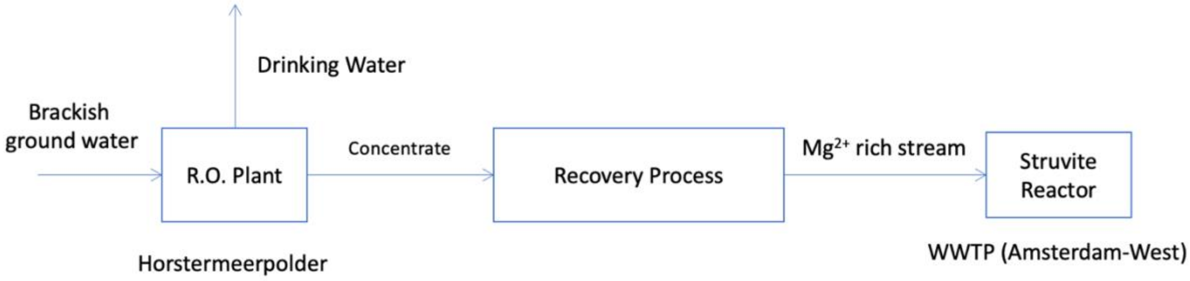

Figure 1.2: Recovery System Flow Chart

1.2 Problem Statement

The struvite reactor is working efficiently for many years. The important part of struvite precipitation is the dosing of magnesium ions. The magnesium ions are currently dosed in the form of magnesium chloride ($MgCl_2$). The newly formed recovery process for magnesium should be compatible with the existing system. The dosing solution could be changed as the underlying requirement is the presence of magnesium ions, and that could be in form of many different magnesium salts other than magnesium chloride. But the underlying restriction is that replacing the dosing solution should not affect the struvite production in any way and should not account for any upgrades to the dosing system or the struvite reactor. The struvite production process works very well with $MgCl_2$. It is essential to find out whether other magnesium salts, such as magnesium hydroxide, magnesium carbonate, and magnesium sulfate would work as well in the current system. It is not just the struvite reactor that has to be taken into consideration, the downstream wastewater treatment processes also have to be considered. The downstream wastewater treatment processes include dewatering using decanters followed by incineration of the solid sludge.

It is also imperative to know in which form the magnesium can be recovered from the R.O. concentrate. At the same time, whether that would be compatible with the existing system of magnesium dosing and struvite precipitation is an important concern. Therefore, a qualitative study is required to figure out the possible recovery technologies (and recovered salts) and compatible dosing scenarios, and then recovery pathways could be hypothesized.

Another important factor is the quantity of magnesium that could be recovered. Is it even worth pursuing a recovery option if the supply does not meet the current demand? Seasonal variations in dosing also must be considered while developing a recovery process. Since the composition of the concentrate stream is like that of brine, it consists of many sodium (Na^+) and calcium (Ca^{2+}) ions in addition to magnesium ions. It also has very high quantities of anions such as chloride and sulfate. With the recovery of magnesium, there would most probably be impurities consisting of other cations and anions. Even if a 32% magnesium chloride solution is obtained, there may be an excess of chloride ions or impurities from other cations. How that would affect the struvite production or the downstream dewatering process in the wastewater treatment plant is not known and must be considered. For example, the polymer used for coagulation in the dewatering process is sensitive to the salinity in the incoming sludge. Hence the presence of salt or higher anionic concentrations of chloride or sulfate may cause a problem in the dewatering process. Cations such as iron (Fe^{3+}) and calcium (Ca^{2+}) have been known to inhibit the struvite crystallization process (Yan and Shih, 2016). Hence the quantity of these ions in the new magnesium dose and its effect on the struvite crystallization is an essential factor. Another important aspect is that the concentrate of the R.O. unit is anaerobic and while the water is anaerobic, iron exists in Fe^{2+} form, which is soluble in water. When it comes in contact with oxygen, it is oxidized to Fe^{3+} which is insoluble in water and tends to precipitate (Kaplan and Ward, 2013). Since the current plan is to treat the R.O. concentrate with aeration and filtration to remove iron and ammonia and discharge it; it is important to analyze whether to keep the concentrate anaerobic or aerobic when the magnesium recovery process is applied.

The R.O. concentrate consists of several monovalent and divalent cations. Considering that the target is to separate magnesium ions from other ions, it is relatively easy to separate divalent cations from other monovalent cations since many technologies such as nanofiltration exists in the market which can complete this task. But separating two divalent cations in an aqueous stream is difficult. Hence the separation of magnesium ions from calcium ions with high efficiency is challenging.

Hence the aim of this thesis is to develop a technologically feasible process of magnesium recovery from the concentrate of the reverse osmosis unit, which can be used for struvite production at the wastewater treatment plant at Amsterdam West.

1.3 Research Aim and Questions

The present study aims to find a technologically feasible recovery process for magnesium that can be used for struvite production. To accomplish this, the first task is to analyze the dosing requirements for the struvite reactor and then analyze the concentrate quality and quantity. After that, the objective is to determine technologically feasible ways by which magnesium ions could be recovered. And then form a bridge between recovery and dosing.

If technologically sound recovery processes that are realistic and seem economically feasible are developed, then proof of the theory is required. This can be done either experimentally and/or modeling and simulation. The aim is not to optimize the said process but to prove to establish a proof of work for a recovery pathway. This leads to the formulation of the main research question:

> *"What would be the most technologically effective way to recover magnesium from the concentrate stream of the reverse osmosis plant to be used for struvite production in the wastewater treatment plant at Amsterdam-West."*

To obtain an answer to the main research question, three groups of sub-research questions are assessed. The first group of sub-research questions investigates the magnesium recovery processes from the R.O. concentrate and are given below:

1) What is the composition of the R.O. concentrate?
2) What is the annually recoverable amount of magnesium from the R.O. concentrate?
3) What are the proven industrial processes of magnesium recovery from brine?
4) What are potential processes for magnesium recovery which could work in this case?
5) Which salts of magnesium could be recovered from the R.O. concentrate?

The second group of sub-research questions is concerned with the struvite precipitation and magnesium dosing and are given below:

6) Which factors inhibit the struvite precipitation process?
7) Which factors could affect the downstream wastewater treatment processes?
8) Which salts of magnesium could be dosed for struvite precipitation?
9) What are the possible states (solid, aqueous, slurry, etc.) for dosing the magnesium ions compatible with the dosing system?

The third group of sub-research questions involves forming a bridge between recovery and dosage of magnesium salts and are given below:

10) What are the possible hypothesized recovery pathways?
11) Which recovery pathway is technologically most feasible, and can a proof of work be obtained for the said pathway?

1.4) Research Methodology

A multi-layer approach is adopted to answer all the sub-research questions. The approach consists of the following parts:

1) Literature review to find possible recovery processes for $Mg^{2+}$and inhibitors to struvite precipitation.

2) System Analysis: Gathering data on the current system to establish its limitations. Then combining the data assessment with the literature review to select possible recovery pathways.
3) Performing software simulations for the potential recovery pathways
4) Performing laboratory experiments to obtain proof of theory for the potential recovery pathways.

1.4.1 Literature Review

An in-depth literature study was conducted to analyze possible ways to recover magnesium salts. This included well-established technologies that have been used for many decades and also new advancements in the field. A comprehensive review of every existing technology that can recover magnesium ions from brine in any form such as magnesium hydroxide, magnesium carbonate, magnesium sulfate, and magnesium chloride was done.

1.4.2 System Analysis

The present study represents a specific scenario within a particular utility. The study involves two departments, the first being the drinking water production department and the second being the wastewater treatment department. The personnel, engineers, and teams within both departments are different and rarely have work overlaps. For the successful completion of this study, technical and chemical limitations have been identified in the R.O. unit and the struvite reactor. Only then can a bridge between recovery and dosing can be formulated. Hence numerous meetings were set up with both departments to gather all the relevant data and understand what they hope to achieve from the recovery process. This often required effective inter-departmental communication and collaboration.

1.4.3 Software Simulations

Every brine (like seawater) is broadly similar in composition but has differences. A technology that is quite effective for recovering nutrients from one brine may be less effective for the other. It is essential to understand if a well-established proven technology can be applied to our specific case. Instead of spending vast amounts of money on laboratory research or pilot studies, software simulations are often preferred for such scenarios. This study used various software to study the concentrate's chemical nature and simulate multiple recovery processes. The software used in this study were: PHREEQC, Wave, and IMS design.

1.4.4 Laboratory Experiments

The laboratory experiments were performed to prove that a particular technology works i.e., to obtain proof of work for the recovery process. This is because software simulations sometimes have limitations and may not be an accurate tool to assess a specific technology's usage for something other than it was initially intended for. In addition, if a process is theoretically sound enough to work, that does not guarantee that it will work. Hence conceptual proof backed by experimental results is necessary to propose a technology as the solution. Although process optimization was not in the scope of this study, it would be conducted in the following research based on this study. Laboratory experiments were performed to obtain proof of work for the ion exchange recovery pathway. The nature of the experiment is described below:

An Ion exchange experiment was performed using a column of diameter 2 cm filled with 40.82 cm^3 of a chelating resin (AmberLite IRC747) in the Na^+ form. The water was pumped using a Watson Marlow 323 peristaltic pump, which is a microprocessor-controlled variable speed pump with a variable speed range of 3.0 to 400 rpm , translating into a dosing speed range of 0.09 to 2000 ml/min. The column was first regenerated with acid and then with base (NaOH). The experiment was performed three times, the first two times HCL was used as the acid regenerant and the third time H_2SO_4 was used as the acid regenerant. The purpose of the experiment was to reach saturation of divalent cations in the resin. These divalent cations come out in the acid regeneration stage which could be used the potential Mg Dose. The experimental analysis and description are described in detail in Section 5.5

1.4.5 Thesis Outline

This thesis embodies the subject matter resulting from this study and is conveyed in 5 separate chapters. In chapter 2, a literature study focuses on available recovery technologies and inhibitions for struvite precipitation. Chapter 3 describes the findings of the struvite reactor, magnesium dosing system, the R.O. unit, and the concentrate are described. Qualitative and quantitative analysis is done. In the last section of Chapter 3, findings from Chapter 2 and the remaining sections of Chapter 3 are combined to discuss the merits and demerits of possible technology which could be used for resource recovery. Based on the discussion, the final technologies selected for the recovery process are described. In chapter 4, the first recovery technology, i.e., Nano-filtration is discussed in detail. The chapter includes the theory about implementing the process, software simulations, results, and conclusions. In Chapter 5, the second recovery technology, i.e., ion exchange system, is discussed; everything from theory, software simulation, laboratory experiments, results, and conclusions are discussed. The final conclusions and outlook of this study are portrayed in the Chapter 6.

The Research Methodology combined with the thesis outline is described in Figure 1.3.

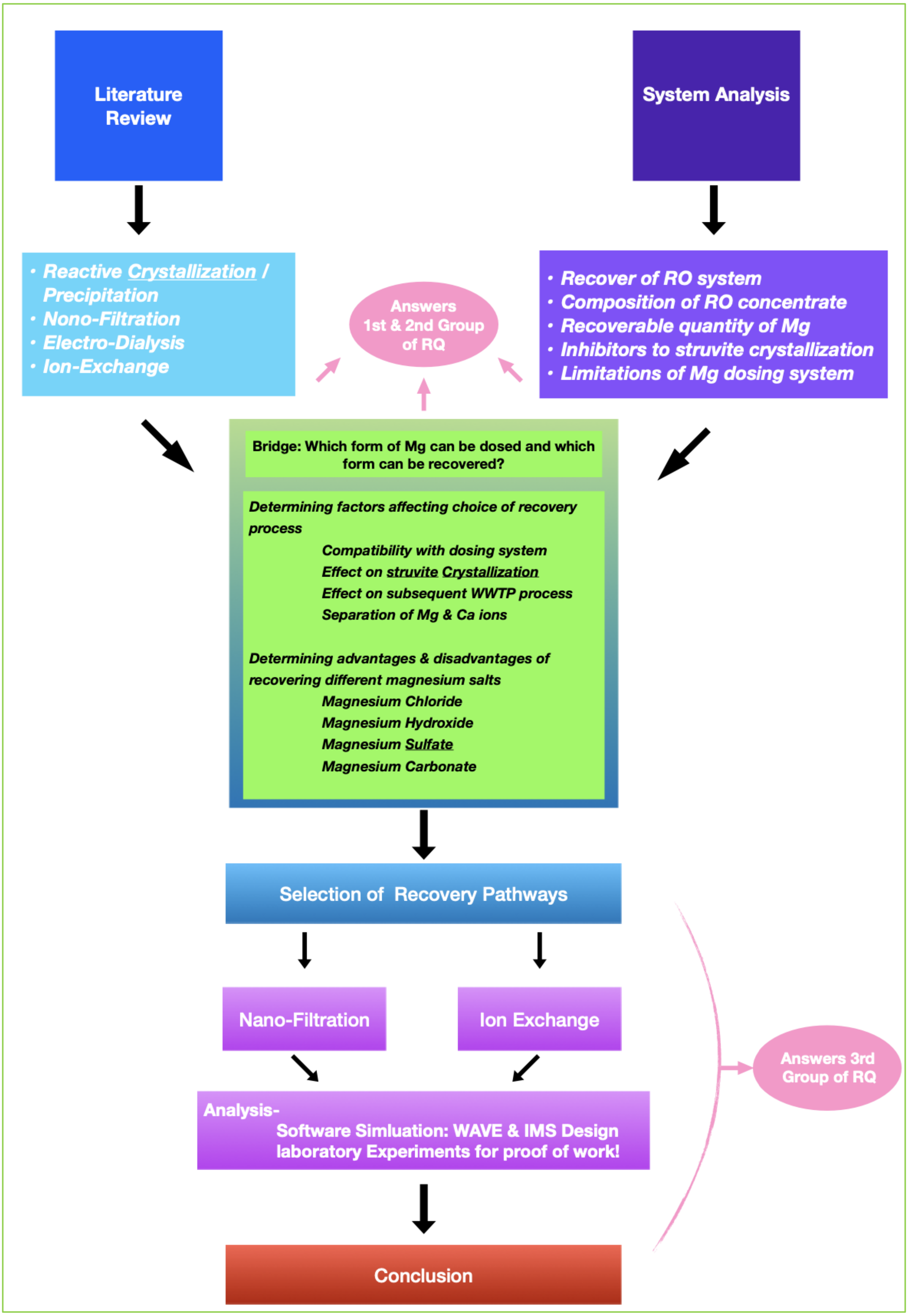

Figure 1.3: Outline of Research Methodology

Chapter 2:

Literature Review

This Chapter provides a framework for the theoretical knowledge derived from existing literature. It comprises possible technologies which have been adopted in the past to recover various salts of magnesium in different forms from different types of brines. It also discusses the theory behind struvite crystallization and the inhibitors to the process.

This Chapter presents a review of the available literature on the methods to extract magnesium from various types of brines. Various methods and technologies exist in the market to extract magnesium from brines generated from membrane processes treating brackish and seawater. Some of these methods are relatively new, while others have been used for many decades and have been thoroughly tested. In the upcoming sections, the functioning, readiness level, merits, and demerits of more than a dozen technologies will be discussed. Also, the factors affecting the struvite crystallization process are discussed toward the end of the Chapter.

2.1 Reactive Crystallization (R.C.)/ Precipitation

Reactive Crystallization (R.C.), or precipitation, involves a reaction leading to the formation of a solute, which crystallizes into a solid product. It is suitable to obtain a sparingly soluble or insoluble compound that leads to phase separation after reacting with an appropriate reactant. There are many ways to achieve the precipitation of magnesium ions, which are discussed in upcoming sections.

2.1.1 Dow Process

This process was developed in the 1940s to extract magnesium from seawater (US2405055A, 1942). The flow diagram of the process is shown in figure 2.1.

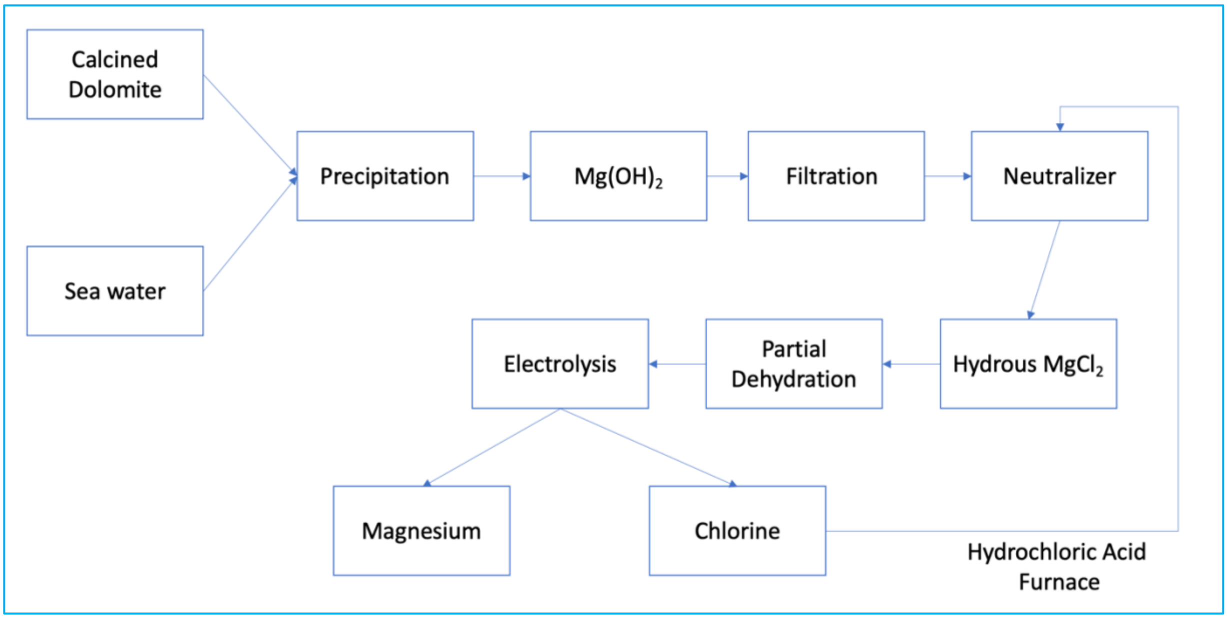

Figure 2.1: Dow Process flow chart (A1)

In this process (Fig 2.1), the seawater is mixed with calcined dolomite ($CaMg(CO_3)_2$) in a flocculator which results in the production of insoluble magnesium hydroxide. This precipitates in a settling tank, and then extracted. Magnesium hydroxide is in the form of a slurry. After filtration, it is mixed with hydrochloric acid, which results in the formation of magnesium chloride. The next step is evaporation which dries the mixture to 25% water content in a series of evaporation steps. The last step is electrolysis to separate magnesium and chloride ions. This results in the production of magnesium ions. This process uses an elaborate setup, including a flocculation tank, settling tank, filtration tank, evaporation unit, electrolysis unit, and hydrochloric acid furnace. It also uses significant resources like calcined dolomite. It is generally used on an industrial scale to produce commercially available magnesium.

2.1.2 Using Ammonium hydroxide

Another way to recover magnesium is via recovering magnesium hydroxide ($Mg(OH)_2$) by the reaction of magnesium carbonate ($MgCO_3$) present in the brine with ammonium hydroxide (NH_4OH). Ammonia is highly soluble in water and is a weak base. At 25°C, about 460 liters of ammonia gas is soluble in 1 liter of water (Chemistry of Gases, 2003). A solution of ammonia in water is known as ammonium hydroxide (NH_4OH). A dual equilibrium is formed as depicted in equation 1

$$NH_3(aq) + H_20 \leftrightarrows NH_4^+(aq) + OH^-(aq) \tag{R1}$$

The reaction with magnesium carbonate ($MgCO_3$) is as follows:

$$NH_3 + 2H_2O + MgCO_3 \longrightarrow NH_4HCO_3 + Mg(OH)_2 \tag{R2}$$

A recent study (Mohammad et al., 2019), used this approach with desalination reject brine and even statistically optimized it using response surface methodology. At a brine salinity of 85 g/l and a temperature of 15 ℃, the study achieved a magnesium recovery of 99% with a molar ratio of 4.4 NH_3 : 1 Mg. Another study (Dong et al., 2017) analyzed the feasibility of recovering high reactivity MgO using the same process as described above but then calcination at 500 ℃ for two hours is done. This technique depends on the concentration of $MgCO_3$ in the brine and can have limitations if the quantity of carbonates of magnesium is less.

2.1.3 Using sodium hydroxide

Reactive magnesium hydroxide precipitation ($Mg(OH)_2$) can also be done by adding sodium hydroxide to the brine solution. It has been historically done for different brines before. One study (Turek and Gnot, 1995) successfully precipitated $Mg(OH)_2$ from coal mine brine by adding NaOH. In this study, it was seen that if the mixture was left to stand for 24 hours before stirring, the sedimentation and filtration rate increased by a factor of 5 and 60 respectively, and hence increasing recovery efficiency. In another study (Cipollina et al., 2014), brine was collected from saltworks in the district of Trapani (Sicily, Italy) with a magnesium concentration of 30-40 kg/m3 (20 – 30 times that of seawater). NaOH was mixed with it in a continuously stirred tank reactor (CSTR). The magnesium was recovered in the form of a powder of $Mg(OH)_2$, with the purity of the precipitates around 98%. This approach has generally been tested for specific brines.

2.1.4 Using Disodium Phosphate

Magnesium phosphates and magnesium ammonium phosphates can be precipitated under certain conditions using disodium phosphate (Na_2HPO_4). It has been tried in calcium-free super-saturated aqueous solutions (Golubev et al., 2001). The main solid phase obtained in the study was, $Mg_3(PO_4)_2{\cdot}8H_2O$. One of the problems is that since the hydration of magnesium is more vital, it is difficult to incorporate it into precipitates compared to calcium salts (Bush, 1974). This approach is very specific to calcium-free water. The study also found that the nucleation rate of magnesium phosphates is several orders of magnitude lower than that of Ca (at the same pH and phosphate concentration). Hence, in brine containing both Ca^{2+} and Mg^{2+} ions, precipitating phosphates of magnesium is highly unlikely.

2.2 Nano-Filtration (N.F.)

N.F. is a pressure-driven membrane separation method with pore sizes ranging from 1-10 nanometers. There are two principles that apply to the N.F. membrane – Size exclusion and Donnan exclusion. Size exclusion separates particles based on size; the larger particles (divalent ions) cannot pass through the membrane. Donnan exclusion, on the other hand, is exclusion based on the charge effect. Donnan exclusion occurs when a semi-permeable membrane forms an electric potential due to the presence of impermeable cations or anions. Hence the membrane becomes charged. There are two ways in which N.F. membranes could be used: salt rejection and separation of monovalent and divalent ions.

In a study (Bruggen et al., 2004), synthetic salt solutions of NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$, and $NaNO_3$ were separated using N.F. membranes, and a 60% separation efficiency was observed for monovalent and divalent cations as well as anions. In another study (Peeters et al., 1998), retention measurements using commercial polymeric N.F. were done with single salt solutions of NaCl, $CaCl_2$, and Na_2SO_4. The study revealed that in positively and negatively charged membranes, the Donnan exclusion plays the dominant role. The following salt recovery (R) sequence was observed $R(Na_2SO_4) > R(NaCl) > R(CaCl_2)$ for negatively charged membranes, $R(CaCl_2) > R(NaCl) > R(Na_2SO_4)$ for positively charged membranes. In another study (Hilal et al., 2005), three commercial N.F. membranes were tested to treat highly concentrated salt solutions: $NaCO_3$, $MgCl_2$, and $CaSO_4$. The salinity level was about the same as that of seawater. The N.F. membranes tested were NF90 (by Dow chemical), NF270 (by Dow chemical), and NF30 (by Microdyn-Nadir). The main result showed that NF90 produced a high rejection rate of 97% for all salts. This shows that salt recovery is a good use for N.F. membranes, although these were pure salt solutions, and predicting the retention of a particular salt from brine may be difficult.

One of the significant applications of N.F. is softening of hard waters i.e. when divalent cations are separated from monovalent cations (Ismail and Matsuura, 2022). This helps create a stream of magnesium and calcium ions, thus separating the sodium ions. This could be useful for the present study, especially if the quantity of magnesium ions is significantly greater than that of calcium ions, in the concentrate. In a study (Oumar Anne et al., 2001), various types of N.F. was tested for fractionation of mono and multivalent cations (monovalent: Na^+, K^+; divalent: Ca^{2+}, Mg^{2+}). It aimed at selectively demineralizing saltwater containing these cations. The results indicated a rejection rate of 50% for the monovalent ions and 90% for the divalent ions.

Hence there are two ways in which N.F. could be used: either fractionation of monovalent and divalent cations and obtaining a Na-free stream, or targeting a particular salt e.g., rejection of magnesium salt. The type of N.F. membrane used is important, as well as the concentration of the salt stream and the main principle behind the rejection (Donnan exclusion or Size rejection).

2.3 Electro-Dialysis (E.D.)

Electro-Dialysis (E.D.) is a membrane process during which ions are transported through the semi-permeable membrane under an electric potential (Water treatment solutions, n.d.). In E.D., ions are transported through the membrane while water is kept in the feed phase. The interaction of ions with the membrane determines their separation. An E.D. membrane stack consists of an alternation of anion and cation exchange membranes (Bruggen et al., 2004). E.D. employs specifically engineered ion exchange membranes (IEM) and an externally applied electric field to facilitate ion migration. IEM that are selective for monovalent ions are used to separate monovalent ions from divalent ions. This can result in a separated stream of Mg^{2+} and other divalent cations. Also, these could then be crystallized independently using a traditional approach such as evaporation or chemical precipitation. The E.D. in such systems contains four membranes: an anion exchange membrane, cation exchange membrane, monovalent selective anion exchange and monovalent selective cation exchange (Davis and Rayman, 2006, Davis, 2013, Bond, 2011, Morillo et al., 2014).

Zero Discharge Desalination (Z.D.D.) process includes the use of electro-dialysis to recover metals and minerals from the brine which is generated from reverse osmosis treatment of brackish water to produce drinking water. A University of South Carolina patent (Davis and Rayman, 2006) described a Z.D.D. process (Fig 2.2) in which E.D. was used to concentrate the brine produced by the R.O. unit. The process produces NaCl, $Mg(OH)_2$, and Br_2. Monovalent selective E.D. was used to separate Na^+ and Cl^- ions from divalent ions. From the divalent stream, Ca was removed by adding Na_2CO_3, leaving the stream with majorly Mg ions that were recovered in the form of $Mg(OH)_2$ using NaOH. In another patent (Davis, 2013) by the same university, a Z.D.D. process was developed by utilizing electrodialysis flowed by crystallization and precipitation to generate salt streams of $CaCl_2$ and Na_2SO_4.

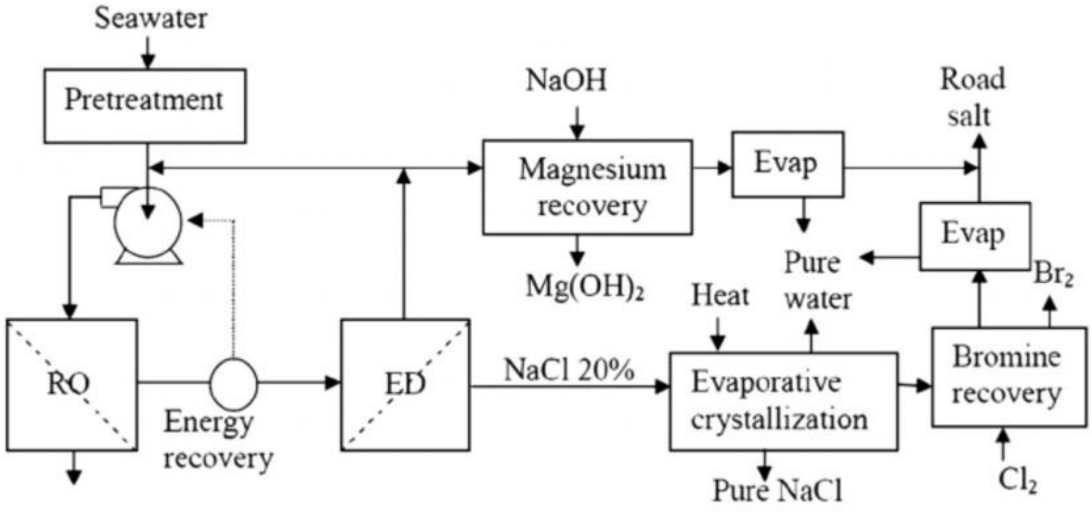

Figure 2.2: A Z.D.D process flow chart (Davis and Rayman, 2006)

In another study (Tran et al., 2012), the feasibility of a hybrid system was investigated. The system comprised of a pellet reactor and an E.D. system to treat the concentrate from the R.O. plant. The purpose of the pellet reactor was to reduce scaling potential, i.e., calcium ions. The results showed the removal of up to 95% of calcium. If magnesium and calcium are two major divalent cationic populations in the concentrate, then using this method, we can obtain a magnesium-rich stream. However, the addition of a pellet reactor would be an expensive proposition.

Another study (Sano et al., 2018), investigated a continuous resource recovery system to continuously extract magnesium from the seabed using water electrolysis. The magnesium hydroxide was formed at the cathode channel, which was separated by an ion exchange membrane. The hydroxide ions was the electrolyte, so magnesium formation was directly related to the electricity used per unit volume of seawater. Interestingly, it was found that if deep-ocean water is subjected to deaeration, it prevents the formation of calcium carbonate since CO_2 is removed, which results in obtaining 99% pure $Mg(OH)_2$.

Hence ED with other technologies could be used with different combinations and in different configurations to recover different metals and minerals from brine. The configuration used and the minerals to be recovered depend highly on the brine concentration and the market values of the recovered minerals. The main technological obstacles are the high cost of electric energy and scale formation (Obotey Ezugbe and Rathilal, 2020).

2.4 Ion Exchange

In simple terms, an ion exchange reaction is any chemical reaction involving an exchange of one or more ionic compounds between two substances, each consisting of negatively and positively charged ions (Cummins et al., 2016). In the water treatment and resource recovery industry, ion exchange is done to obtain a specific compound or to eliminate unwanted compounds from the water stream. This could be achieved in two ways: via an ion exchange membrane and ion exchange chromatography.

Ion exchange chromatography has many uses, including but not limited to water softening, water purification, metal separation, condensate polishing, and industrial demineralization (IEX, Dupont). In ion exchange chromatography, a column is filled with a resin (this could be either positively or negatively charged). There are two types of ion exchange resins: anion exchange and cation exchange. They are further classified into weak and strong exchanges based on the functional groups. Weak exchanges work over a limited range of pH, while strong exchanges show no changes in ion exchange capacity to changes in pH (Cummins et al., 2016). Hence the categories of ion exchange resin are strong acid cation exchange resin, weak acid cation exchange resin, strong base anion exchange resin, and weak base anion exchange resin. Ion exchange resins are made up of polymers attached to the functional groups (Dardel, 2022). About 85% of resins are composed of polystyrene matrix, 10% of acrylic and polyacrylate matrix and the rest are composed of other special polymer matrixes like phenol-formaldehyde (IEX, Dupont). The functional groups are phosphonic (-PO_3^{2-}), carboxylic (-COOH), and sulfonic (-SO_3H) for cation exchangers and a quaternary ammonium or amine functional groups for anion exchangers (Korkisch, 2017, Smith and Chang,1983). Some exchange resins contain both acidic and basic inorganic groups, hence having the capability to exchange both cations and anions. There are also chelating resins containing a functional group explicitly targeting alkaline earth metals.

In one study (Pérez-González et al., 2014), cationic and anionic ion exchange systems were used to separate magnesium, calcium, and sulfate from the brine as a pre-treatment step to obtain a highly concentrated stream of NaCl. The cationic ion exchange system was used to separate magnesium and calcium. The resin used was Lewatit TP208 (Lewatit--Monoplus-TP-208). This is a weak acid macroporous cation exchange resin. It is a chelating resin with iminodiacetic acid groups. This helps in the selective removal of alkaline earth metals. The removal efficiency of metal cations was of the order: Copper (Cu) > Lead (Pb)> Nickel (Ni) > Zinc (Zn) > Cadmium (Cd) > Cobalt (Co) > Iron (II) (Fe^{2+}) > Beryllium (Be) > Manganese (Mn) » Calcium (Ca) > Magnesium (Mg) > Strontium (Sr) > Barium (Ba) > Sodium (Na) (Lewatit--Monoplus-TP-208).

In another study published in 2022, which was carried out at Delft University of Technology (Haidari et al., 2022), silica scaling was investigated in a seawater (salinity >12000 mg/l TDS) R.O. installation used as a pretreatment to Eutectic Freeze Crystallization (E.F.C.). E.F.C is a separation process that separates salt and water and is more energy efficient than methods such as evaporative crystallization. Divalent cations were removed beforehand using a cation ion exchange column to reduce silica scaling on the membranes. The column was filled with Amberlite-IRC747 (DuPont) resin to remove multivalent cations such as $Fe^{2+,}$ $Ca^{2+,}$ and Mg^{2+}. The resin is a chelating resin which macroporous and amino phosphonic (Cummins et al., 2016). It is designed explicitly for softening saturated brine solutions (Dupont). The calcium and magnesium concentrations were successfully reduced from 481 mg/l and 297 mg/ to 0.43 mg/l and 0.16 mg/l, respectively, in the first experiment. This shows that this resin is highly effective at capturing divalent cations for softening purposes.

Hence ion exchange columns are highly effective in removing divalent cations from a solution. After the column is saturated, the column can be regenerated with acid to bring it to H^+ form. When the column is regenerated with an acid (HCl or H_2SO_4), the divalent cations would react with the acid and leave the column in the form of chlorides or sulfates. Hence, a highly concentrated stream of divalent cations could be obtained via this method. If the calcium concentration is low, a highly concentrated aqueous stream of Mg^{2+} ions can be obtained.

2.5 Miscellaneous

2.5.1 Ion Exchange Membrane Crystallizer (CrIEM)

A novel ion exchange membrane crystallizer (CrIEM) was developed and patented in 2015 (La Corte et al., 2020). The CrIEM facilitates the passage of ions of interest (i.e., OH^- ions) for crystallization without the requirement for direct mixing between the two solutions (alkaline solution and brine), thus eliminating the possibility of co-precipitation. The passage is facilitated by using an anionic exchange membrane. The alkaline solution consists of OH^- ions. Generally, this leads to the precipitation of other compounds, such as calcium sulfates and carbonates. It enables reactive crystallization to separate important species (e.g., magnesium from brines) with a wide range of options for reactants. This also permits the use of low-cost, high-quality reactants or alkaline industrial waste without compromising the purity of the end product. A mathematical model of the CrIEM process was recently proposed as a tool for its design in different working conditions with showed good agreement with the laboratory results (Vassallo et al., 2021). Although if the brine contains significant quantities of calcium, the process may need to be revised. The process is described in Figure 2.3

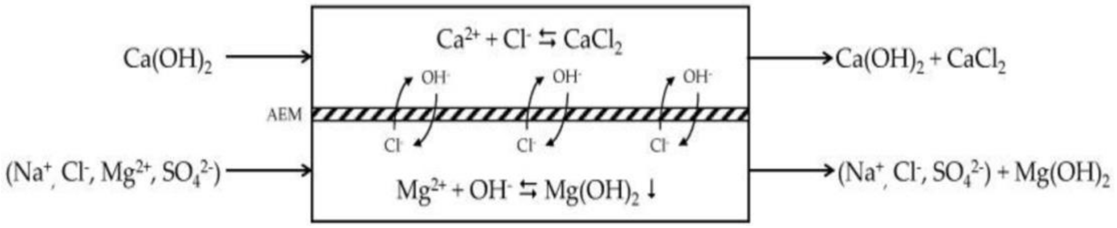

Fig 2.3: CrIEM Process (La Corte et al., 2020)

2.5.2 Membrane Distillation Crystallization (M.D.C.)

One more relatively less used technology is membrane distillation crystallization (MDC). Membrane distillation is used in MDC to recover water and create appropriate supersaturation in the crystallizer, allowing product crystals to form. To attain supersaturation conditions, M.D.C. uses hydrophobic microporous membranes and thermal energy. This is a method of increasing salt concentration by evaporating the solvent used in membrane distillation. The temperatures on the two sides of the membrane are different. On the warmer side, the solvent evaporates, while on the colder side, it condenses. The membrane's hydrophobic nature allows vapor to travel while preventing condensed water from returning. It has been demonstrated that this approach can ensure fine control of supersaturation and, as a result, control over the crystal size distribution and shape (Drioli et al., 2012). Recovery of NaCl and $MgSO_4$ from concentrated streams using M.D.C. has been reported (Mene and Murthy, 2018).

2.6 Struvite Crystallization

Struvite is magnesium ammonium phosphate. The formula is $NH_4MgPO_4{\cdot}6H_2O$. It is a phosphate mineral (Struvite-An Overview). Struvite precipitation involves nucleation and then crystal growth. These processes are affected by various physiochemical factors such as temperature, pH, supersaturation ratio, and, most important for present study: the existence of foreign ions (Yan and Shih, 2016). It is known that ferric (Fe^{3+}) and calcium (Ca^{2+}) ions inhibit the struvite precipitation process and the quantity and quality of crystals formed (Kabdaszli et al., 2006). There is also a negative linear correlation between the solution Ca/Mg molar ratio and struvite weight content. Fe^{3+} and Ca^{2+} also lead to irregular precipitate shapes (Kabdaszli et al., 2006, Le Corre et al., 2009, Yan and Shih, 2016). The effect of Na^+ and Ca^{2+} have been studied quite intensively, and their presence has always been shown to result in the retardation of struvite crystallization (Kabdaszli et al., 2006, Le Corre et al., 2009).

In the wastewater treatment process, calcium concentrations is consistently observed in the settled sludge liquors, and the Ca/Mg molar ratio could range from 1.4 to 3.7 (Yan and Shih, 2016). Calcium Phosphate ($CaPO_4$) precipitation is often reported in wastewater treatment and is regarded as another important route for phosphorous removal and recovery. Iron (Fe) chemicals are used in wastewater treatment for various purposes, such as coagulation, flocculation, and phosphorous removal (Mishima et al., 2018). More commonly, ferric salts are used in the anaerobic digestion of sludge to control the emission of hydrogen sulfide (H_2S) into biogas (Charles et al., 2006, Ge et al., 2013). Ferric ions affect crystal growth in many ways, such as altering needle-shaped crystals into tapered prisms (Mullin, 2001). Hence there are always quantities of Fe and Ca when struvite is precipitated in wastewater treatment, but their amounts should not inhibit struvite production. The magnesium-dose developed from the recovery of magnesium ions from brine may contain impurities (other cations present in the brine). Their quantity should be assessed, and if they are significant, the implication on struvite precipitation should be studied.

A qualitative and quantitative analysis comprising information about the R.O. unit, struvite precipitation, and magnesium dosing is shown in the successive chapter leading to the selection of recovery processes.

Chapter 3:

System Analysis

This Chapter first provides the discovery of various facts and analysis of the current systems of struvite precipitation, magnesium dosing, and the R.O. unit. It provides an understanding of the research and the context and limitations of the recovery processes. Thereafter, the research findings of Chapter 2 and the initial section of this chapter are combined to answer the first and second sets of research questions and provide possible recovery pathways which will be investigated in further chapters.

Chapter 3 System Analysis

3.1 System Data

3.1.1. R.O. Pilot Plant

The pilot plant consists of a reverse osmosis unit (Fig 3.1) and a candle filter for turbidity check (Fig 3.2). The pilot is treating brackish groundwater. The permeate is used for drinking water production. The concentrate is potentially a source of magnesium.

Figure 3.1: R.O. unit

Figure 3.2: Candle Filter

The R.O. membranes have a pressure limit of 40 bar. The gauge in the pilot system has a capacity of 35 bar. Currently, the R.O. unit is being tested at 24 bar for treatment of brackish seepage water. An antiscalant is dosed to prevent scaling issues in the membranes, and this antiscalant is environmentally friendly. The quality of the brackish groundwater is the same on average throughout the depth of the aquifer. Two RO configurations have been tested until now: one-stage and two-stage. The recovery of one stage RO system stood at 67% and that of the two-stage stood at 71%.

The target is to treat 8 Mm^3 (Million-meter cube)of brackish groundwater annually. The R.O. is still undergoing optimization but the final recovery would stand between 60% and 80%. This means that the quantity of concentrate annually would be between 1.6 and 3.2 Mm^3, respectively.

The concentrate would be anaerobic. The tentative plan is to treat the concentrate with aeration and filtration to remove Iron (Fe) and Ammonium (NH_4) before sending it for discharge. So, for the recovery of magnesium, the process could be applied either with anaerobic water or aerobic water which would be free of iron.

3.1.2 Composition of R.O. concentrate

The simulated chemical composition of the R.O. concentrate, as done by the pilot plant team at Waternet, is provided in **Appendix A1.** The simulated concentrations were used since the pilot plant was out of commission for several months. The water quality of the brackish water was tested, and exact compositions was known. Based on the R.O. recovery of 67% for one stage and 71% for two-stage, the quality (composition) was calculated and provided by the utility (Appendix A1). The composition of the major anions and cations for a recovery of 71% are shown in Table 3.1. These compositions were taken as the starting point for the present study while also considering the boundary conditions (Recovery at 60%-80%). The pH was 7.24.

Table 3.1: Composition of R.O. concentrate

Serial No.	Ion	Symbol	Concentration (mg/l)
1	Ammonium	NH_4	8.4
2	Potassium	K	94.2
3	Sodium	Na	6744.4
4	Magnesium	Mg	890.9
5	Calcium	Ca	1506
6	Strontium	Sr	8.5
7	Barium	Ba	0.5
8	Carbonate	CO_3	9.9
9	Bicarbonate	HCO_3	1179.9
10	Nitrate	NO_3	12.9
11	Chlorine	Cl	14970.5
12	Fluorine	F	1.6
13	Sulfate	SO_4	1295.5
14	Phosphate	PO_4	0.7

Table 3.1 shows that the calcium concentration (1509 mg/l) is 1.6 times that of magnesium concentration (890.9 mg/l). The sodium concentration is very high at 6744.4 mg/l, which is about 7.5 times that of the magnesium concentration. The chlorine concentration is significantly high at about 15000 mg/l.

3.1.3 Magnesium dosing system

The magnesium dosed in the struvite reactor is in the form of $MgCl_2$. A stock solution of 32% $MgCl_2$ is bought for this purpose and stored in the silos shown in Figure 3.3. The dosing system is aqueous (Fig 3.4). This system would remain the same, and updating it is not an option presently. The recovery process from R.O. concentrate should produce a magnesium-dose compatible with the existing system, i.e., it must be in aqueous form and contain a similar concentration of Mg^{2+} ions.

Figure 3.3: Storage of $MgCl_2$

Figure 3.4: Loading system of $MgCl_2$

Figure 3.5 shows the daily dosage of $MgCl_2$ for the last seven years. Several large gaps could be seen from 2015-2018 period; these are attributed to the shutdown of the struvite reactor either due to some ongoing work, upgrades, technical difficulties, or testing new operating conditions. The dosing has been more or less constant since April 2022. If the data from April 2022 is taken into account, excluding the days when the dosing was not done, the average dosing has been 10,734 liters/day, with the median being 11,014 liters/day and the maximum at any day ever being 19,450 liters/day.

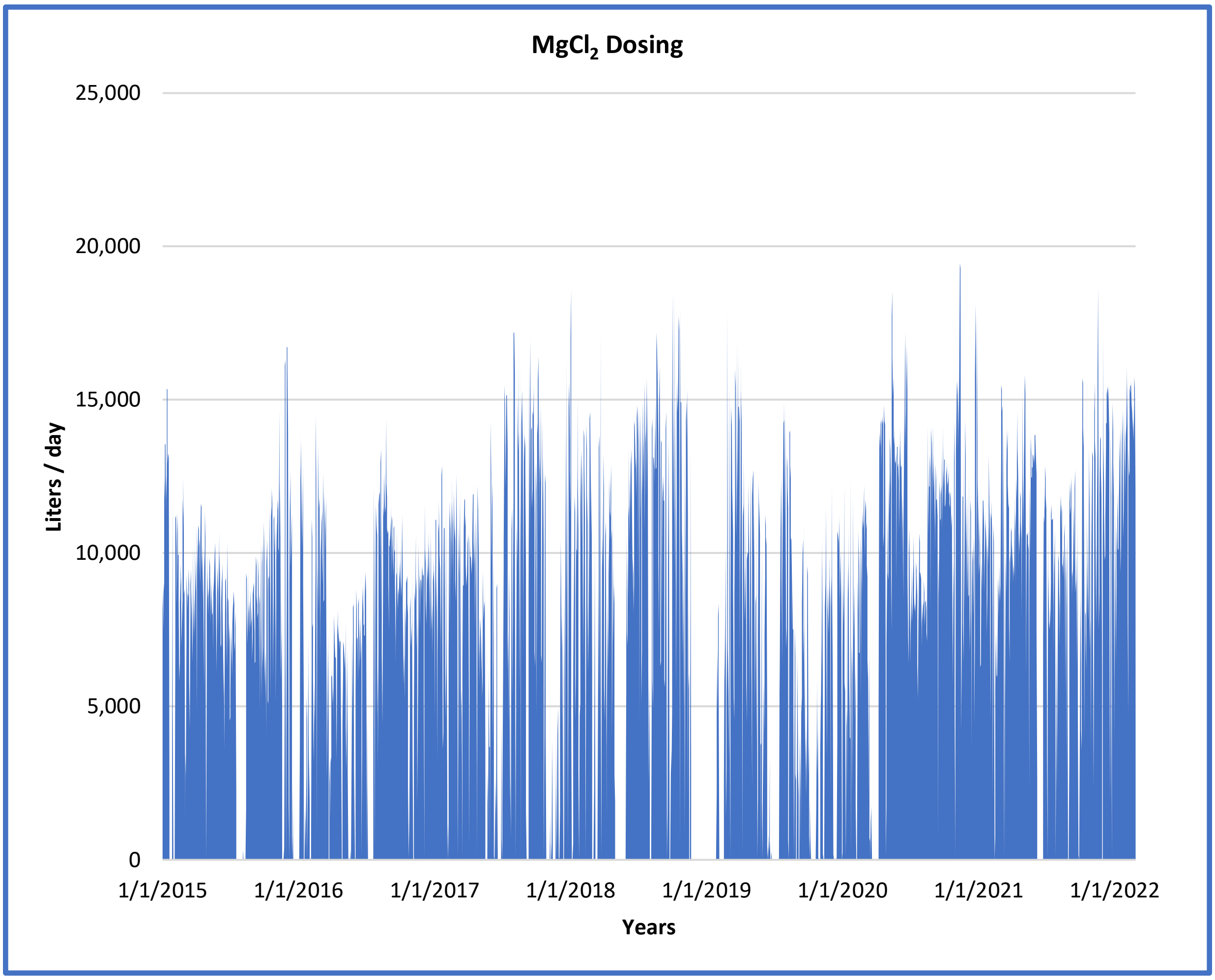

Figure 3.5: $MgCl_2$ dosing per day

Figure 3.6 shows the yearly purchase quantity data for the stock solution of $MgCl_2$ for the 2015-2021 period. The highest amount was purchased in 2020, which was 4442 tons. If the amount of magnesium potentially recovered is more than 4500 tones (equivalent to 32% $MgCl_2$ solution), then the recovery process would act as a one-stop solution for magnesium dosing. It wouldn’t be necessary to buy any additional magnesium solution from the market.

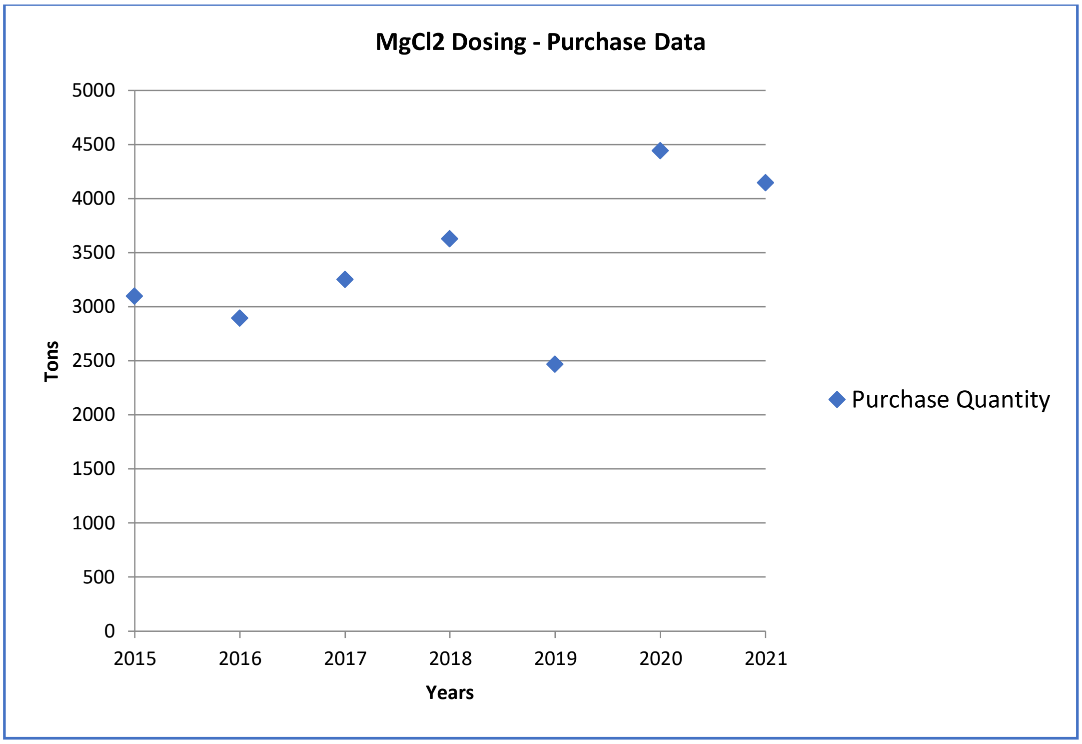

Figure 3.6: Annual purchase data of $MgCl_2$

3.1.4 Struvite reactor

After the anaerobic digestor, the homogenous digestate is sent to the struvite reactor (Fig 3.7) for struvite production. The struvite crystals produced are shown in Figure 3.8. After struvite is produced and separated, the digestate goes to dewatering decanters (Fig 3.9). After dewatering, the solid sludge goes for incineration.

Figure 3.7: Struvite Reactor at WWTP Amsterdam-West

Figure 3.8: Struvite Crystals

In the decanters, a coagulant (LC 699 A from VTA Austria GmbH) is used to coagulate the digestate. This coagulant is sensitive to salinity i.e., the concentration of NaCl. The current salinity in the incoming anaerobic digestate is 5 g/l. The sodium concentration should be minimal in the magnesium dose recovered from the R.O. concentrate (which has very high salinity). The magnesium dose recovered should not have a significant effect on the salinity level.

Figure 3.9: Decanters

During the abovementioned process, Ca_2PO_4 crystals are found in the system. This implies there is calcium present in the digestate. Presently, it does not affect the struvite precipitation and forms crystals with phosphate ions. Hence small quantities of Ca^{2+} should not be a problem, but if a significant amount of Ca^{2+} is dosed with the new Mg^{2+} dose (since divalent cations are challenging to separate from brine, as discussed in Chapter 2), then it may pose a problem.

In the wastewater treatment plant at Amsterdam-West, to tackle the production of hydrogen sulfide (H_2S), more than 100 tons of ferric salts are added to the aerators annually. This is because hydrogen sulfide gas in lower concentrations smells like rotten eggs and could be hazardous to health in higher concentrations. It also leads to corrosion in the sewer system. Iron has a high affinity for sulfides. Regardless of the compound or valence of iron, iron sulfides always form when sulfides are present. Iron sulfide (FeS) has extremely low solubility. Hence competitive reaction with other constituents does not occur. Therefore, there is a minute concentration of Fe, but it is not affecting the struvite precipitation, as of now. Iron is a vital metal to monitor in the magnesium dosing since the R.O. concentrate is anaerobic and contains Fe^{3+} ions.

3.2 Qualitative Assessment

The chemical composition of the concentrate was modeled in PHREEQC to determine the stability of the elements and the saturation levels. PHREEQC is a software used for the speciation of a sample indicating the saturation indices and distribution of aqueous species. The PHREEQC model is shown in **Appendix A2**. This was done because, generally, the compounds are near their saturation limits after the membrane filtration process; if that is the case, it is essential to know which compounds are already oversaturated in the R.O. concentrate. This will help determine the recovery process for magnesium.

The results indicated that every compound's Saturation Index (SI) was within limits. No major compounds had any tendency to precipitate. This means that the R.O. concentrate is relatively stable and could undergo additional magnesium recovery treatment without scaling/jamming issues.

3.3 Quantitative Assessment

The magnesium concentration in the groundwater was 259 mg/l (**Appendix A1**). The simulation showed that in a brand new, two-stage R.O. unit with a 71% permeate recovery, the magnesium concentration in the concentrate would be 890.9 mg/l (Table 3.1). On the other hand, in an R.O. unit with an element age of 5 years, with a 71% permeate recovery, the magnesium concentration in the concentrate was 890.6 mg/l (**Appendix A1**). Hence an element age of 5 years doesn’t make any difference in magnesium recovery.

For the boundary limits of recovery is between 60% and 80%, the magnesium concentration in the concentrate would be between 647.5 mg/l and 1295 mg/l respectively based on groundwater concentration of 259 mg/l.

The amount of 32% $MgCl_2$ magnesium chloride solution, which is available for recovery (assuming 100% availability of chloride ions and full magnesium recovery), is 25,364 tons annually. The calculation is shown in **Appendix A3**. Even if the recovery is 20% of the above value, it is still greater than what is needed for struvite production (4500 tons). Suffice it to say there is more than enough magnesium available to recover for dosing in the struvite reactor. If we talk about Mg^{2+} ions (since maybe the salt of magnesium recovered is other than $MgCl_2$), and the current $MgCl_2$ dose (4500 tons), the Mg^{2+} concentration is 81.68 grams/liter, which translates to 8.168% solution of Mg^{2+} being dosed. From the concentrate, assuming full Mg^{2+} recovery; 25,367 tons of 8.168% solution of Mg ions could be recovered. Even if the actual recovery is 20 % of it, it is still enough to meet the demand for magnesium dosing.

3.4 Criteria for Selection

One of the most crucial tasks is to determine which form of magnesium could be dosed in the struvite reactor and which form could be recovered from the brine. The current situation is as follows: A 32% stock solution of magnesium chloride is dosed in the struvite reactor. The other compounds of magnesium are magnesium hydroxide ($Mg(OH)_2$), magnesium carbonate ($MgCO_3$), and magnesium sulfate ($MgSO_4$). As far as struvite crystallization is concerned, the only important factor is the presence of magnesium ions. But the downstream wastewater treatment process, namely dewatering, could be affected by the type of magnesium compound. Based on the data gathered and shown in the above sections, several deciding factors are formulated, which collectively answer the question of which magnesium salt to be recovered and what would be limitations on the recovery process and dosage. The factors and their relevance are described in Table 3.2.

Table 3.2: Factors affecting the choice of the recovery process

Serial No.	Factor	Relevance
1	Compatibility with the dosing system	The dosing system is aqueous. Hence precipitation/crystallization during recovery from brine is counterproductive. It makes sense to obtain a stream of high-concentration magnesium ions. Also, the dosage cannot be a slurry; it must be aqueous.

2	Effect on struvite crystallization	The recovery of a magnesium compound from brine would not be pure unless precipitation is applied (still, there is generally massive co-precipitation). Hence there will be impurities present. These could be cations such as Na^+, Ca^{2+}, and Fe^{3+}, which inhibit the struvite crystallization process.
3	Effect on the dewatering process	As mentioned before, the dewatering process uses a coagulant that is sensitive to anionic concentrations. Hence excess anion concentrations in the magnesium dose could lead to affecting the dewatering process. It is also imperative to remove the salinity (NaCl) completely from the magnesium dose.
4	Separation from calcium	The R.O. concentrate contains more calcium concentration than magnesium. Separation of divalent cations through any membrane process is not possible. The only way is precipitation. Either precipitate out the calcium ions or precipitate out the magnesium ions. It is much more sensible to separate out calcium precipitates and obtain an aqueous stream of high magnesium concentration. Now the salts of magnesium and calcium namely: chlorides, sulfates, hydroxides, and carbonates vary in solubility. Between calcium and magnesium salts, calcium salts are likely to precipitate first except in case of hydroxides. Among the calcium salts, the solubility is as follows: $CaSO_4 > Ca(OH)_2 > CaCO_3 > CaCl_2$ (Ksp values in **Appendix A4**, (KSP solubility constant for common salts).
5	Feasibility for recovery	The R.O. concentrate composition is important in determining which compounds of magnesium are feasible to recover in most recovery processes. Hence the chloride, sulphate and carbonate concentrations in the brine are also an important factor. Because otherwise, additional resources would be required. The highest quantity in the brine is of Chloride ions.
6	Solubility	The magnesium salts should be soluble in water at the dosing concentration and temperature. All the investigated salts are soluble in that range.

Table 3.3 summarizes the advantages and disadvantages of each of the magnesium salts based on Chapter 2 and findings of initial sections of Chapter 3.

Table 3.3: Advantages and disadvantages of magnesium salts

Compound	Advantages	Disadvantages
$MgCl_2$	Tried and tested for struvite crystallization	Separating of $CaCl_2$ from $MgCl_2$ is not possible as they are both highly soluble in water.
$Mg\ (OH)_2$	There is tremendous literature available to obtain $Mg(OH)_2$ from brine existing since 1940s as shown in Chapter 2.	This salt is not selected since it is not compatible with the existing dosing system.
$MgSO_4$	There is literature indicating possible ways to recover $MgSO_4$ from brine and use it for struvite production (Chapter 2). $CaSO_4$ in the form of gypsum could easily precipitate out.	The sulfate concentration in the brine is limited.
$MgCO_3$	This salt won't affect struvite crystallization process.	$CaCO_3$ precipitation is not as significant as in the case of gypsum. Also, very limited literature is present indicating ways to recover $MgCO_3$ precisely because other compounds are relatively easy to recover and carbonate concentration is limited in brine.

3.5 Selection of possible recovery processes

Based on the literature review and the findings of previous sections, the merits and demerits of each technology are summarized.

All precipitation processes require a considerable number of resources and always pose the risk of massive co-precipitation. The Dow process is not ideal for the present study because it requires substantial setup and significant resources. The goal is to produce a concentrated aqueous stream of magnesium salt by recovering magnesium from the R.O. concentrate economically. The energy-intensive electrolysis step is not suitable. Even if the steps till magnesium chloride production are considered, a considerable quantity of hydrochloric acid would be required. This is an excellent method to produce $Mg(OH)_2$, but that is not compatible with the dosing system since the dosing can also be aqueous and $Mg(OH)_2$ solution is a form of slurry. Hence a setup involving a flocculation tank, settling tank, filtration unit, and neutralizer tank to produce $MgCl_2$ is not desirable when there is a more straightforward way of achieving that. Also, first creating $Mg(OH)_2$ and then converting it to $MgCl_2$ is also a bit counterproductive; it would be more beneficial to obtain $MgCl_2$ directly.

The magnesium salts that could be recovered must be in a form that can be dosed in the existing dosing system: i.e., it must be aqueous. This is why recovering magnesium in the form of magnesium hydroxide ($Mg(OH)_2$) is not a good option since it is in slurry form and hence not compatible with the existing dosing system. The dosing system is not open for upgradation. This is why precipitation and crystallization methods are not appropriate. This is because first, a lot of energy and resources would be required to create and separate precipitates, and then they would have to be converted into aqueous form again. Hence the best option is to obtain a stream of highly concentrated magnesium ions from the concentrate. The precipitation option, although can be considered for separating calcium precipitates.

An E.D. with monovalent selective cation exchange membranes that can generate a stream of divalent cations is very electricity-intensive and has only been theorized or experimented with at a laboratory scale. No full-scale installations are operational, and much research is going into optimizing such a process. This is because both the capital and operating costs are high. Hence, much research spanning many years is required before a full-scale installation comes into being. Also, this would not solve the problem of separating calcium ions from magnesium ions. Hence it was decided to wait to follow through on this technology for now and would only consider it if the rest of the options do not yield actionable results.

The remaining technologies are ion exchange and nano-filtration.

Nano-filtration can be used to concentrate the magnesium particles while at the same time diluting the sodium and chloride concentrations. This would require a two-step process consisting of concentration and dilution stages. The rejection rate is often slightly different for calcium and magnesium ions. Hence calcium concentration could also decrease overall in several cycles. A detailed description of the process is given in Chapter 4.

An ion exchange column containing an ion exchange resin is traditionally used for water treatment. It does so by removing contaminants or unwanted ions from the water. Cation exchange resins are used for softening processes, specifically removing divalent cations such as magnesium and calcium from the water. In a normal softening process, when the breakthrough of divalent cations occurs in the outlet, the process is stopped, and the resin is regenerated. In the present study, the process will be stopped when the magnesium concentration in the inlet and outlet is the same. This would ensure saturation in the resin with divalent cations. Then, when the resin is regenerated with acid, the stream generated would be rich in divalent ions. It is generally discarded as a waste stream. But in this case, it will be the magnesium-rich stream for struvite production. This process, with its limitations and complete analysis, is discussed in Chapter 5.

Chapter 4:

Nano-Filtration

This Chapter investigates the technology of nano-filtration for the recovery of magnesium ions. It first explains the theory behind the recovery pathway, then the methodology for investigating it. After that, it discusses the results obtained.

Chapter 4 Nano-Filtration

4.1 Theory and Hypothesizes

To obtain an aqueous stream rich in magnesium ions, it is imperative to reduce the concentration of sodium and calcium ions. For this, a two-step Nano-Filtration (N.F.) process was thought of as a potential solution to reduce the concentration of sodium and calcium ions.

Step 1: Concentration

In this step, the R.O. concentrate is concentrated further using the N.F. unit. The criteria for selecting the N.F. membrane are as follows:

1) High Magnesium rejection: The rejection of divalent cations in N.F. membranes can be as high as 99%. The current magnesium concentration in R.O. concentrate is 890.9 mg/l, and the goal is to reach a concentration of 81.68 g/l for struvite precipitation. That is a concentration factor of 91. Hence the N.F. membrane chosen should have very high magnesium rejection.

2) Low Sodium Rejection: The rejection of monovalent cations in N.F. membranes could be between 20% - 70%. The current sodium concentration in the concentrate is about 6744.4 mg/l. The goal is to have negligible sodium concentration for struvite precipitation. Hence the N.F. membrane chosen should have as low sodium rejection as possible.

3) Calcium rejection < Magnesium rejection (Preferred): Although the rejection of all divalent cations is relatively high in N.F. membranes, there are still differences present between the specific divalent cations. The calcium concentration in the R.O. concentrate is 1.6 times that of the magnesium concentration, and ideally, for the recovery, it should be negligible or way less than the magnesium concentration. Hence the N.F. membrane chosen should ideally have relatively higher rejection for magnesium ions than calcium ions.

Step 2: Dilution

Once the R.O. concentrate is passed through the N.F. unit having recovery of around 50-70%, the N.F. concentrate produced would be 30-50% of the R.O. concentrate. This must be sent back to the N.F. unit for more concentration. Before it is sent back, it should be diluted with ultra-pure water back to its original quantity.

When repeated 6-7 times, this two-step process should produce an aqueous stream with very low sodium and calcium concentrations while magnesium concentration remains as near to the original as possible. Then the obtained stream could be concentrated with another N.F. unit to increase the magnesium concentration. The process is described in Figure 4.1 and explained with an example below.

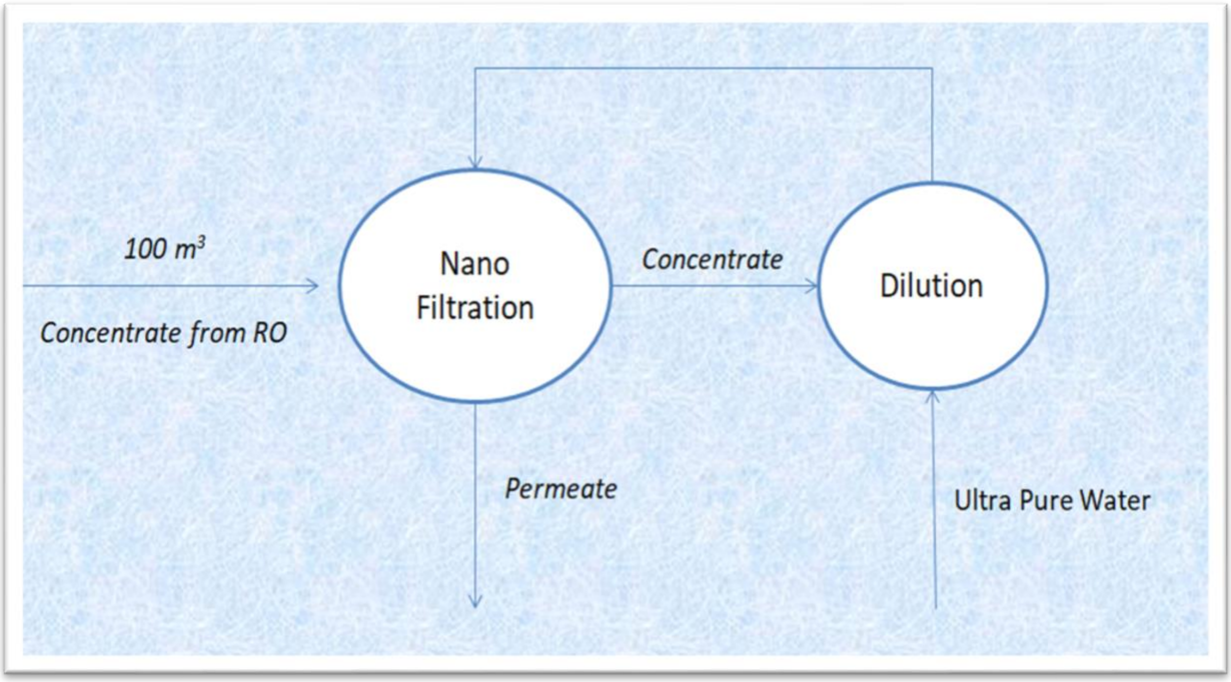

Figure 4.1: N.F. process flow chart

For instance, a 100 m^3/h flow of R.O. concentrate is sent through the N.F. unit. The permeate of the N.F. unit is discharged, and the concentrate is diluted back to its original quantity so that it can be sent through the N.F. again. The dilution step decreases the concentrations of every ion by 50%. The dilution step is imperative; otherwise, the N.F. membrane will stop working after 1-2 cycles. This is because the recovery is generally near 50-70%. So from 100 m^3 feed in the first cycle, assuming a recovery of 60%, only 40 m^3 is sent to the next cycle and only 16 m^3 to the cycle after that. This leads to precipitation, scaling, and design warnings in the N.F. unit.

This recovery process was investigated via software simulations. Two software were used for this purpose which are commonly used to design N.F. systems: WAVE and IMS design.

4.2 Results

4.2.1 Membrane Selection

Several N.F. membranes are available in the WAVE software, while their number is lower in the IMS design software. Each membrane was tested in same simulation. The simulation used a 1 stage N.F. membrane system. The feed water was identical to the composition of the R.O. concentrate. The rejection percentages of all the anions and cations were obtained successfully. The data is plotted in Figure 4.2. The x-axis represents the different N.F. membranes (namely NF90B-400, NF90-400/34i, NF90-4040, NF90-400/34, Nf200-4040, NF270-400/34i, NF270-400/34, NF270-440, and NF270-4040) and the y-axis displays the rejection percentages. The orange square depicts magnesium ions, the green triangle is for calcium ions, and the blue diamond represents sodium ions.

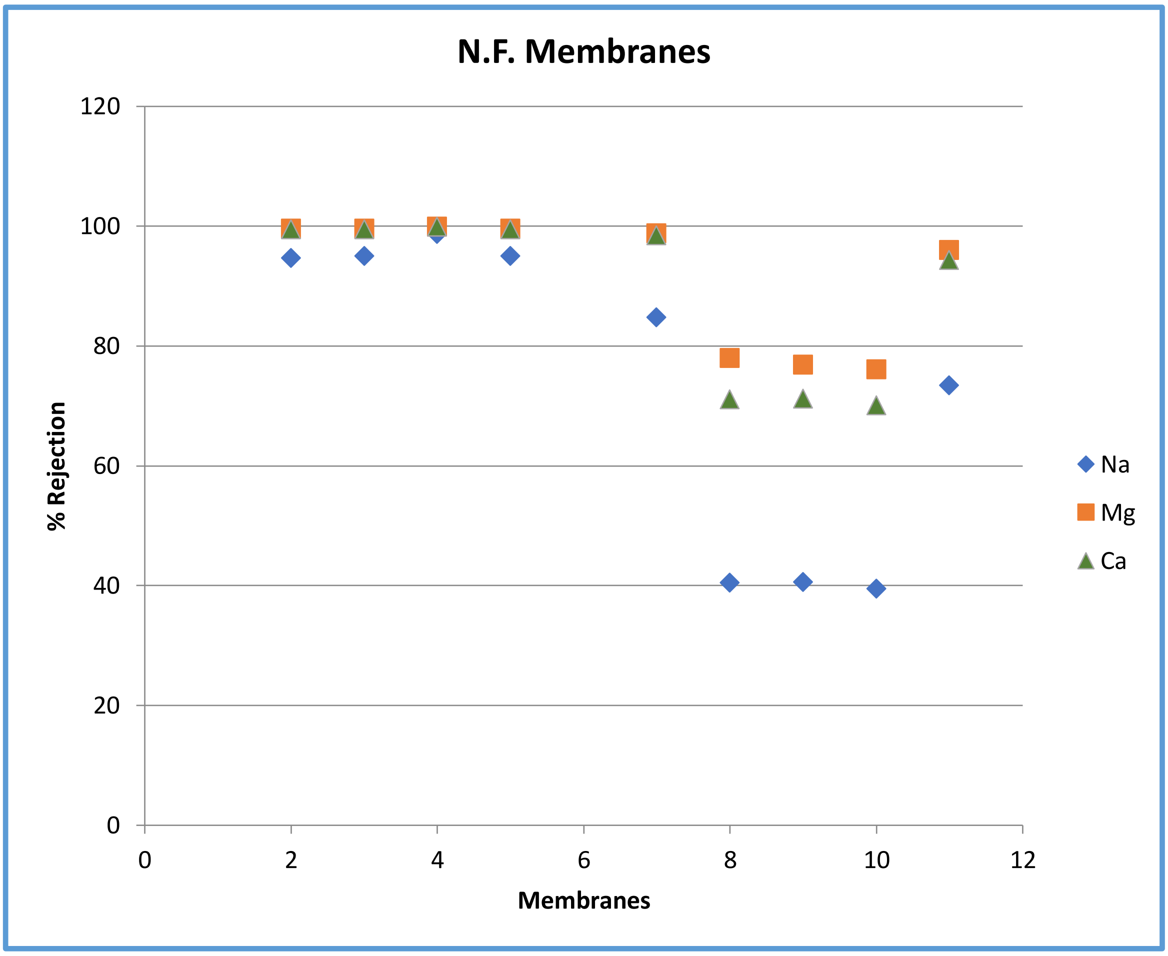

Figure 4.2: % Rejection for different cations in different membranes

It can be seen from Figure 4.2, that the membranes with a very high rejection percentage of magnesium (about 99%); also have a high rejection percentage of calcium (about 99%) and sodium ions (about 95%). These are therefore not suited for the required purpose. The membrane at number eleven on the x-axis has a significant separation of about 25% between sodium and magnesium rejection percentages. Still, the corresponding difference between magnesium and calcium rejection percentages is negligible.

Hence the membrane at number 8 (NF270-440/34) was selected for magnesium recovery. It has a high magnesium rejection of 78.0%, a relatively lower calcium rejection of 71.1%, and a much lower sodium rejection of 40.5 %. Different configurations were tested for the N.F. unit, as described in the sections below.

4.2.2 One Stage N.F. unit system

In the first configuration, a 1-stage N.F. unit was simulated. The details of the unit are described in Table 4.1.

Table 4.1: 1-Stage N.F. Unit characteristics

Characteristic	Description
Membrane selected:	NF270-400/34
Inlet flow:	100 m^3/h
Recovery:	50%
Stages:	One
Dilution after every cycle:	Back to 100 m^3
Number of cycles:	1

After inputting the composition of the concentrate, the concentration of some ions was adjusted by the software to achieve charge balance. The charge was not balanced because the software accepts ion concentrations of limited cations and anions. In addition, the software does not work if the concentration of an ion has decimal points. Hence the concentration of all ions was rounded off to the nearest whole number. Due to this, charge equilibrium was not established initially, so the software adjusted the concentration of certain cations and anions to account for charge equilibrium. The Na concentration changed from 6744 mg/l to 7312 mg/l, Mg concentration from 890.9 to 900 mg/l, and calcium concentration from 1506 to 1500mg/l. The results after the first cycle are shown in Table 4.2.

Table 4.2: Results after 1st cycle for simulation of 1- stage N.F. system

Ion	Initial Concentration ($100m^3$) (mg/l)	% Rejection	Permeate concentration ($50m^3$) (mg/l)	Concentrate concentration ($50m^3$) (mg/l)
Sodium (Na)	7312	40.5	4351.0	10199.0
Magnesium (Mg)	900.0	78.0	197.7	1584.0
Calcium (Ca)	1500.0	71.1	433.6	2539.0

This simulation was tested for ten cycles. The composition of the concentrate obtained after the 10th cycle is described in Table 4.3.

Table 4.3: Results after the 10th cycle for simulation of 1-stage N.F. system

Ion	Initial Concentration (mg/l)	Final Concentration of concentrate (after 10th cycle) (mg/l)
Sodium (Na)	7312	161
Magnesium (Mg)	900	250
Calcium (Ca)	1500	240

From Table 4.3, after ten cycles, the magnesium concentration decreased by a factor of 3.6, the calcium concentration decreased by a factor of 6.25, and the sodium concentration decreased by a factor of 45.4.

In addition to the above results, no design warnings were encountered. Hence the simulation is technologically feasible. However, many other warning signs were encountered, such as:

- Langelier Saturation Index > 1: The Langelier saturation index measures calcium carbonate saturation in water. If it is greater than 1, that means water is oversaturated with $CaCO_3$, and scaling will develop in the system.

- Stiff-Davis Stability Index > 0: This index overcomes the shortcoming of the Langelier index, considering the impact of the "common ion" effect on the driving force for scale formation and high total dissolved solids. Generally, this index predicts less scale forming for the same water chemistry than the Langelier index. But if this index is >0, that means water is scale forming.

- Gypsum ($CaSO_4$) saturation
- $BaSO_4$ saturation

An antiscalant can indeed handle the saturations. Although, that was not possible to test in the simulations. But the fact that it took ten cycles for the calcium and sodium concentration to be lower than that of magnesium is not desirable. Moreover, there isn't any significant difference between the concentration of magnesium and calcium ions. Therefore, simulations with multiple stages and higher recovery were attempted.

4.2.3 Two Stage N.F. System

Using the same N.F. membrane, a 2-stage N.F. unit was simulated. The characteristics of the simulation are described in Table 4.4.

Table 4.4: 2-Stage N.F. Unit characteristics

Characteristic	Description
Membrane selected	NF270-400/34
Inlet	100 m^3/h
Recovery	65%
Stages	Two
Dilution after every cycle	Back to 100 m^3
Number of cycles	8

A recovery of 65% means 35 m^3 of concentrate will be generated for a feed of 100 m^3. First, a dilution of 100% was tried, which means that the obtained concentrate (35 m^3) was diluted to 70 m^3 and sent back to the N.F. unit. Then for the next cycle, a concentrate of 24.5 m^3 (35% of 70 m3) was obtained, which was diluted to 49 m^3. This resulted in the system stopping after three cycles because many design warnings were unsolvable. Most of the time, the flow in some elements was less than the minimum flow required. Hence the system stopped working. So, the N.F. concentrate was diluted back to 100 m^3 after every cycle.

The ion concentrations in the concentrate obtained after each cycle are described in Figure 4.3**.** The x-axis represents the number of cycles, and the y-axis represent the concentration of ions in mg/l. The blue diamond represents sodium, the orange square represents magnesium, and the green triangle represents calcium.

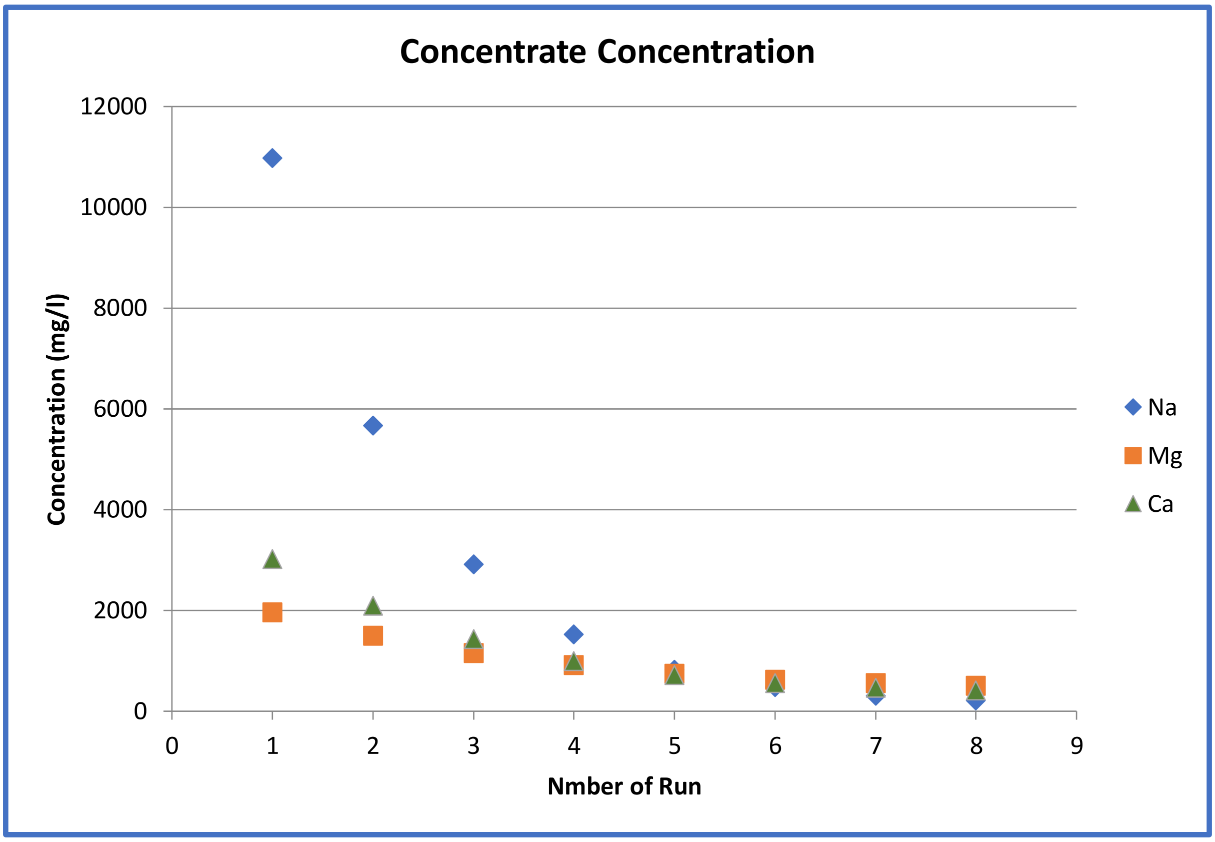

Figure 4.3: Ion concentration after each cycle

As seen in Figure 4.3, the sodium concentration decreased with every run, and the calcium concentration eventually got lower than magnesium, which was the idea behind implementing the N.F. process. The final concentration of the ions at the end of the 8th cycle is shown in Table 4.5.

Table 4.5: Results after the 8th cycle for simulation of 2-Stage N.F. system

Ion	Initial Concentration (beginning of 1st Cycle) (mg/l)	Final Concentration of concentrate (End of 8th Cycle) (mg/l)
Sodium (Na)	7312	218

Magnesium (Mg)	900	509
Calcium (Ca)	1500	408

The magnesium concentration decreased by a factor of 1.5, the calcium concentration decreased by a factor of 3.67, and the sodium concentration decreased by a factor of 33.5. The results are relatively better than one stage N.F. system, and it took eight cycles instead of ten to get the calcium concentration lower than magnesium. The sodium and calcium concentration was expected to be much lower than the magnesium concentration in 5-6 cycles. The fact that it took eight cycles to accomplish the results shown in Table 4.5 is not preferable.

N.F. systems with more stages were also simulated after this but increasing the number of stages of the N.F. unit to more than two resulted in too many undesirable design warnings, which meant that the system was not compatible anymore.

4.2.4 Concentrating Magnesium

Once the aqueous stream is obtained with minimal calcium and sodium concentration, the next step is concentrating it so that magnesium concentration increases. This is because magnesium still needs to be concentrated by a factor of 160 to reach 81.68 g/l from 0.509 g/l. For this purpose, a Christmas tree configuration was used, i.e., the elements of the N.F. unit is decreasing as the stages increase (Figure 4.4). Each Stage consists of a certain number of elements (N.F. membranes).

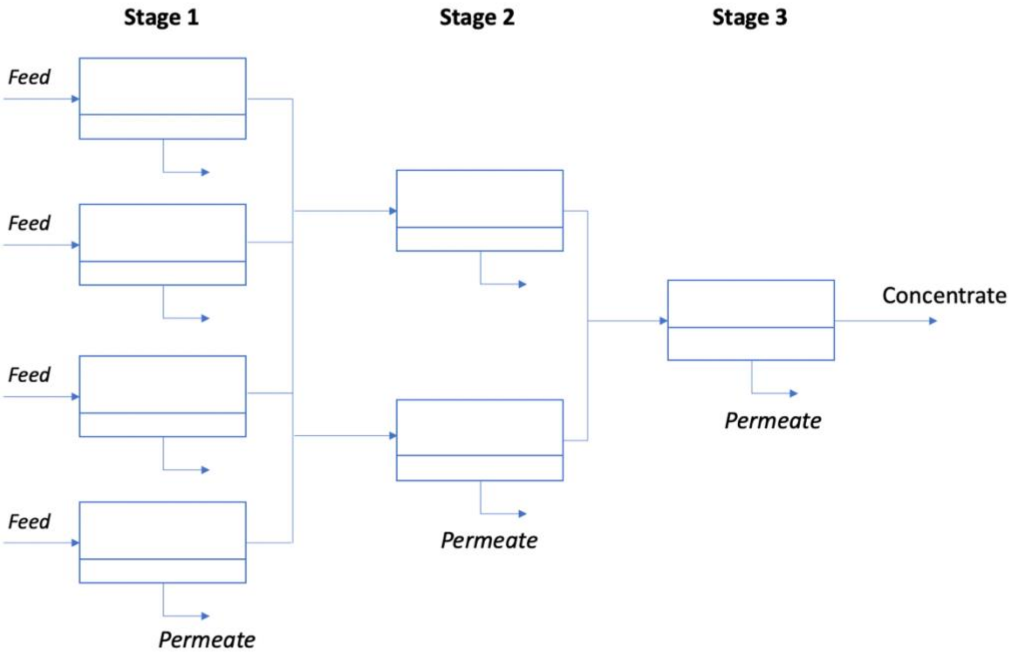

Figure 4.4: Christmas Tree Configuration

Every possible configuration with 2, 3, 4, and even five stages were simulated. The results were negative. The configurations with more than three stages always failed. With a configuration with three stages, numerous design warnings were encountered after the first cycle. The design warnings included but were not limited to the concentrate flow rate being less than the minimum element limit, the element recovery surpassing the maximum limit, etc.

It is important to note that the starting volume was 35 m^3/h. Dilution is not an option here because the goal is the increase the magnesium concentration tremendously. Even after the second run on the Christmas tree configuration with two stages, the volume was insufficient to keep the system running. The system needs to run multiple concentration cycles to reach the required magnesium concentration, which is not feasible. The only way to concentrate the stream is via some form of evaporation, which is usually not a desirable option due to the high electricity consumption.

4.3 Discussion

The current results indicate that the N.F. process is not efficient enough. However if the N.F. membranes available were highly selective, with a high rejection rate for magnesium ions and very low for sodium and calcium ions. In that case, this approach may have worked.

There is another point of concern with this approach which is the usage of ultra-pure water. For every 100 m^3 of R.O. concentrate, 520 m^3 of ultra-pure water is needed to complete eight cycles in the 2-stage N.F. system. The expected quantity of R.O. concentrate is 1.6 Mm^3 to 3.2 Mm^3 annually. To implement the N.F. process, 8.32 Mm^3 to 16.64 Mm^3 of ultra-pure water would be required. The drinking water production is expected to be about 5.6 Mm^3. Since the permeate of the N.F. unit is high in sodium (due to low rejection), the permeate is not useful and is considered a waste.

Chapter 5:

Ion-Exchange

This Chapter investigates the technology of ion exchange for the recovery of magnesium ions. It investigates both weak and strong acid cation exchange processes. It first explains the theory behind the proposed recovery pathway, then the methodology about how it will be investigated. Thereafter, it describes the results and the discussion for the recovery pathway including its efficiency and potential for optimization.

Chapter 5 Ion-Exchange

Ion exchange has been widely used for softening and purification purposes since last many decades. It can be classified into weak/strong cation and weak/strong anion exchange processes. For the recovery of magnesium ions, the cation exchange processes were investigated.

5.1 Aim and Hypothesis

Generally, the aim of an ion exchange process is to treat water, but for the purpose of magnesium recovery, the method will be used in a different manner than it is normally applied. Normally, the aim is to stop the process i.e., the flow of water through the column, at breakthrough (detection of Na^+ or Ca^{2+}/Mg^{2+} ions in the effluent). But for the present study, the feed water was stopped when the magnesium concentration in the outlet equals the magnesium concentration in the feed water. That would mean the resin is saturated with magnesium ions. The resin always has a greater affinity for divalent cations. So though at first sodium ions will also be attached to the resin, over time, it will get saturated with just Mg^{2+} and Ca^{2+} ions. If the column is operated in H^+ form, it will be regenerated with an acid (HCL or H_2SO_4). If the column is operated in the Na^+ form, then it can be regenerated with NaCl or with an acid (HCL or H_2SO_4) and a base (NaOH). The regenerant stream produced would be rich in Ca^{2+} and Mg^{2+} ions. If H2SO4 is used as the regenerant, there is a possibility that gypsum would precipitate out. This would result in a stream rich in Mg^{2+} ions only which is the aim of the present study.

Software simulations were conducted in the WAVE software both in weak and strong cation exchange resins. The weak cation exchange resins were available to be operated in the H^+ form which means regeneration with an acid. The strong cation exchange resins were available to be operated in the Na^+ form. The results are described in the further sections.

5.2 Weak Acid Cation Exchange

Normally a cation exchange process works as follows in a weak acid cation exchange: A column is filled with a weak acid cation exchange resin. Water with high TDS content is passed through the column. Generally, a traditional weak acid cation exchange resin is almost always operated in the H+ form. H^+ ions replace the cations (Ca^{2+}, Na^+, Mg^{2+}) in the water to produce decationised water. Since the affinity is greater for divalent cations, over time, the column could be completely saturated with divalent cations. The exchange capacity depends on alkalinity. It removes the hardness associated with alkalinity. The resin is regenerated with an acid (HCl or H_2SO_4). The process is described in figure 5.1.

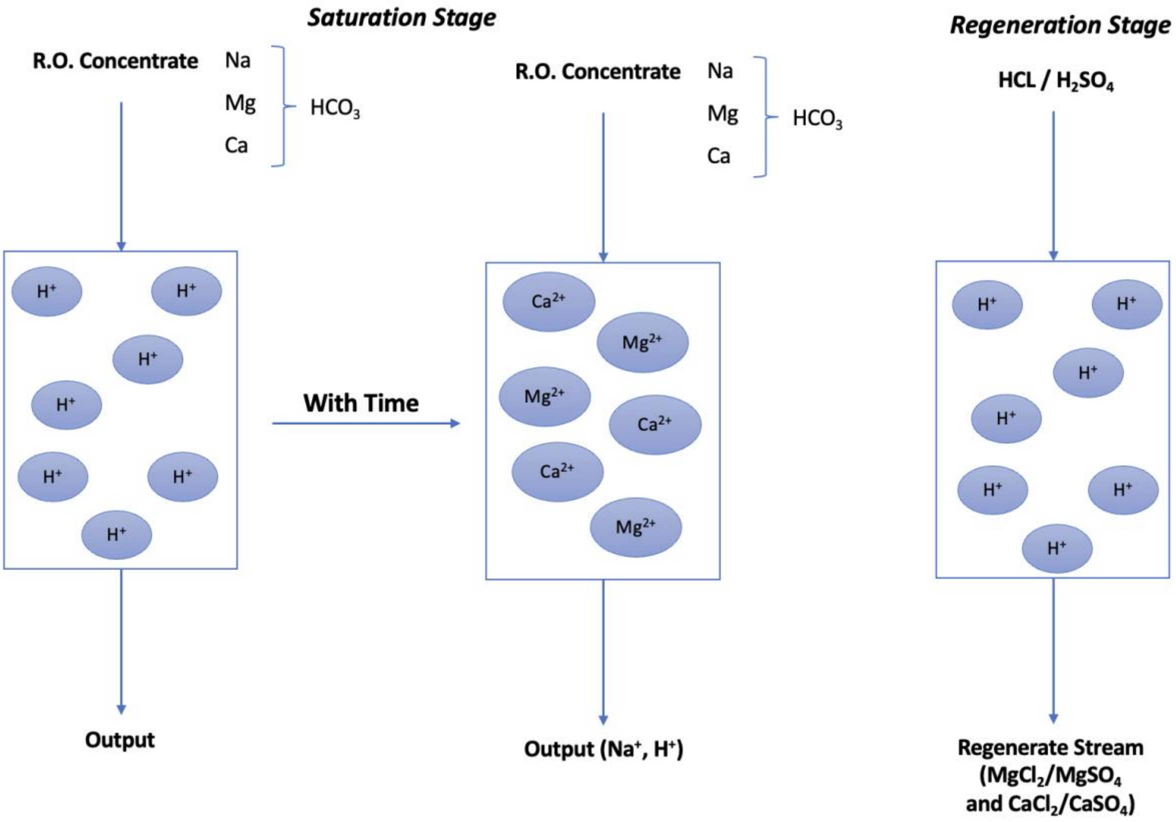

Figure 5.1: Recovery Process using cation exchange resin in H^+ form

A model was made for the same in the WAVE software. The software contained the data for the following resins: AmberLite HPR8300H, AmberLite HPR 8400 H, AmberLite IRC83H, and AmberLite Mac-3H. Simulations with all these available resins were carried out but the result was the same.

5.2.1 Results

The results of the simulation are described in Table 5.1.

Table 5.1: Results for simulation of weak acid cation exchange

Parameter	Feed	Outlet (Estimated Average)
pH	7.68	4.52
Hardness (ppm $CaCO_3$)	7462	6507

Alkalinity (ppm $CaCO_3$)	1004	32

The software doesn't tell the exact concentration of ions as it did with N.F. It only tells the feed and the outlet concentration of hardness and alkalinity in terms of ppm $CaCO_3$. Hardness represents the Ca^{2+} and Mg^{2+} ions whereas alkalinity represents the hardness associated with carbonate and bicarbonate ions. 954.88 ppm $CaCO_3$ of hardness was successfully removed but the ratio of Mg and Ca removal is not known. In terms of alkalinity, 971.7 ppm $CaCO_3$ was removed.

With weak acid cation exchange, the divalent cations can only be removed as long as the carbonate and bicarbonate are present i.e., it removes hardness associated with alkalinity. Since the concentration of these ions is limited in the R.O. concentrate, only limited hardness could be removed. Changing the resin packaging size was tested in the hope of increasing the efficiency of the process. It did not affect the outcome. Changing the resin packaging size only changes the design of the bed (bed diameter, resin volume, etc.,)

Weak acid cation exchange was originally thought because it could be easily operated in H^+ form. If the resin is in Na^+ form, then it means that the effluent during the saturation stage would have an even greater Na^+ concentration. Since the weak cation exchange process is limited due to the alkalinity, strong cation exchange processes were simulated.

5.3 Strong Acid Cation Exchange

The recovery process is shown in Figure 5.2. This process was simulated using WAVE software. The software only gave the option to operate the resin in the Na^+ form. Very limited strong acid cation exchange resins were available for simulations. Moreover, a very limited choice of regeneration chemicals was present. The simulations failed to give any useful results. For the removal of divalent cations, a chelating resin is best suited for this purpose.

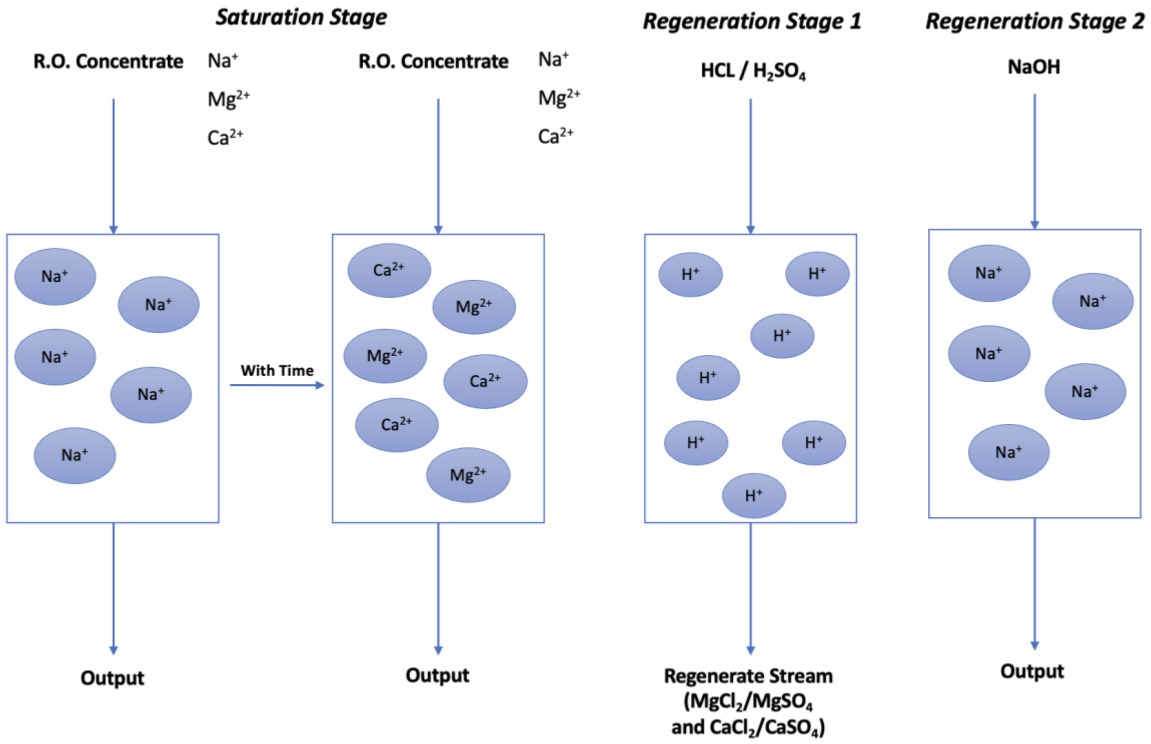

Figure 5.2: Recovery Process using cation exchange resin in Na^+ form

5.4 Chelating Resin

The software had its limitations because it was designed to simulate the process in such a way that the process is stopped at the breakthrough of ions which was not the aim of the experiment. Moreover, the best-suited resin for such a process would be a cheating resin. The software did not have a chelating resin in its library. Even if it had, the process again would only have gone until the breakthrough of divalent cations, and the aim is to continue the flow of water through the ion exchange column till saturation of divalent cations is reached.

For the purpose of the experiment, chelating resins are specifically useful for separating divalent cations. They are a class of cation exchange resins that utilize chelating resins covalently bonded to a polymer matrix. Chelation is the bonding of ions and molecules to metal ions in which two or more separate coordinate bonds are formed between a multiple-bonded ligand and a metal atom. They basically form complexes with alkaline earth metals. And they work well in high salinity and capture only divalent cations unlike softening resins which work in low salinity.

The resin which was selected was: AmberLite IRC747. This is a chelating resin. It is a weak macroporous, aminophosphonic resin designed specifically for softening saturated brine solutions. It delivers extremely low calcium and magnesium levels while providing a high operating capacity.

Macroporous resins have discrete holes in the polymer matrix. They act as stress relievers and provide physical toughness. They also have higher cross-link levels in the polymer. The structure also provides a greater surface area. An aminophosphonic resin is less selective for other metals in a hardness-rich environment than an iminodiacetate resin. Hence this type of resin is primarily used in brine softening. These form complexes with metal ions. This resin is not available in any software for simulation. The relative affinity of the AmberLite IRC747 resin for the different cations is shown below in decreasing order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mg^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Sr^{2+} > Ba^{2+}$. The fact that the affinity for calcium is less than that for magnesium is beneficial for the recovery process. Reaction:

$$R\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}PO_3Na_{2.} \;+.\; M^{2+.} = R\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}PO_3M + 2\,Na^{+} \qquad \text{(R3)}$$

Hypothetically, the process should work but the proof of concept was needed. Weak acid cation exchange experiments were performed in the laboratory at TU Delft with the chosen chelating resin to test the proof of concept. Optimizing the experiment/process was not the goal but to see if the recovery process is viable enough for further investigations.

5.5 Laboratory Experiment

A setup for an ion exchange column experiment is shown in Figure 5.3. The resin used was a weak chelating resin called AmberLite.

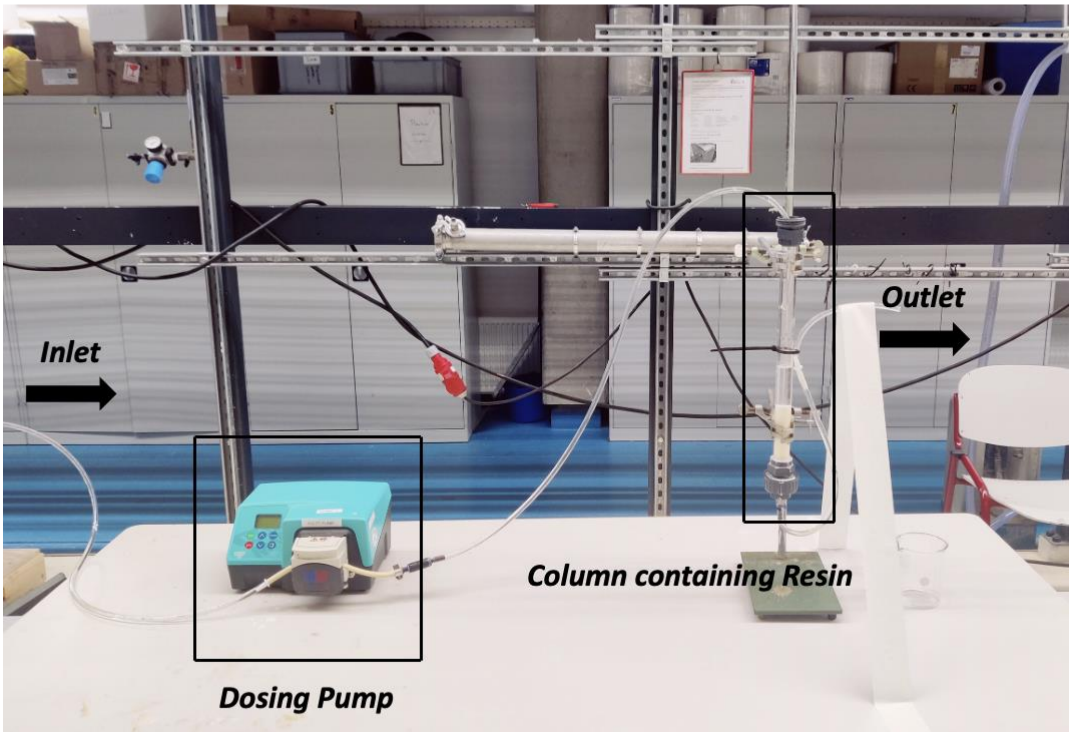

Figure 5.3: Experimental Setup

The sample water is pumped via a dosing pump (Figure 5.4). The dosing pump is Watson Marlow 323 peristaltic pump, which is a microprocessor-controlled variable speed pump with a variable speed range of 3.0 to 400 rpm ,translating into a dosing speed range of 0.09 to 2000 ml/min. The sample would be pumped to the top of a column containing the resin AmberLite IRC747 (Figure 5.5). The column containing the resin has been shown in Figure 5.6. There is a mesh at the bottom of the column to keep the resin from flowing out, but it allowed the water to pass. An exit tube was attached to the bottom of the column. The outlet was kept at a height equal to the top of the resin, this ensured that the water level is always greater than that of the resin so the resin never gets dry. It is important for the resin to not get dry to avoid air bubbles from forming in the resin. The sample exit through the outlet pipe into a collection vessel.

Figure 5.4: Watson Marlow Pump

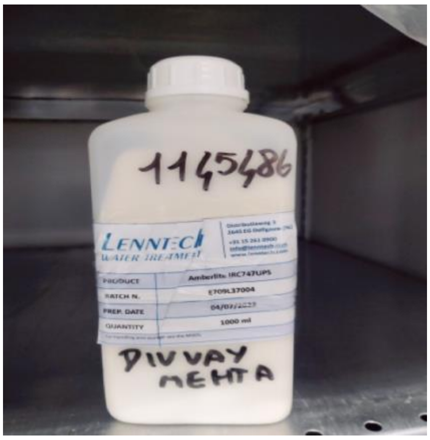

Figure 5.5: Amberlite IRC747 Resin

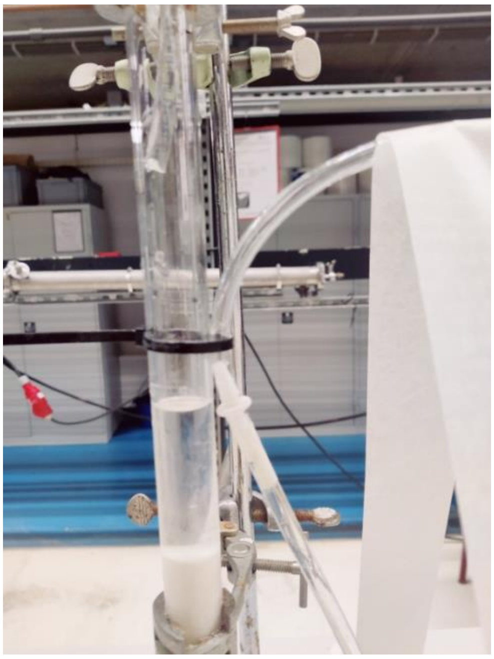

Figure 5.6: Column containing the Resin

For the regeneration of the resin, the following acids and bases were used:

- Sodium Hydroxide (NaOH): 1 N
- Sulphuric Acid (H_2SO_4): 2 N
- Hydrochloric Acid (HCl): 1N

5.5.1 Groundwater Sample Collection

The R.O. pilot was not in a functional state and would not have been for a few months. The water from the aquifer was collected for the experiments. The same logic works for aquifer water. The only difference is the R.O. concentrate would have higher concentrations for ions and hence less amount would be needed to saturate the ion exchange column. The important part is to figure out the saturation ratio of Mg/Ca ions. The well pumping the water from the aquifer is shown in Figure 5.7 and the sample collection is portrayed in Figure 5.8.

Figure 5.7: Pumping System for Aquifer

Figure 5.8: Sample Collection

The sample collection wells (blue in color, Fig 5.7) were used to collect the sample for analysis. The sample was collected from 2 different depths: One from a depth between 98-150 meters, and the other between 58-92 meters. Since the composition of the aquifer is similar throughout the depth, the samples were combined for the experimental analysis. 10-liter sample was collected for each of the depth ranges. The samples are shown in Figure 5.9.

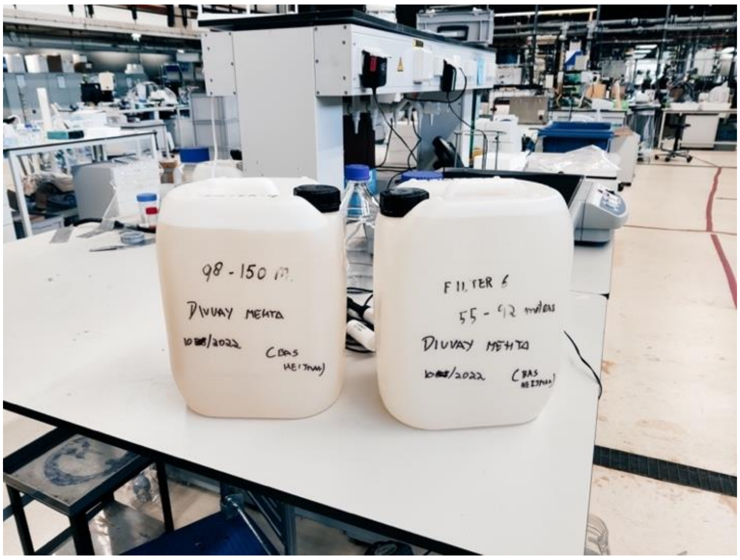

Figure 5.9: Groundwater Samples

The brownish-orange color in the water represents Iron (Fe^{3+}). This was brought in contact with oxygen during collection, hence the iron particles oxidized from Fe^{2+} to Fe^{3+} and started to precipitate. The groundwater sample had the following concentrations of the major anions and cations are shown in Table 5.2;

Table 5.2: Ion Concentrations in groundwater

Element	Concentration (g/l)
Sodium (Na^+)	2.030
Magnesium (Mg^{2+})	0.259
Calcium (Ca^{2+})	0.437
Chlorine (Cl^-)	4.450
Sulphate ($SO4^{2-}$)	0.368

5.5.2 Filtration for Iron Removal

Before ion exchange, the iron particles must be removed otherwise they would jam the IEX column. For this, a cartridge filter was used. The cartridge filter used was a spun polypropylene filter manufactured by Pentair Water, which had a rating of 1 micron, temperature range of 4.4-62.8℃, and used for sediment separation. The filter as in the new state and after filtration are shown in Figure 5.10.

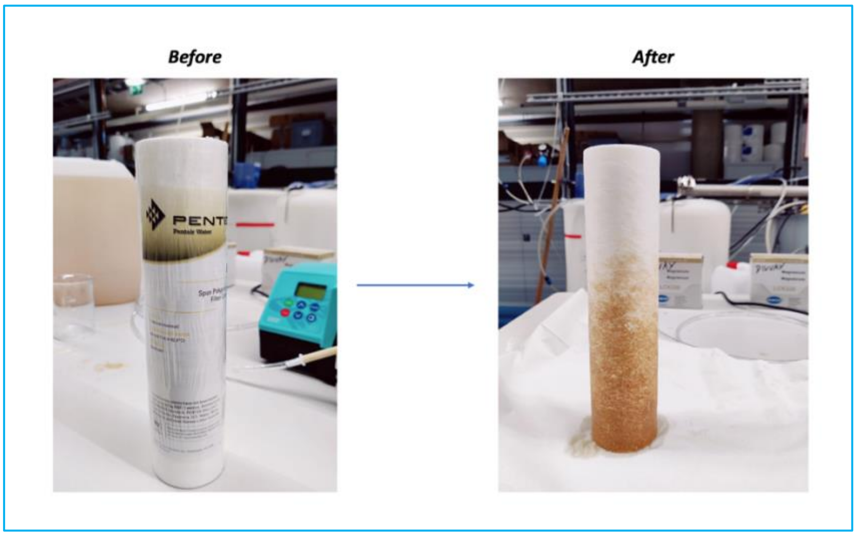

Figure 5.10: Cartridge Filter

5.5.3 Column Selection

The columns which were available in the laboratory for experimental analysis are shown in Figure 5.11. The columns are numbered one to five from left to right. The column selection depended on the following criteria:

- The cross-sectional diameter of the column should not be too small, otherwise, water flow through the resin may be interrupted due to the resin getting blocked and jammed.

- D/d i.e., column diameter to diameter of resin particles should ideally be >50, otherwise, the wall effect becomes important. The Wall effect is when the friction due to the wall surface has to be considered for calculating the pressure drop flow rate using the Ergun equation. This is normally a concern during water treatment using IEX that water does not pass the resin uninterrupted near the walls but for the recovery process it is not a concern, hence D/d ratio could be lower than 50.

- Availability of connection parts for the column

Figure 5.11: Available Columns

Columns 1 and 2 had quite small cross-sectional diameters, hence were not considered for the process. Columns 3, 4, and 5 have the same diameter. Due to the availability of connection parts for column 4, it was selected for the experiments. It’s characteristics are described in Table 5.3.

Table 5.3: Column characteristics

Parameter	Value	Units
Diameter	2	cm
Column height	32	cm
Available column volume	100.48	cm^3
Column height filled with resin	13	cm
Headspace available	19	cm
Volume of resin used	40.82	cm^3

5.5.4 Resin Properties

The resin had various characteristics which defined the experimental limits and duration for feed flow and regeneration, and these are described in Table 5.4.

Table 5.4: Characteristics of the resin

Parameter	Value	units
Particle diameter	0.05-0.06	cm
Ionic form	Na^+	
Total exchange capacity	>1.75	Equivalent/ liter of resin
Acceptable flow rate	20-40	BV/hour
Acceptable flow rate	816.4 – 1632.8	cm^3/hr
Regeneration (HCl)	1-2	N
Conversion to Na^+ (NaOH)	1-2	N

5.5.5 Experimental Analysis

The experiment was repeated three times. It was done two times (EXP1 and EXP2) by using HCl as the acid regenerant and one time by using H_2SO_4 (EXP3)as the acid regenerant.

The groundwater sample would hereby be referred to as the sample. The experiment was performed in 3 stages. In the first stage, the saturation stage, the resin was saturated with divalent cations from the sample. This can be ensured by measuring the concentration of magnesium ions in the outlet. For example, if the concentration of magnesium ions in the sample is x, then as the sample passes through the column, the magnesium ions would get attached to the resin. Hence the concentration in the outlet would be much lower than x in the beginning. The resin would start to get saturated and exhaust its exchange capacity with time. This means that it would replace fewer magnesium ions, and the concentration in the outlet would increase. When the concentration of magnesium ions in the outlet reaches x or 95% of x, the resin is fully saturated.

There is another way to calculate how much amount of sample would be needed for full saturation. The exchange capacity of the resin and the amount of the resin used are known. It is also known that the resin would only exchange magnesium and calcium ions since they were the majority of divalent cations in the sample. The ratio of Mg/Ca, which would be exchanged, was not known, and that was, in fact the goal of the experiment. So the maximum amount of Ca^{2+} and Mg^{2+} ions separately the resin could exchange can be calculated. Since the concentrations of these ions in the sample are known, the sample amount which would contain the calculated concentration could be easily found out. Both above-mentioned exercises were carried out to satisfactorily reach saturation in the resin.

Based on the volume of resin, its exchange capacity, and ion concentration in the sample, about 3.26 liters of sample would be required to fully saturate the column with just Ca^{2+} ions and about 3.35 liters of sample would be required to fully saturate the column with just Mg^{2+} ions. So 3.35 liters of the sample should definitely saturate the column with divalent cations. At 15 RPM, a flow rate of 43 BV/ hr was achieved, which translates to a flow of 1756 ml/h. All calculations with explanations are shown in **Appendix A5**. This meant a flow time of 1.9 hours. Taking safety margin, the experiment was run for 2 hours and 20 minutes. The other parameter for reaching saturation is the practical measurement of magnesium concentration in the outlet and inlet. This was done via using Hach kit LCK326. The saturation curve obtained via magnesium measurements in the outlet is shown in Figure 5.12.

In the second stage, regeneration with acid, the resin was dosed with acid. The H^+ ions in the acid would replace the Mg^{2+} and Ca^{2+} ions attached to the functional groups of the resin. The amount of acid to be dosed could be calculated using the exchange capacity of the resin. The amount was 71.45 ml for HCL and 35.7 ml for H_2SO_4. Due to a dosing error in practical BV/h, the actual volume of the acids dosed was 119.9 ml and 53.2 ml, respectively. These are still acceptable since the goal of saturation was achieved. The regenerant waste generated from this stage is hereby referred to as regenerant. This regenerant is filled with $MgCl_2$ and $CaCl_2$ when HCl was used for regeneration and $MgSO_4$ and $CaSO_4$ when H_2SO_4 was used for regeneration. This regenerant also contains the initial sample which was left in the outlet pipe from 1st stage of the experiment.

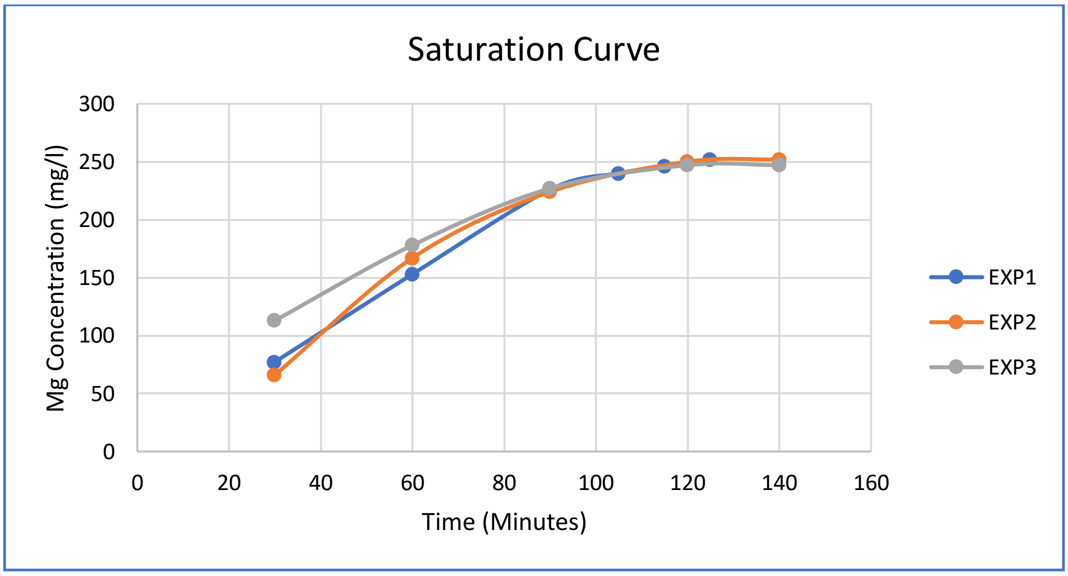

Figure 5.12: Saturation Curve

In the second stage, regeneration with base stage, Na^+ ions replace the H^+ ions in the resin. After this, the resin is fully regenerated and ready to be used again. The samples obtained were tested using in an Ion Chromatography (IC) (Figure 5.13) machine which tells the concentration of cations and anions in the water sample. The ions which were measured were Na^+, Mg^{2+}, Ca^{2+}, $Cl^{-,}$ and SO_4^{2-}. The standard sample loop used for the system is 5 μl with a range of 1 to 100 ppm. 2 columns were used for the analysis:

- A Supp 5 150/4.0
  - ⇒ standard anion column used for inorganic matrices such as drinking water or groundwater.
  - ⇒ Eluent Used: 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$
  - ⇒ Eluent running speed: 0.7 ml/min
- C6 Cation 150/4.0
  - ⇒ the standard cation column, suitable for the separation of both inorganic cations and amines.
  - ⇒ Eluent Used: 3mM HNO_3
  - ⇒ Eluent running speed: 0.9 ml/min

Figure 5.13: IC Machine

5.5.6 Results

The results (ion concentration in the regenerant stream) are described in Table 5.5 for EXP1 and EXP2 (when HCL was used for regeneration) and in Table 5.6 for EXP3 (when H_2SO_4 was used for regeneration

Table 5.5: Results of EXP1 and EXP2

Element	EXP1 - Concentration (g/l)	EXP2 – Concentration (g/l)	Remarks and Reflections
Sodium (Na^+)	0.724 ± 0.01	0.908 ± 0.03	According to mass balance, the sodium concentration from the sample remaining in the outlet pipe was 39.3% for EXP1 and 56.3% for EXP2, respectively. The rest of the sodium concentration comes from the resin. This means some sodium ions were still attached to the resin. Hence the results could be optimized further in the future.
Magnesium (Mg^{2+})	1.639 ± 0.09	1.658 ± 0.08	The magnesium concentration in the result is diluted due to 2 constraints of laboratory experiments and would not be present in the actual set-up. The actual concentration of magnesium should be higher than the obtained value. The first reason is volume dilution due to the sample volume left in the outlet pipe from stage 1. The second reason is the high accidental dosing of HCL as a reagent. Due to this, the total volume of the collected sample was higher than it should have been. In addition, this concentration also has magnesium ions partly from the sample left in the outlet pipe, which is 2.2% for EXP1 and 3.9% for EXP2, respectively. Taking all three factors into account, the actual magnesium concentrations are reported in Table 5.7.
Calcium (Ca^{2+})	4.561 ± 0.35	4.716 ± 0.34	The three factors which affected magnesium concentration have the same effect on calcium concentration. The concentration of ions from the outlet pipe accounted for 1.3% for EXP1 and 2.3% for EXP2, respectively. The calcium concentration is 2.8 times higher than magnesium concentration. This means that the regenerant obtained cannot be used for magnesium dosing for struvite precipitation without undergoing further treatment to remove calcium ions.
Chloride (Cl^-)	25.637 ± 0.21	24.140 ± 0.14	The chloride concentration from the outlet pipe only accounted for 2.5% for EXP1 and 4.6% for EXP2, respectively.
Sulphate ($SO4^{2-}$)	0.401 ± 0.13	0.457 ± 0.13	The sulfate concentration from the outlet pipe only accounted for 53.4% for EXP1 and 20.1% for EXP2 respectively. This means that the sulphate concentration

			in the groundwater sample must be higher than the provided concentration since there is not other source for sulphate ions in the regenerant stream.

Table 5.6: Results for EXP3

Element	EXP3 - Concentration (g/l)	Remarks
Sodium (Na^+)	1.398 ± 0.03	According to mass balance, the sodium concentration due to the sample remaining in the outlet pipe was 59.3%. The rest of the sodium concentration comes from the resin. This means some sodium ions were still attached to the resin. Hence the results could be optimized further in the future.
Magnesium (Mg^{2+})	1.768± 0.08	As discussed before in Table 5.5, the magnesium concentration in the result is diluted due to two reasons which are constraints of laboratory experiments and would not be present in the actual set-up. The actual concentration of magnesium should be higher than this. The first reason is volume dilution due to the sample present in the outlet pipe. The second reason is the high accidental volume of H_2SO_4 as a reagent. Due to this, the total volume of the sample which was collected was higher than it should have been. In addition to this, this concentration also has magnesium ions partly from the sample left in the outlet pipe which is 6.0%. Taking all three factors into account, the actual magnesium concentrations are reported in Table 5.7.
Calcium (Ca^{2+})	Not Measurable (< 0.25)	The calcium precipitated out as gypsum (Fig 5.14). Since the Ion Chromatography (IC) machine can only measure samples filtered through a 0.2-micron filter, the gypsum particles got separated out. Hence the calcium concentration was below the measuring limit of the IC (1 ppm), considering the dilution factor, the concentration was less than 0.25 g/l. This is a much better result than EXP1 and EXP2 when HCL was used for regeneration. The magnesium concentration is atleast 17 times greater than the calcium concentration in this case. No additional precipitation processes to separate out calcium ions are required, only a filtration process would

		suffice. Gypsum formation was seen immediately even in the outlet pipe. There is a concern for gypsum formation blocking the resin but no visible formations in the resin was seen during the experiment. Even if such a case arises, there are ways to tackle that such as using a fluidized bed ion exchange reactor.
Chloride (Cl^-)	2.567 ± 0.06	The chloride concentration from the outlet pipe accounted for 70% of this chlorine value. This could mean two things: the chloride concentration in the groundwater sample was more than the measurements provided by the company. Or the sample in the outlet pipe was more in volume that originally measured which could be due to error in measurement since the sample volumes are extremely small. But for now, it is not a cause for concern since the focus in currently on Mg^{2+} and Ca^{2+} concentrations.
Sulphate ($SO4^{2-}$)	27.697 ± 0.412	The sulfate concentration from the outlet pipe only accounted for 0.5% of the total sulfate concentration.

The regenerant output of EXP3 is shown in Figure 5.14 where gypsum particles could be seen to already settle.

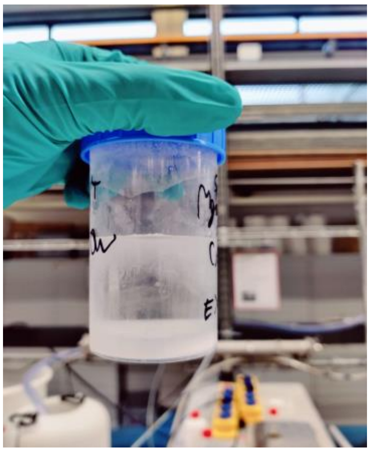

Figure 5.14: Regenerant of EXP3

The charge balance based on values obtained from IC analysis is shown in **Appendix A6**. The charge balance turns out to be negative 0.34 ± $2*10^{-2}$ equivalent/l for EXP1, negative 0.28 ± $1.8*10^{-2}$ equivalent/l for EXP2and negative 0.44 ± $1.1*10^{-2}$ equivalent/l for EXP3. The reason for net negative balance is not known.

The actual concentration of the target ions is described in table 5.7 and the pH in the following in Table 5.8

Table 5.7: Actual Concentrations

Element / Sample	Magnesium (Mg^{2+}) (g/l)	Calcium (Ca^{2+}) (g/l)	Mg/Ca Ratio
EXP1	3.21	8.94	0.36
EXP2	3.71	10.56	0.35
EXP3	4.45	<0.25 (Negligible)	At least 17.68

Table 5.8: pH Values

Serial No.	Sample	pH
1	Groundwater Sample	7.855
2	Regeneration Acids: HCl/H_2SO_4 (1 mole/Liter):	0
3	EXP1: Regenerant ($MgCl_2$+ $CaCl_2$)	0.259
4	EXP2: Regenerant ($MgCl_2$ + $CaCl_2$)	0.378
5	EXP3: Regenerant ($MgSO_4$ + $CaSO_4$)	0.451

5.6. Discussion

5.6.1 Composition of the acquired Aqueous Mg^{2+} Stream

AmberLite IRC 747 (a chelating weak acid cation exchange resin) works well in producing an aqueous stream concentrated in Mg^{2+} ions. The most important aspect of the produced aqueous stream is that it was possible to get rid of Ca^{2+} and Na^{+} ions in a 1-step process and with minimal use of resources. The gypsum particles produced could be separated by a simple sedimentation process. One concern is that gypsum particles in the resin could potentially jam the water flow. During the experiments, no visible precipitates were seen inside the resin, but precipitates were observed in the outlet pipe. This is not a cause for concern since techniques exist to target this exact problem, such as a fluidized bed reactor.

5.6.2 The concentration of Mg^{2+} Ions

The target concentration of Mg^{2+} ions (currently dosed in the struvite reactor) is 81.68 g/l. The concentration in the obtained aqueous stream from EXP3 is now 4.45 g/l. It still needs to be concentrated by a factor of 18. This could be achieved in via 3 ways described below

Increasing the efficiency of the process

The exchange capacity of the resin is greater than 1.75 equivalent/liter of resin, as described by the supplier. Given the bed volume of 40.82 cm^3 used in the experiment, 0.071435 equivalents could have been replaced. Since it has been established in section 5.5.6 that the majority of the ions in the effluent are Mg^{2+} and Ca^{2+} ions. The combined equivalents in the effluent for EXP 1 and EXP2 are 0.05049 and 0.05916 respectively. Hence % of efficiency for the resin was at 70.7 %and 82.8% respectively. Detailed calculations are shown In **Appendix A7.** The calculation could not be done for EXP3 since the gypsum particles were precipitated. This proves that the efficiency of the process could be enhanced. This is further supported by the low sodium concentration in the aqueous stream, partly due to the resin (Section 5.5.6). Hence the process shows potential for optimization.

Counter-Current Regeneration

Acids with higher concentrations can also be used for regeneration depending on the limitations of the resin. With a higher concentration of acid, H^+ ions used in one round of regeneration would be relatively quite low. Hence the same volume of acid could be used again for regeneration in a counter-current regeneration system. An example of such a process tested on a pilot scale could be seen in the research study by Wolter Siegers, and Jacques van Paassen and Bas Heijman titled “Color removal from drinking water by anion exchange and wet oxidation” (Siegers et al., n.d.). In the study, an anion exchange resin was used to remove humic substances responsible for color in the drinking water. The regenerative fluid was used five times before it was discarded. The regeneration process was counter-current, i.e. the most contaminated part of the resin (resin column) was treated first with the most contaminated regenerative fluid. The counter-current process is shown in Figure 5.15, and the regenerative fluid at different stages is shown in Figure 5.16.

Figure 5.15: Counter-Current process Figure 5.16: Regenerative fluid at different stages

The technique of counter-current regeneration allows the use of the same quantity of the regeneration (Acid) to regenerate the ion exchange column multiple times. This could be done when an acid with a higher concentration (6-10N) is used and after one round of regeneration, only a small amount of H^+ ions are utilized. This could increase the concentration in the regenerant stream by even a factor of 5. The amount of H^+ ions utilized for each EXP is shown in Table 5.9.

Table 5.9: Usage of H^+ ions

Serial No.	**Sample**	**pH**	**H^+ concentration left (mole/l)**
1	EXP1	0.259	0.55
2	EXP2	0.378	0.42
3	EXP3	0.451	0.35

The hydrochloric acid used was 1 N while the sulfuric acid used was 2 N. The accidental overdosing of acid was different for experiments 1 and 2 compared to EXP3 (Section 5.5.6). In addition to that, the amount of sample left in the outlet pipe also acted as further dilution (Section 5.5.6). Hence the comparison of H^+ concentration left for further regeneration between the experiments in terms of equivalents is not ideal but is shown in **Appendix A8.** For EXP3, 35 ml of 2 N H_2SO_4 was dosed and 70% of available equivalents were utilized. Hence during counter regeneration, if the regenerant is concentrated up to 5 times, assuming all the available equivalents of H^+ are replaced, then a 7 N H_2SO_4 solution would be required as the regenerant. The calculation is shown in **Appendix A8**.

Further concentration using an additional technology

The study revealed a process to separate to obtain $MgSO_4$ via a 1 step process. This salt ($MgSO_4$) could be further concentrated using an additional step. The technologies which could accomplish this are reverse osmosis (RO), vacuum membrane distillation (VMD), and Electro-Dialysis (ED). These technologies are capable of concentrating a given salt to higher concentrations. All the processes could achieve a concentration of 80g/l based on starting point of 20g/l. 2 Stage process RO and ED process show better results than 1 stage process. Both RO and ED systems use considerably less energy than a VMP system. Depending on the type of system, membrane and pressure, and the starting and final concentration achieved; the RO and ED could vary between 10-30 KWH/m3 while the VMD requires energy in the range of about 1000 kWh/m^3 (Woen, 2022)

Conclusion

Considering all the factors for improvisation listed above, it is possible to reach a concentration of 81.68 g/l as required. Although first, the focus should be on increasing the efficiency and using counter-current regeneration. Then the basis for further concentration could be established. For this, structured experimental laboratory research is required aimed at optimizing the suggested process, which is not covered under the scope of this study. In general, numerous full-scale counter-current systems using ion exchange processes have been deployed; the research is just needed to realize and adapt the efficiency in this specific case.

Amount of Acid

The amount of sulfuric acid required to obtain an Mg^{2+} dose of 81.68 g/l with an annual amount of 4500 tons is 841 m^3 (98% purity and 36 N H_2SO_4). The calculation is shown in **Appendix A9**.

Chapter 6:

Conclusions and Outlook

This chapter summarizes the results and conclusion of the present study. It also provides insights into the framework of further research on the topic.

Chapter 6 Conclusion and Outlook

6.1 Conclusion

6.1.1 Possible Recovery Process

In answering the first and second group of research questions in Chapter 2 and Chapter 3, the study revealed that the possible realistic recovery pathways which could be used to extract Mg^{2+} from the RO concentrate in such a form that it is compatible with the existing magnesium dosing system and struvite precipitation reactor in WWTP at Amsterdam West, are nano-filtration and ion exchange.

6.1.2 N.F.

The conclusion from the evaluation of an N.F. recovery process is as follows:

- On evaluating the N.F. recovery pathway using software simulations done in WAVE and IMS design software, a stream containing 0.218 g/l Na^{+}, 0.509 Mg^{2+}, and 0.408 Ca^{2+} concentration was obtained after eight cycles of concentration and dilution using a 2 stage N.F. system (membrane - NF270-400/34).

- The efficacy of the N.F. system is not sufficient for desirable magnesium recovery. However, if more selective (rejection of magnesium ions > calcium ions, rejection of magnesium ions at least more than 90%, and rejection of sodium ion about 20%) N.F. membranes could be produced, then the efficacy may be sufficient.

- Even if the efficacy is sufficient, the ultra-pure water requirement for the whole system is very high. For the available quantity of R.O. concentrate is between 1.6 Mm^3 to 3.2 Mm^3 annually, implementing the N.F. process would require 8.32 Mm^3 to 16.64 Mm^3 of ultra-pure water, which is very high given the fact that the drinking water production is targeted at between 4.8 Mm3 and 6.4 Mm^3 annually.

The process is not feasible as a potential recovery pathway for recovering Mg^{2+} from RO concentrate.

6.1.3 Ion exchange

The conclusion from the evaluation of an ion exchange recovery process is as follows:

- An acid cation exchange process using traditional resin operating in the H+ form removes hardness only associated with alkalinity. Since alkalinity is limited in the concentrate, these resins are not feasible for the recovery process.

- A chelating resin is most suitable for recovery since it forms complexes with alkaline earth metals, efficiently removing divalent cations from the water and letting the Na^+ pass.

- Software simulations have limitations: the processes are stopped at the breakthrough of divalent cations, whereas the aim is to reach saturation. No chelating resins are available in the software database, and the choice of regeneration chemicals is also limited.

- The laboratory experiments using the chelating resin IRC 747 yielded excellent results that could be further optimized and enhanced to reach the target magnesium concentration. The experiments produced an aqueous stream of 4.5 g/l Mg^{2+} ions with negligible sodium and very low calcium concentrations.

The proposed recovery pathway is described below.

The Ion exchange process consists of a weak chelating cation exchange resin (AmberLite IRC747) in the Na^+. This resin form complexes with alkaline earth metals and lets the sodium pass through. Instead of stopping the process at the breakthrough of divalent cations, the process is continued till the column is saturated with divalent cations (i.e., Mg^{2+} concentration in the effluent is the same as that of influent). Then the column is regenerated with the acid H_2SO_4. The regenerant stream produced is rich in $MgSO_4$ and $CaSO_4$. The gypsum precipitates could be separated via a sedimentation process. In the end, a Na^+ free stream of 4.45 g/l Mg^{2+} and Ca^{2+} less than 0.25 g/l is obtained.

The concentration of the Mg^{2+} ions could be increased by making the process more efficient, by implementing counter-current regeneration, and by adding a technology such as RO, ED, or VMP to further concentrate the salt ($MgSO_4$). The proposed recovery process is ideal as it covers all the underlying constraints and requirements, namely:

- The recovery pathway does not employ multiple units and consumes abundant resources.

- The recovery pathway is successful in producing a concentrated stream of Mg^{2+} ions.

- The recovery pathway successfully almost removes all the other cations that can act as inhibitors to the struvite crystallization process, such as Na^+ and Ca^{2+} ions.

The recovery process would initiate circularity in the magnesium cycle within the borders of Waternet.

An essential resource like magnesium is typically extracted via mining according to a conventional linear industrial approach. Seawater and brackish brines are the keys to moving towards more sustainable exploitation of available resources as they represent an inexhaustible source of magnesium. The present study resulted in a new recovery method for Mg^{2+} from RO concentrate. The results of this study could act as a benchmark to further investigate the application of this method for recovering Mg^{2+} from concentrates of desalination plants, other RO concentrates, and different types of brines.

6.2 Further Research Questions

The outcome of the present study led to the formation of a new approach to a standard ion exchange process. Optimizing the process is a topic for further research. The following research questions could be the focus point of future research:

- What is the maximum efficiency of the ion exchange process using a counter-current regeneration system? Is this efficiency enough to generate an Mg^{2+} dose of 81.68 g/l? Which technology should be considered if the further concentration is required?
- What would be the environmental impacts/benefits of such a process?
- What would be the capital and operating expenses of such a process?
- Is the pH of the obtained Mg^{2+} make the dose acidic in nature? If yes, would it affect the struvite crystallization process? If yes, what is the most optimal method to make it neutral?
- The flexibility of the process for adoption to other brackish brines and desalination brines.

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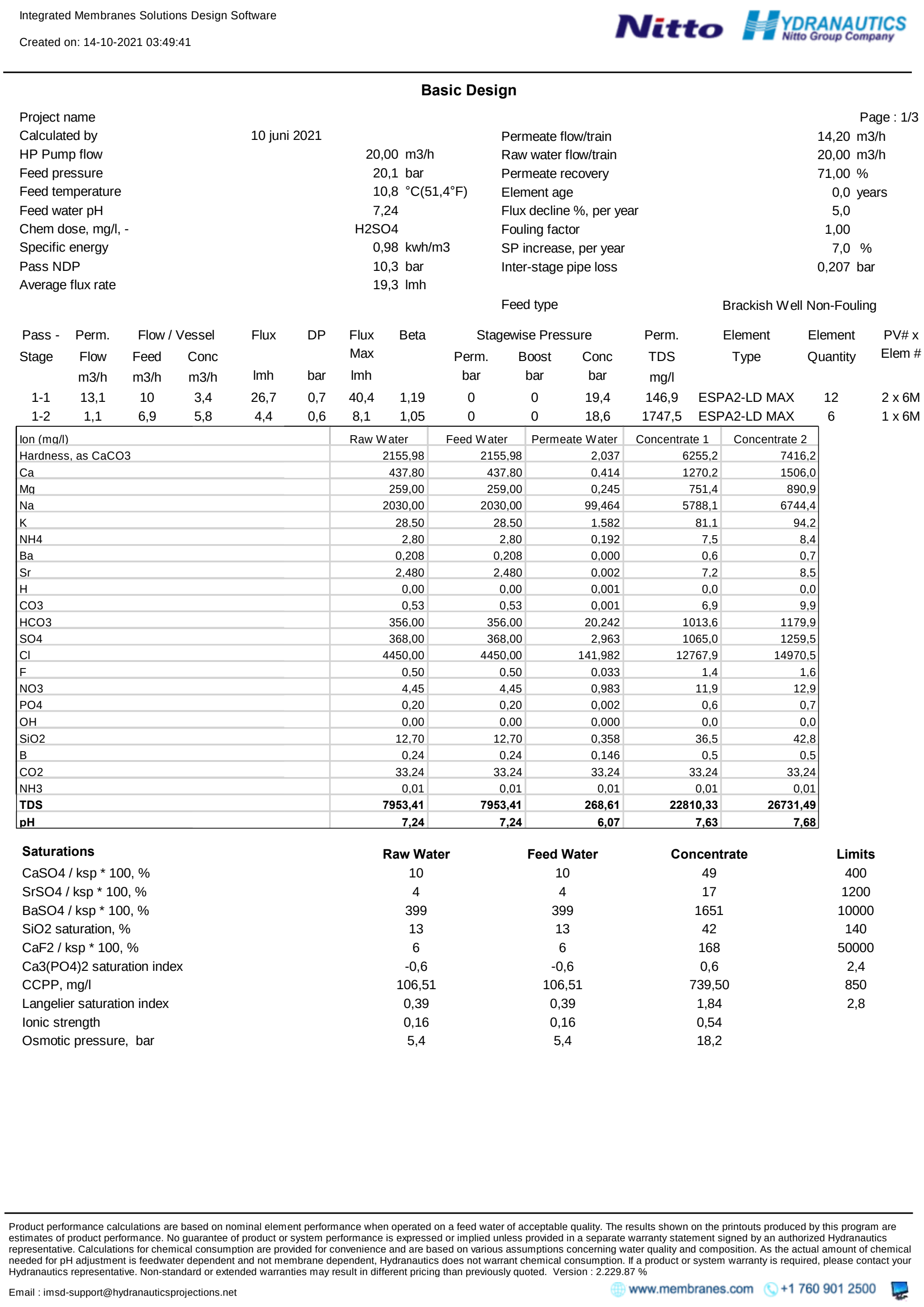
Appendix

A1: Data on the composition of groundwater and R.O. concentrate

The data with the R.O. element age of 0 years is shown in Fig A.1-A.3. The data with the R.O. element age of 5 years is shown in Fig A.4-A.6.



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Basic Design

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Project name			
Calculated by	10 juni 2021	Permeate flow/train	14,20 m3/h
HP Pump flow	20,00 m3/h	Raw water flow/train	20,00 m3/h
Feed pressure	20,1 bar	Permeate recovery	71,00 %
Feed temperature	10,8 °C(51,4°F)	Element age	0,0 years
Feed water pH	7,24	Flux decline %, per year	5,0
Chem dose, mg/l, -	H2SO4	Fouling factor	1,00
Specific energy	0,98 kwh/m3	SP increase, per year	7,0 %
Pass NDP	10,3 bar	Inter-stage pipe loss	0,207 bar
Average flux rate	19,3 lmh		
		Feed type	Brackish Well Non-Fouling

Pass - Stage	Perm. Flow m3/h	Flow / Vessel Feed m3/h	Flow / Vessel Conc m3/h	Flux lmh	DP bar	Flux Max lmh	Beta	Stagewise Pressure Perm. bar	Stagewise Pressure Boost bar	Stagewise Pressure Conc bar	Perm. TDS mg/l	Element Type	Element Quantity	PV# x Elem #
1-1	13,1	10	3,4	26,7	0,7	40,4	1,19	0	0	19,4	146,9	ESPA2-LD MAX	12	2 x 6M
1-2	1,1	6,9	5,8	4,4	0,6	8,1	1,05	0	0	18,6	1747,5	ESPA2-LD MAX	6	1 x 6M

Ion (mg/l)	Raw Water	Feed Water	Permeate Water	Concentrate 1	Concentrate 2
Hardness, as CaCO3	2155,98	2155,98	2,037	6255,2	7416,2
Ca	437,80	437,80	0,414	1270,2	1506,0
Mg	259,00	259,00	0,245	751,4	890,9
Na	2030,00	2030,00	99,464	5788,1	6744,4
K	28,50	28,50	1,582	81,1	94,2
NH4	2,80	2,80	0,192	7,5	8,4
Ba	0,208	0,208	0,000	0,6	0,7
Sr	2,480	2,480	0,002	7,2	8,5
H	0,00	0,00	0,001	0,0	0,0
CO3	0,53	0,53	0,001	6,9	9,9
HCO3	356,00	356,00	20,242	1013,6	1179,9
SO4	368,00	368,00	2,963	1065,0	1259,5
Cl	4450,00	4450,00	141,982	12767,9	14970,5
F	0,50	0,50	0,033	1,4	1,6
NO3	4,45	4,45	0,983	11,9	12,9
PO4	0,20	0,20	0,002	0,6	0,7
OH	0,00	0,00	0,000	0,0	0,0
SiO2	12,70	12,70	0,358	36,5	42,8
B	0,24	0,24	0,146	0,5	0,5
CO2	33,24	33,24	33,24	33,24	33,24
NH3	0,01	0,01	0,01	0,01	0,01
TDS	**7953,41**	**7953,41**	**268,61**	**22810,33**	**26731,49**
pH	**7,24**	**7,24**	**6,07**	**7,63**	**7,68**

Saturations	**Raw Water**	**Feed Water**	**Concentrate**	**Limits**
CaSO4 / ksp * 100, %	10	10	49	400
SrSO4 / ksp * 100, %	4	4	17	1200
BaSO4 / ksp * 100, %	399	399	1651	10000
SiO2 saturation, %	13	13	42	140
CaF2 / ksp * 100, %	6	6	168	50000
Ca3(PO4)2 saturation index	-0,6	-0,6	0,6	2,4
CCPP, mg/l	106,51	106,51	739,50	850
Langelier saturation index	0,39	0,39	1,84	2,8
Ionic strength	0,16	0,16	0,54	
Osmotic pressure, bar	5,4	5,4	18,2	

Product performance calculations are based on nominal element performance when operated on a feed water of acceptable quality. The results shown on the printouts produced by this program are estimates of product performance. No guarantee of product or system performance is expressed or implied unless provided in a separate warranty statement signed by an authorized Hydranautics representative. Calculations for chemical consumption are provided for convenience and are based on various assumptions concerning water quality and composition. As the actual amount of chemical needed for pH adjustment is feedwater dependent and not membrane dependent, Hydranautics does not warrant chemical consumption. If a product or system warranty is required, please contact your Hydranautics representative. Non-standard or extended warranties may result in different pricing than previously quoted. Version : 2.229.87 %

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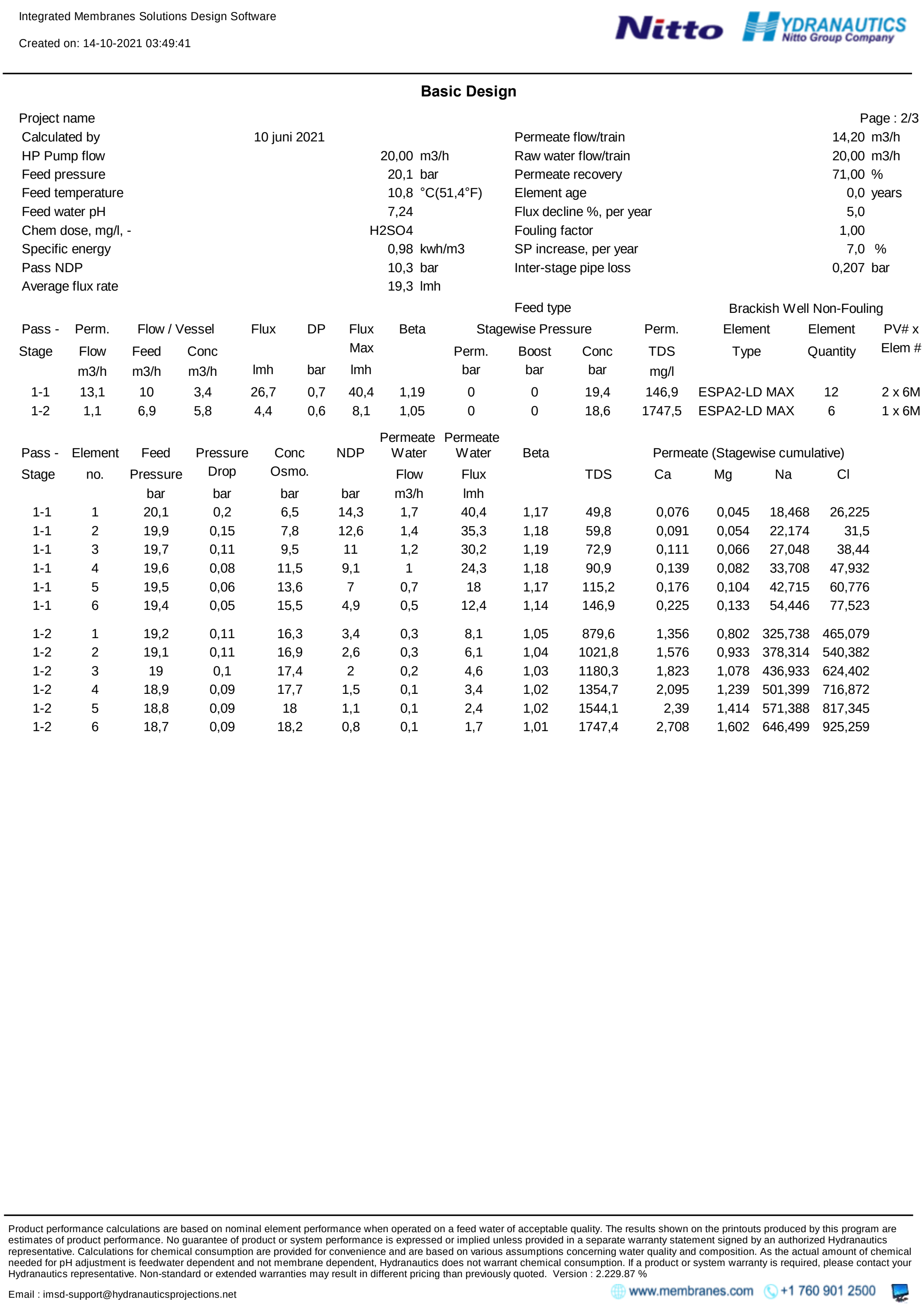
Figure A1.1: Data on the composition of groundwater and R.O. concentrate -1



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Project name			Page : 2/3
Calculated by	10 juni 2021	Permeate flow/train	14,20 m3/h
HP Pump flow	20,00 m3/h	Raw water flow/train	20,00 m3/h
Feed pressure	20,1 bar	Permeate recovery	71,00 %
Feed temperature	10,8 °C(51,4°F)	Element age	0,0 years
Feed water pH	7,24	Flux decline %, per year	5,0
Chem dose, mg/l, -	H2SO4	Fouling factor	1,00
Specific energy	0,98 kwh/m3	SP increase, per year	7,0 %
Pass NDP	10,3 bar	Inter-stage pipe loss	0,207 bar
Average flux rate	19,3 lmh		
		Feed type	Brackish Well Non-Fouling

Pass -	Perm.	Flow / Vessel		Flux	DP	Flux	Beta	Stagewise Pressure			Perm.	Element	Element	PV# x
Stage	Flow	Feed	Conc			Max		Perm.	Boost	Conc	TDS	Type	Quantity	Elem #
	m3/h	m3/h	m3/h	lmh	bar	lmh		bar	bar	bar	mg/l			
1-1	13,1	10	3,4	26,7	0,7	40,4	1,19	0	0	19,4	146,9	ESPA2-LD MAX	12	2 x 6M
1-2	1,1	6,9	5,8	4,4	0,6	8,1	1,05	0	0	18,6	1747,5	ESPA2-LD MAX	6	1 x 6M

Pass -	Element	Feed	Pressure	Conc	NDP	Permeate Water	Permeate Water	Beta		Permeate (Stagewise cumulative)			
Stage	no.	Pressure	Drop	Osmo.		Flow	Flux		TDS	Ca	Mg	Na	Cl
		bar	bar	bar	bar	m3/h	lmh						
1-1	1	20,1	0,2	6,5	14,3	1,7	40,4	1,17	49,8	0,076	0,045	18,468	26,225
1-1	2	19,9	0,15	7,8	12,6	1,4	35,3	1,18	59,8	0,091	0,054	22,174	31,5
1-1	3	19,7	0,11	9,5	11	1,2	30,2	1,19	72,9	0,111	0,066	27,048	38,44
1-1	4	19,6	0,08	11,5	9,1	1	24,3	1,18	90,9	0,139	0,082	33,708	47,932
1-1	5	19,5	0,06	13,6	7	0,7	18	1,17	115,2	0,176	0,104	42,715	60,776
1-1	6	19,4	0,05	15,5	4,9	0,5	12,4	1,14	146,9	0,225	0,133	54,446	77,523
1-2	1	19,2	0,11	16,3	3,4	0,3	8,1	1,05	879,6	1,356	0,802	325,738	465,079
1-2	2	19,1	0,11	16,9	2,6	0,3	6,1	1,04	1021,8	1,576	0,933	378,314	540,382
1-2	3	19	0,1	17,4	2	0,2	4,6	1,03	1180,3	1,823	1,078	436,933	624,402
1-2	4	18,9	0,09	17,7	1,5	0,1	3,4	1,02	1354,7	2,095	1,239	501,399	716,872
1-2	5	18,8	0,09	18	1,1	0,1	2,4	1,02	1544,1	2,39	1,414	571,388	817,345
1-2	6	18,7	0,09	18,2	0,8	0,1	1,7	1,01	1747,4	2,708	1,602	646,499	925,259

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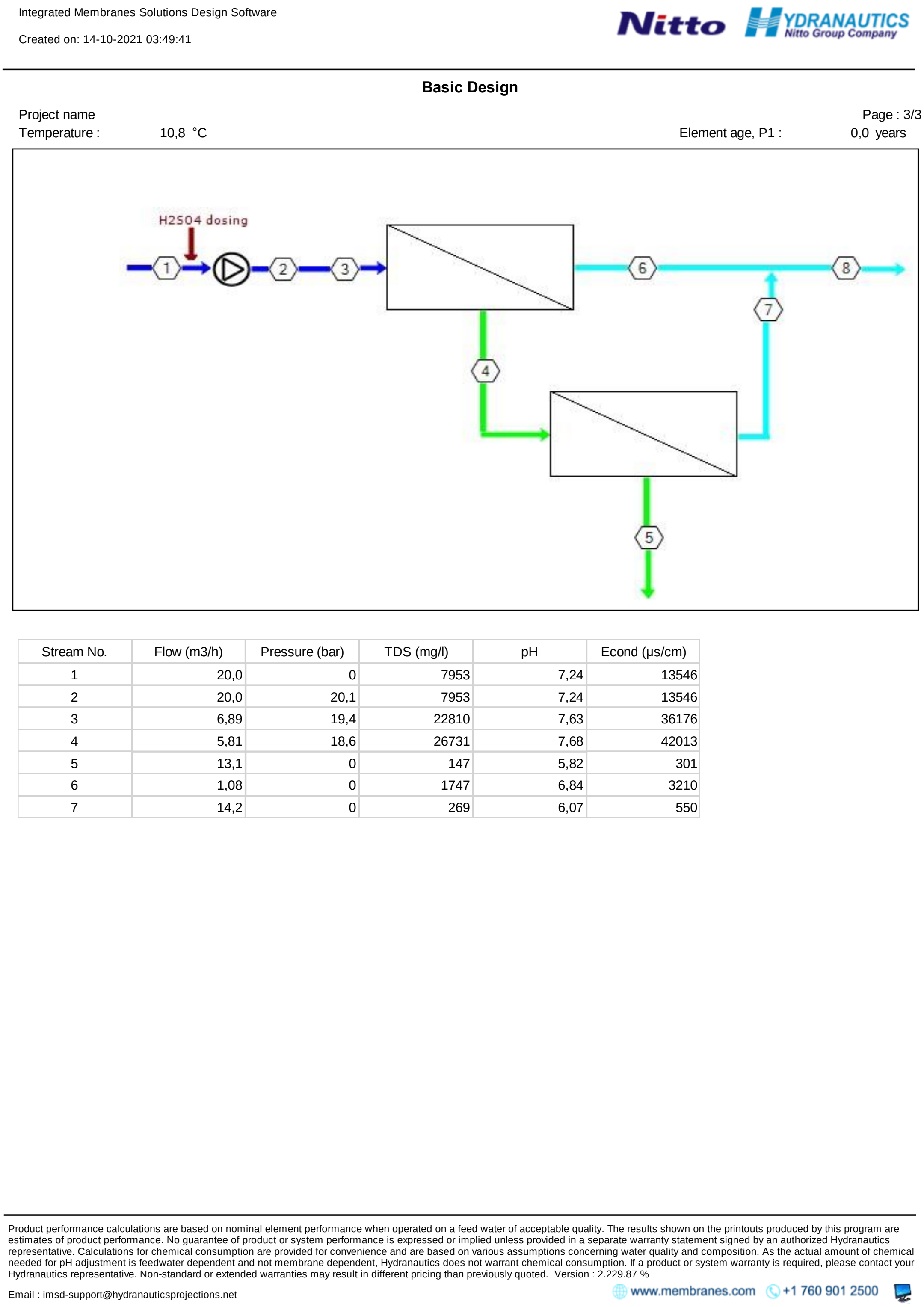
Figure A1.2: Data on the composition of groundwater and R.O. concentrate - 2



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Project name

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Temperature : 10,8 °C

Element age, P1 : 0,0 years

Stream No.	Flow (m3/h)	Pressure (bar)	TDS (mg/l)	pH	Econd (µs/cm)
1	20,0	0	7953	7,24	13546
2	20,0	20,1	7953	7,24	13546
3	6,89	19,4	22810	7,63	36176
4	5,81	18,6	26731	7,68	42013
5	13,1	0	147	5,82	301
6	1,08	0	1747	6,84	3210
7	14,2	0	269	6,07	550

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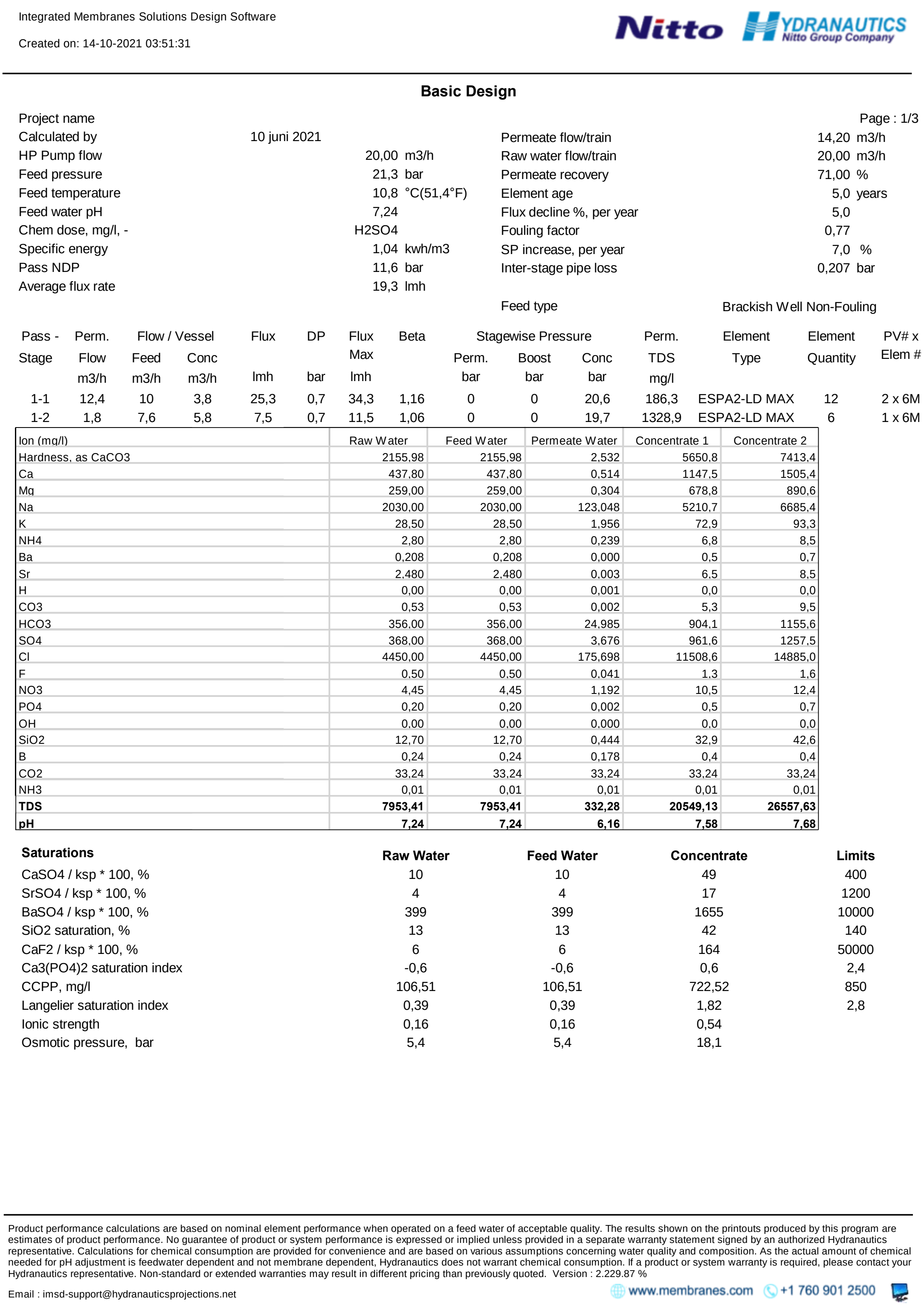
Figure A1.3: Data on the composition of groundwater and R.O. concentrate - 3



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Basic Design

Project name				Page : 1/3	
Calculated by	10 juni 2021		Permeate flow/train	14,20	m3/h
HP Pump flow	20,00	m3/h	Raw water flow/train	20,00	m3/h
Feed pressure	21,3	bar	Permeate recovery	71,00	%
Feed temperature	10,8	°C(51,4°F)	Element age	5,0	years
Feed water pH	7,24		Flux decline %, per year	5,0	
Chem dose, mg/l, -	H2SO4		Fouling factor	0,77	
Specific energy	1,04	kwh/m3	SP increase, per year	7,0	%
Pass NDP	11,6	bar	Inter-stage pipe loss	0,207	bar
Average flux rate	19,3	lmh			
			Feed type	Brackish Well Non-Fouling	

Pass - Stage	Perm. Flow m3/h	Flow / Vessel Feed m3/h	Flow / Vessel Conc m3/h	Flux lmh	DP bar	Flux Max lmh	Beta	Stagewise Pressure Perm. bar	Stagewise Pressure Boost bar	Stagewise Pressure Conc bar	Perm. TDS mg/l	Element Type	Element Quantity	PV# x Elem #
1-1	12,4	10	3,8	25,3	0,7	34,3	1,16	0	0	20,6	186,3	ESPA2-LD MAX	12	2 x 6M
1-2	1,8	7,6	5,8	7,5	0,7	11,5	1,06	0	0	19,7	1328,9	ESPA2-LD MAX	6	1 x 6M

Ion (mg/l)	Raw Water	Feed Water	Permeate Water	Concentrate 1	Concentrate 2
Hardness, as CaCO3	2155,98	2155,98	2,532	5650,8	7413,4
Ca	437,80	437,80	0,514	1147,5	1505,4
Mg	259,00	259,00	0,304	678,8	890,6
Na	2030,00	2030,00	123,048	5210,7	6685,4
K	28,50	28,50	1,956	72,9	93,3
NH4	2,80	2,80	0,239	6,8	8,5
Ba	0,208	0,208	0,000	0,5	0,7
Sr	2,480	2,480	0,003	6,5	8,5
H	0,00	0,00	0,001	0,0	0,0
CO3	0,53	0,53	0,002	5,3	9,5
HCO3	356,00	356,00	24,985	904,1	1155,6
SO4	368,00	368,00	3,676	961,6	1257,5
Cl	4450,00	4450,00	175,698	11508,6	14885,0
F	0,50	0,50	0,041	1,3	1,6
NO3	4,45	4,45	1,192	10,5	12,4
PO4	0,20	0,20	0,002	0,5	0,7
OH	0,00	0,00	0,000	0,0	0,0
SiO2	12,70	12,70	0,444	32,9	42,6
B	0,24	0,24	0,178	0,4	0,4
CO2	33,24	33,24	33,24	33,24	33,24
NH3	0,01	0,01	0,01	0,01	0,01
TDS	**7953,41**	**7953,41**	**332,28**	**20549,13**	**26557,63**
pH	**7,24**	**7,24**	**6,16**	**7,58**	**7,68**

Saturations	**Raw Water**	**Feed Water**	**Concentrate**	**Limits**
CaSO4 / ksp * 100, %	10	10	49	400
SrSO4 / ksp * 100, %	4	4	17	1200
BaSO4 / ksp * 100, %	399	399	1655	10000
SiO2 saturation, %	13	13	42	140
CaF2 / ksp * 100, %	6	6	164	50000
Ca3(PO4)2 saturation index	-0,6	-0,6	0,6	2,4
CCPP, mg/l	106,51	106,51	722,52	850
Langelier saturation index	0,39	0,39	1,82	2,8
Ionic strength	0,16	0,16	0,54	
Osmotic pressure, bar	5,4	5,4	18,1	

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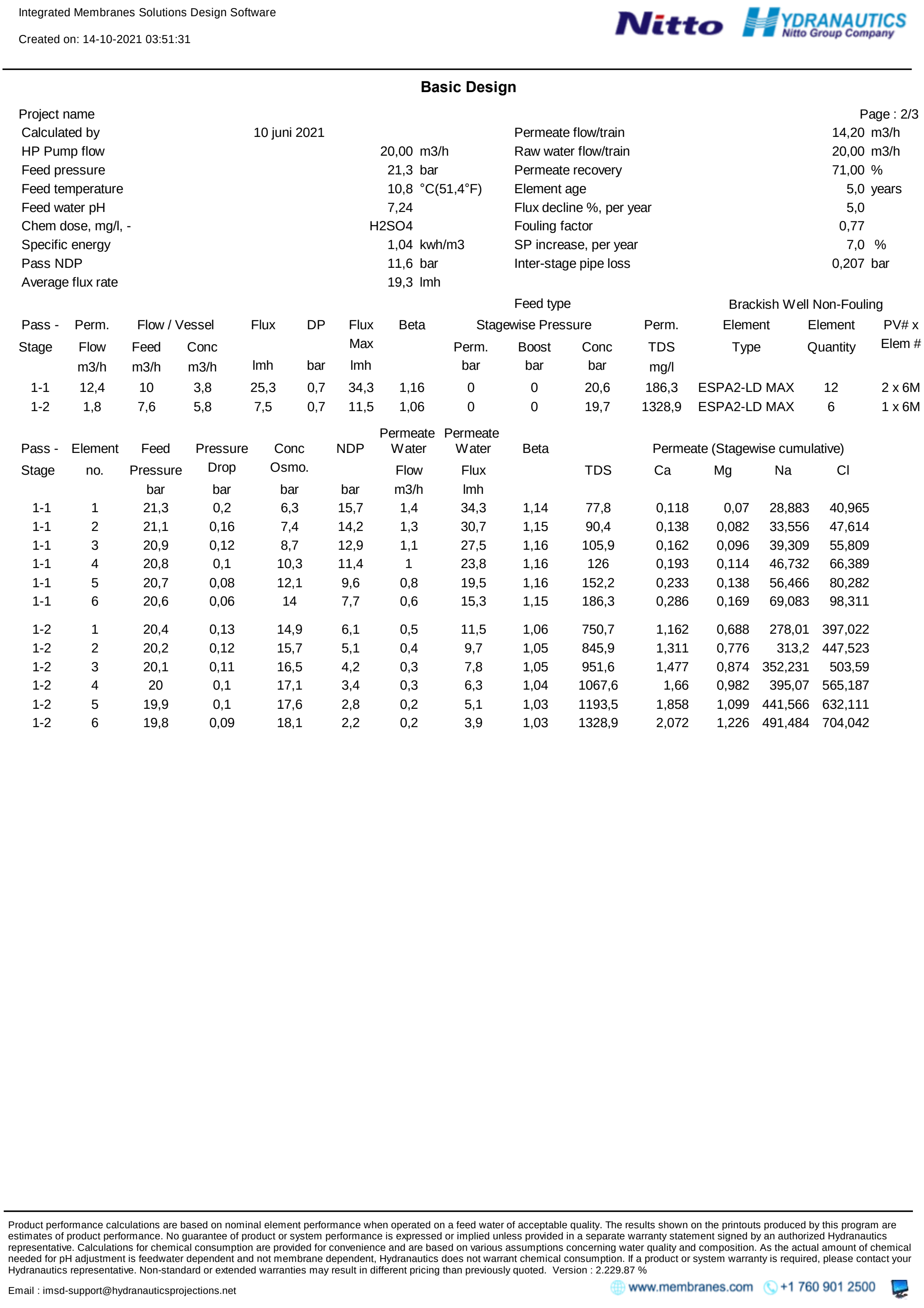
Figure A1.4: Data on the composition of groundwater and R.O. concentrate - 4



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Calculated by	10 juni 2021	Permeate flow/train	14,20 m3/h
HP Pump flow	20,00 m3/h	Raw water flow/train	20,00 m3/h
Feed pressure	21,3 bar	Permeate recovery	71,00 %
Feed temperature	10,8 °C(51,4°F)	Element age	5,0 years
Feed water pH	7,24	Flux decline %, per year	5,0
Chem dose, mg/l, -	H2SO4	Fouling factor	0,77
Specific energy	1,04 kwh/m3	SP increase, per year	7,0 %
Pass NDP	11,6 bar	Inter-stage pipe loss	0,207 bar
Average flux rate	19,3 lmh	Feed type	Brackish Well Non-Fouling

Pass - Stage	Perm. Flow m3/h	Flow / Vessel Feed m3/h	Flow / Vessel Conc m3/h	Flux lmh	DP bar	Flux Max lmh	Beta	Stagewise Pressure Perm. bar	Stagewise Pressure Boost bar	Stagewise Pressure Conc bar	Perm. TDS mg/l	Element Type	Element Quantity	PV# x Elem #
1-1	12,4	10	3,8	25,3	0,7	34,3	1,16	0	0	20,6	186,3	ESPA2-LD MAX	12	2 x 6M
1-2	1,8	7,6	5,8	7,5	0,7	11,5	1,06	0	0	19,7	1328,9	ESPA2-LD MAX	6	1 x 6M

Pass - Stage	Element no.	Feed Pressure bar	Pressure Drop bar	Conc Osmo. bar	NDP bar	Permeate Water Flow m3/h	Permeate Water Flux lmh	Beta	Permeate (Stagewise cumulative) TDS	Ca	Mg	Na	Cl
1-1	1	21,3	0,2	6,3	15,7	1,4	34,3	1,14	77,8	0,118	0,07	28,883	40,965
1-1	2	21,1	0,16	7,4	14,2	1,3	30,7	1,15	90,4	0,138	0,082	33,556	47,614
1-1	3	20,9	0,12	8,7	12,9	1,1	27,5	1,16	105,9	0,162	0,096	39,309	55,809
1-1	4	20,8	0,1	10,3	11,4	1	23,8	1,16	126	0,193	0,114	46,732	66,389
1-1	5	20,7	0,08	12,1	9,6	0,8	19,5	1,16	152,2	0,233	0,138	56,466	80,282
1-1	6	20,6	0,06	14	7,7	0,6	15,3	1,15	186,3	0,286	0,169	69,083	98,311
1-2	1	20,4	0,13	14,9	6,1	0,5	11,5	1,06	750,7	1,162	0,688	278,01	397,022
1-2	2	20,2	0,12	15,7	5,1	0,4	9,7	1,05	845,9	1,311	0,776	313,2	447,523
1-2	3	20,1	0,11	16,5	4,2	0,3	7,8	1,05	951,6	1,477	0,874	352,231	503,59
1-2	4	20	0,1	17,1	3,4	0,3	6,3	1,04	1067,6	1,66	0,982	395,07	565,187
1-2	5	19,9	0,1	17,6	2,8	0,2	5,1	1,03	1193,5	1,858	1,099	441,566	632,111
1-2	6	19,8	0,09	18,1	2,2	0,2	3,9	1,03	1328,9	2,072	1,226	491,484	704,042

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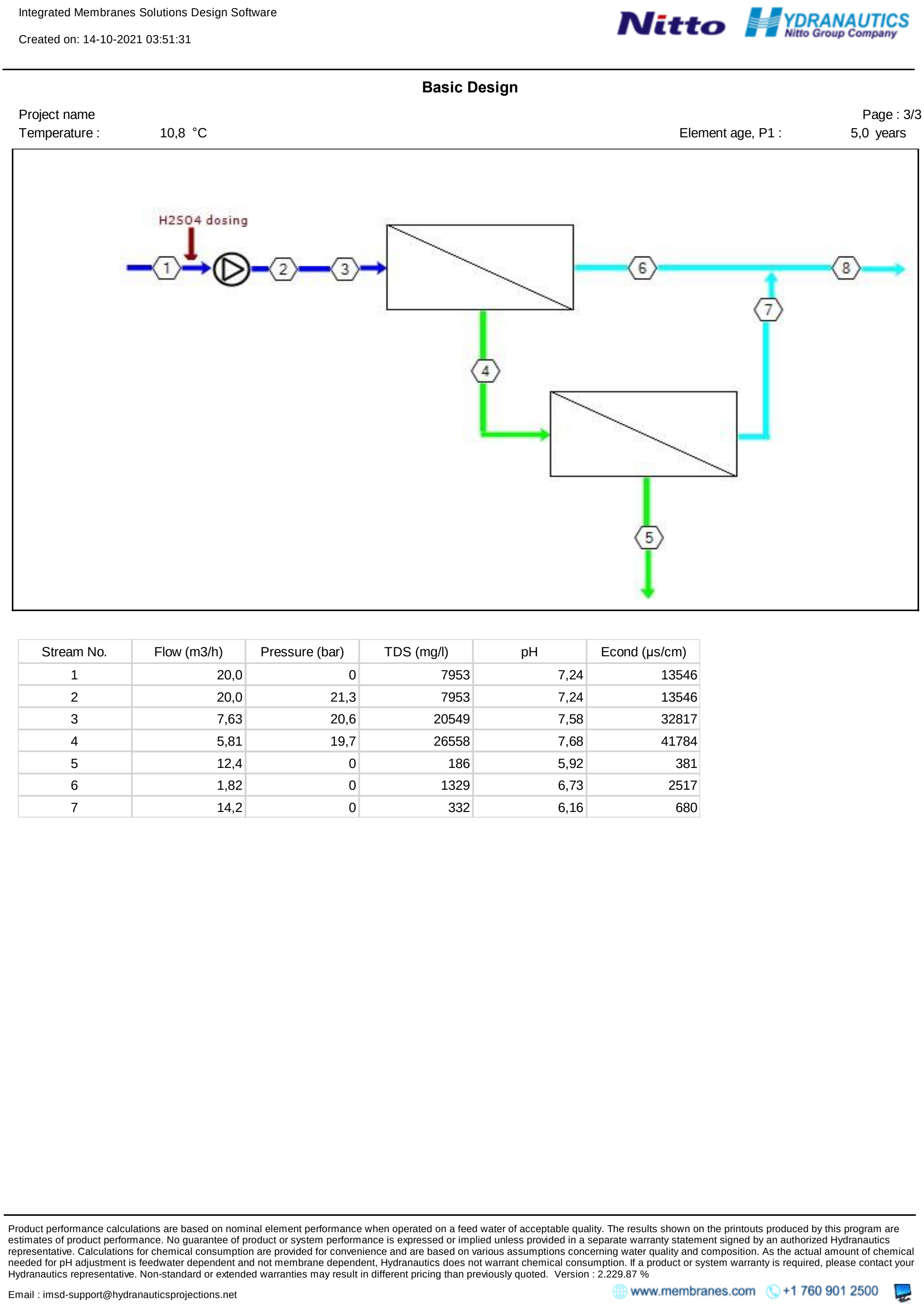
Figure A1.5: Data on the composition of groundwater and R.O. concentrate - 5



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Basic Design

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Temperature : 10,8 °C Element age, P1 : 5,0 years

Stream No.	Flow (m3/h)	Pressure (bar)	TDS (mg/l)	pH	Econd (µs/cm)
1	20,0	0	7953	7,24	13546
2	20,0	21,3	7953	7,24	13546
3	7,63	20,6	20549	7,58	32817
4	5,81	19,7	26558	7,68	41784
5	12,4	0	186	5,92	381
6	1,82	0	1329	6,73	2517
7	14,2	0	332	6,16	680

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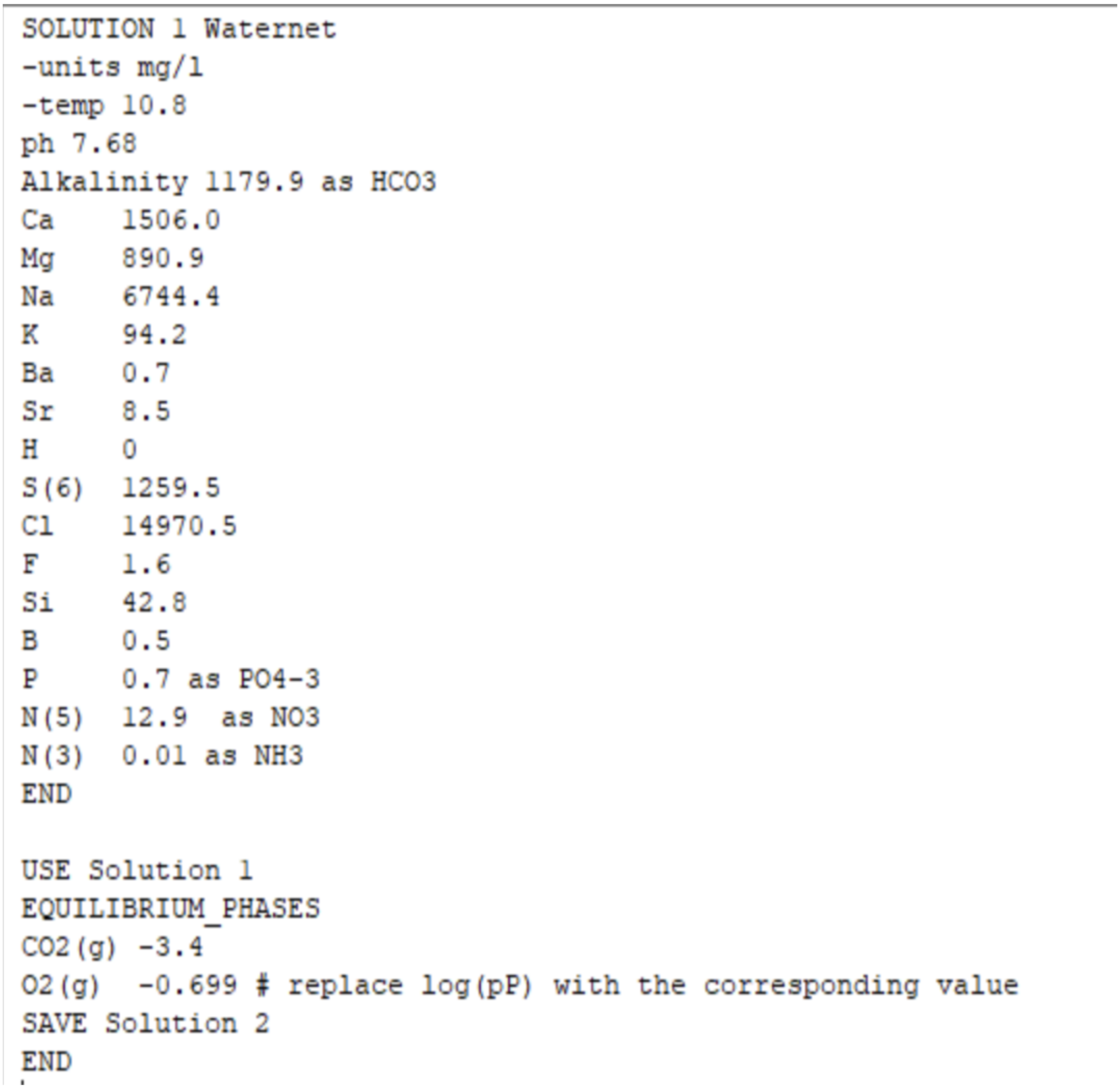
Figure A1.6: Data on the composition of groundwater and R.O. concentrate - 6

A2: PHREEQC

The PHREEQC model is described in Figure A2.



```
SOLUTION 1 Waternet
-units mg/l
-temp 10.8
ph 7.68
Alkalinity 1179.9 as HCO3
Ca    1506.0
Mg    890.9
Na    6744.4
K     94.2
Ba    0.7
Sr    8.5
H     0
S(6)  1259.5
Cl    14970.5
F     1.6
Si    42.8
B     0.5
P     0.7 as PO4-3
N(5)  12.9  as NO3
N(3)  0.01 as NH3
END

USE Solution 1
EQUILIBRIUM_PHASES
CO2(g) -3.4
O2(g)  -0.699 # replace log(pP) with the corresponding value
SAVE Solution 2
END
```

Figure A2.1: PHREEQC Input

A3: Calculations for Magnesium Dose

In terms of $MgCl_2$:
Amount of Brackish groundwater to be treated = 8 Mm^3/year

Concentrate of R.O. generated = 3.2 Mm^3/year = $3.2 * 10^9$ liters/year

The concentration of Magnesium in the concentrate = 647.5 mg/l

Concentration of Magnesium in the concentrate in moles/l = (647.5 mg/l) / ($24.305*10^3$ mg/mole) = $26.64 * 10^{-3}$ moles/l

Maximum $MgCl_2$ which can be generated (assuming 100% availability of chloride ions and full magnesium recovery) = $26.64 * 10^{-3}$ moles/l

In 1 year: $3.2 * 10^9$ liters/year * $26.64 * 10^{-3}$ moles/l = $85.248 * 10^6$ moles
= $85.248 * 10^6$ moles * 95.211 g/mole = $8{,}116.547328 * 10^6$ grams = 8,116,547.3 Kg = 8116 tons

A 32% mixture of $MgCl_2$ = 25,364,210.3 Kg of solution per year = 25364 tons/year

In terms of Mg^{2+} ions:
Brackish groundwater treated = 8 Mm^3/year

Concentrate of R.O. generated = 3.2 Mm^3/year = $3.2 * 10^9$ liters/year

The concentration of Magnesium in the concentrate = 647.5 mg/l

Concentration of Magnesium in the concentrate in moles/l = (647.5 mg/l) / ($24.305*10^3$ mg/mole) = $26.64 * 10^{-3}$ moles/l

In 1 year: $3.2 * 10^9$ liters/year * $26.64 * 10^{-3}$ moles/l = $85.248 * 10^6$ moles
= $85.248 * 10^6$ moles * 24.305 g/mole = $2{,}071.95264 * 10^6$ grams = 2,071,952.64 Kg = 2072 tons

8.2% Mg solution – 25,367.29 tons of Mg ions

A 32% mixture of $MgCl_2$ = 320 grams/liter MgCl2 = 81.68 grams/liter Mg
Dosage is 4500 tons of mgcl2 = 1148 tons of Mg

A4: Values for the solubility product constant (Ksp)

The solubility product constant, Ksp, is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more soluble a substance is, the higher its Ksp value. Ksp at 25℃. The

Table A4: Ksp Values

Compounds	Chemical Formula	Ksp Value
Calcium carbonate (calcite)	$CaCO_3$	3.36×10^{-9}
Calcium carbonate (aragonite)	$CaCO_3$	6.0×10^{-9}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}
Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}
Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}

A5: Experiment Calculations

Height filled with resin = 13 cm, giving a headspace of 19 cm.

The volume of resin used = 40.82 cubic cm.

The testing sample (groundwater) is, at this moment, referred to as a sample. Magnesium and calcium concentrations in the sample are as follows:

- *Mg: 259 mg/l*
- *Ca: 437.8 mg/l*

Resin Properties:

- *The top of the resin should never be dry!*
- *Ionic form: Na+*
- *Total Exchange capacity: >1.75 equivalent/l (This is per Liter of resin)*

From 1 liter of resin = 1.75 equivalent of Mg/Ca be replaced.

For 40.82 ml of resin = 1.75*0.0408 = 0.071435 equivalent can be replaced

*Equivalent = moles *valence*

Moles = equivalents/valency

Moles = weight/molecular weight

Magnesium

0.071435 equivalent of Mg = 0.071425/2 moles of Mg = 0.071425/2*24.3 grams of Mg = 0.86793525 gram

So 0.85679g of Mg can be exchanged for 40.82 cubic cm of resin.

That means:

1 liter – 0.259 gram/l. (Mg concentration)

X liter – 0.8679 gram/l. (sample required)

X = 3.35 liter

3.35 liter of sample is required to fully saturate a resin column of 13 cm (40.82 cubic cm) with Magnesium ions.

Calcium

0.071435 equivalent of Ca = 0.071435/2 moles of Ca = 0.071435/2*40 = 1.4287 grams of Ca

1.4287 g of Ca be exchanged for 40.82 cubic cm of resin. That means we need

1 liter – 0.438 gram/l. (Ca concentration)

X liter – 1.4287 gram/l.   (sample required)

X = 3.26 liters of sample

3.26 liter of sample is required to thoroughly saturate a resin column of 13 cm (40.82 cubic cm) with Calcium Ions.

Since the ratio of Mg/Ca ions are unknown, which will be attached to the resin (which is the aim of the experiment), it can be safely said that about 3.35 liter of sample to reach the saturation point.

Flow Rate

The flow rate is between 20-40 BV per hour.

If 25 BV/hr is taken as our flow rate: (BV = 40.82 cubic cm or ml)

Then, 40 BV/hour = 1632.8 cubic cm per hour

In the experiment, the rate achieved was close to 1756 cubic cm/h (43 BV/h). Since the limits were prescribed efficient removal of ions until a breakthrough is achieved which was not the purpose of this experiment, a slightly higher rate did not affect the experiment.

Saturation Time or Sample running time: 1 Hour 53 minute.

Regeneration

HCl 1N

1 N of HCl / l = 1 mole of HCl / l = 1 mole of H^+ ions =

1 gram of H^+ions per Liter

Resin: 0.071435 equivalent capacity.

0.071435 equivalent of H^+ means 0.071435/1 moles of H^+ = 0.071435 grams of H^+

0.071435 gram of v ions has to be exchanged. So

1 Liter = 1 gram (1 N HCl Solution)

X Liter = 0.071435 gram (Required)

X = 0.071435 Liter of acid is needed to regenerate the column fully.

That means approx. 71.43 ml! And similarly,

H_2SO_4 2N

2 N of H_2SO_4 / l = 1 mole of H_2SO_4 / l = 2 moles of H^+ ions/l =

2 grams of H^+ ions per Liter

Resin: 0.071435 equivalent capacity.

0.071435 equivalent of H^+ means 0.071435/1 moles of H^+ = 0.071435 grams of H^+ are required.

0.071435 gram of H^+ ions has to be exchanged. So

1 Liter = 2 gram

X Liter = 0.071435 *gram (Required)*

X = 0.0357175 Liter of acid is needed to regenerate the column fully.

That means approx. 35.71 ml!

Flow Rate for Regeneration

The flow rate is between 2-4 BV/hour. If 4 BV/Hour is taken

That translates to 163.28 ml per hour.

So the regeneration should be for 25.7 minutes.

But the experiment's flow rate was 280 ml/hr, which means around 6.8 BV/Hour.

So the resin was regenerated for 23 minutes, but it should have been regenerated for 15 minutes. So there is about 100% dilution of the sample, which could have been avoided.

So the regenerant solution had a regenerant of 119.93 ml. The total regenerant collected was closer to 140 ml for EXP1. Hence the rest is sample water from the outlet pipe.

Similarly, dilutions for EXP2 and EXP3 could be found.

NaOH

NaOH: 1 N = 1 mole / l of Na = 23 gram/L

0.071435 equivalent is the resin capacity.

That translates to (0.07435*23) grams of Na, which is 1.61 grams.

1 Liter = 23 g (1 N NaOH solution)

X Liter = 1.61 g (Required)

X = 0.07435 l

71 ml of Na

So the regeneration with base should have been for 15 minutes, but it was actually regenerated for 23 minutes. But in this case, it doesn't matter since the stream generated is a waste stream.

A6: Charge Balance

Table A6.1: Charge Balance for EXP1

Element	Measurement (*10^{-3} g/l)	Molecular weight (g/mole)	*10^{-3} Moles/l	Valency	*10^{-3} Equivalent/l
Na	724.5 ± 12.60	22.98	31.53 ± 0.55	1	31.53 ± 0.55
Mg	1639.25 ± 91.33	24.30	67.46 ± 3.76	2	134.92 ± 7.52
Ca	4561.62 ± 350.23	40.08	113.81 ± 8.73	2	227.62 ± 17.46
Cl	25637.56 ± 209.13	35.45	723.20 ± 5.89	1	723.20 ± 5.89
SO_4	401.12 ± 126.66	96.06	4.17 ± 1.31	2	8.34 ± 2.62

Value = (31.5134.92+227.62-723.20-8.34)*10^{-3} = -337.47 *10^{-3}

SD = SQRT ((0.55)^2+(7.52)^2+(17.46)^2+(5.89)^2+(2.62)^2) = 20.08 *10^{-3}

Charge Balance = -337.47 ± 20.08 *10^{-3} = -0.34 ± 2*10^{-2} equivalent/l

Table A6.2: Charge Balance for EXP2

Element	Measurement (*10^{-3} g/l)	Molecular weight (g/mole)	*10^{-3} Moles/l	Valency	*10^{-3} Equivalent/l
Na	908.25 ± 28.02	22.98	39.52 ± 1.22	1	39.52 ± 1.22
Mg	1658.19 ± 88.44	24.30	68.24 ± 3.64	2	136.48 ± 7.28
Ca	4716.56 ± 335.34	40.08	117.68 ± 8.36	2	235.36 ± 16.72
Cl	24140.75 ± 144.44	35.45	680.95 ± 4.07	1	680.95 ± 4.07
SO_4	457.44 ± 126.72	96.06	4.76 ± 1.32	2	9.52 ± 2.64

Value = (39.52 + 136.48 + 235.36 – 680.95 – 9.52) *10^{-3} = 279.11 *10^{-3}

SD = SQRT ((1.22)^2+(7.28)^2+(16.72)^2+(4.07)^2+(2.64)^2) = 18.91 *10^{-3}

Charge Balance = 0.28 ± 1.8*10^{-2} equivalent/l

Table A6.3: Charge Balance for EXP3

Element	**Measurement (*10^{-3} g/l)**	**Molecular weight (g/mole)**	***10^{-3} Moles/l**	**Valency**	***10^{-3} Equivalent/l**
Na	1398.62 ± 33.79	22.98	60.86 ± 1.47	1	60.86 ± 1.47
Mg	1768.25 ± 88.71	24.30	72.77 ± 3.65	2	145.53 ± 7.30
Ca	Unknown				
Cl	2567.68 ± 64.65	35.45	72.43 ± 1.83	1	72.43 ± 1.83
SO_4	27696 ± 412.02	96.06	288.32 ±4.29	2	576.64 ± 8.58

Value = (60.86 + 145.53 – 72.43 – 576.64) *10^{-3} = - 442.68 *10^{-3}

SD = SQRT ($(1.47)^2+(7.30)^2+(1.83)^2+(8.58)^2$) = 11.51 *$10^{-3}$

Charge Balance = 0.44 ± 1.1*10^{-2} equivalent/l

A7: Efficiency of Ion Exchange Column

The ion exchange capacity of the resin > 1.75 equivalent/liter of resin

The volume of resin used = 40.82 cm^3

Ion exchange capacity of the column = 1.75 *40.82/1000 equivalents = 0.071435 equivalent/liter

EXP1

Concentration of Mg^{2+} = 3.21 g/l

Equivalents of Mg^{2+} = 3.21 g/l * (0.071 l) / (24.305 g/mole) * 2 = 0.01875 equivalents

Concentration of Ca^{2+} = 8.94 g/l

Equivalents of Ca^{2+} = 8.94 g/l * (0.071 l) / (40 g/mole) * 2 = 0.03174 equivalents

Total Equivalents = 0.05049

Exchange Efficiency = 0.05049 / 0.071435 * 100 = 70.68 %

EXP2

Concentration of Mg^{2+} = 3.71 g/l

Equivalents of Mg^{2+} = 3.21 g/l * (0.071 l) / (24.305 g/mole) * 2 = 0.02167 equivalents

Concentration of Ca^{2+} = 8.94 g/l

Equivalents of Ca^{2+} = 10.56 g/l * (0.071 l) / (40 g/mole) * 2 = 0.03748 equivalents

Total Equivalents = 0.05916

Exchange Efficiency = 0.05916 / 0.071435 * 100 = 82.82 %

EXP3

Since calcium concentration for EXP3 is not known, the above equivalent balance could not be performed. But on the basis of EXP1 and EXP 2 results, it could be said that the ion exchange column could perform more efficiently.

A8 Equivalents of H+ used

EXP 1

The pH of obtained stream = 0.259

H^+ concentration in the obtained stream = 0.55 moles/l

The volume of the whole sample obtained = 140 ml

Equivalents of H^+ in the obtained stream = 0.55*0.140*1 = 0.077 equivalents

H^+ Concentration in the acid dosed (HCL) = 1 mole/l

The volume of HCL dosed (including accidental over-dosing) = 120 ml

Equivalents of H^+ dosed = 1*0.12*1 = 0.12 equivalents

Equivalents Used up for regeneration = 0.12 – 0.077 = 0.043 equivalents

EXP 2

The pH of obtained stream = 0.378

H^+ concentration in the obtained stream = 0.42 moles/l

The volume of the whole sample obtained = 160 ml

Equivalents of H^+ in the obtained stream = 0.42*0.160*1 = 0.0672 equivalents

H^+ Concentration in the acid dosed (HCL) = 1 mole/l

The volume of HCL dosed (including accidental over-dosing) = 120 ml

Equivalents of H^+ dosed = 1*0.12*1 = 0.12 equivalents

Equivalents Used up for regeneration = 0.12 – 0.0672 = 0.0528 equivalents

EXP 3

The pH of obtained stream = 0.451

H^+ concentration in the obtained stream = 0.35 moles/l

The volume of the whole sample obtained = 90 ml

Equivalents of H^+ in the obtained stream = 0.35*0.09*1 = 0.0315 equivalents

H^+ Concentration in the acid dosed (H_2SO_4) = 2 mole/l

The volume of H_2SO_4 dosed (including accidental over-dosing) = 53.2 ml

Equivalents of H^+ dosed = 2*0.0532*1 = 0.1064 equivalents

Equivalents Used up for regeneration = 0.1064 – 0.0315 = 0.0749 equivalents

Concentrating regenerant 5 times = 5 * 0.0749 = 0.3745 equivalents needed

That translate to 0.3745/0.1064 = 3.5 times the current concentration.

That translates to using a 7 N H_2SO_4 solution.

A9 Amount of Acid Required

Concentration of Mg^{2+} ions in current dose = 81.68 g/l

Annual consumption = 4500 tons = $4.5 * 10^6$ kg

Annual consumption of Mg^{2+} Ions = $4.5 * 10^6 * 81.68$(g/kg)/1000 kg = $39.06 * 10^7$ g

Annual consumption of Mg^{2+} Ions = 39.06/24.3 moles/g * 10^7 moles = $15.1 * 10^6$ moles

Annual requirement of H_2SO_4 to replace these Mg^{2+} ions = $15.1 * 10^6$ moles of H_2SO_4

Annual requirement of H_2SO_4 = $1510 * 10^6$ grams of H_2SO_4 = $1510 * 10^3$ Kg of H_2SO_4

= 1510 tons

H_2SO_4 is available in 98% by weight with a density of 1.8g/cm^3

Annual requirement adjusted for purity = 1540 tons

The annual requirement in m^3 = 841 m^3

This calculation is based on 36 N H_2SO_4