

REMOVAL OF CALCIUM FROM INDUSTRIAL-GRADE MAGNESIUM SULFATE SOLUTION



Åbo Akademi University

Faculty of Science and Engineering

John Paulo Samin

Student No.: 2100771



Master's programme in Excellence in Analytical Chemistry

Master's Thesis in Analytical Chemistry, 30 credits

Supervisor: Prof. Johan Bobacka (Åbo Akademi University)

Co-supervisors: Dr. Jouni Karhu (Renotech Oy)

Dr. Irja Helm (University of Tartu)

June 2022

PREFACE

The research work presented in this master's thesis was carried out at the Laboratory of Molecular Science and Engineering (Analytical Chemistry) at Åbo Akademi University in collaboration with Renotech Oy as part of the Erasmus Mundus Joint Master's Degree Programme - Excellence in Analytical Chemistry (EMJMD EACH).

I would like to express my deepest gratitude to my supervisor Professor Johan Bobacka and my co-supervisor Dr. Jouni Karhu for generously providing me with their invaluable knowledge, expertise, support, guidance, and encouragement during the conduct of this research work. I would also like to thank my co-supervisor Dr. Irja Helm, for giving me valuable feedback on the writing of this thesis.

I am grateful to Bob Talling and Renotech for providing me the opportunity to work on this project. I learned a lot through the process and it was a great experience working with you.

Many thanks to Dr. Zekra Mousavi, Tor Laurén, Ville Yrjänä, Jaypee Oña, and Luis Bezerra for their assistance in the laboratory.

I would like to express my sincere gratitude to Professor Ivo Leito, Dr. Anu Teearu-Ojakäär, and all the people involved in the EACH programme for teaching and helping us be experts in the field of analytical chemistry.

To my friends in the EACH programme, especially Naela, Raegan, Majid, Bojidar, and Angelo, thank you for making my two years interesting, fun, and memorable.

Last but not the least, I express my deepest gratitude to my family and friends for their unfailing support and continuous encouragement throughout my life and in this moment.

Turku/Åbo, June 2022

John Paulo Samin

ABSTRACT

Title of the thesis: Removal of calcium from industrial-grade magnesium sulfate solution

Author: John Paulo Samin

Thesis supervisors: Professor Johan Bobacka
Åbo Akademi University, Turku, Finland
 Dr. Jouni Karhu
Renotech Oy, Turku, Finland
 Dr. Irja Helm
University of Tartu, Tartu, Estonia

Date: June 2022

The aim of this work was to find a method to remove calcium impurities from a concentrated magnesium sulfate solution. Different methods were evaluated, including (i) selective precipitation using ethanol, sodium carbonate, oxalic acid, and sodium hydroxide, (ii) partial crystallization, and dissolution of magnesium sulfate solutions, (iii) ion-exchange using cationic exchange resin, and (iv) membrane separation using a calcium ion-selective membrane. The changes of Ca^{2+} and Mg^{2+} ions in each method were evaluated using ICP-OES analysis. Among the additives used in the selective precipitation experiments, ethanol and sodium hydroxide were the most efficient in removing calcium up to 65% and concentrating magnesium ions by six times (Mg/Ca molar ratio) as compared to the original solution, respectively. Sodium carbonate and oxalic acid did not cause any precipitation of calcium due to the high ionic strength as well as the inhibitory effect of Mg^{2+} ions present in the solution. Furthermore, partial crystallization and Ca^{2+} -selective membrane separation were found to be ineffective in removing calcium. Ion-exchange, using Amberlite® IR 120 resin, reduced the concentration of calcium ions in the solution by 30%, but also removed 20% of the magnesium ions in the solution, which signifies inadequate selectivity of the ion-exchanger. Lastly, partial dissolution of magnesium heptahydrate salts showed that calcium solubility decreases at low temperatures.

Keywords: selective precipitation, ion exchange, partial dissolution, partial crystallization, Ca-selective membrane, crystallization fouling, magnesium sulfate, calcium impurity removal, purification

TABLE OF CONTENTS

PREFACE	ii
ABSTRACT	iii
TABLE OF CONTENTS	iv
LIST OF ABBREVIATIONS	vi
1. INTRODUCTION	1
2. REVIEW OF RELATED LITERATURE	2
2.1 Removal of calcium impurities	2
2.2 Selective precipitation of calcium using additives	3
2.3 Ion-exchange	4
2.4 Ion-selective membranes.....	5
2.5 Inductively-coupled plasma – optical emission spectroscopy technique.....	6
3. MATERIALS AND METHOD	6
3.1 Materials.....	6
3.2 Inductively coupled plasma – optical emission spectrometry (ICP-OES).....	7
3.3 Selective precipitation experiments	8
3.3.1 <i>Ethanol</i>	8
3.3.2 <i>Oxalic acid</i>	9
3.3.3 <i>Sodium carbonate</i>	9
3.3.4 <i>Sodium hydroxide</i>	10
3.4 Partial crystallization of MgSO ₄ solution through evaporation	10
3.5 Preparation of magnesium sulfate solution from the heptahydrate salt	10
3.6 Removal of calcium using ion-exchange resin	11
3.7 Removal of calcium using a Ca-selective membrane	11
3.8 Determination of Mg, Ca, and S contents using ICP-OES	13
4. RESULTS AND DISCUSSION	13
4.1 Ca ²⁺ precipitation by ethanol.....	15
4.2 Ca ²⁺ precipitation by oxalic acid solution	18
4.3 Ca ²⁺ precipitation by sodium carbonate	20
4.4 Ca ²⁺ removal through magnesium hydroxide precipitation	21

4.5 Ca ²⁺ removal by partial crystallization of MgSO ₄ solution	23
4.6 Ca ²⁺ removal by partial dissolution of MgSO ₄ · 7H ₂ O salt.....	24
4.8 Ca ²⁺ removal by a PVC-based Ca-selective membrane.....	26
5. CONCLUSION	28
6. LITERATURE CITED	30
7. APPENDICES	37

LIST OF ABBREVIATIONS

DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EGTA	Ethylene glycol bis (2-aminoethyl ether)- N, N, N',N'-tetraacetic acid
ETH 129	N, N, N', N'-Tetracyclohexyl-3-oxapentanediamide
FAAS	Flame atomic absorption spectroscopy
HEDTA	N-(2-hydroxyethyl)ethylene diamine-N,N,N'-triacetic acid
ICP – MS	Inductively-coupled plasma – mass spectrometry
ICP – OES	Inductively-coupled plasma – optical emission spectroscopy
ISM	Ion-selective membrane
LOD	Limit of detection
o-NPOE	2-nitrophenyl octyl ether
PTFE	Polytetrafluoroethylene
PVC	Poly (vinyl chloride)
THF	Tetrahydrofuran

1. INTRODUCTION

Magnesium is the eighth-most abundant mineral in the earth's crust by mass while its cation (Mg^{2+}) is the second-most abundant cation present in seawater. Magnesium is found in the form of magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$) and in mineral waters where the magnesium ion is soluble. As a metal, magnesium is mainly used in lightweight materials and alloys, die-casting [1], and the desulfurization process in the production of iron and steel [2]. Its compounds are diversely applied in agriculture, medicine, and the development of construction materials. The addition of magnesium hydroxide in plastics makes them fire retardants [3]. Magnesium oxide is determined to possess antibacterial properties and also acts as a fire-resistant and insulating material [4]. Since magnesium is involved in many physiological and biochemical processes in plants, it plays an important role in plant growth and development [5]. Furthermore, magnesium compounds such as sulfate (Epsom salt), hydroxide (milk of magnesia), chloride, and citrate are all used in the field of medicine in the form of laxatives or antacids [6].

Purity is an essential factor in determining the possible application of these magnesium compounds and their price in the market. Among the possible impurities, the presence of calcium during downstream processing in industries is problematic due to calcification [7]. Calcium carbonate deposits on vessels and equipment may increase the cost of maintenance and the downtimes in manufacturing resulting in production loss. Several studies were conducted to remove calcium in the production of magnesium-rich solutions. Selective precipitation is the most common processing method, because it gives a significant advantage by increasing the ease of operation and reducing the cost and by diminishing the production of secondary pollutants [8]. Xia et al. used four additives (sodium carbonate, sodium oxalate, sodium fluoride, and sodium sulfate) to selectively remove calcium, and sodium hydroxide to recover magnesium by precipitation from flue gas desulfurization wastewater [9]. They reported that a 96% Ca removal efficiency was achieved using oxalate with 1.4-times stoichiometric dosage at pH 6.0. They recovered magnesium hydroxide with 99.3% (w/w) purity. Kim et al. developed a technology to recover Mg from seawater desalination brine in the form of high-purity $MgSO_4$ [8]. It consisted of three steps: pre-precipitation of $Mg(OH)_2$ using alkali, preparation of Mg concentrate using sulfuric acid, and precipitation of $MgSO_4$ using ethanol. Another study had developed a process scheme for the selective precipitation of calcium (Ca) and magnesium (Mg) from Red Sea water and reverse

osmosis brine using a dual precipitation/chelation unit [10]. Two precipitation stages were employed using sodium carbonate and sodium hydroxide for the sequential removal of Ca and Mg, respectively. They reported that the Ca removal could achieve 93.2-96.6% efficiency, while Mg removal achieved 74-99.6% efficiency. The use of chelating agents (EGTA, DTPA, and HEDTA) achieved almost complete removal of Mg with a maximum capacity of 490 mg/g.

Besides selective precipitation, other pre-treatment processes, such as ion exchange and electrodeionization, were investigated for calcium removal. However, some of these methods aimed at producing pure water and their selectivity between calcium and magnesium was not considered. In the present work, different methods, namely selective precipitation, partial crystallization and dissolution, ion-exchange, and ion-selective membrane, were tested and investigated for the removal of calcium from industrial-grade magnesium sulfate solutions. To reduce the loss of magnesium, experiments were conducted at different pH, temperature, and molar ratios, which will help in understanding the behavior of calcium impurities in concentrated magnesium sulfate solution.

2. REVIEW OF RELATED LITERATURE

2.1 Removal of calcium impurities

Crystallization fouling is a common problem in domestic, commercial, and industrial processes where water is involved. Also known as scaling, it is caused by the crystallization of dissolved salts from the heat exchange medium onto the heat transfer surface of industrial processes. The crystallization results from the supersaturation of the salt solution due to the following: (1) the evaporation of solvent, (2) cooling of a solution containing otherwise soluble salts below their solubility temperature, (3) heating a solution of inverse solubility salts above the solubility temperature, and (4) mixing of solutions with different composition or variation of the solution's pH [11]. The primary substances responsible for this problem are the carbonate and sulfate salts of calcium and magnesium [12]. The formation of mineral scales creates technical problems including pipe or valve blockage, under-deposit corrosion, and unscheduled equipment shutdown [13]. This leads to an increase in costs for industries due to higher fuel usage, production losses, and maintenance [14].

Calcium sulfate and its hydrated forms are one of the major components of scale in many industrial processes [15]. Unlike many other salts, the solubility of calcium sulfate decreases with increasing temperature from 40 °C which is why most scale deposits are composed of calcium sulfate anhydrous (anhydrite) and calcium sulfate dihydrate (gypsum) [16]. Several studies have attempted to control the scaling process. These strategies include the addition of additives that slow down or inhibit the precipitation of calcium sulfate [17,18] and pre-treatment of the water source to remove the calcium and other ions responsible for the formation of scales in industrial and domestic processes [19].

2.2 Selective precipitation of calcium using additives

Selective precipitation is a procedure of separating ions in an aqueous medium by using reagents that precipitate one or more of the target ions while leaving other ions in the solution. Numerous papers in the scientific literature investigated the use of additives in the removal of calcium from seawater desalination brines and effluents from the wastewater treatment process. Such additives include ethanol, carbon dioxide, sodium carbonate, sodium bicarbonate, sodium fluoride, sodium sulfate, and oxalic acid.

An investigation of the solid-liquid equilibrium of water-ethanol-NaCl-CaSO₄ at 25 °C was performed [20]. It showed that as ethanol concentration increases in the solution, the CaSO₄ solubility decreases. It concluded that it is possible to utilize ethanol to precipitate salts from brine samples to obtain more effective conversion in a reverse osmosis desalination plant. Kim and his colleagues developed a technology to recover magnesium from seawater desalination brine as high purity MgSO₄ without calcium impurities. The recovery method consisted of pre-precipitation of Mg(OH)₂ using alkali, preparation of Mg concentrate with sulfuric acid, and precipitation of MgSO₄ using ethanol [8]. When the volume ratio of ethanol to Mg eluate was 0.4 and higher, most of the calcium ions precipitated in the form of calcium sulfate dihydrate (gypsum). Moreover, they stated that the two-step addition of ethanol ensures better removal of Ca²⁺ impurities without Mg loss than using the one-step addition of ethanol. The purity of the recovered MgSO₄ was reported to be up to 99.8%.

Chemical precipitation is an approach that offers significant advantages for the selective removal of calcium due to its ease of operation, low cost, and absence of secondary pollution [9]. Calcium ions (Ca²⁺) from nanofiltration retentate were removed through reactive unseeded precipitation

using sodium bicarbonate/sodium carbonate. The reduction of Ca^{2+} ions varied from 56 to 89% for initial pH values of 9.05 and 9.90. At this pH, the calcium carbonate precipitate was in the form of calcite [21]. The use of sodium carbonate was also investigated in the recovery of salts from brines in desalination plants. Na_2CO_3 was added at the first stage of reactive precipitation at pH 9.2. The recovery of calcium reached about 95.5%, 89%, and 95% for seawater, Mediterranean, and Red Sea reverse osmosis brines, respectively [22]. Wang et al. introduced a modified sodium carbonate method to remove calcium from seawater and found that temperature was the most crucial factor affecting its efficiency. The optimum operating conditions were determined to include an equimolar dosage of sodium carbonate with a brine salinity of >56 g/kg at 85°C [23].

Oxalic acid was also used to extract calcium from seawater and brine solutions. Natasha and Lalasari investigated the effect of variations in the volume of oxalic acid at a constant concentration to form calcium oxalate [24]. The ICP-OES analysis of the filtrate from seawater showed a significant decrease from an initial calcium concentration of 826 ppm to 0.04 ppm, while brine water had a decrease from 170 ppm to 1.96 ppm [24]. Although effective in removing calcium ions, there is still a small number of magnesium ions that is co-precipitated when oxalic acid is used as the precipitant. Particle sizes of calcium oxalate and magnesium oxalate are also extremely small, resulting in difficulty for solid/liquid separation [25].

2.3 Ion-exchange

Ion exchange is a process of exchanging ions from a solution with the ions that are electrostatically bound to the functional groups of an ion exchanger. Those groups can be in a solid matrix [26]. An ion exchange resin is an insoluble polymer matrix that is normally in the form of beads. The beads are typically porous to provide a large surface area and many accessible functional groups for the ion exchange process [27]. The functional groups are intended to interact with the ion of interest. Matrices could be made of polystyrene, polyacrylic, phenolic resin, or polyalkylamine resins. Resins can be classified either as cationic or anionic with different intensities of acid/base exchange abilities depending on the nature of their functional group [28].

Ion exchange resins are significantly utilized in commercial and industrial processes, particularly in water purification and metal ion removal in the chemical industry [29]. Removal of calcium and magnesium from lithium bicarbonate solution using Amberlite™ IRC 747 was investigated in a

study. The resin was reported to be a suitable material to remove calcium and magnesium ions from their sample solution [30].

Amberlite® IR 120 is a strongly acidic cation exchange resin consisting of polystyrene divinyl benzene polymer with sulfonic (-SO₃H) functional groups [31]. The resin's effectiveness in removing calcium was studied in the presence of magnesium and softening of waters [32,33]. It was found that this resin was more selective to calcium as compared to magnesium ions and a pH higher than 2.0 had the greatest effect on the selectivity of the resin [32].

2.4 Ion-selective membranes

Ion-selective membranes (ISMs) are polymeric membranes that exclude all ions except the ion of interest. ISMs are typically used in potentiometric sensors [34]. The membranes are composed of a matrix/supporting material, plasticizer, lipophilic salts, and the ionophore. The matrix component is usually made of high molecular weight poly (vinyl chloride) because of its low toxicity, strength, and chemical and redox inertness [35]. Plasticizers are used as additives to produce the desired flexibility and durability of the membrane. When added, plasticizers increase the volume of the membrane by embedding themselves between the chains of the polymer. As the plasticizer component of ISM is increased, the more flexible and durable the membrane will become. Plasticizers could be phthalates, ethers, or esters of either aromatic and aliphatic acids [36]. The main function of lipophilic salts is to improve the detection limit and selectivity of the electrodes and decrease the resistance of the sensing membrane [37]. Furthermore, ionophores are lipophilic complexing agents that can reversibly bind ions of interest. They may be charged or electrically neutral when not in the complex form [38]. The ionophore is responsible for ion selectivity and is the actual sensing component of the membrane [35].

The ionophore used in this study is calcium ionophore II or ETH 129 (Figure 1). It is a neutral carrier that forms a 1:3 cation/ionophore complex with Ca²⁺ and 1:2 complexes with Mg²⁺, making it highly selective for calcium rather than magnesium [39]. It was also reported to have little or no activity for the transport of Na⁺, K⁺, and Mg²⁺. Since ETH 129 contains no ionizable functions and forms cation complexes, the membrane potential is important in the case of this kind of ionophore [40].

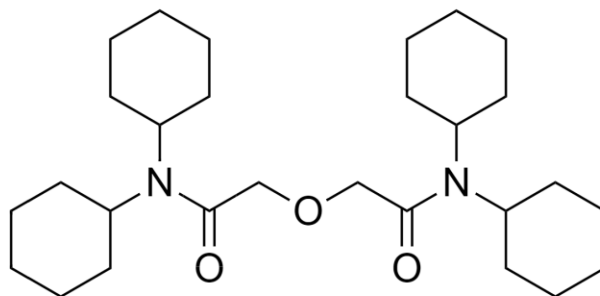


Figure 1. Calcium ionophore II (ETH 129).

2.5 Inductively-coupled plasma – optical emission spectroscopy technique

Inductively-coupled plasma – optical emission spectroscopy (ICP-OES) is an analytical technique used to identify the atomic composition of a particular sample. Samples are introduced as acid solutions and then nebulized into a stable stream to form a fine aerosol that is transported into the plasma by a carrier gas, typically argon. The sample will then undergo desiccation, vaporization to molecular gases, and dissociated into ionizable atoms. Atoms and ions become excited, and will thereafter revert to the ground state simultaneously emitting light that can be measured by an optical spectrometer.

There are two geometries when measuring atomic emissions, the axial view and the radial view. The axial view is when the torch is turned 90° towards the spectrometer. This allows the measurement to achieve a lower detection limit. In radial viewing, the torch is perpendicular to the spectrometer, thus allowing better stability and higher precision during the analysis [41]. ICP-OES analysis has a limit of detection at the level of mg/L and µg/L which is in between the detection limit of ICP-mass spectrometry (ICP-MS) and flame atomic absorption spectroscopy (FAAS) [42].

3. MATERIALS AND METHOD

3.1 Materials

Industrial-grade magnesium sulfate (MgSO_4) solution and magnesium sulfate heptahydrate salt were obtained from industrial production. Magnesium sulfate anhydrous, calcium citrate tetrahydrate, oxalic acid anhydrous, sodium hydroxide (NaOH) pellets, calcium chloride anhydrous (CaCl_2), poly (vinyl chloride) (PVC), 2-nitrophenyl octyl ether (o-NPOE), Calcium-

Ionophore II, ethylenediaminetetraacetic acid (EDTA) disodium salt, sulfuric acid (H₂SO₄), nitric acid (HNO₃), and hydrochloric acid (HCl) were purchased from Sigma Aldrich (Germany). The purity of all chemicals was of analytical grade. Amberlite® Ion exchanger IR-120 (strongly acidic cation exchanger) in the H⁺ form was purchased from Sigma Aldrich (Germany). All aqueous solutions for the experiments were made from deionized water from ELGA PureLab Ultra with resistivity of 18.2 MΩ·cm.

Before the industrial-grade magnesium sulfate solution was used for the experiments, it was first filtered using quantitative filter paper (4-12 μm pore size, 589/2 Whatman Ashless Filter paper) to remove existing precipitates from the solution. The filtered solution was then transferred into a plastic container, labelled and stored at room temperature before use. A model magnesium sulfate solution (250 g/L MgSO₄ and 500 ppm Ca) and a calcium solution (500 ppm Ca only) were also prepared for preliminary experiments. The calcium from these solutions were prepared from analytical grade calcium nitrate.

3.2 Inductively coupled plasma – optical emission spectrometry (ICP-OES)

The ICP-OES measurements were carried out with a PerkinElmer Optima DV equipped with an autosampler. The instrument was operated under suitable conditions and three wavelengths at axial and radial view were recorded for each element. The most suitable wavelength was selected for each element and the result was reported as the average of five measurements. Standard solutions of each element were also prepared and measured.

Magnesium sulfate samples, namely industrial-grade magnesium sulfate solution and magnesium sulfate heptahydrate salt, were subjected to multi-element ICP-OES analysis. A 10 mL aliquot of the industrial-grade magnesium sulfate solution was transferred in a 100 mL volumetric flask and was diluted to mark with 1.5% (w/w) nitric acid solution. For the preparation of magnesium sulfate heptahydrate salt solution, 5 g of the salt was weighed and transferred to a 100 mL beaker. The salt was dissolved with 50 mL 1.5% (w/w) nitric acid solution. When the salt was fully dissolved, the resulting solution was transferred to a 100 mL volumetric flask and was diluted to mark using the same acid solution. The sample solutions were then stored at room temperature prior to ICP-OES analysis.

3.3 Selective precipitation experiments

Different additives (ethanol, sodium carbonate, oxalic acid, and sodium hydroxide) were used to selectively remove the calcium impurities from the industrial-grade MgSO_4 solution. Precipitation of calcium was investigated for the addition of ethanol, sodium carbonate, and oxalic acid. Calcium retention in the filtrate was evaluated for the magnesium hydroxide produced after the addition of sodium hydroxide in the solution.

Moreover, a 25% MgSO_4 solution was prepared for ethanol experiments, while the rest of the experiments used the filtered industrial-grade MgSO_4 solution. Since the precipitation using ethanol is based on the ionic strength of the solution, a 25% magnesium sulfate solution containing 500 ppm calcium was used as the model solution for the industrial-grade MgSO_4 .

3.3.1 Ethanol

An aliquot of 10 mL 25% MgSO_4 solution was transferred in a 20 mL glass vial. Different volumes of ethanol were added to the vial, as shown in Table 1. A small magnetic bar was added and the vial was tightly capped. The solution was then magnetically stirred at 600 rpm for 10 min. The prepared solutions were left to stand for 70-72 hours to facilitate the complete precipitation of calcium sulfate. The solutions were filtered by gravity using a quantitative filter paper (4-12 μm pore size, 589/2 Whatman Ashless Filter paper). The filtrate was collected in a 100 mL volumetric flask. After filtration, about 75 mL of deionized water was added to the flask followed by the addition of 2.145 mL of 70% nitric acid solution using an automatic pipettor. The solutions were diluted to mark by deionized water, mixed well, and transferred in a 250 mL plastic container for ICP-OES analysis. These solutions were prepared for calcium analysis. For magnesium and sulfur analysis, 0.8 mL was pipetted out from these solutions and transferred to a 100 mL volumetric flask. The flasks were diluted to mark with 1.5% (w/w) nitric acid solution. The diluted solutions were then stored in 250 mL plastic bottle container before ICP-OES analysis.

Table 1. Treatments for ethanol addition.

Ratio of ethanol to MgSO_4 solution	Code	Volume of MgSO_4 solution, mL	Volume of ethanol, mL
0:1 (Control)	E1	10	0
0.10:1.0	E2	10	1.0
0.15:1.0	E3	10	1.5
0.20:1.0	E4	10	2.0

3.3.2 Oxalic acid

In a 20 mL vial, 8 ml of the filtered MgSO_4 solution and 4.2 mL of 0.2M oxalic acid solution (pH 7.0) were mixed. The molar ratio of calcium to oxalic acid was around 1:16. The pH of the solutions was adjusted to pH 8 and pH 9 using 1M NaOH solution. After the pH adjustment, the samples were left overnight to observe if precipitation occurs. Another set of experiments was conducted where the molar ratio of oxalic acid to calcium was doubled without pH adjustments. The solutions were left overnight to observe if precipitation occurs by increasing the amount of oxalic acid without pH adjustments.

A third set of experiments was conducted to identify any possible precipitate observed in the previous experiments. About 20 mL filtered MgSO_4 solution and 10 mL 0.2 M oxalic acid (pH 7) were magnetically stirred for 10 min at 850 rpm using a heating magnetic stirrer without heating. While mixing, the pH was adjusted to 9.0 using 1M NaOH solution and was, then, left to stand for 48 hours. After 24 hours, one of the treatments was filtered using a quantitative filter paper (4-12 μm pore size, 589/2 Whatman Ashless Filter paper). The filtrate was stored in a 25-mL centrifuge tube and was left to stand for another 24 hours to observe any further precipitation. The treatments are shown in Table 2.

Table 2. Treatments for oxalic acid addition.

Treatments	Description
W0	Control – no addition of oxalic acid (pH 9)
W1	1:16 molar ratio calcium: oxalic acid (pH 9)
W2	1:16 molar ratio calcium: oxalic acid (pH 9) – filtered twice

3.3.3 Sodium carbonate

For the carbonate experiment, 40 mL filtered MgSO_4 solution (containing approximately 250 ppm Ca) was mixed with 40 mL 5 g/L Na_2CO_3 solution (1:7.6 molar ratio Ca:carbonate). The solution was then adjusted to pH 9.2 using 1M NaOH solution and the resulting solution was mixed for 10 min at 600 rpm using a hotplate stirrer. The solution was left overnight to allow for precipitation to occur. After 24 hours, the solution was filtered and the filtrate was collected for ICP-OES analysis.

3.3.4 Sodium hydroxide

In contrast to the previous precipitation experiment, the hydroxide approach was used to precipitate magnesium into its hydroxide form, while leaving the calcium ions in the solution. A 10 mL aliquot of the filtered MgSO_4 solution was measured using a volumetric pipette and was transferred to a 50 mL beaker. Then, 20 mL of 2 M NaOH solution was added dropwise using a 25 mL burette to the magnesium sulfate solution. While adding the NaOH solution, the solution was magnetically stirred at 240 rpm using a magnetic stirrer. It was slowly stirred to prevent the formation of a thick gel-like suspension, which is difficult to filter. The mixture was then vacuum filtered using a Whatman filter paper (589/1 quantitative) and washed twice with 10 mL of deionized water. The precipitate was dried in an oven at 105 °C for 1 hour or until the precipitate was fully dried. A small amount of the precipitate was dissolved in 1.5% (w/w) nitric acid solution for ICP-OES analysis.

3.4 Partial crystallization of MgSO_4 solution through evaporation

A 50 mL aliquot of the industrial-grade MgSO_4 solution was measured using a 50-mL volumetric pipette and was transferred to a 100 mL beaker. The solution was then heated at 80 °C for 30 min. The solution was weighed before and after heating to estimate the percent of water evaporated from the sample, which was approximately 10% of the solution. After heating, the solution was cooled and 5 mL of the sample was taken initially for ICP-OES analysis using a syringe fitted with a syringe filter (Puradisc™, 0.45 μm polypropylene, 25 mm diameter). The solutions were left overnight to allow precipitation to occur. If a precipitate was observed, 5 mL of the supernatant was taken using a syringe fitted with a syringe filter and was prepared for ICP-OES analysis.

3.5 Preparation of magnesium sulfate solution from the heptahydrate salt

This method aimed to dissolve the magnesium sulfate crystals while leaving the calcium sulfate in the solid phase. About 15 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt was dissolved by pipetting out 50 mL of deionized water at different initial temperatures (2, 20, and 70 °C). The solution was magnetically stirred for 5 min at 350 rpm. Any remaining solids were left undissolved. An aliquot was taken from the supernatant using a syringe fitted with a filter (Puradisc™, 0.45 μm polypropylene, 25 mm diameter) and was prepared for ICP-OES analysis.

3.6 Removal of calcium using ion-exchange resin

Another method to selectively remove calcium impurities is through the use of a cation exchange resin. Amberlite® IR-120 ion-exchange resin in protonated form was used in this experiment. The resin was preconditioned by washing with deionized water three times to remove adhered impurities from the resin as described by Naushad and Al-Othman [43]. About 5.0 g Amberlite® IR-120 resin in H⁺ form was packed in a glass column with a fritted disc at the end. The column was washed 2-3 times with deionized water. About 10 mL of the magnesium sulfate at different pH (4, 5, and 8) was pipetted to the column and allowed to flow at a constant rate. The column was rinsed with 10 mL of deionized water and the effluent was collected in a 100-mL volumetric flask. About 75 mL deionized water was added to the flask followed by the addition of 2.145 mL of 70% nitric acid solution using an automatic pipettor. The solutions were diluted to mark by deionized water, mixed well, and transferred to a 250 mL plastic container for ICP-OES analysis. After every replicate, the resin was regenerated by adding 10 mL 8% hydrochloric acid (HCl) solution twice. The excess acid was then washed by 10 mL deionized water two times and the column was now ready for the next sample. Control solutions of magnesium sulfate adjusted at pH 4, 5, and 8 were also prepared and subjected to ICP-OES analysis.

3.7 Removal of calcium using a Ca-selective membrane

Membranes with and without calcium-ionophore were prepared in a glass vial with compositions, as shown in Table 3. The membrane was composed of three components: PVC, plasticizer (2-nitrophenyl octyl ether), and ionophore (ETH 129). The total mass of each membrane was 120 mg. About 2.5 mL tetrahydrofuran (THF) was added to each vial and vortex-mixed until all the substance was dissolved. The vials were then placed in a rocker to slowly shake the solution for an hour to ensure complete dissolution of the substances.

Table 3. Composition of membranes.

Substance	Mass and percent composition	
	Dummy membrane	Calcium-selective membrane
Polyvinyl chloride (PVC)	40.8 mg (34%)	38.6 mg (32%)
o-NPOE (plasticizer)	79.2 mg (66%)	79.2 mg (66%)
Calcium-ionophore II (ETH 129)	0.0 mg (0%)	2.4 mg (2%)

After shaking, the membrane solution was poured into a glass cylinder secured on a glass plate with a rubber band (Figure 2). The set-up was covered with a transparent glass tray and left for 3 days to allow evaporation of THF. The resulting thin film membrane of approximately 0.38 mm thickness was carefully removed from the cylinder. The membrane was then fitted in between two cells made of polytetrafluoroethylene (PTFE). The source cell contained a solution of 0.01 M calcium chloride solution or industrial-grade magnesium sulfate solution and the receiving cell contained deionized water or 0.05 M EDTA (pH 8). Each cell contained 15 mL of each solution, as shown in Table 4. Samples were collected after 24 and 72 hr for the dummy membrane treatments, while samples with the Ca-selective membrane were collected after 24 and 48 hr.



Figure 2. Set-up for membrane preparation.

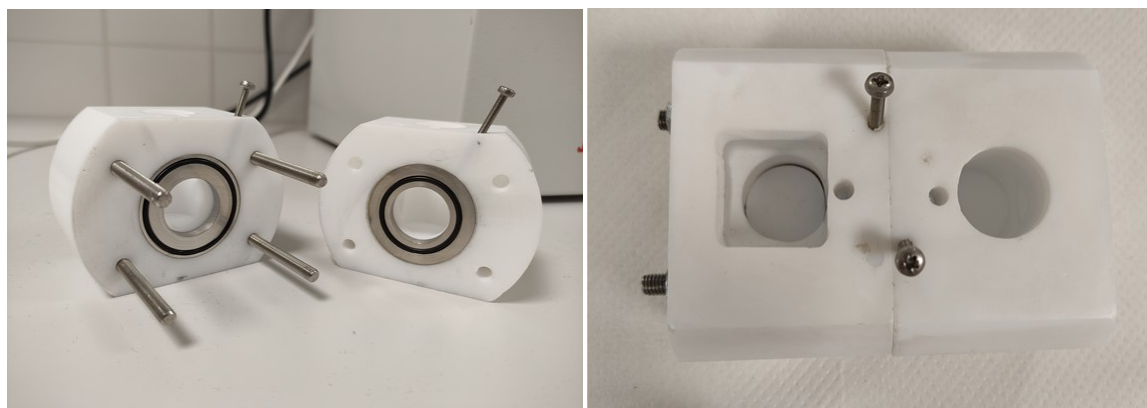


Figure 3. Ion-selective membrane set-up.

Table 4. Treatments for the removal of calcium using membranes.

Membrane	Composition	
	Source cell	Receiving cell
Dummy membrane	0.01 M CaCl ₂ solution	Deionized water
	0.01 M CaCl ₂ solution	0.05 M EDTA (pH 8)
Ca-selective membrane	0.01 M CaCl ₂ solution	Deionized water
	0.01 M CaCl ₂ solution	0.05 M EDTA (pH 8)
	10% MgSO ₄ solution	Deionized water
	10% MgSO ₄ solution	0.05 M EDTA (pH 8)
	Original filtered MgSO ₄ solution	Deionized water
	Original filtered MgSO ₄ solution	0.05 M EDTA (pH 8)

3.8 Determination of Mg, Ca, and S contents using ICP-OES

The samples were diluted in 1.5% (w/w) nitric acid solution and were analyzed for Mg, Ca and S content using the PerkinElmer Optima 5300 DV ICP-OES system. The samples were analyzed in triplicates against a blank containing 1.5% (w/w) nitric acid solution. All experiments were performed in triplicates except for the ion-selective membrane experiment. Data was reported as the mean of three measurements and their standard deviation.

Moreover, some deviations on the expected stoichiometric ratio of some elements were noticed. The analysed concentration of sulfur was in many analyses noticeably higher than the concentration of magnesium (and other possible counter ions). Thus, the industrial-grade magnesium sulfate solution and magnesium sulfate heptahydrate samples were submitted for ICP-OES analysis to external laboratories for comparison to the values reported in this study. It was observed that calcium and magnesium contents were smaller compared to the results from external laboratories, while sulfur content was higher for both samples (Appendix Table 2). The stoichiometric ratio of magnesium to sulfur reported in this study was about 1:1.3, while the external laboratory results were much closer to 1:1 and in better agreement with the expected ratio.

4. RESULTS AND DISCUSSION

The elemental composition of magnesium sulfate solution and magnesium sulfate heptahydrate salt from industrial production was determined using ICP-OES, as shown in Table 5. The magnesium sulfate solution contained a small amount of precipitate which could cause further

precipitation of magnesium sulfate through seeding. Filtration was therefore necessary to have a homogenous sample for the experiments. Initially, the MgSO_4 solution appeared to be brownish. After filtration, the brownish solution turned clearer and a yellow to brown precipitate was observed on the filter paper. Moreover, the analysis of the filtered solution showed that the concentration of manganese had decreased from 0.23 mM to 0.04 mM (11 ppm to 2 ppm) after the filtration. Besides the yellowish precipitate, the unfiltered solution was observed to contain needle-like precipitate after long storage. After filtration, no precipitate formation was found to take place. Magnesium sulfate heptahydrate salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) was used to prepare magnesium sulfate solution by partial dissolution, one of the approaches investigated in this study. Sample solution was prepared for ICP-OES analysis by fully dissolving 5 g of the salt in 1.5% (w/w) nitric acid solution. The result served as the baseline concentration for the partial dissolution experiments. As can be seen in Table 5, the magnesium sulfate heptahydrate contained a higher amount of magnesium, sulfur, and silicon, while calcium content was the same as for the MgSO_4 solution. Calcium is often the main cause of scaling problems in the industrial processes because of the formation of its insoluble salts, calcium carbonate, and calcium sulfate dihydrate (gypsum). In this study, multiple methods were investigated to remove calcium from industrial-grade MgSO_4 solution.

Table 5. Elemental composition of magnesium sulfate samples.

Element	Concentration		
	MgSO_4 solution, mol/L		$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt, mol/kg
	Unfiltered	Filtered	
Magnesium	2.25	2.24	3.73
Calcium	0.0071	0.0063	0.0068
Potassium	0.00194	0.00189	0.00049
Manganese	0.00023	0.000039	0.000333
Sodium	0.0052	0.0052	0.0012
Lead ^a	<LOD	<LOD	--- ^b
Sulfur	3.07	3.08	4.93
Silicon	0.00036	0.00027	0.00068

^a Concentration below the limit of detection, LOD ($<7.2 \times 10^{-7}$ M).

^b Result cannot be calculated because lead concentration is below LOD.

4.1 Ca²⁺ precipitation by ethanol

Addition of ethanol was evaluated as a method to precipitate calcium ions as calcium sulfate. Model magnesium sulfate solutions containing approximately 250 g/L magnesium sulfate and 500 mg/L Ca²⁺ from Ca(NO₃)₂, were subjected to different volume addition of ethanol resulting in a 0.1-0.30:1 ratio at 0.05 interval. At 0.25:1 and 0.30:1 ratio, the salt in the solution immediately started to precipitate after mixing. When left overnight, these mixtures fully precipitated (Figure 4).

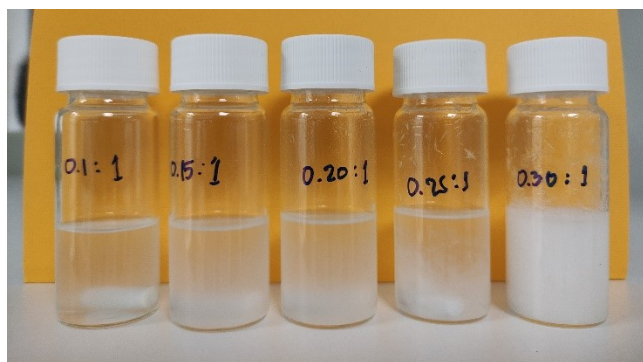


Figure 4. Different volume ratios of ethanol and magnesium sulfate model solution.

Another set of treatments was conducted with volume ratios of 0.1:1, 0.15:1, and 0.2:1 ethanol-model magnesium sulfate (containing 500 ppm Ca²⁺ ions). The model solution had a pH of 8.0 at 25 °C. The formation of the precipitate as a function of time after the addition of ethanol is shown by the sample replicate (together with the initial clear solutions) in Figures 5-8. The figures show the situation directly after ethanol addition (after mixing), after 15 min, after 30 min, and after 60 min. Among the treatments prepared, one replication with 0.2 mL ethanol addition showed a large amount of precipitate after standing for 72 hours, as shown in Figure 8 (photo on the lower right). The treatment with the least amount of ethanol (0.1:1) added was observed to have the slowest rate of precipitate formation. Treatments with 0.15 mL and 0.20 mL ethanol addition resulted in turbid solutions immediately after mixing. After the precipitate was formed, it started to settle at the bottom of the container. The precipitate collected by filtration is shown as an example in Figure 9.

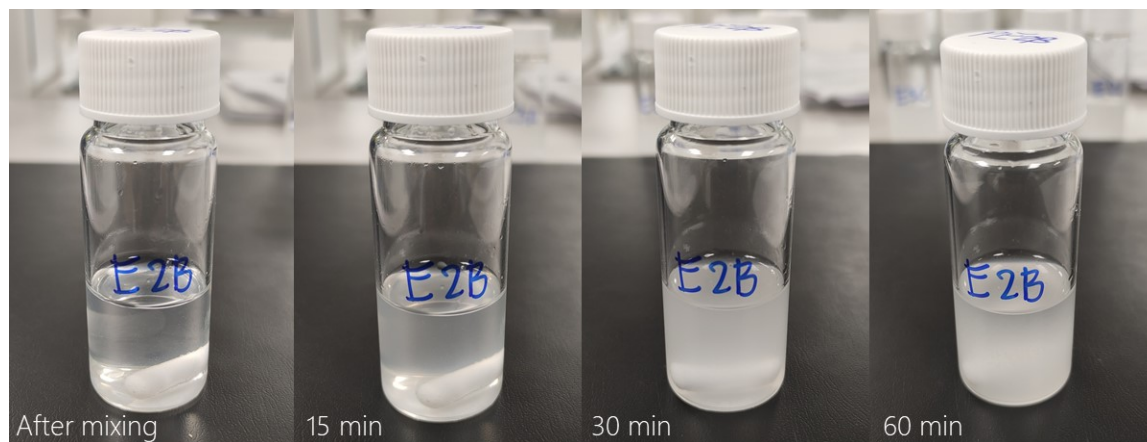


Figure 5. 0.1:1 v/v ethanol: model solution (Replicate 2).

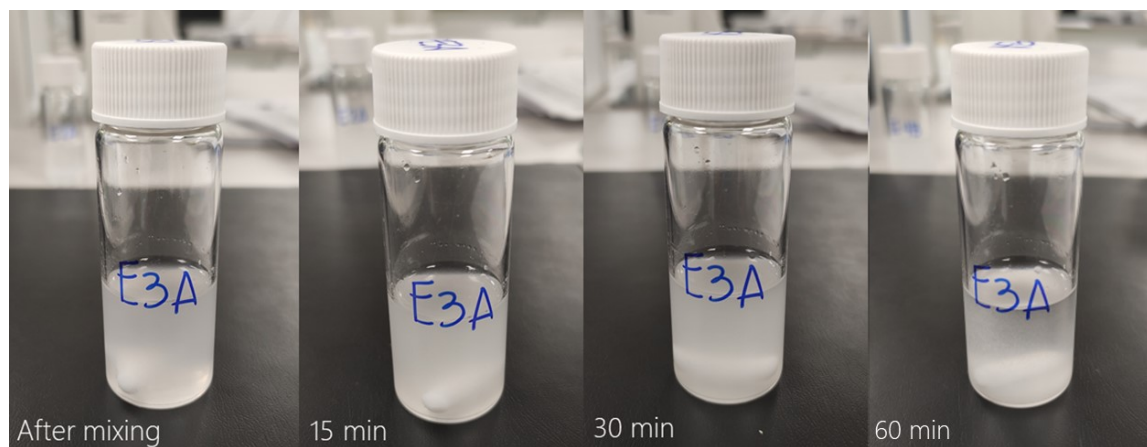


Figure 6. 0.15:1 v/v ethanol: model solution (Replicate 1).

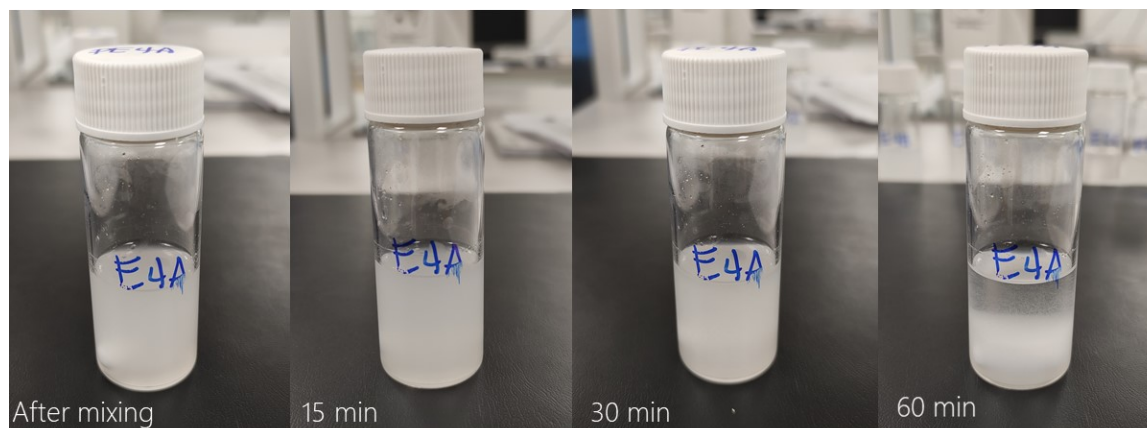


Figure 7. 0.20:1 v/v ethanol: model solution (Replicate 1).

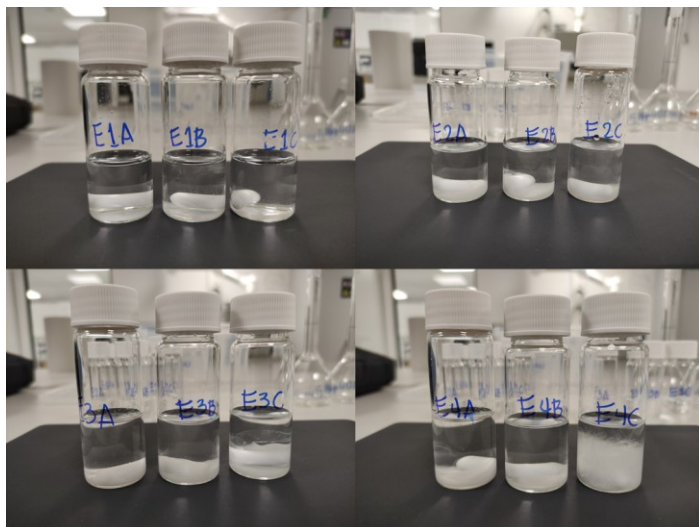


Figure 8. Ethanol treatments after 72 hours.

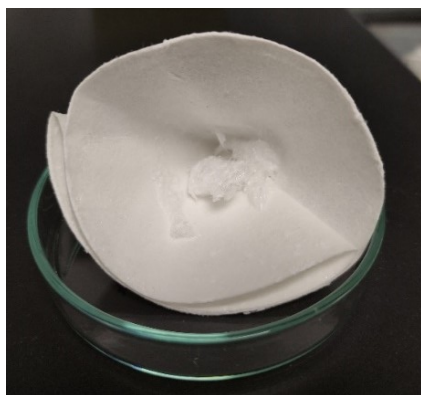


Figure 9. The collected precipitate from one replicate in 0.20:1 v/v ethanol: model solution.

Figure 10 shows the magnesium, sulfur, and calcium content of the filtrates after the precipitation of calcium. The addition of ethanol did not significantly reduce the magnesium and sulfur content of the solution. The results obtained by ICP-OES are ca 20 % lower than the theoretically expected concentration of the prepared model solution, which should contain ca 50,000 ppm of magnesium. Washing of the filter paper during filtration was not done, because the precipitate redissolves when washed with deionized water. If ethanol was used for washing, more salt precipitated and there was more of it left in the filter. Therefore, part of the magnesium content in the solution remained in the filter paper during the process. Treatments with a 0.15:1 volume ratio and above were observed to form a lot of white precipitate after an hour. Thus, it might be recommended to store it for a shorter time after the addition of a larger amount of ethanol to prevent co-precipitation of magnesium.

Increasing the volume of ethanol added to the samples decreases the solubility of calcium sulfate. The calcium content in the model solutions was reduced up to 65.7%. This trend has also been reported by Gomis et al. (2013) while studying the solubility of calcium sulfate (CaSO_4) in water-ethanol mixtures in the presence of sodium chloride at 25 °C [20]. They also stated that increasing the ionic strength of the solution also increases the solubility of CaSO_4 . Thus, more ethanol must be added to precipitate calcium from solutions with high ionic strength. Besides the effect of ionic strength, ethanol can also precipitate magnesium sulfate from the solution when the ethanol: MgSO_4 solution volume ratio is 0.4 or higher [8,44]. Thus, to achieve efficient removal of Ca^{2+} ions, it is necessary to know the ionic strength and magnesium composition of brine samples. From an industrial point of view, another limitation of this method is the cost of ethanol recovery and the safety hazard due to its flammable properties.

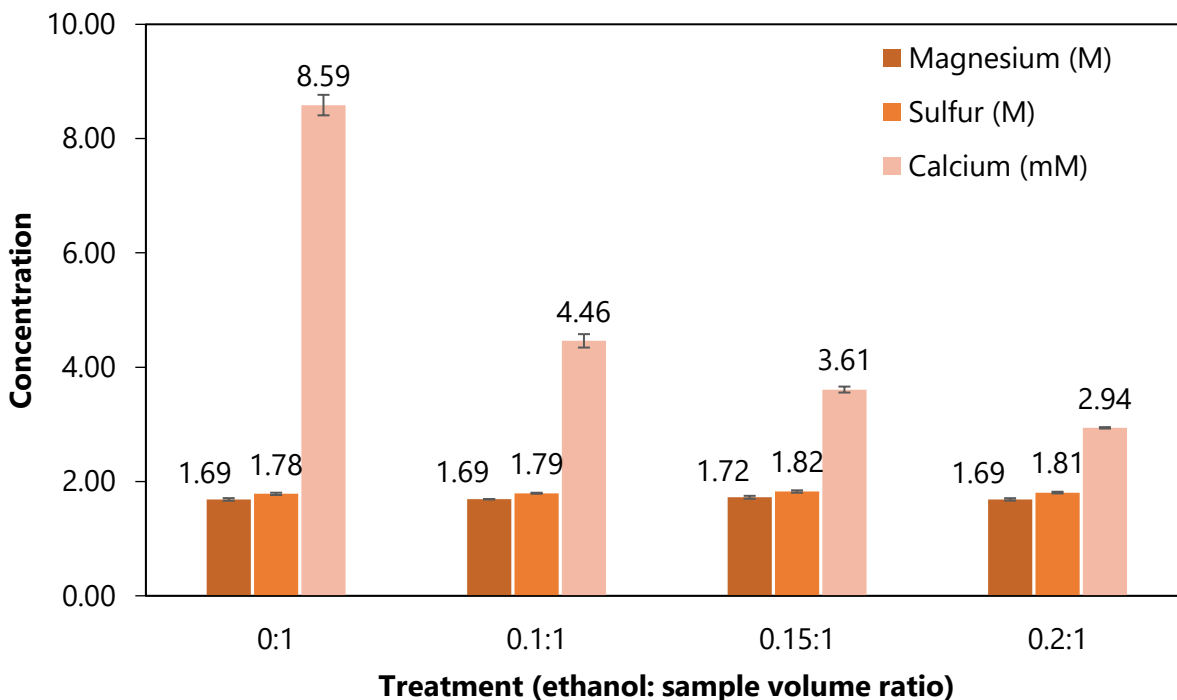


Figure 10. Effect of ethanol addition on the magnesium, sulfur, and calcium contents of the model solution.

4.2 Ca^{2+} precipitation by oxalic acid solution

An initial test was carried out in an attempt to precipitate calcium in the form of calcium oxalate by the addition of oxalic acid. In Figure 11, more than equimolar amount of oxalic acid to calcium ions was added in each solution: model solution and 500 ppm Ca^{2+} solution. No precipitate was

observed from the model solution, while a white precipitate was formed in the 500 ppm Ca^{2+} solution upon the addition of oxalic acid.

Another set of tests was performed using the filtered MgSO_4 solution. Two solutions with molar ratios 1:8 and 1:16 of Ca^{2+} ions to oxalate were prepared using the filtered solution and oxalic acid (pH 7). After leaving the prepared solution for 1 day, no precipitate was observed. The next experiment was to test the effect of pH adjustment. The solutions (1:16 molar ratio Ca: oxalic acid) were adjusted to pH 8.3 and 9.4 using 1.0 M NaOH solution. After leaving the solutions to stand overnight, a precipitate was observed at both pH and the solution at pH 9.4 had a more turbid appearance, indicating that more precipitate was formed overnight.

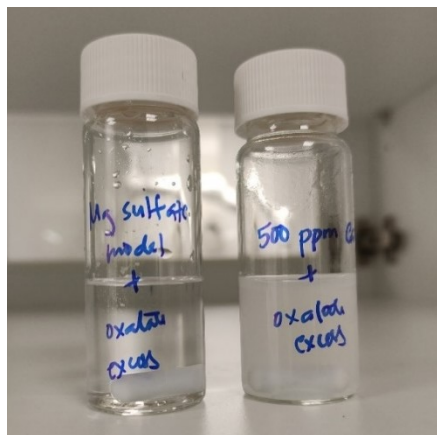


Figure 11. Solutions after mixing oxalate in excess: model solution (Left) and 500 ppm Ca^{2+} solution (right).

Before identifying the precipitate, another set of solutions (1:16 Ca:oxalic acid molar ratio at pH 9) was prepared and filtration was done twice for one of the solutions. This was performed to find out whether precipitation is already at equilibrium after 1 day of standing. The filtered solution, which was clear after the first filtration, became turbid again after 1 day. This signifies that there is the possibility of precipitation of other species than calcium oxalate in the solution. This was confirmed by the ICP-OES analysis, as shown in Figure 12. The results showed no significant difference in Ca content, while a slight decrease in Mg was observed for the solution after filtering twice. The identity of the precipitate could thus be magnesium hydroxide. The use of 1 M NaOH in the pH adjustment could be the reason for the formation of $\text{Mg}(\text{OH})_2$. Upon addition of the alkali, the hydroxide ions might have immediately reacted with the magnesium ions in the solutions to form an insoluble $\text{Mg}(\text{OH})_2$ before the pH of the solution reaches an equilibrium.

Moreover, calcium oxalate was not formed in the model solution because of its high Mg^{2+} content. According to Riley et al. [45], the presence of magnesium ions tends to destabilize calcium oxalate ion pairs and reduce aggregate size. Magnesium ion has a concentration-dependent inhibitory effect. This effect is also effective under an acidic environment in which calcium oxalate precipitates.

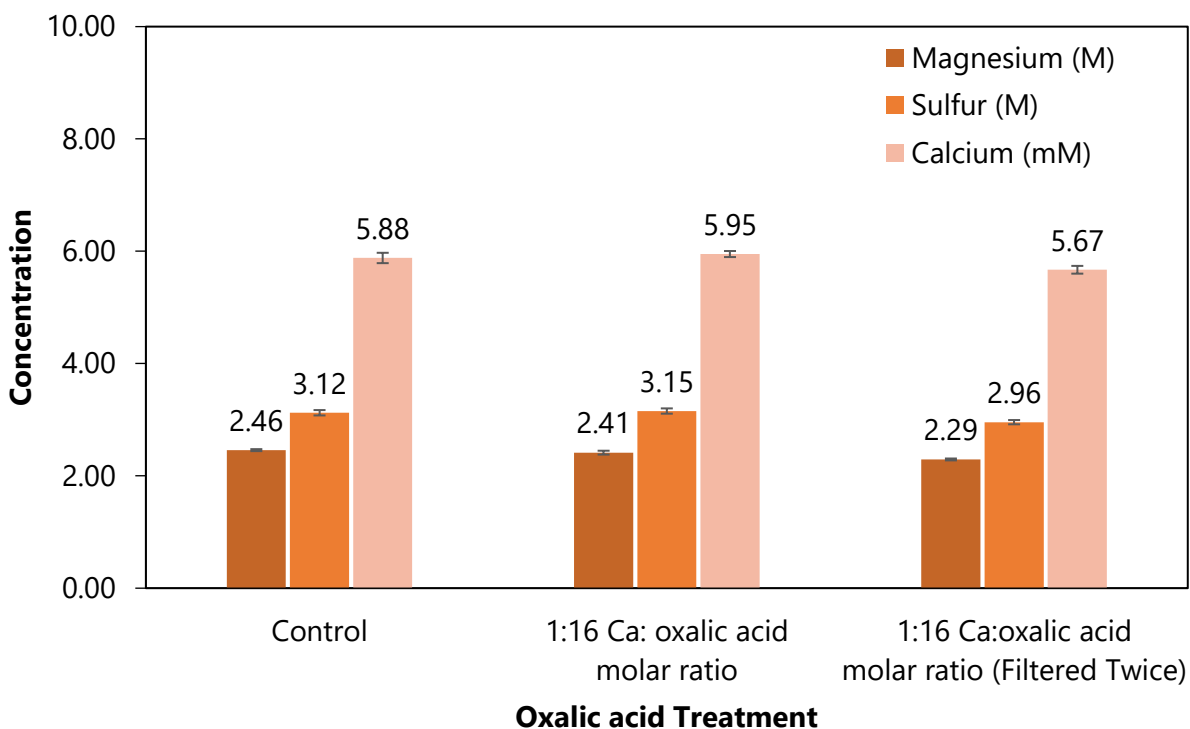


Figure 12. Changes in magnesium, sulfur, and calcium content after filtration of precipitate.

4.3 Ca^{2+} precipitation by sodium carbonate

Among the additives, the addition of sodium carbonate did not produce a precipitate in the model solution (250g/L $MgSO_4$ containing 500 mg/L Ca), while the opposite was observed for the 500 mg/L Ca^{2+} solution (without $MgSO_4$), as shown in Figure 13. Bubbling with carbon dioxide also did not produce any precipitate for the model solution. However, the pH of the solution was observed to decrease, which signifies that CO_2 gas reacted with water in the solution to form carbonic acid species.

A white precipitate was observed when the solution containing 500 ppm Ca was used. The probable reason for this lack of precipitation in the model solution might be its high salt concentration (MgSO_4). The presence of diverse salts increases the solubility of precipitates due to the shielding of the dissociated ion species [46]. Since the 500 mg/L Ca solution only contained a small concentration of calcium and nitrate ions, there was no shielding effect, thus, calcium carbonate precipitated in this solution upon addition of sodium carbonate.

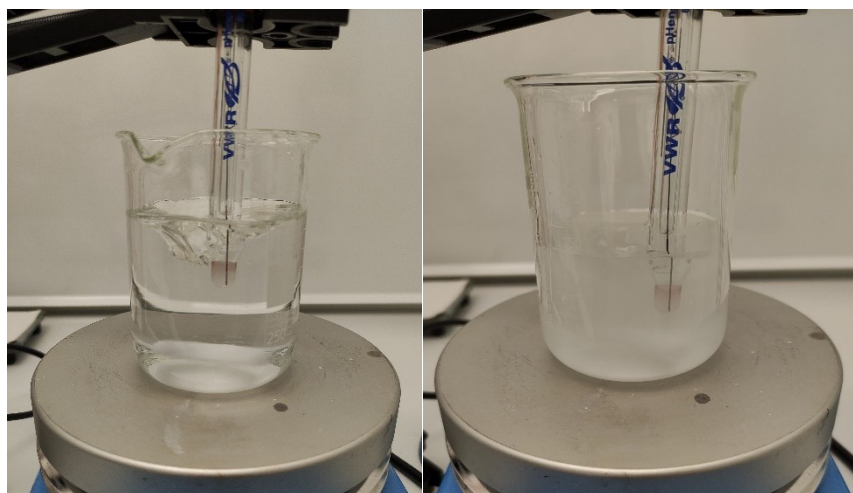


Figure 13. Solution after mixing with sodium carbonate: model solution (Left) and 500 ppm Ca^{2+} solution only (Right).

Using filtered MgSO_4 solution, the addition of sodium carbonate (1:5 molar ratio) still showed no formation of a precipitate. The experimental results agree with the literature. The ionic strength plays a vital role in the activity of ions in the solution. According to Di Lorenzo et al., increasing ionic strength decreases the activity coefficient of ions, as described by the Debye-Huckel and Davies equations; thus, calcite, a form of calcium carbonate becomes more soluble at higher salinity, and calcium and carbonate ions remain in the solution [47]. Additionally, the presence of MgSO_4 itself in the solution inhibits the growth formation of calcite [48,49]. Nielsen et al. reported an inhibition index of 0.99 for calcite formation in the presence of 12.6 mM MgSO_4 [50].

4.4 Ca^{2+} removal through magnesium hydroxide precipitation

Precipitation of magnesium hydroxide was another route in this study to remove Ca^{2+} ions and other impurities in the solution. The addition of sodium hydroxide to a magnesium sulfate solution

was done so that ca 90% of the magnesium ions would react to hydroxide ions to form magnesium hydroxide. Excess hydroxide was avoided to minimize co-precipitation of $\text{Ca}(\text{OH})_2$ with $\text{Mg}(\text{OH})_2$. Results of the experiment showed that the calcium concentration remained the same for both samples, but the method concentrates the magnesium content effectively (Table 6). The Mg/Ca molar ratio increased from 362 for the filtered solution to 2393 for the $\text{Mg}(\text{OH})_2$ precipitate. The use of hydroxide to recover Mg was also reported to be effective by Pujiastuti et al. [51]. The removal of magnesium from their saturated salt solution was about 95.5% using 2 N sodium hydroxide. The washing process might also have aided in removing calcium ions that could be incorporated into the precipitate.

Table 6. Elemental composition and Mg/Ca ratio of filtered MgSO_4 solution and $\text{Mg}(\text{OH})_2$ precipitate.

Element	Concentration ^a			
	Filtered MgSO_4 solution		$\text{Mg}(\text{OH})_2$ precipitate	
	mg/L	mol/L	mg/kg	mol/kg
Calcium	239.62±2.91	0.00598±0.00007	218.59±4.49	0.0055±0.0001
Magnesium	52673±325	2.17±0.01	317214±4125	13.05±0.17
Sulfur	130010±760	4.05±0.02	75403±3911	2.35±0.12
Sodium	119.1±1.6	0.0052±0.0001	26173±3271	1.14±0.14
Potassium	73.9±1.2	0.00194±0.00001	<0.1	---
Manganese	2.16±0.02	$3.9 \times 10^{-5} \pm 4.0 \times 10^{-7}$	19.5±1.1	$3.5 \times 10^{-4} \pm 2.2 \times 10^{-5}$
Silicon	7.49±0.05	$2.67 \times 10^{-4} \pm 2.0 \times 10^{-6}$	3488±1655	0.12±0.06
Aluminum	<0.01	---	<0.01	---
Arsenic	0.42±0.01	$5.61 \times 10^{-6} \pm 1.33 \times 10^{-7}$	<0.016	---
Cadmium	<0.0008	---	<0.0008	---
Cobalt	<0.02	---	<0.02	---
Chromium	<0.02	---	<0.02	---
Copper	<0.003	---	<0.003	---
Iron	<0.0015	---	<0.0015	---
Nickel	<0.05	---	<0.05	---
Lead	<0.03	---	<0.03	---
Antimony	<0.01	---	<0.01	---
Selenium	<0.025	---	<0.025	---
Tin	<0.03	---	<0.03	---
Zinc	<0.002	---	<0.002	---
Mg/Ca ratio	220	362	1451	2393

^a Values reported as the mean of four replicates ± standard deviation.

This process might be an effective way to remove calcium and concentrate magnesium. However, the use of sodium hydroxide has one disadvantage. $\text{Mg}(\text{OH})_2$ particles are hydrophilic [52] and have high surface energy [53], which makes them agglomerate in an aqueous medium creating a very viscous suspension [54]. This makes the suspension settle very slowly and the final sediment is exceedingly difficult to filtrate [55].

4.5 Ca^{2+} removal by partial crystallization of MgSO_4 solution

Partial crystallization of the MgSO_4 solution was tested through evaporation. The sample solutions were heated for a sufficient time to reduce their mass by 9-10%. It was observed that at this range of mass reduction, the solution produced a small amount of precipitate. Since the filtered solution is already near its saturation, reducing the mass by 15% and above causes full precipitation of the salts in the solution. The supernatants were then monitored for changes in magnesium, sulfur, and calcium content, and the results are shown in Figure 14.

The calcium concentration did not decrease after crystallization, which signifies that the salt formed in the solution was not a calcium salt. The slight increase in Ca concentration can be due to the small amount of water lost through evaporation. The concentration of magnesium and sulfur, in contrast, showed a slight decrease in concentration. Thus, it can be inferred from the result that the identity of the salt is solid magnesium sulfate.

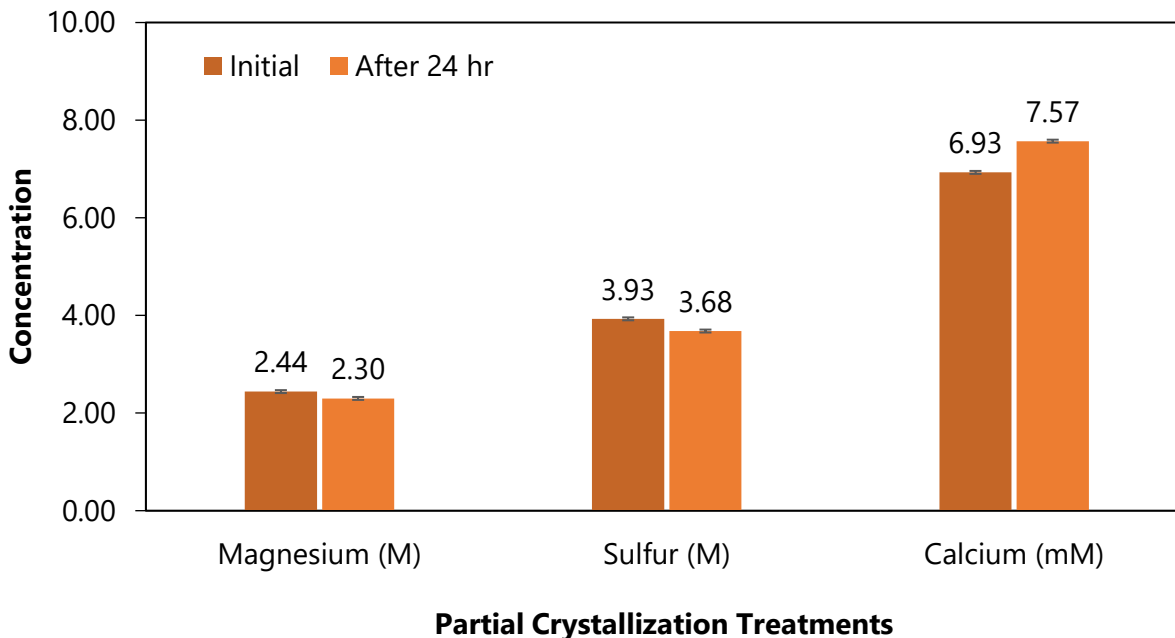


Figure 14. Changes in the magnesium, sulfur, and calcium content of the solution after partial crystallization.

4.6 Ca^{2+} removal by partial dissolution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt

The use of magnesium sulfate heptahydrate salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) as a starting material for producing magnesium sulfate solution was investigated. Partial dissolution was performed using deionized water at different temperatures. The procedure was made to leave some salts undissolved in the solution, especially salts with low solubility such as calcium sulfate dihydrate (gypsum). The results are shown in Figure 15.

The magnesium and sulfur content of the samples showed no significant difference at different temperatures, while the calcium contents showed some significant difference. The solution prepared at low temperature had the lowest amount of dissolved Ca^{2+} ions, followed by the solution at 70 °C. The solution prepared at room temperature had the highest calcium content in its supernatant. This trend could be attributed to the effect of temperature on the solubility of calcium sulfate. According to Hoang et al. (2007), elevated temperature (>40 °C) speeds up the formation of calcium sulfate [56]. Shen et al. (2019) studied the thermodynamics behavior of $\text{CaSO}_4\text{-H}_2\text{O}$ system up to 200 °C [57]. They stated that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is stable at temperatures between 0 and 42.8 °C while above 43 °C, anhydrite (CaSO_4) is the stable form. Thus, it explains

the higher concentration of calcium dissolved at room temperature as compared to the treatment at a higher temperature.

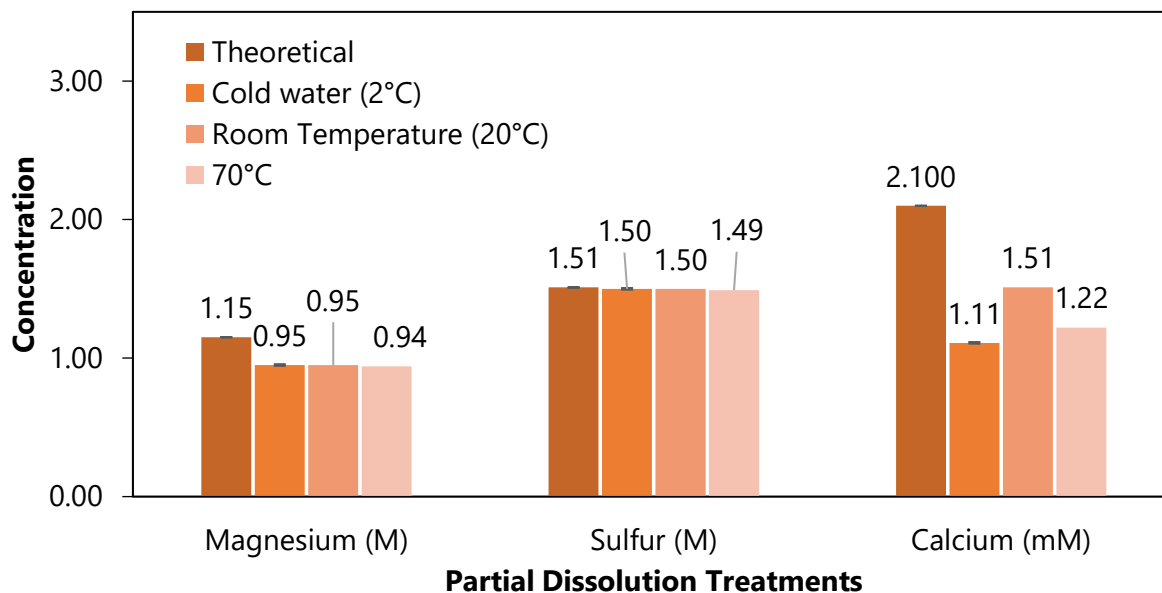


Figure 15. Effect of temperature in the partial dissolution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt.

4.7 Ca^{2+} removal by ion-exchange resin

Removal of Ca^{2+} by ion-exchange was also investigated. To study the effect of pH, different MgSO_4 solutions at pH 4, 5, and 8 were prepared and eluted into a column containing five grams of Amberlite® IR-120 cationic exchange resin, originally in protonated (H^+) form. The pH of the samples was adjusted by the addition of 0.05 M sulfuric acid and served as the control solution. A 10 mL aliquot of the samples at each pH were eluted for 20 min and the eluent was collected for ICP-OES analysis. The results are shown in Figure 16. Overall, changing the pH of the sample solution did not show any significant difference in the calcium and magnesium content after the ion-exchange process. Amberlite® IR 120 is a strongly acidic cation exchange resin consisting of styrene-divinylbenzene with a sulfonic acid functional group. The sulfonic acid group gives the resin a higher affinity for divalent cations (Mg^{2+} , Ca^{2+}) and a low affinity for monovalent ions (H^+ , Na^+) [58]. The obtained results showed that the resin was not selective for Ca^{2+} or Mg^{2+} ions. Around 30% of calcium was removed from the sample solution, while also removing 20% of the magnesium ions. Since the sample solution contains a high concentration of magnesium and an

exceedingly small amount of calcium, the ion-exchange process is not recommended for the removal of Ca^{2+} impurities.

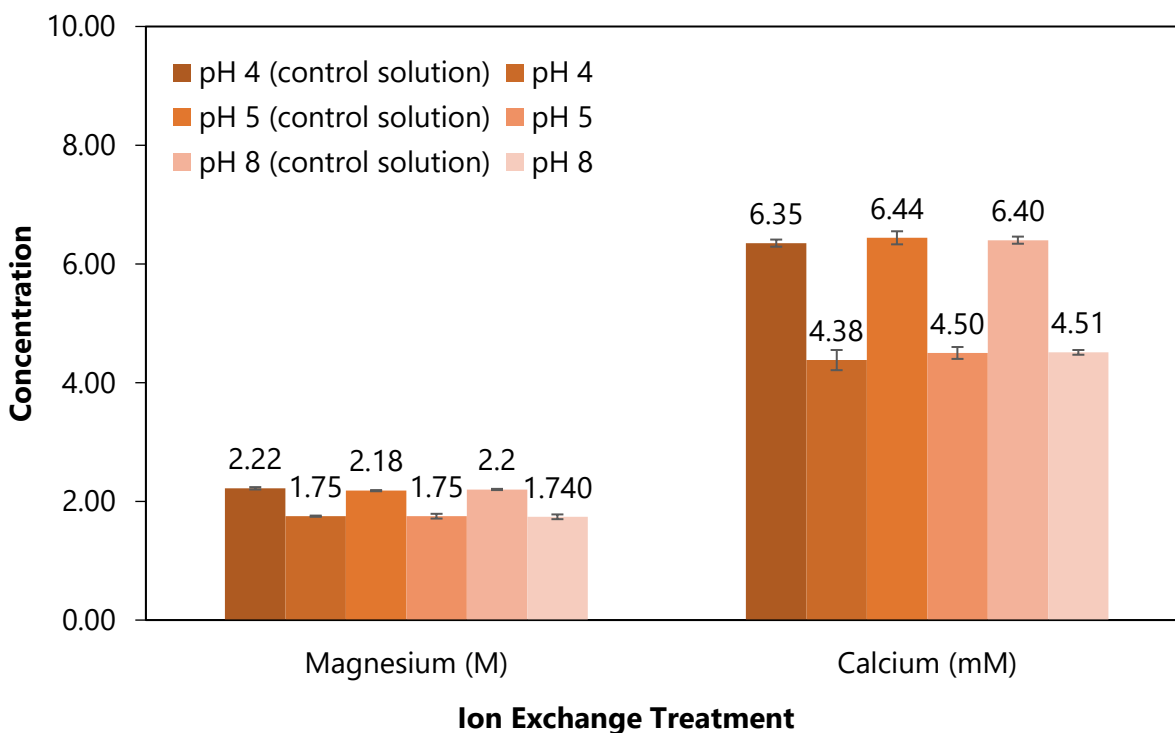


Figure 16. Effect of pH on magnesium and calcium contents using ion-exchange resin.

4.8 Ca^{2+} removal by a PVC-based Ca-selective membrane

A PVC-based calcium-selective membrane was tested for the removal of calcium. The prepared membrane was fitted in between the two cells. The source cell contained Ca^{2+} solution, while the receiving cell contained either deionized water or EDTA solution. The purpose of this investigation was to obtain selective transport of Ca^{2+} ions through the membrane. A dummy membrane was first prepared to check the migration of calcium ions without the help of ionophores. It was shown in Table 7 that there is only a small change in the calcium content in each cell, which signifies little to no transfer of calcium ions between the cells. Replacing deionized water with EDTA solution caused higher flux of Ca through the dummy membrane. However, the transport was slow, which might be due to the lack of ionophore that will carry the ion from the source cell to the receiving cell.

Table 7. Changes in calcium content in source cell (SC) and receiving cell (RC) using PVC-based dummy membrane.

Treatments		Calcium content, mM ^a	
		24 hr	72 hours
1	SC - CaCl ₂ solution	10.13±0.09	11.22±0.11
	RC - Deionized water ^b	<LOD	<LOD
2	SC - CaCl ₂ solution	10.18±0.11	10.60±0.14
	RC - EDTA solution (pH 8.0)	0.027±0.001	0.138±0.001

^a Values reported as the mean of five measurements± standard deviation.

^b Limit of detection ($<7.5 \times 10^{-7}$ M)

Another membrane was tested for the removal of calcium ions but this time, Ca-ionophore II (ETH 129) was added as one of the components in the membrane. The results are shown in Table 8. Although an ionophore was now included in the membrane, there was still no significant transport of calcium through the membrane. By using an EDTA solution in the receiving cell, the transport of calcium was slightly higher as compared to using deionized water in the receiving cell. This behavior is similar to that of the dummy membrane without the ionophore. According to Wang et al., the slow transport of calcium ions through the membrane could be due to the transport property of ETH 129 [40]. ETH 129 transports Ca²⁺ via an electrogenic mechanism in which the rate of transport is dependent on the membrane potential. Thus, there is a need for an applied potential to facilitate the transfer of calcium from the source cell to the receiving cell.

Moreover, the membrane was supposed to selectively transfer only calcium ions, but it was observed that there was a minor transport of magnesium ions in treatments 5 and 6. The minor transport of magnesium ions can be related to the large excess of Mg²⁺ vs. Ca²⁺ due to the highly concentrated MgSO₄ solutions.

Table 8. Changes in the calcium and magnesium content in source cell (SC) and receiving cell (RC) using PVC-based Ca-selective membrane.

Treatments		Concentration ^a			
		Calcium, mM		Magnesium, M ^b	
		24 hr	48 hr	24 hr	48 hr
1	SC - CaCl ₂ solution	9.85±0.12	9.82±0.11	<LOD	<LOD
	RC - Deionized water	0.0087±0.0006	0.0158±0.0006	<LOD	<LOD
2	SC - CaCl ₂ solution	9.85±0.10	10.09±0.05	<LOD	<LOD
	RC - EDTA solution (pH 8.0)	0.0307±0.0005	0.0369±0.0007	<LOD	<LOD
3	SC - 10% MgSO ₄ solution	2.82±0.03	2.80±0.02	0.93±0.02	0.93±0.02

	RC - Deionized water	0.0069±0.0002	0.0140±0.0002	<LOD	<LOD
4	SC- 10% MgSO ₄ solution	2.74±0.03	2.82±0.02	0.92±0.01	0.93±0.01
	RC - EDTA solution (pH 8.0)	0.0114±0.0003	0.0216±0.0005	<LOD	<LOD
5	SC- Filtered MgSO ₄ solution	6.23±0.05	6.28±0.06	2.20±0.03	2.23±0.03
	RC - Deionized water	0.0035±0.0001	0.0089±0.0002	6.71×10 ⁻⁵	5.37×10 ⁻⁵
6	SC - Filtered MgSO ₄ solution	6.30±0.12	6.32±0.09	2.22±0.03	2.23±0.03
	RC - EDTA solution (pH 8.0)	0.0137±0.0005	0.0254±0.0005	6.17×10 ⁻⁵	6.60×10 ⁻⁵

^a Values reported as the mean of five measurements± standard deviation.

^b Limit of detection (<2.1×10⁻⁸ M)

5. CONCLUSION

The removal of calcium ions as an impurity in industrial processes is an important step to minimize crystallization fouling. This study investigated different methods of removing calcium impurity from industrial-grade magnesium sulfate solution. The methods were selective precipitation using precipitating agents, partial crystallization, partial dissolution of magnesium sulfate heptahydrate salts, ion exchange, and ion-selective membrane.

Among the precipitating agents, oxalic acid and sodium carbonate did not produce any calcium precipitate due to the high salinity of the solution. The presence of a high concentration of ionic species, especially magnesium ions, provided a shielding effect that prevented the interaction of calcium ions with the carbonates and oxalates to form precipitates. The addition of ethanol to the MgSO₄ samples was successful in forming precipitates. The removal efficiency for calcium was found to be 65.7% for the mixture containing a 0.20:1.00 volume ratio of ethanol to sample solution. Ethanol would be a good precipitating agent for calcium. However, ethanol poses some safety risks owing to its flammable property. For sodium hydroxide, the process produced high purity magnesium precipitate with a Mg/Ca molar ratio that was six times that of the original solution. Thus, sodium hydroxide was the most promising among the precipitating agents studied for removing calcium from the sample.

Partial crystallization of MgSO₄ solution through evaporation produced magnesium sulfate crystals only. There was a decrease in the concentration of magnesium and sulfur, while no significant change in calcium concentration was observed in the supernatant. Therefore, it can be concluded that no calcium sulfate was co-precipitated or incorporated into the MgSO₄ crystals. For the partial dissolution method, the difference in the temperature of deionized water showed an

interesting trend in the calcium content during dissolution. At 2 °C, the calcium dissolved from the heptahydrate salt of MgSO_4 had the lowest concentration. This was followed by samples dissolved at 70 °C, while deionized water at room temperature produced the highest calcium content. Calcium sulfate decreases its solubility at high temperatures, which explained why dissolution at 70 °C had lower calcium content than at room temperature.

A cation-exchange resin (Amberlite® IR 120) was also investigated. It revealed that the resin did not have enough selectivity between Ca^{2+} and Mg^{2+} . About 30% of calcium was removed by the resin, but it also reduced the magnesium content by 20% in the sample. Since magnesium is in high concentration in the sample, the ion-exchange process is not efficient and not practical to use. Furthermore, the results for the Ca^{2+} -selective membrane with ETH 129 (Ca-ionophore II) showed no significant transfer of calcium through the membrane from one cell to the other. ETH 129 was reported to transport Ca^{2+} ions through an electrogenic mechanism, which means that it is dependent on the applied potential in the membrane. That explains the lack of transport of Ca^{2+} ions using the ion-selective membrane.

Among the methods investigated, selective precipitation showed to be the most promising process for calcium removal. Since the MgSO_4 sample contained a high concentration of Mg^{2+} as compared to Ca^{2+} , concentrating Mg^{2+} using sodium hydroxide was found to be the most effective approach to reduce the amount of Ca^{2+} ions in the solution.

6. LITERATURE CITED

- [1] A.A. Luo, Magnesium casting technology for structural applications, *J. Magnes. Alloys.* 1 (2013) 2–22. <https://doi.org/10.1016/j.jma.2013.02.002>.
- [2] F.N.H. Schrama, E.M. Beunder, B. Van den Berg, Y. Yang, R. Boom, Sulphur removal in ironmaking and oxygen steelmaking, *Ironmak. Steelmak.* 44 (2017) 333–343. <https://doi.org/10.1080/03019233.2017.1303914>.
- [3] R. Gul, A. Islam, T. Yasin, S. Mir, Flame-retardant synergism of sepiolite and magnesium hydroxide in a linear low-density polyethylene composite, *J. Appl. Polym. Sci.* 121 (2011) 2772–2777. <https://doi.org/10.1002/app.33767>.
- [4] A.A. Pilarska, Ł. Klapiszewski, T. Jesionowski, Recent development in the synthesis, modification and application of Mg(OH)₂ and MgO: A review, *Powder Technol.* 319 (2017) 373–407. <https://doi.org/10.1016/j.powtec.2017.07.009>.
- [5] M. Senbayram, A. Gransee, V. Wahle, H. Thiel, Role of magnesium fertilisers in agriculture: plant–soil continuum, *Crop Pasture Sci.* 66 (2015) 1219. <https://doi.org/10.1071/CP15104>.
- [6] W. Jahnen-Dechent, M. Ketteler, Magnesium basics, *Clin. Kidney J.* 5 (2012) i3–i14. <https://doi.org/10.1093/ndtplus/sfr163>.
- [7] F. Hammes, A. Seka, S. de Knijf, W. Verstraete, A novel approach to calcium removal from calcium-rich industrial wastewater, *Water Res.* 37 (2003) 699–704. [https://doi.org/10.1016/S0043-1354\(02\)00308-1](https://doi.org/10.1016/S0043-1354(02)00308-1).
- [8] M.-J. Kim, S. Kim, S. Shin, G. Kim, Production of high-purity MgSO₄ from seawater desalination brine, *Desalination.* 518 (2021) 115288. <https://doi.org/10.1016/j.desal.2021.115288>.
- [9] M. Xia, C. Ye, K. Pi, D. Liu, A.R. Gerson, Ca removal and Mg recovery from flue gas desulfurization (FGD) wastewater by selective precipitation, *Water Sci. Technol.* 76 (2017) 2842–2850. <https://doi.org/10.2166/wst.2017.452>.

- [10] M.H. Sorour, H.A. Hani, H.F. Shaalan, Separation of calcium and magnesium using dual precipitation/chelation scheme from saline solutions, *Desalination Water Treat.* 57 (2016) 22818–22823. <https://doi.org/10.1080/19443994.2015.1114170>.
- [11] J. Berce, M. Zupančič, M. Može, I. Golobič, A Review of Crystallization Fouling in Heat Exchangers, *Processes.* 9 (2021) 1356. <https://doi.org/10.3390/pr9081356>.
- [12] J. MacAdam, S.A. Parsons, Calcium carbonate scale formation and control, *Rev. Environ. Sci. Biotechnol.* 3 (2004) 159–169. <https://doi.org/10.1007/s11157-004-3849-1>.
- [13] Q. Yang, Y. Liu, A. Gu, J. Ding, Z. Shen, Investigation of Calcium Carbonate Scaling Inhibition and Scale Morphology by AFM, *J. Colloid Interface Sci.* 240 (2001) 608–621. <https://doi.org/10.1006/jcis.2001.7669>.
- [14] T.K. Hou, S.N. Kazi, A.B. Mahat, C.B. Teng, A. Al-Shamma'a, A. Shaw, Industrial Heat Exchanger: Operation and Maintenance to Minimize Fouling and Corrosion, in: S.M.S. Murshed, M.M. Lopes (Eds.), *Heat Exch. - Adv. Featur. Appl., InTech*, 2017. <https://doi.org/10.5772/66274>.
- [15] J. MacAdam, P. Jarvis, Water-Formed Scales and Deposits, in: *Miner. Scales Depos.*, Elsevier, 2015: pp. 3–23. <https://doi.org/10.1016/B978-0-444-63228-9.00001-2>.
- [16] M. Prisciandaro, A. Santucci, A. Lancia, D. Musmarra, Role of Citric Acid in Delaying Gypsum Precipitation, *Can. J. Chem. Eng.* 83 (2008) 586–592. <https://doi.org/10.1002/cjce.5450830325>.
- [17] Z. Amjad, P.G. Koutsoukos, Evaluation of maleic acid based polymers as scale inhibitors and dispersants for industrial water applications, *Desalination.* 335 (2014) 55–63. <https://doi.org/10.1016/j.desal.2013.12.012>.
- [18] D.E. Abd-El-Khalek, B.A. Abd-El-Nabey, M.A. Abdel-kawi, Sh. Ebrahim, S.R. Ramadan, The inhibition of crystal growth of gypsum and barite scales in industrial water systems using green antiscalant, *Water Supply.* 19 (2019) 2140–2146. <https://doi.org/10.2166/ws.2019.094>.
- [19] D.H. Kim, B.M. Jenkins, J.H. Oh, Gypsum scale reduction and collection from drainage water in solar concentration, *Desalination.* 265 (2011) 140–147. <https://doi.org/10.1016/j.desal.2010.07.044>.

- [20] V. Gomis, M.D. Saquete, J. García-Cano, CaSO₄ solubility in water–ethanol mixtures in the presence of sodium chloride at 25°C. Application to a reverse osmosis process, *Fluid Phase Equilibria*. 360 (2013) 248–252. <https://doi.org/10.1016/j.fluid.2013.09.063>.
- [21] E. Drioli, E. Curcio, A. Criscuoli, G.D. Profio, Integrated system for recovery of CaCO₃, NaCl and MgSO₄·7H₂O from nanofiltration retentate, *J. Membr. Sci.* 239 (2004) 27–38. <https://doi.org/10.1016/j.memsci.2003.09.028>.
- [22] M.H. Sorour, H.A. Hani, H.F. Shaalan, G.A. Al-Bazedi, Schemes for salt recovery from seawater and RO brines using chemical precipitation, *Desalination Water Treat.* 55 (2015) 2398–2407. <https://doi.org/10.1080/19443994.2014.946720>.
- [23] Y. Wang, Y. Qin, B. Wang, J. Jin, B. Wang, D. Cui, Selective removal of calcium ions from seawater or desalination brine using a modified sodium carbonate method, *DESALINATION WATER Treat.* 174 (2020) 123–135. <https://doi.org/10.5004/dwt.2020.24828>.
- [24] N.C. Natasha, L.H. Lalasari, Calcium extraction from brine water and seawater using oxalic acid, in: West Java, Indonesia, 2017: p. 070002. <https://doi.org/10.1063/1.4974443>.
- [25] Y. Wang, X. Guo, Y. Bai, X. Sun, Effective removal of calcium and magnesium sulfates from wastewater in the rare earth industry, *RSC Adv.* 9 (2019) 33922–33930. <https://doi.org/10.1039/C9RA05615G>.
- [26] C. Cobzaru, V. Inglezakis, Ion Exchange, in: *Prog. Filtr. Sep.*, Elsevier, 2015: pp. 425–498. <https://doi.org/10.1016/B978-0-12-384746-1.00010-0>.
- [27] F. de Dardel, T.V. Arden, Ion Exchangers, in: Wiley-VCH Verlag GmbH & Co. KGaA (Ed.), *Ullmanns Encycl. Ind. Chem.*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2008: p. a14_393.pub2. https://doi.org/10.1002/14356007.a14_393.pub2.
- [28] B. Török, C. Schäfer, A. Kokel, Solid catalysts for environmentally benign synthesis, in: *Heterog. Catal. Sustain. Synth.*, Elsevier, 2022: pp. 23–80. <https://doi.org/10.1016/B978-0-12-817825-6.00013-6>.
- [29] E. Pehlivan, T. Altun, The study of various parameters affecting the ion exchange of Cu²⁺, Zn²⁺, Ni²⁺, Cd²⁺, and Pb²⁺ from aqueous solution on Dowex 50W synthetic resin, *J. Hazard. Mater.* 134 (2006) 149–156. <https://doi.org/10.1016/j.jhazmat.2005.10.052>.

- [30] W. Yi, C. Yan, P. Ma, Removal of calcium and magnesium from LiHCO_3 solutions for preparation of high-purity Li_2CO_3 by ion-exchange resin, *Desalination*. 249 (2009) 729–735. <https://doi.org/10.1016/j.desal.2009.01.034>.
- [31] A. Devi, Shallu, M.L. Sharma, J. Singh, Paal–Knorr Pyrrole Synthesis Using Recyclable Amberlite IR 120 Acidic Resin: A Green Approach, *Synth. Commun.* 42 (2012) 1480–1488. <https://doi.org/10.1080/00397911.2010.540766>.
- [32] G. Cetin, Removal of Hardness of Earth Alkaline Metals from Aqueous Solutions by Ion Exchange Method, *ISRN Anal. Chem.* 2014 (2014) 1–7. <https://doi.org/10.1155/2014/621794>.
- [33] P.U. Singare, R.S. Lokhande, N.G. Samant, M.R. Dhatrak, Selectivity study of strongly acidic cation exchange resin Amberlite IR-120, *Colloid J.* 72 (2010) 538–543. <https://doi.org/10.1134/S1061933X10040150>.
- [34] K. Maksymiuk, E. Stelmach, A. Michalska, Unintended Changes of Ion-Selective Membranes Composition—Origin and Effect on Analytical Performance, *Membranes*. 10 (2020) 266. <https://doi.org/10.3390/membranes10100266>.
- [35] D.T. Jackson, P.N. Nelson, Preparation and properties of some ion selective membranes: A review, *J. Mol. Struct.* 1182 (2019) 241–259. <https://doi.org/10.1016/j.molstruc.2019.01.050>.
- [36] M. M., Plasticizers and Their Role in Membrane Selective Electrodes, in: M. Luqman (Ed.), *Recent Adv. Plast., InTech*, 2012. <https://doi.org/10.5772/36620>.
- [37] J.M. Zook, J. Langmaier, E. Lindner, Current-polarized ion-selective membranes: The influence of plasticizer and lipophilic background electrolyte on concentration profiles, resistance, and voltage transients, *Sens. Actuators B Chem.* 136 (2009) 410–418. <https://doi.org/10.1016/j.snb.2008.12.047>.
- [38] J.A. Ortuño, F. Tomás-Alonso, A.M. Rubio, Ion-Selective Electrodes Based on Ionic Liquids, in: *Ion. Liq. Sep. Technol.*, Elsevier, 2014: pp. 275–299. <https://doi.org/10.1016/B978-0-444-63257-9.00009-2>.

- [39] Urs. Schefer, Daniel. Ammann, Ernoe. Pretsch, Urs. Oesch, Wilhelm. Simon, Neutral carrier based calcium(2+)-selective electrode with detection limit in the sub-nanomolar range, *Anal. Chem.* 58 (1986) 2282–2285. <https://doi.org/10.1021/ac00124a036>.
- [40] E. Wang, W.L. Erdahl, S.A. Hamidinia, C.J. Chapman, R.W. Taylor, D.R. Pfeiffer, Transport Properties of the Calcium Ionophore ETH-129, *Biophys. J.* 81 (2001) 3275–3284. [https://doi.org/10.1016/S0006-3495\(01\)75961-9](https://doi.org/10.1016/S0006-3495(01)75961-9).
- [41] D.A. Skoog, *Fundamentals of analytical chemistry*, 9th Ed, Cengage - Brooks/Cole, Belmont, CA, 2012.
- [42] C. Grochowski, E. Blicharska, P. Krukow, K. Jonak, M. Maciejewski, D. Szczepanek, K. Jonak, J. Flieger, R. Maciejewski, Analysis of Trace Elements in Human Brain: Its Aim, Methods, and Concentration Levels, *Front. Chem.* 7 (2019) 115. <https://doi.org/10.3389/fchem.2019.00115>.
- [43] Mu. Naushad, Z.A. Al-Othman, Separation of toxic Pb^{2+} metal from aqueous solution using strongly acidic cation-exchange resin: analytical applications for the removal of metal ions from pharmaceutical formulation, *Desalination Water Treat.* 53 (2015) 2158–2166. <https://doi.org/10.1080/19443994.2013.862744>.
- [44] H.-R. Na, M.-J. Kim, Determination of optimal conditions for magnesium recovery process from seawater desalination brine using paper sludge ash, sulfuric acid, and ethanol, *Desalination Water Treat.* 157 (2019) 324–331. <https://doi.org/10.5004/dwt.2019.23791>.
- [45] J.M. Riley, H. Kim, T.D. Averch, H.J. Kim, Effect of magnesium on calcium and oxalate ion binding, *J. Endourol.* 27 (2013) 1487–1492. <https://doi.org/10.1089/end.2013.0173>.
- [46] G. Christian, *Analytical Chemistry*, 6th Ed., John Wiley & Sons, Inc., 2004.
- [47] F. Di Lorenzo, K. Steiner, S.V. Churakov, The Effect of pH, Ionic Strength and the Presence of PbII on the Formation of Calcium Carbonate from Homogenous Alkaline Solutions at Room Temperature, *Minerals.* 11 (2021) 783. <https://doi.org/10.3390/min11070783>.
- [48] A. Mucci, R. Canuel, S. Zhong, The solubility of calcite and aragonite in sulfate-free seawater and the seeded growth kinetics and composition of the precipitates at 25°C, *Chem. Geol.* 74 (1989) 309–320. [https://doi.org/10.1016/0009-2541\(89\)90040-5](https://doi.org/10.1016/0009-2541(89)90040-5).

- [49] W. Mejri, A. Korchef, M. Tlili, M. Ben Amor, Effects of temperature on precipitation kinetics and microstructure of calcium carbonate in the presence of magnesium and sulphate ions, *Desalination Water Treat.* 52 (2014) 4863–4870. <https://doi.org/10.1080/19443994.2013.808813>.
- [50] M.R. Nielsen, K.K. Sand, J.D. Rodriguez-Blanco, N. Bovet, J. Generosi, K.N. Dalby, S.L.S. Stipp, Inhibition of Calcite Growth: Combined Effects of Mg^{2+} and SO_4^{2-} , *Cryst. Growth Des.* 16 (2016) 6199–6207. <https://doi.org/10.1021/acs.cgd.6b00536>.
- [51] C. Pujiastuti, Y. Ngatilah, K. Sumada, S. Muljani, The effectiveness of sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) on the impurities removal of saturated salt solution, *J. Phys. Conf. Ser.* 953 (2018) 012215. <https://doi.org/10.1088/1742-6596/953/1/012215>.
- [52] X. Lv, Hari-Bala, M. Li, X. Ma, S. Ma, Y. Gao, L. Tang, J. Zhao, Y. Guo, X. Zhao, Z. Wang, In situ synthesis of nanolamellas of hydrophobic magnesium hydroxide, *Colloids Surf. Physicochem. Eng. Asp.* 296 (2007) 97–103. <https://doi.org/10.1016/j.colsurfa.2006.09.029>.
- [53] G. Song, S. Ma, G. Tang, X. Wang, Ultrasonic-assisted synthesis of hydrophobic magnesium hydroxide nanoparticles, *Colloids Surf. Physicochem. Eng. Asp.* 364 (2010) 99–104. <https://doi.org/10.1016/j.colsurfa.2010.04.043>.
- [54] K. Tong, X. Song, G. Xiao, J. Yu, Colloidal Processing of $Mg(OH)_2$ Aqueous Suspensions Using Sodium Polyacrylate as Dispersant, *Ind. Eng. Chem. Res.* 53 (2014) 4755–4762. <https://doi.org/10.1021/ie5002857>.
- [55] M. Turek, W. Gnot, Precipitation of Magnesium Hydroxide from Brine, *Ind. Eng. Chem. Res.* 34 (1995) 244–250. <https://doi.org/10.1021/ie00040a025>.
- [56] T.A. Hoang, H.M. Ang, A.L. Rohl, Effects of temperature on the scaling of calcium sulphate in pipes, *Powder Technol.* 179 (2007) 31–37. <https://doi.org/10.1016/j.powtec.2006.11.013>.
- [57] L. Shen, H. Sippola, X. Li, D. Lindberg, P. Taskinen, Thermodynamic Modeling of Calcium Sulfate Hydrates in the $CaSO_4-H_2O$ System from 273.15 to 473.15 K with Extension to 548.15 K, *J. Chem. Eng. Data.* 64 (2019) 2697–2709. <https://doi.org/10.1021/acs.jced.9b00112>.

- [58] H.B. Ulusoy Erol, C.N. Hestekin, J.A. Hestekin, Effects of Resin Chemistries on the Selective Removal of Industrially Relevant Metal Ions Using Wafer-Enhanced Electrodeionization, *Membranes*. 11 (2021) 45. <https://doi.org/10.3390/membranes11010045>.

7. APPENDICES



Appendix Figure 1. (A) Unfiltered and filtered MgSO_4 solution, (B) Residue during filtration, (C) Residue after drying.

Appendix Table 1. Elemental composition of magnesium sulfate samples.

Element	Concentration ^a		
	MgSO ₄ solution, mg/L		MgSO ₄ · 7H ₂ O salt, mg/kg ^c
	Unfiltered ^b	Filtered	
Magnesium	54659	54483	90644
Calcium	282.98	252.85	273.95
Potassium	75.86	73.86	19.35
Manganese	11.18	2.16	18.32
Sodium	120.25	119.11	28.25
Sulfur	98438	98845	158012
Silicon	10.11	7.49	19.02
Aluminum	---	<0.01	---
Arsenic	---	0.42±0.01	---
Cadmium	---	<0.0008	---
Cobalt	---	<0.02	---
Chromium	---	<0.02	---
Copper	---	<0.003	---
Iron	---	<0.0015	---
Nickel	---	<0.05	---
Lead	---	<0.03	---
Antimony	---	<0.01	---
Selenium	---	<0.025	---
Tin	---	<0.03	---
Zinc	---	<0.002	---

^a Values (in mg/L and mg/kg) reported as the mean of five measurements.

^b Some elements were not analyzed.

^c Results for some elements cannot be reported because their concentration was below LOD.

Appendix Table 2. Comparison of ICP-OES results from different laboratories.

Laboratories	Concentration					
	Magnesium, g/L		Sulfur, g/L		Calcium, mg/L	
<i>Magnesium sulfate heptahydrate</i>						
Analysis in this thesis	90.6		158		274	
Laboratory A	107		143		302	
Laboratory B	100		130		500	
<i>Magnesium sulfate solution^a</i>						
Laboratories	Concentration ^b					
	Magnesium		Sulfur		Calcium	
	g/kg	g/L	g/kg	g/L	mg/kg	mg/L
Analysis in this thesis	---	54.7	---	98.4	---	283
Laboratory A	50.6	64.3	61.2	77.7	297	377

^a Magnesium sulfate solution was only submitted to one external laboratory.

^b Laboratory A results were converted from g/kg to g/L using the sample density of 1.27 g/mL.

Appendix Table 3. Effect of ethanol addition.

Treatments	Concentration ^a		
	Magnesium, g/L	Sulfur, g/L	Calcium, mg/L
0:1	41.0±0.6	57.2±0.6	344.1±7.2
0.1:1	41.1±0.9	57.5±0.3	178.8±4.7
0.15:1	41.9±0.6	58.5±0.7	144.6±2.1
0.2:1	41.0±0.5	57.9±0.5	117.8±0.5

^a Values reported as the mean of three replications ± standard deviation.

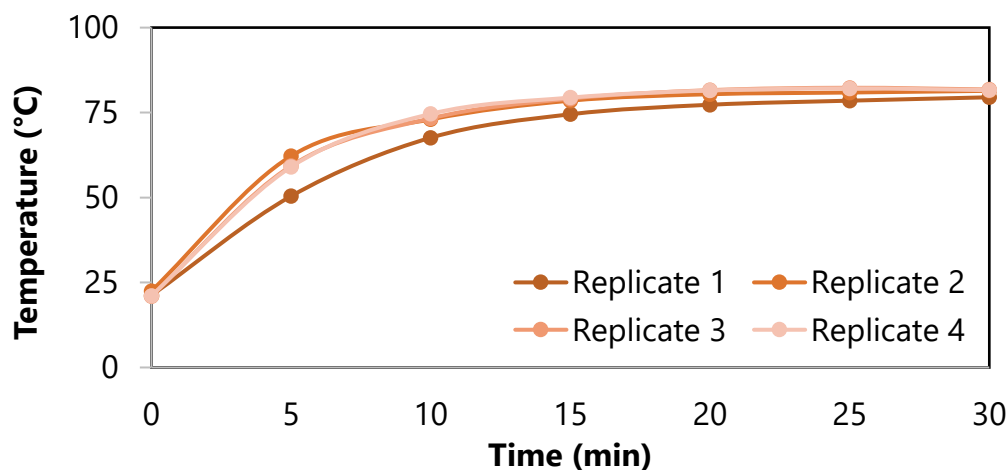
Appendix Table 4. Changes in magnesium, sulfur, and calcium content after filtration of precipitate.

Treatments	Concentration ^a		
	Magnesium, g/L	Sulfur, g/L	Calcium, mg/L
Control	59.7±0.4	100.2±1.5	235.7±3.7
1:16 Ca: oxalic acid molar ratio	58.7±0.8	101.2±1.5	238.4±2.2
1:16 Ca:oxalic acid molar ratio (Filtered Twice)	55.7±0.4	94.9±1.2	227.2±2.8

^a Values reported as the mean of three replications ± standard deviation.

Appendix Table 5. Mass reduction of magnesium sulfate solution during partial crystallization experiment.

Replication	Weight beaker (g)	Wt. sample (g)	Final Wt. Beaker and sample (g)	Final Weight of sample (g)	Weight difference (g)	% Mass reduction
1	53.30	63.03	110.82	57.52	5.51	8.74
2	67.86	62.97	125.11	57.25	5.72	9.08
3	49.75	63.11	106.65	56.90	6.21	9.84
4	46.02	63.05	103.14	57.12	5.93	9.41

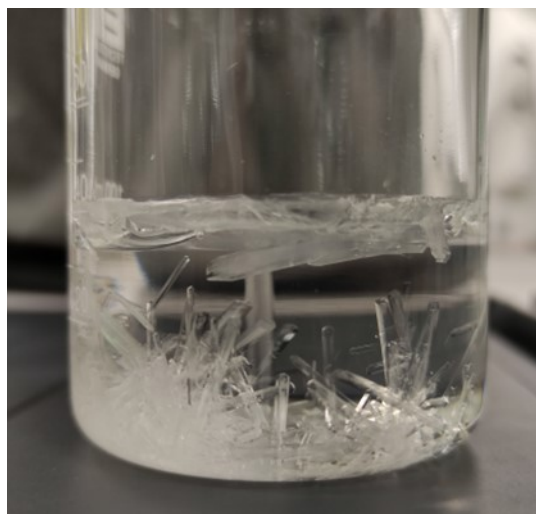


Appendix Figure 2. Temperature increase of solutions during partial crystallization.

Appendix Table 6. Changes in the magnesium, sulfur, and calcium content of the solution after partial crystallization.

Treatments	Concentration ^a		
	Magnesium, g/L	Sulfur, g/L	Calcium, mg/L
Initial	59.3±0.8	125.9±1.5	277.8±2.0
After 24 hours	55.8±0.6	118.0±1.4	303.3±5.4

^a Values reported as the mean of four replications ± standard deviation.



Appendix Figure 3. Precipitate formed from partial crystallization experiment after 24 hours.

Appendix Table 7. Effect of temperature in the partial dissolution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt.

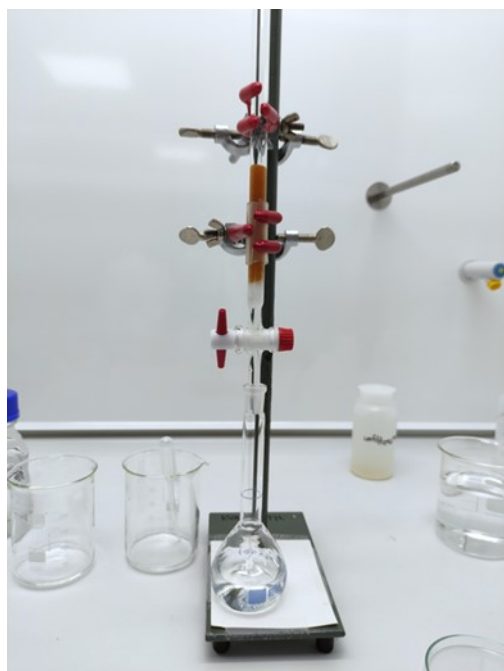
Composition (mg/L)	Theoretical content	Treatments		
		Cold water (2.3±0.2 °C)	Room Temperature (20.6±0.5 °C)	70 °C (70.3±0.1 °C)
Magnesium, g/L	27.8	23.0±0.1	23.2±0.6	22.8±0.1
Sulfur, g/L	48.5	48.1±0.3	48.2±1.2	47.7±0.5
Calcium	84.2	44.6±8.2	47.7±0.5	48.8±2.0
Sodium	8.68	6.41±0.23	6.41±0.23	6.09±0.18
Potassium	5.94	4.18±0.18	4.06±0.27	3.78±0.14
Manganese	5.63	<0.005	<0.005	<0.005
Silicon	5.84	4.59±0.06	5.28±0.10	4.88±0.09
Aluminum	<0.01	<0.01	<0.01	<0.01
Arsenic	<0.016	<0.016	<0.016	<0.016
Cadmium	<0.0008	<0.0008	<0.0008	<0.0008
Cobalt	<0.02	<0.02	<0.02	<0.02
Chromium	<0.02	<0.02	<0.02	<0.02
Copper	<0.003	<0.003	<0.003	<0.003
Iron	<0.0015	<0.0015	<0.0015	<0.0015
Nickel	<0.05	<0.05	<0.05	<0.05
Lead	<0.03	<0.03	<0.03	<0.03
Antimony	<0.01	<0.01	<0.01	<0.01
Selenium	<0.025	<0.025	<0.025	<0.025
Tin	<0.03	<0.03	<0.03	<0.03
Zinc	<0.002	<0.002	<0.002	<0.002

^a Values reported as the mean of three replications ± standard deviation.

Appendix Table 8. Effect of pH on magnesium and calcium contents using ion-exchange resin.

Treatments	Concentration ^a	
	Magnesium, g/L	Calcium, mg/L
pH 4 (control)	53.9±0.4	254.6±2.6
pH 4	42.5±0.3	175.6±7.0
pH 5 (control)	52.9±0.3	258.0±4.3
pH 5	42.6±0.9	180.2±4.0
pH 8 (control)	53.6±0.3	256.5±2.5
pH 8	42.3±0.9	180.7±1.8

^a Values reported as the mean of three replications ± standard deviation.



Appendix Figure 4. Ion-exchange column set-up using Amberlite® IR-120 H⁺ form resin.

Appendix Table 9. Changes in calcium content in source cell (SC) and receiving cell (RC) using PVC-based dummy membrane.

Treatments		Calcium content, mg/L ^a	
		24 hr	72 hours
1	SC - CaCl ₂ solution	406.1±3.8	449.7±4.6
	RC - Deionized water ^b	<LOD	<LOD
2	SC - CaCl ₂ solution	407.9±4.4	424.9±5.5
	RC - EDTA solution (pH 8.0)	1.08±0.02	1.25±0.03

^a Values reported as the mean of five measurements± standard deviation.

^b Limit of detection (<0.03 mg/L)

Appendix Table 10. Changes in the calcium and magnesium content in source cell (SC) and receiving cell (RC) using PVC-based Ca-selective membrane.

Treatments		Concentration ^a			
		Calcium, mg/L		Magnesium, g/L ^b	
		24 hr	48 hr	24 hr	48 hr
1	SC - CaCl ₂ solution	394.9±4.8	393.7±4.3	<LOD	<LOD
	RC - Deionized water	0.35±0.03	0.64±0.02	<LOD	<LOD
2	SC - CaCl ₂ solution	394.9±4.0	404.3±2.1	<LOD	<LOD
	RC - EDTA solution (pH 8.0)	1.23±0.02	1.48±0.03	<LOD	<LOD
3	SC - 10% MgSO ₄ solution	111.2±1.3	112.3±0.7	22.7±0.4	22.6±0.4
	RC - Deionized water	0.28±0.01	0.56±0.01	<LOD	<LOD
4	SC - 10% MgSO ₄ solution	109.9±1.2	113.1±0.7	22.3±0.4	22.6±0.3
	RC - EDTA solution (pH 8.0)	0.46±0.01	0.86±0.02	<LOD	<LOD
5	SC - Filtered MgSO ₄ solution	249.6±2.2	251.7±2.3	53.6±0.8	54.2±0.8
	RC - Deionized water	0.14±0.01	0.36±0.01	1.63±0.10	1.31±0.09
6	SC - Filtered MgSO ₄ solution	252.6±4.8	253.5±3.5	53.9±0.5	53.7±0.6
	RC - EDTA solution (pH 8.0)	0.55±0.02	1.02±0.02	1.50±0.08	1.60±0.09

^a Values reported as the mean of five measurements± standard deviation.

^b Limit of detection (<0.005 mg/L)